

Evaluated kinetic and photochemical data for atmospheric chemistry: Volume II – reactions of organic species

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Abstract

This article, the second in the series, presents kinetic and photochemical data evaluated by the IUPAC Subcommittee on Gas Kinetic Data Evaluation for Atmospheric Chemistry. It covers the gas phase and photochemical reactions of Organic species, which were last published in 1999, and were updated on the IUPAC website in late 2002. The article consists of a summary sheet, containing the recommended kinetic parameters for the evaluated reactions, and eight appendices containing the data sheets, which provide information upon which the recommendations are made.

1 Introduction

In the mid 1970s it was appreciated that there was a need for the establishment of an international panel to produce a set of critically evaluated rate parameters for reactions of interest for atmospheric chemistry. To this end the CODATA Task Group on Chemical Kinetics, under the auspices of the International Council of Scientific Unions (ICSU), was constituted in 1977, and tasked to produce an evaluation of relevant, available kinetic and photochemical data. The first evaluation by this international committee was published in *J. Phys. Chem. Ref. Data* in 1980 (Baulch et al., 1980), followed by Supplements in 1982 (Baulch et al., 1982) and 1984 (Baulch et al., 1984). In 1986 the IUPAC Subcommittee on Data Evaluation superseded the original CODATA Task Group for Atmospheric Chemistry, and the Subcommittee has continued its data evaluation program with Supplements published in 1989 (Atkinson et al., 1989), 1992 (Atkinson et al., 1992), 1997 (Atkinson et al., 1997a), 1997 (Atkinson et al., 1997b), 1999 (Atkinson et al., 1999), and 2000 (Atkinson et al., 2000). Following the last of these reports, Supplement VIII (Atkinson et al., 2000), the evaluation has continued to be updated and published on the worldwide web (<http://www.iupac-kinetic.ch.cam.ac.uk/>). The IUPAC website hosts an interactive data base with a search facility and implemented hyperlinks between the summary table and the data sheets, both of which can be

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downloaded as individual PDF files. In order to further enhance the accessibility of this updated material to the scientific community, the evaluation is being published as a series of articles in *Atmospheric Chemistry and Physics*. This article is the second of the series, Volume II.

2 Summary of recommended rate coefficients for organic reactions recommended rate coefficients

The ordering of families in the Summary Table is O(³P) and O(¹D) atom reactions, HO radical reactions, RO reactions, RO₂ reactions, O₃ reactions, halogen atom reactions and photochemical reactions. Reactions are numbered sequentially in each family. Chemical reactions are listed as first reactant (usually an atom or radical) + second reactant (usually a molecule). Each datasheet has a unique identifier: 'Volume: Appendix: reaction number'. For example, the first reaction in the summary sheet below refers to Datasheet 'II.A1.1'.

reaction number	Reaction	k_{298} cm ³ molecule ⁻¹ s ⁻¹	$\Delta \log k_{298}^a$	Temp. dependence of k /cm ³ molecule ⁻¹ s ⁻¹	Temp. range/K	$\Delta(E/R)/K^2$
O atom Reactions based on data sheets in Appendix 1						
1	O + CH ₃ → products	1.3 × 10 ⁻¹⁰	± 0.1	1.3 × 10 ⁻¹⁰	290-900	±100
2	O(¹ D) + CH ₄ → HO + CH ₃	1.05 × 10 ⁻¹⁰		1.05 × 10 ⁻¹⁰	200-350	
	→ CH ₃ O or CH ₂ OH + H	3.45 × 10 ⁻¹¹		3.45 × 10 ⁻¹¹	200-350	
	→ HCHO + H ₂	7.50 × 10 ⁻¹²		7.50 × 10 ⁻¹²	200-350	
15	overall	1.50 × 10 ⁻¹⁰	±0.10	1.50 × 10 ⁻¹⁰	200-350	±100

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reaction number	Reaction	k_{298} cm ³ molecule ⁻¹ s ⁻¹	$\Delta \log k_{298}^a$	Temp. dependence of k /cm ³ molecule ⁻¹ s ⁻¹	Temp. range/K	$\Delta(E/R)/K^a$
HO Reactions based on data sheets in Appendix 2						
3	HO + CH ₄ → H ₂ O + CH ₃	6.4 × 10 ⁻¹⁵	±0.08	1.85 × 10 ⁻¹² exp(-1690/T)	200–300	±100
4	HO + C ₂ H ₂ + M → C ₂ H ₂ OH + M	5 × 10 ⁻³⁰ [N ₂] 1.8 × 10 ⁻¹² $F_c = 0.35$	(k_0) ±0.1 (k_∞) ±0.5	5 × 10 ⁻³⁰ (T/300) ^{-1.5} [N ₂] 3.8 × 10 ⁻¹¹ exp(-910/T)	300–800 200–400	$\Delta n = \pm 1.5$ ±200
5	HO + C ₂ H ₄ + M → C ₂ H ₄ OH + M	7 × 10 ⁻²⁹ [N ₂] 9.0 × 10 ⁻¹² $F_c = 0.48$	(k_0) ±0.3 (k_∞) ±0.3	7 × 10 ⁻²⁹ (T/300) ^{-3.1} [N ₂] 9 × 10 ⁻¹²	200–300 200–300	$\Delta n = \pm 2$ $\Delta n = \pm 0.5$
6	HO + C ₂ H ₆ → H ₂ O + C ₂ H ₅	2.4 × 10 ⁻¹³	±0.08	6.9 × 10 ⁻¹² exp(-1000/T)	200–300	±100
7	HO + C ₃ H ₆ + M → C ₃ H ₆ OH + M	8 × 10 ⁻²⁷ [N ₂] 3.0 × 10 ⁻¹¹ $F_c = 0.5$	(k_0) ±1.0 (k_∞) ±0.1	8 × 10 ⁻²⁷ (T/300) ^{-3.5} [N ₂] 3.0 × 10 ⁻¹¹ (T/300) ^{-1.0}	200–300 200–300	$\Delta n = \pm 1$ $\Delta n = \pm 1$
8	HO + C ₃ H ₈ → H ₂ O + C ₃ H ₇	1.1 × 10 ⁻¹²	±0.08	7.6 × 10 ⁻¹² exp(-585/T)	200–300	±100
9	HO + CH ₃ CH ₂ CH ₂ CH ₃ → products	2.3 × 10 ⁻¹²	±0.10	9.1 × 10 ⁻¹² exp(-405/T)	230–300	±150
10	HO + CH ₂ =C(CH ₃)CH=CH ₂ (isoprene) → products	1.0 × 10 ⁻¹⁰	±0.10	2.7 × 10 ⁻¹¹ exp(390/T)	240–430	±100
11	HO + α -Pinene → products	5.3 × 10 ⁻¹¹	±0.15	1.2 × 10 ⁻¹¹ exp(440/T)	290–430	±200
12	HO + CO → H + CO ₂ HO + CO + M → HOCO + M	1.3 × 10 ⁻¹³ (1 + 0.6 P/bar) see data sheet for OH + CO + M	±0.05	1.3 × 10 ⁻¹³ (1 + 0.6 P/bar)	200–300	$\Delta \log k \pm 0.2$
13	HO + HCHO → H ₂ O + HCO	8.5 × 10 ⁻¹²	±0.08	5.4 × 10 ⁻¹² exp(135/T)	200–300	±100
14	HO + CH ₃ CHO → H ₂ O + CH ₃ CO	1.5 × 10 ⁻¹¹	±0.08	4.4 × 10 ⁻¹² exp(365/T)	200–350	±100
15	HO + C ₂ H ₅ CHO → products	2.0 × 10 ⁻¹¹	±0.1	5.1 × 10 ⁻¹² exp(405/T)	240–380	±200
16	HO + CH ₃ CH ₂ CH ₂ CHO → products	2.4 × 10 ⁻¹¹	±0.1	6.0 × 10 ⁻¹² exp(410/T)	250–430	±250
17	HO + CH ₂ =C(CH ₃)CHO → products	2.9 × 10 ⁻¹¹	±0.15	8.0 × 10 ⁻¹² exp(380/T)	230–380	±200

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reaction number	Reaction	k_{298} cm ³ molecule ⁻¹ s ⁻¹	$\Delta \log k_{298}^a$	Temp. dependence of k /cm ³ molecule ⁻¹ s ⁻¹	Temp. range/K	$\Delta(E/R)/K^a$
18	HO + Pinonaldehyde → products	4.2 × 10 ⁻¹¹	±0.25			
19	HO + (CHO) ₂ → H ₂ O + CH(O)CO	1.1 × 10 ⁻¹¹	±0.3			
20	HO + HOCH ₂ CHO → H ₂ O + HOCH ₂ CO → H ₂ O + HOCHCHO	1.0 × 10 ⁻¹¹ 2.6 × 10 ⁻¹²	±0.2			
	overall	1.3 × 10 ⁻¹¹	±0.2			
21	HO + CH ₃ C(O)CHO → H ₂ O + CH ₃ C(O)CO	1.5 × 10 ⁻¹¹	±0.2			
22	HO + CH ₃ C(O)CH ₃ → H ₂ O + CH ₂ C(O)CH ₃	1.7 × 10 ⁻¹³	±0.10	8.8 × 10 ⁻¹² exp(-1320/T) + 1.7 × 10 ⁻¹⁴ exp(420/T)	200–400	$\Delta \log k = \pm 0.1$
23	HO + CH ₃ C(O)CH ₂ CH ₃ → products	1.2 × 10 ⁻¹²	±0.15	1.3 × 10 ⁻¹² exp(-25/T)	240–300	±200
24	HO + CH ₂ =CHC(O)CH ₃ → products	2.0 × 10 ⁻¹¹	±0.15	2.6 × 10 ⁻¹² exp(610/T)	230–380	±200
25	HO + CH ₃ OH → H ₂ O + CH ₂ OH → H ₂ O + CH ₃ O	7.9 × 10 ⁻¹³ 1.4 × 10 ⁻¹³				
	overall	9.3 × 10 ⁻¹³	±0.15	3.1 × 10 ⁻¹² exp(-360/T)	240–300	±200
26	HO + C ₂ H ₅ OH → H ₂ O + CH ₂ CH ₂ OH → H ₂ O + CH ₃ CHOH → H ₂ O + CH ₃ CH ₂ O	1.6 × 10 ⁻¹³ 2.9 × 10 ⁻¹² 1.6 × 10 ⁻¹³				
	overall	3.2 × 10 ⁻¹²	±0.15	4.1 × 10 ⁻¹² exp(-70/T)	270–340	±200
27	HO + CH ₃ CH ₂ CH ₂ OH → products	5.8 × 10 ⁻¹²	±0.10	4.6 × 10 ⁻¹² exp(70/T)	260–380	±100
28	HO + CH ₃ CH(OH)CH ₃ → products	5.1 × 10 ⁻¹²	±0.08	2.6 × 10 ⁻¹² exp(200/T)	250–360	±100
29	HO + CH ₃ CH ₂ CH ₂ CH ₂ OH → products	8.5 × 10 ⁻¹²	±0.15	5.3 × 10 ⁻¹² exp(140/T)	260–380	±200
30	HO + CH ₃ CH(OH)CH ₂ CH ₃ → products	8.7 × 10 ⁻¹²	±0.15			
31	HO + (CH ₃) ₂ C(OH)CH=CH ₂ → products	6.4 × 10 ⁻¹¹	±0.15	8.2 × 10 ⁻¹² exp(610/T)	230–300	±200
32	HO + CH ₃ OCH ₃ → H ₂ O + CH ₃ OCH ₂	2.8 × 10 ⁻¹²	±0.08	5.7 × 10 ⁻¹² exp(-215/T)	230–300	±100

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reaction Reaction	k_{298} $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$\Delta \log k_{298}^a$	Temp. dependence of $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp. range/K	$\Delta(E/R)/\text{K}^2$
		number			
33	HO + 3-methylfuran → products	9.3×10^{-11}	±0.3		
34	HO + CH ₃ C(O)CH ₂ OH → products	3.0×10^{-12}	±0.15		
35	HO + (CH ₃) ₂ C(OH)CHO → products	1.5×10^{-11}	± 0.3		
36	HO + CH ₃ OOH → H ₂ O + CH ₂ OOH → H ₂ O + CH ₃ OO	1.9×10^{-12} 3.6×10^{-12}			
	overall	5.5×10^{-12}	±0.2	$2.9 \times 10^{-12} \exp(190/T)$	220–430 ±150
37	HO + HC(O)OH → products	4.5×10^{-13}	± 0.15	4.5×10^{-13}	290–450 ± 250
38	HO + CH ₃ C(O)OH → products	8.0×10^{-13}	±0.3		
39	HO + C ₂ H ₅ C(O)OH → products	1.2×10^{-12}	±0.2	1.2×10^{-12}	290–450 ± 300
40	HO + CH ₃ ONO ₂ → products	2.3×10^{-14}	^{+0.5} -0.2	$4.0 \times 10^{-13} \exp(-845/T)$	220–300 ± 400
41	HO + C ₂ H ₅ ONO ₂ → products	1.8×10^{-13}	±0.3	$6.7 \times 10^{-13} \exp(-395/T)$	230–300 ± 400
42	HO + 1-C ₃ H ₇ ONO ₂ → products	5.8×10^{-13} (1 bar air)	±0.3		
43	HO + 2-C ₃ H ₇ ONO ₂ → products	2.9×10^{-13}	±0.2	$6.2 \times 10^{-13} \exp(-230/T)$	230–300 ± 300
44	HO + 1-C ₄ H ₉ ONO ₂ → products	1.6×10^{-12}	±0.2		
45	HO + 2-C ₄ H ₉ ONO ₂ → products	8.6×10^{-13}	±0.3		
46	HO + CH ₃ C(O)OONO ₂ → products	$<3 \times 10^{-14}$			
47	HO + CH ₃ C(O)CH ₂ ONO ₂ → products	$<1 \times 10^{-12}$			
48	HO + CH ₃ CH ₂ C(O)CH ₂ ONO ₂ → products	8.2×10^{-13}	±0.3		
49	HO + CH ₃ CH(ONO ₂)C(O)CH ₃ → products	1.2×10^{-12}	±0.3		
50	HO + CH ₂ =C(CH ₃)C(O)OONO ₂ → products	2.9×10^{-11}	^{+0.2} ± -0.5		
51	HO + HCN → products	3.0×10^{-14} (1 bar)	±0.5	$1.2 \times 10^{-13} \exp(-400/T)$ (1 bar)	290–440 ± 300
52	HO + CH ₃ CN → products	2.2×10^{-14} (1 bar)	±0.15	$8.1 \times 10^{-13} \exp(-1080/T)$	250–390 ± 200

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reaction number	Reaction	k_{298} $\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	$\Delta \log k_{298}^a$	Temp. dependence of $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp. range/K	$\Delta(E/R)/\text{K}^2$
HO₂ Reactions – based on data sheets in Appendix 2a						
53	HO ₂ + CH ₃ O ₂ → O ₂ + CH ₃ OOH	5.2×10^{-12}	± 0.3	$3.8 \times 10^{-13} \exp(780/T)$	225–580	± 500
54	HO ₂ + HOCH ₂ O ₂ → O ₂ + HOCH ₂ OOH → O ₂ + HCOOH + H ₂ O					
	overall	1.2×10^{-11}	± 0.3	$5.6 \times 10^{-15} \exp(2300/T)$	275–335	± 1500
55	HO ₂ + C ₂ H ₅ O ₂ → O ₂ + C ₂ H ₅ OOH	7.7×10^{-12}	±0.2	$3.8 \times 10^{-13} \exp(900/T)$	200–500	± 400
56	HO ₂ + CH ₃ CO ₃ → O ₂ + CH ₃ C(O)OOH → O ₃ + CH ₃ C(O)OH	1.1×10^{-11} 2.8×10^{-12}				
	overall	1.4×10^{-11}	±0.3	$5.2 \times 10^{-13} \exp(983/T)$	250–400	± 500
57	HO ₂ + HOCH ₂ CH ₂ O ₂ → products	1.0×10^{-11}	± 0.3			
58	HO ₂ + CH ₃ OCH ₂ O ₂ → O ₂ + CH ₃ OCH ₂ OOH → O ₂ + CH ₃ OCHO + H ₂ O	See data sheet				
59	HO ₂ + CH ₃ COCH ₂ O ₂ → O ₂ + CH ₃ COCH ₂ OOH	9.0×10^{-12}	± 0.3			
60	HO ₂ + HCHO → HOCH ₂ OO	7.9×10^{-14}	± 0.3	$9.7 \times 10^{-15} \exp(625/T)$	275–333	± 600
61	HOCH ₂ OO → HO ₂ + HCHO	1.5×10^2	(k/s^{-1}) ± 0.3	$2.4 \times 10^{12} \exp(-7000/T)$	275–330	± 2000

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reaction number	Reaction	k_{298} cm ³ molecule ⁻¹ s ⁻¹	$\Delta \log k_{298}^a$	Temp. dependence of k /cm ³ molecule ⁻¹ s ⁻¹	Temp. range/K	$\Delta(E/R)/K^a$
NO₃ Reactions – based on data sheets in Appendix 3						
62	NO ₃ + CH ₄ → HNO ₃ + CH ₃	<1 × 10 ⁻¹⁸				
63	NO ₃ + C ₂ H ₂ → products	<1 × 10 ⁻¹⁶				
64	NO ₃ + C ₂ H ₄ → products	2.1 × 10 ⁻¹⁶	± 0.2	3.3 × 10 ⁻¹² exp(-2880/T)	270–340	± 500
65	NO ₃ + C ₂ H ₆ → HNO ₃ + C ₂ H ₅	<1 × 10 ⁻¹⁷				
66	NO ₃ + C ₃ H ₆ → products	9.5 × 10 ⁻¹⁵	± 0.2	4.6 × 10 ⁻¹³ exp(-1155/T)	290–430	± 300
67	NO ₃ + C ₃ H ₈ → HNO ₃ + C ₃ H ₇	<7 × 10 ⁻¹⁷				
68	NO ₃ + <i>n</i> -C ₄ H ₁₀ → products	4.6 × 10 ⁻¹⁷	± 0.2	2.8 × 10 ⁻¹² exp(-3280/T)	290–430	± 400
69	NO ₃ + CH ₂ =C(CH ₃)CH=CH ₂ (isoprene) → products	7.0 × 10 ⁻¹³	± 0.2	3.15 × 10 ⁻¹² exp(-450/T)	250–390	± 200
70	NO ₃ + α -Pinene → products	6.2 × 10 ⁻¹²	± 0.1	1.2 × 10 ⁻¹² exp(490/T)	260–390	± 300
71	NO ₃ + HCHO → HNO ₃ + HCO	5.6 × 10 ⁻¹⁶	± 0.3			
72	NO ₃ + CH ₃ CHO → HNO ₃ + CH ₃ CO	2.7 × 10 ⁻¹⁵	± 0.2	1.4 × 10 ⁻¹² exp(-1860/T)	260–380	± 500
73	NO ₃ + C ₂ H ₅ CHO → products	6.4 × 10 ⁻¹⁵	± 0.2			
74	NO ₃ + CH ₃ C(O)CH ₃ → HNO ₃ + CH ₃ COCH ₂	<3 × 10 ⁻¹⁷				
75	NO ₃ + C ₃ H ₇ CHO → products	1.1 × 10 ⁻¹⁴	± 0.15	1.7 × 10 ⁻¹² exp(-1500/T)	260–340	± 500
76	NO ₃ + (CH ₃) ₂ CHCHO → products					
77	NO ₃ + CH ₂ =C(CH ₃)CHO → products	3.4 × 10 ⁻¹⁵	± 0.15			
78	NO ₃ + CH ₃ C(O)CH=CH ₂ → products	<6.0 × 10 ⁻¹⁶				
79	NO ₃ + Pinonaldehyde → products	2.0 × 10 ⁻¹⁴	± 0.25			
80	NO ₃ + 3-methylfuran → products	1.9 × 10 ⁻¹¹	± 0.5			
81	NO ₃ + CH ₂ =C(CH ₃)C(O)OONO ₂ → products	1.6 × 10 ⁻¹⁶	± 0.7			
82	NO ₃ + CH ₃ OH → products	1.3 × 10 ⁻¹⁶	± 0.5	9.4 × 10 ⁻¹³ exp(-2650/T)	250–370	± 700
83	NO ₃ + C ₂ H ₅ OH → products	<2 × 10 ⁻¹⁵				
84	NO ₃ + CH ₃ CH(OH)CH ₃ → products	1.4 × 10 ⁻¹⁵	± 0.3			
85	NO ₃ + CH ₃ CH(OH)CH ₂ CH ₃ → products	2.0 × 10 ⁻¹⁵	± 0.3			
86	NO ₃ + (CH ₃) ₂ C(OH)CH=CH ₂ → products	1.2 × 10 ⁻¹⁴	± 0.2	4.6 × 10 ⁻¹⁴ exp(-400/T)	260–400	± 200

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reaction number	Reaction	k_{298} cm ³ molecule ⁻¹ s ⁻¹	$\Delta \log k_{298}^a$	Temp. dependence of k /cm ³ molecule ⁻¹ s ⁻¹	Temp. range/K	$\Delta(E/R)/K^a$
Carbon Radical Reactions – based on data sheets in Appendix 4						
87	CH ₃ + O ₂ + M → CH ₃ O ₂ + M	1.0 × 10 ⁻³⁰ [N ₂]	(<i>k</i> ₀)	± 0.2	1.0 × 10 ⁻³⁰ (<i>T</i> /300) ^{-3.3} [N ₂]	200–300 $\Delta n = \pm 1$
		1.8 × 10 ⁻¹²	(<i>k</i> _∞)	± 0.3	1.8 × 10 ⁻¹² (<i>T</i> /300) ^{1.1}	200–300 $\Delta n = \pm 1$
		<i>F</i> _c = 0.27				
88	CH ₃ + O ₃ → products	2.3 × 10 ⁻¹²		± 0.3	4.7 × 10 ⁻¹² exp(-210/T)	240–400 ± 200
89	C ₂ H ₅ + O ₂ → C ₂ H ₄ + HO ₂	3.8 × 10 ⁻¹⁵	(1 bar air)	± 0.5		
		1.9 × 10 ⁻¹⁴	(0.133 bar air)	± 0.5		
90	C ₂ H ₅ + O ₂ + M → C ₂ H ₅ O ₂ + M	5.9 × 10 ⁻²⁹ [N ₂]	(<i>k</i> ₀)	± 0.3	5.9 × 10 ⁻²⁹ (<i>T</i> /300) ^{-3.8} [N ₂]	200–300 $\Delta n = \pm 1$
		7.8 × 10 ⁻¹²	(<i>k</i> _∞)	± 0.2	7.8 × 10 ⁻¹²	200–300
		<i>F</i> _c = 0.58exp(- <i>T</i> /1250)			200–300	
		+ 0.42exp(- <i>T</i> /183)			200–300	
91	<i>n</i> -C ₃ H ₇ + O ₂ + M → <i>n</i> -C ₃ H ₇ O ₂ + M	8.0 × 10 ⁻¹²	(<i>k</i> _∞)	± 0.2	8.0 × 10 ⁻¹²	200–300
92	<i>i</i> -C ₃ H ₇ + O ₂ + M → <i>i</i> -C ₃ H ₇ O ₂ + M	1.1 × 10 ⁻¹¹	(<i>k</i> _∞)	± 0.3	1.1 × 10 ⁻¹¹	200–300 $\Delta \log k = \pm 0.3$
93	1-C ₄ H ₉ + O ₂ + M → 1-C ₄ H ₉ O ₂ + M	7.5 × 10 ⁻¹²	(<i>k</i> _∞)	± 0.5		
94	2-C ₄ H ₉ + O ₂ + M → 2-C ₄ H ₉ O ₂ + M	1.7 × 10 ⁻¹¹	(<i>k</i> _∞)	± 0.5		
95	CH ₃ C(O)CH ₂ + O ₂ + M → CH ₃ C(O)CH ₂ O ₂ + M	1.5 × 10 ⁻¹²	(<i>k</i> _∞)	± 0.5		
96	HCO + O ₂ → CO + HO ₂	5.1 × 10 ⁻¹²		± 0.15	5.1 × 10 ⁻¹²	200–300 ± 150
97	CH ₃ CO + O ₂ + M → CH ₃ C(O)O ₂ + M	5.1 × 10 ⁻¹²	(<i>k</i> _∞)	± 0.2	5.1 × 10 ⁻¹²	220–300
98	CH ₂ OH + O ₂ → HCHO + HO ₂	9.7 × 10 ⁻¹²		± 0.12		
99	CH ₃ CHOH + O ₂ → CH ₃ CHO + HO ₂	1.9 × 10 ⁻¹¹		± 0.3		
100	CH ₂ CH ₂ OH + O ₂ → products	3.0 × 10 ⁻¹²		± 0.3		

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reaction number	Reaction	k_{298} cm ³ molecule ⁻¹ s ⁻¹	$\Delta \log k_{298}^a$	Temp. dependence of $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp. range/K	$\Delta(E/R)/K^a$
RO Radical Reactions – based on data sheets in Appendix 5						
101	CH ₃ O + O ₂ → HCHO + HO ₂	1.9 × 10 ⁻¹⁵	±0.2	7.2 × 10 ⁻¹⁴ exp(-1080/T)	290–610	±300
102	C ₂ H ₅ O + O ₂ → CH ₃ CHO + HO ₂	8.1 × 10 ⁻¹⁵	±0.2	2.4 × 10 ⁻¹⁴ exp(-325/T)	295–355	±300
103	1-C ₃ H ₇ O + O ₂ → C ₂ H ₅ CHO + HO ₂	1.0 × 10 ⁻¹⁴	±0.2	2.6 × 10 ⁻¹⁴ exp(-253/T)	220–380	±500
104	2-C ₃ H ₇ O + O ₂ → CH ₃ COCH ₃ + HO ₂	7.0 × 10 ⁻¹⁵	±0.2	1.5 × 10 ⁻¹⁴ exp(-230/T)	210–370	±200
105	CH ₃ CH ₂ CH ₂ CH ₂ O + O ₂ → CH ₃ CH ₂ CH ₂ CHO + HO ₂	1.4 × 10 ⁻¹⁴	±0.3			
106	CH ₃ CH ₂ CH ₂ CH ₂ O + M → CH ₃ CH ₂ CH ₂ CH ₂ OH + M	2.3 × 10 ⁵	(s ⁻¹)(1 bar) ±0.5	2.4 × 10 ¹¹ exp(-4130/T)(1 bar)	295–400	±1000
107	CH ₃ OCH ₂ O + O ₂ → CH ₃ OCHO + HO ₂ CH ₃ OCH ₂ O + M → CH ₃ OCHO + H + M	see data sheet				
108	CH ₃ C(O)CH ₂ O + O ₂ → CH ₃ C(O)CHO + HO ₂ CH ₃ C(O)CH ₂ O + M → CH ₃ CO + HCHO + M	see data sheet				
109	CH ₃ CH(O)CH ₂ CH ₃ + M → CH ₃ CHO + C ₂ H ₅ + M	2.0 × 10 ⁴	(s ⁻¹)(1 bar) ±0.3	2 × 10 ¹⁴ exp(-6860/T)(1 bar)	300–500	±500
110	CH ₃ O + NO + M → CH ₃ ONO + M	2.6 × 10 ⁻²⁹ [N ₂] 3.3 × 10 ⁻¹¹	(k ₀) ±0.1 (k _∞) ±0.5	2.6 × 10 ⁻²⁹ (T/300) ^{-2.6} [N ₂] 3.3 × 10 ⁻¹¹ (T/300) ^{-0.6} F _c = exp(-7/900)	200–400	Δn = ±0.5 Δn = ±0.5
	CH ₃ O + NO → HCHO + HNO	see data sheet				
111	C ₂ H ₅ O + NO + M → C ₂ H ₅ ONO + M	2.2 × 10 ⁻²⁸ [N ₂] 4.4 × 10 ⁻¹¹ F _c = 0.6	(k ₀) ±0.3 (k _∞) ±0.3	4.4 × 10 ⁻¹¹	200–400	
	C ₂ H ₅ O + NO → CH ₃ CHO + HNO	see data sheet				
112	<i>n</i> -C ₃ H ₇ O + NO + M → <i>n</i> -C ₃ H ₇ ONO + M	3.8 × 10 ⁻¹¹	(k _∞) ±0.3			
113	<i>i</i> -C ₃ H ₇ O + NO + M → <i>i</i> -C ₃ H ₇ ONO + M	3.4 × 10 ⁻¹¹	(k _∞) ±0.3			

6305

reaction number	Reaction	k_{298} cm ³ molecule ⁻¹ s ⁻¹	$\Delta \log k_{298}^a$	Temp. dependence of $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp. range/K	$\Delta(E/R)/K^a$
114	(CH ₃) ₃ CO + NO + M → (CH ₃) ₃ CONO + M	2.6 × 10 ⁻¹¹	±0.3	2.6 × 10 ⁻¹¹ (T/300) ^{-1.4}	200–400	Δn = ±0.5
115	2-C ₄ H ₉ O + NO + M → 2-C ₄ H ₉ ONO + M	2.5 × 10 ⁻¹¹	±0.5			
116	CH ₃ O + NO ₂ + M → CH ₃ ONO ₂ + M	8.1 × 10 ⁻²⁹ [N ₂] 2.1 × 10 ⁻¹¹ F _c = 0.44	(k ₀) ±0.3 (k _∞) ±0.3	8.1 × 10 ⁻²⁹ (T/300) ^{-4.5} [N ₂] 2.1 × 10 ⁻¹¹	200–400	Δn = ±1 Δn = ±0.5
	CH ₃ O + NO ₂ → HCHO + HONO	see data sheet				
117	C ₂ H ₅ O + NO ₂ + M → C ₂ H ₅ ONO ₂ + M C ₂ H ₅ O + NO ₂ → CH ₃ CHO + HONO	2.8 × 10 ⁻¹¹ see data sheet	(k _∞) ±0.3	2.8 × 10 ⁻¹¹	200–300	Δn = ±0.5
118	1-C ₃ H ₇ O + NO ₂ + M → 1-C ₃ H ₇ ONO ₂ + M	3.6 × 10 ⁻¹¹	(k _∞) ±0.3			
119	2-C ₃ H ₇ O + NO ₂ + M → 2-C ₃ H ₇ ONO ₂ + M	3.4 × 10 ⁻¹¹	(k _∞) ±0.2	3.4 × 10 ⁻¹¹	200–300	

RO₂ Reactions – based on data sheets in Appendix 6

120	CH ₃ O ₂ + NO → CH ₃ O + NO ₂	7.7 × 10 ⁻¹²	±0.05	2.95 × 10 ⁻¹² exp(285/T)	200–430	±100
121	C ₂ H ₅ O ₂ + NO → products	9.2 × 10 ⁻¹²	±0.1	2.6 × 10 ⁻¹² exp(380/T)	200–410	±50
122	HOCH ₂ CH ₂ O ₂ + NO → HOCH ₂ CH ₂ O + NO ₂	9 × 10 ⁻¹²	±0.5			
123	<i>n</i> -C ₃ H ₇ O ₂ + NO → products	9.4 × 10 ⁻¹²	±0.2	2.9 × 10 ⁻¹² exp(350/T)	200–410	±100
124	<i>i</i> -C ₃ H ₇ O ₂ + NO → products	9.0 × 10 ⁻¹²	±0.1	2.7 × 10 ⁻¹² exp(360/T)	200–410	±100
125	CH ₃ C(O)CH ₂ O ₂ + NO → CH ₃ C(O)CH ₂ O + NO ₂	8 × 10 ⁻¹²	±0.3			
126	CH ₃ C(O)O ₂ + NO → CH ₃ C(O)O + NO ₂	2.0 × 10 ⁻¹¹	±0.15	7.5 × 10 ⁻¹² exp(290/T)	200–350	±250
127	C ₂ H ₅ C(O)O ₂ + NO → C ₂ H ₅ C(O)O + NO ₂	2.1 × 10 ⁻¹¹	±0.15	6.7 × 10 ⁻¹² exp(340/T)	220–410	±200

6306

reaction number	Reaction	k_{298} cm ³ molecule ⁻¹ s ⁻¹	$\Delta \log k_{298}^a$	Temp. dependence of $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp. range/K	$\Delta(E/R)/K^a$
128	$\text{CH}_3\text{O}_2 + \text{NO}_2 + \text{M} \rightarrow \text{CH}_3\text{O}_2\text{NO}_2 + \text{M}$	$2.5 \times 10^{-30}[\text{N}_2]$ 1.8×10^{-11} $F_c = 0.36$	(k_0) ± 0.3 (k_∞) ± 0.3	$2.5 \times 10^{-30}(T/300)^{-5.5}[\text{N}_2]$ 1.8×10^{-11}	250–350 250–350	$\Delta n \pm 1$ $\Delta n \pm 0.5$
129	$\text{CH}_3\text{O}_2\text{NO}_2 + \text{M} \rightarrow \text{CH}_3\text{O}_2 + \text{NO}_2 + \text{M}$	$6.8 \times 10^{-19}[\text{N}_2]$ 4.5 $F_c = 0.6$	(k_0/s^{-1}) ± 0.3 (k_∞/s^{-1}) ± 0.3	$9 \times 10^{-5} \exp(-9690/T)[\text{N}_2]$ $1.1 \times 10^{16} \exp(-10560/T)$	250–300 250–300	± 500 ± 500
130	$\text{C}_2\text{H}_5\text{O}_2 + \text{NO}_2 + \text{M} \rightarrow \text{C}_2\text{H}_5\text{O}_2\text{NO}_2 + \text{M}$	$1.3 \times 10^{-29}[\text{N}_2]$ 8.8×10^{-12} $F_c = 0.31$	(k_0) ± 0.3 (k_∞) ± 0.3	$1.3 \times 10^{-29}(T/300)^{-6.2}[\text{N}_2]$ 8.8×10^{-12}	200–300 200–300 200–300	$\Delta n = \pm 1$ $\Delta \log k = \pm 0.3$
131	$\text{C}_2\text{H}_5\text{O}_2\text{NO}_2 + \text{M} \rightarrow \text{C}_2\text{H}_5\text{O}_2 + \text{NO}_2 + \text{M}$	$1.4 \times 10^{-17}[\text{N}_2]$ 5.4 $F_c = 0.31$	(k_0/s^{-1}) ± 0.5 (k_∞/s^{-1}) ± 0.5	$4.8 \times 10^{-4} \exp(-9285/T)[\text{N}_2]$ $8.8 \times 10^{15} \exp(-10440/T)$	250–300 250–300 250–300	± 1000 ± 1000
132	$\text{CH}_3\text{C(O)O}_2 + \text{NO}_2 + \text{M} \rightarrow \text{CH}_3\text{C(O)O}_2\text{NO}_2 + \text{M}$	$2.7 \times 10^{-28}[\text{N}_2]$ 1.2×10^{-11} $F_c = 0.3$	(k_0) ± 0.4 (k_∞) ± 0.2	$2.7 \times 10^{-28}(T/300)^{-7.1}[\text{N}_2]$ $1.2 \times 10^{-11}(T/300)^{-0.9}$	250–300 250–300	$\Delta n = \pm 2$ $\Delta n = \pm 1$
133	$\text{CH}_3\text{C(O)O}_2\text{NO}_2 + \text{M} \rightarrow \text{CH}_3\text{C(O)O}_2 + \text{NO}_2 + \text{M}$	$1.1 \times 10^{-20}[\text{N}_2]$ 3.8×10^{-4} $F_c = 0.3$	(k_0/s^{-1}) ± 0.5 (k_∞/s^{-1}) ± 0.3	$4.9 \times 10^{-3} \exp(-12100/T)[\text{N}_2]$ $5.4 \times 10^{16} \exp(-13830/T)$	300–330 300–330	± 1000 ± 300
134	$\text{C}_2\text{H}_5\text{C(O)O}_2\text{NO}_2 + \text{M} \rightarrow \text{C}_2\text{H}_5\text{C(O)O}_2 + \text{NO}_2 + \text{M}$	$6.2 \times 10^{-20}[\text{N}_2]$ 4.0×10^{-4} $F_c = 0.36$	(k_0/s^{-1}) ± 0.5 (k_∞/s^{-1}) ± 0.2	$1.7 \times 10^{-3} \exp(-11280/T)[\text{N}_2]$ $8.3 \times 10^{16} \exp(-13940/T)$	290–320 290–320	± 2000 ± 1000
135	$\text{CH}_3\text{C(O)CH}_2\text{O}_2\text{NO}_2 + \text{M} \rightarrow$ $\text{CH}_3\text{C(O)CH}_2\text{O}_2 + \text{NO}_2 + \text{M}$			$1.0 \times 10^{16} \exp(-10630/T)(1 \text{ bar})$	240–260	± 2000
136	$\text{CH}_2=\text{C}(\text{CH}_3)\text{C(O)OONO}_2 + \text{M} \rightarrow$ $\text{CH}_2=\text{C}(\text{CH}_3)\text{C(O)OO} + \text{NO}_2$	3.5×10^{-4}	$(s^{-1})(1 \text{ bar})$ ± 0.3	$1.6 \times 10^{16} \exp(-13500/T)(1 \text{ bar})$	290–330	± 1000
137	$\text{H}_3\text{O}_2 + \text{NO}_3 \rightarrow \text{CH}_3\text{O} + \text{NO}_2 + \text{O}_2$	1.3×10^{-12}	± 0.3			

6307

reaction number	Reaction	k_{298} cm ³ molecule ⁻¹ s ⁻¹	$\Delta \log k_{298}^a$	Temp. dependence of $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp. range/K	$\Delta(E/R)/K^a$
138	$\text{C}_2\text{H}_5\text{O}_2 + \text{NO}_3 \rightarrow \text{C}_2\text{H}_5\text{O} + \text{NO}_2 + \text{O}_2$	2.3×10^{-12}	± 0.2			
139	$\text{CH}_3\text{O}_2 + \text{CH}_3\text{O}_2 \rightarrow \text{CH}_3\text{OH} + \text{HCHO} + \text{O}_2$ $\rightarrow 2 \text{CH}_3\text{O} + \text{O}_2$ $\rightarrow \text{CH}_3\text{OOCCH}_3 + \text{O}_2$	1.3×10^{-13}	± 0.15	$7.4 \times 10^{-13} \exp(-520/T)$	220–330	± 300
140	overall $\text{CH}_3\text{O}_2 + \text{CH}_3\text{C(O)O}_2$ $\rightarrow \text{CH}_3\text{O} + \text{CH}_3\text{CO}_2 + \text{O}_2$ $\rightarrow \text{CH}_3\text{COOH} + \text{HCHO} + \text{O}_2$	3.5×10^{-13} 9.9×10^{-12} 1.1×10^{-12} 1.1×10^{-11}	± 0.12	$1.0 \times 10^{-13} \exp(365/T)$	200–400	± 200
141	$\text{CH}_3\text{O}_2 + \text{CH}_3\text{C(O)CH}_2\text{O}_2$ $\rightarrow \text{CH}_3\text{OH} + \text{CH}_3\text{C(O)CHO} + \text{O}_2$ $\rightarrow \text{HCHO} + \text{CH}_3\text{C(O)CH}_2\text{OH} + \text{O}_2$ $\rightarrow \text{CH}_3\text{O} + \text{CH}_3\text{C(O)CH}_2\text{O} + \text{O}_2$	1.9×10^{-12} 7.6×10^{-13} 1.1×10^{-12} 3.8×10^{-12}	± 0.15	$2.0 \times 10^{-12} \exp(500/T)$	200–350	± 250
142	overall $\text{HOCH}_2\text{O}_2 + \text{HOCH}_2\text{O}_2$ $\rightarrow \text{HC(O)OH} + \text{CH}_2(\text{OH})_2 + \text{O}_2$ $\rightarrow 2 \text{HOCH}_2\text{O} + \text{O}_2$	7.0×10^{-13} 5.5×10^{-12}	± 0.3 ± 0.3	$5.7 \times 10^{-14} \exp(750/T)$	270–330	± 750
143	$\text{C}_2\text{H}_5\text{O}_2 + \text{C}_2\text{H}_5\text{O}_2 \rightarrow \text{C}_2\text{H}_5\text{OH} + \text{CH}_3\text{CHO} + \text{O}_2$ $\rightarrow 2 \text{C}_2\text{H}_5\text{OH} + \text{O}_2$	2.4×10^{-14} 4.0×10^{-14} 6.4×10^{-14}	± 0.12	6.4×10^{-14}	250–450	$\begin{matrix} +300 \\ -100 \end{matrix}$
144	overall $\text{C}_2\text{H}_5\text{O}_2 + \text{CH}_3\text{C(O)O}_2$ $\rightarrow \text{C}_2\text{H}_5\text{O} + \text{CH}_3\text{C(O)O} + \text{O}_2$ $\rightarrow \text{CH}_3\text{CHO} + \text{CH}_3\text{C(O)OH} + \text{O}_2$	1.6×10^{-11}	± 0.5	$4.4 \times 10^{-13} \exp(1070/T)$	220–440	± 500

6308

reaction number	Reaction	k_{298} cm ³ molecule ⁻¹ s ⁻¹	$\Delta \log k_{298}^a$	Temp. dependence of k/cm^3 molecule ⁻¹ s ⁻¹	Temp. range/K	$\Delta(E/R)/K^a$
145	CH ₃ OCH ₂ O ₂ + CH ₃ OCH ₂ O ₂ → CH ₃ OCH ₂ OH + CH ₃ OCHO + O ₂ → 2 CH ₃ OCH ₂ O + O ₂	1.4 × 10 ⁻¹²				
	overall	2.1 × 10 ⁻¹²	± 0.3			
146	CH ₃ C(O)O ₂ + CH ₃ C(O)O ₂ → 2 CH ₃ C(O)O + O ₂	1.6 × 10 ⁻¹¹	± 0.1	2.9 × 10 ⁻¹² exp(500/T)	200–370	± 200
147	CH ₃ CO ₃ + CH ₃ C(O)CH ₂ O ₂ → CH ₃ C(O)OH + CH ₃ C(O)CHO + O ₂ → CH ₃ CO ₂ + CH ₃ C(O)CH ₂ O + O ₂	2.5 × 10 ⁻¹²				
	overall	5.0 × 10 ⁻¹²	± 0.3			
148	HOCH ₂ CH ₂ O ₂ + HOCH ₂ CH ₂ O ₂ → HOCH ₂ CH ₂ OH + HOCH ₂ CHO + O ₂ → 2 HOCH ₂ CH ₂ O + O ₂	1.1 × 10 ⁻¹² 1.1 × 10 ⁻¹²				
	overall	2.2 × 10 ⁻¹²	± 0.1	7.8 × 10 ⁻¹⁴ exp(1000/T)	250–450	± 300
149	<i>n</i> -C ₃ H ₇ O ₂ + <i>n</i> -C ₃ H ₇ O ₂ → <i>n</i> -C ₃ H ₇ OH + C ₂ H ₅ CHO + O ₂ → 2 <i>n</i> -C ₃ H ₇ O + O ₂					
	overall	3.0 × 10 ⁻¹³	± 0.5			
150	<i>i</i> -C ₃ H ₇ O ₂ + <i>i</i> -C ₃ H ₇ O ₂ → <i>i</i> -C ₃ H ₇ OH + CH ₃ C(O)CH ₃ + O ₂ → 2 <i>i</i> -C ₃ H ₇ O + O ₂	4.4 × 10 ⁻¹⁶ 5.6 × 10 ⁻¹⁶				
	overall	1.0 × 10 ⁻¹⁵	± 0.3	1.6 × 10 ⁻¹² exp(-2200/T)	300–400	± 300
151	CH ₃ C(O)CH ₂ O ₂ + CH ₃ C(O)CH ₂ O ₂ → CH ₃ C(O)CH ₂ OH + CH ₃ C(O)CHO + O ₂ → 2 CH ₃ C(O)CH ₂ O + O ₂	2.0 × 10 ⁻¹² 6.0 × 10 ⁻¹²				
	overall	8.0 × 10 ⁻¹²	± 0.3			

6309

reaction number	Reaction	k_{298} cm ³ molecule ⁻¹ s ⁻¹	$\Delta \log k_{298}^a$	Temp. dependence of k/cm^3 molecule ⁻¹ s ⁻¹	Temp. range/K	$\Delta(E/R)/K^a$
152	RCHO + O ₃ → RCHO + 2O ₂ RCHO + H ₂ O → products RCHO + CO → products RCHO + HCHO → products RCHO + C ₂ H ₄ → products RCHO + NO → RCHO + NO ₂ RCHO + NO ₂ → RCHO + NO ₃ RCHO + SO ₂ → products RCHO + HC(O)OH → products RCHO + CH ₃ CHO → secondary ozonide RCHO → products RRCOO → products	No recommendations (see data sheet)				

O₃ Reactions – based on data sheets in Appendix 1

153	O ₃ + alkene → HO + products	see data sheet				
154	O ₃ + C ₂ H ₂ → products	1.0 × 10 ⁻²⁰	± 1.0			
155	O ₃ + C ₂ H ₄ → products	1.6 × 10 ⁻¹⁸	± 0.1	9.1 × 10 ⁻¹⁵ exp(-2580/T)	180–360	± 100
156	O ₃ + C ₃ H ₆ → products	1.0 × 10 ⁻¹⁷	± 0.1	5.5 × 10 ⁻¹⁵ exp(-1880/T)	230–370	± 200
157	O ₃ + CH ₂ =C(CH ₃)CH=CH ₂ → products	1.27 × 10 ⁻¹⁷	± 0.1	1.03 × 10 ⁻¹⁴ exp(-1995/T)	240–360	± 200
158	O ₃ + α -Pinene → products	9.0 × 10 ⁻¹⁷	± 0.2	6.3 × 10 ⁻¹⁶ exp(-580/T)	270–370	± 300
159	O ₃ + CH ₂ =C(CH ₃)CHO → products	1.2 × 10 ⁻¹⁸	± 0.2	1.4 × 10 ⁻¹⁵ exp(-2100/T)	240–330	± 300
160	O ₃ + CH ₂ =CHC(O)CH ₃ → products	5.2 × 10 ⁻¹⁸	± 0.2	8.5 × 10 ⁻¹⁶ exp(-1520/T)	240–330	± 200
161	O ₃ + 3-methylfuran → products	2.0 × 10 ⁻¹⁷	± 0.3			
162	O ₃ + CH ₂ =C(CH ₃)C(O)OONO ₂ → products	8.2 × 10 ⁻¹⁸	± 0.3			
163	O ₃ + Pinonaldehyde → products	< 2 × 10 ⁻²⁰				
164	O ₃ + (CH ₃) ₂ C(OH)CH=CH ₂ → products	1.0 × 10 ⁻¹⁷	± 0.2			

6310

reaction number	Reaction	k_{298} cm ³ molecule ⁻¹ s ⁻¹	$\Delta \log k_{298}^a$	Temp. dependence of k /cm ³ molecule ⁻¹ s ⁻¹	Temp. range/K	$\Delta(E/R)/K^a$
Halogen atom Reactions – based on data sheets in Appendix 7						
165	F + CH ₄ → HF + CH ₃	6.3 × 10 ⁻¹¹	± 0.15	1.3 × 10 ⁻¹⁰ exp(-215/T)	180–410	± 200
166	Cl + CH ₄ → HCl + CH ₃	1.0 × 10 ⁻¹³	± 0.06	6.6 × 10 ⁻¹² exp(-1240/T)	200–300	± 200
167	Cl + C ₂ H ₂ + M → C ₂ H ₂ Cl + M	6.1 × 10 ⁻³⁰ [N ₂] 2.0 × 10 ⁻¹⁰	(k ₀) ± 0.3 (k _∞) ± 0.3	6.1 × 10 ⁻³⁰ (T/300) ⁻³ [N ₂] 2.0 × 10 ⁻¹⁰	200–300 200–400	Δn = ± 1 Δn = ± 1
168	Cl + C ₂ H ₄ + M → C ₂ H ₄ Cl + M	1.85 × 10 ⁻²⁹ [air] 6 × 10 ⁻¹⁰ [air]	(k ₀) ± 0.5 (k _∞) ± 0.3	1.85 × 10 ⁻²⁹ (T/300) ^{-3.3} [air] 6 × 10 ⁻¹⁰	250–300 250–300	Δn = ± 1 Δn = ± 1
169	Cl + C ₂ H ₆ → HCl + C ₂ H ₅	5.9 × 10 ⁻¹¹	± 0.06	8.3 × 10 ⁻¹¹ exp(-100/T)	220–600	± 100
170	Cl + C ₃ H ₈ + M → C ₃ H ₇ Cl + M	4.0 × 10 ⁻²⁸ [N ₂] 2.8 × 10 ⁻¹⁰	(k ₀) ± 0.5 (k _∞) ± 0.3			
171	Cl + C ₃ H ₈ → HCl + C ₃ H ₇	1.4 × 10 ⁻¹⁰	± 0.06	1.4 × 10 ⁻¹⁰	200–700	± 100
172	Cl + n-C ₄ H ₁₀ → HCl + C ₄ H ₉	2.05 × 10 ⁻¹⁰	± 0.06	2.05 × 10 ⁻¹⁰	290–600	± 100
173	Cl + HCHO → HCl + HCO	7.3 × 10 ⁻¹¹	± 0.06	8.2 × 10 ⁻¹¹ exp(-34/T)	200–500	± 100
174	Cl + CH ₃ CHO → HCl + CH ₃ CO	7.9 × 10 ⁻¹¹	± 0.1	7.9 × 10 ⁻¹¹	210–340	± 300
175	Cl + C ₂ H ₅ CHO → products	1.3 × 10 ⁻¹⁰	± 0.2			
176	Cl + CH ₃ C(O)CH ₃ → HCl + CH ₃ C(O)CH ₂	2.5 × 10 ⁻¹²	± 0.15	3.9 × 10 ⁻¹¹ exp(-815/T)	215–300	± 300
177	Cl + CH ₃ C(O)C ₂ H ₅ → products	3.8 × 10 ⁻¹¹	± 0.15			
178	Cl + CH ₃ OH → HCl + CH ₂ OH	5.5 × 10 ⁻¹¹	± 0.1	5.5 × 10 ⁻¹¹	200–500	± 200
179	Cl + C ₂ H ₅ OH → products	9.6 × 10 ⁻¹¹	± 0.1	8.2 × 10 ⁻¹¹ exp(45/T)	295–600	± 100

6311

reaction number	Reaction	k_{298} cm ³ molecule ⁻¹ s ⁻¹	$\Delta \log k_{298}^a$	Temp. dependence of k /cm ³ molecule ⁻¹ s ⁻¹	Temp. range/K	$\Delta(E/R)/K^a$
180	Cl + n-C ₃ H ₇ OH → products	1.6 × 10 ⁻¹⁰	± 0.15	2.5 × 10 ⁻¹⁰ exp(-130/T)	270–350	± 100
181	Cl + i-C ₃ H ₇ OH → products	8.8 × 10 ⁻¹¹	± 0.3			
182	Cl + CH ₃ OOH → products	5.9 × 10 ⁻¹¹	± 0.5			
183	Cl + HC(O)OH → products	1.9 × 10 ⁻¹³	± 0.15			
184	Cl + CH ₃ C(O)OH → products	2.8 × 10 ⁻¹⁴	± 0.3			
185	Cl + CH ₃ ONO ₂ → products	2.4 × 10 ⁻¹³	± 0.15			
186	Cl + C ₂ H ₅ ONO ₂ → products	4.7 × 10 ⁻¹²	± 0.2			
187	Cl + n-C ₃ H ₇ ONO ₂ → products	2.7 × 10 ⁻¹¹	± 0.2			
188	Cl + i-C ₃ H ₇ ONO ₂ → products	5.8 × 10 ⁻¹²	± 0.3			
189	Cl + 1-C ₄ H ₉ ONO ₂ → products	8.5 × 10 ⁻¹¹	± 0.3			
190	Cl + CH ₃ C(O)OONO ₂ → products	< 2 × 10 ⁻¹⁴				
191	Cl + CH ₃ CN → products	1.2 × 10 ⁻¹⁴	± 0.3	1.6 × 10 ⁻¹¹ exp(-2140/T)	270–350	± 300
192	Br + C ₂ H ₂ → products	2.6 × 10 ⁻¹⁴	(1 bar air) ± 0.2	6.35 × 10 ⁻¹⁵ exp(440/T)	230–300	± 200
193	Br + C ₂ H ₄ → products	1.3 × 10 ⁻¹³	(1 bar air) ± 0.15	2.80 × 10 ⁻¹³ exp(224/T)B/ (B + 8.5 × 10 ¹² exp(-3200/T)) B = 7.5 × 10 ⁻¹² [O ₂]s ⁻¹	240–300	
194	Br + C ₃ H ₆ → products	3.6 × 10 ⁻¹²	(1 bar air) ± 0.2			
195	Br + HCHO → HBr + HCO	1.1 × 10 ⁻¹²	± 0.15	7.7 × 10 ⁻¹² exp(-580/T)	220–300	± 200
196	Br + CH ₃ CHO → HBr + CH ₃ CO	3.9 × 10 ⁻¹²	± 0.2	1.8 × 10 ⁻¹¹ exp(-460/T)	250–400	± 200

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reaction number	Reaction	k_{298} cm ³ molecule ⁻¹ s ⁻¹	$\Delta \log k_{298}^a$	Temp. dependence of $k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp. range/K	$\Delta(E/R)/\text{K}^a$
Data for the following Photochemical Reactions are based on data sheets in Appendix 8						
197	HCHO + hv → products					
198	CH ₃ CHO + hv → products					
199	C ₂ H ₅ CHO + hv → products					
200	pinonaldehyde ^a + hv → products					
201	(CHO) ₂ + hv → products					
202	HOCH ₂ CHO + hv → products					
203	CH ₃ C(O)CHO + hv → products					
204	CH ₃ C(O)CH ₃ + hv → products					
205	CH ₃ C(O)C ₂ H ₅ + hv → products					
206	CH ₂ =C(CH ₃)CHO + hv → products					
207	CH ₃ C(O)CH=CH ₂ + hv → products					
208	<i>n</i> -C ₃ H ₇ CHO + hv → products					
209	CH ₃ OOH + hv → products					
210	HOCH ₂ OOH + hv → products					
211	CH ₃ ONO ₂ + hv → products					
212	C ₂ H ₅ ONO ₂ + hv → products					
213	<i>n</i> -C ₃ H ₇ ONO ₂ + hv → products					
214	<i>i</i> -C ₃ H ₇ ONO ₂ + hv → products					
215	<i>i</i> -C ₄ H ₉ ONO ₂ + hv → products					
216	2-C ₄ H ₉ ONO ₂ + hv → products					
217	CH ₃ O ₂ NO ₂ + hv → products					
218	CH ₃ C(O)OONO ₂ + hv → products					

^aThe cited uncertainty is an expanded uncertainty corresponding approximately to a 95% confidence limit.

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3 Guide to the data sheets

The data sheets are principally of two types: (i) those for individual thermal reactions and (ii) those for the individual photochemical reactions.

3.1 Thermal reactions

- 5 The data sheets begin with a statement of the reactions including all pathways which are considered feasible. This is followed by the corresponding enthalpy changes at 298 K, calculated from the enthalpies of formation summarized in the Thermodynamics Data summary.

- The available kinetic data on the reactions are summarized under two headings: (i) Absolute Rate Coefficients, and (ii) Relative Rate Coefficients. Under these headings, we include new data which have been published since the last published IUPAC evaluation as well as the data used in deriving the preferred values. Under both of the headings above, the data are presented as absolute rate coefficients. If the temperature coefficient has been measured, the results are given in a temperature dependent form over a stated temperature range. For bimolecular reactions, the temperature dependence is usually expressed in the normal Arrhenius form, $k = A \exp(-B/T)$, where $B = E/R$. For a few bimolecular reactions, we have listed temperature dependences in the alternative form, $k = A'T^n$ or $CT^n \exp(-D/T)$, where the original authors have found this to give a better fit to the data. For pressure dependent combination and dissociation reactions, the non-Arrhenius temperature dependence is used. This is discussed more fully in a subsequent section of this Introduction.

- Single temperature data are presented as such and wherever possible the rate coefficient at, or close to, 298 K is quoted directly as measured by the original authors. This means that the listed rate coefficient at 298 K may differ slightly from that calculated from the Arrhenius parameters determined by the same authors. Rate coefficients at 298 K marked with an asterisk indicate that the value was calculated by extrapolation of a measured temperature range which did not include 298 K. The tables of data are

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supplemented by a series of comments summarizing the experimental details. The following list of abbreviations, relating to experimental techniques, is used in the Techniques and Comments sections:

- A – absorption
- 5 AS – absorption spectroscopy
- CCD – charge coupled detector
- CIMS – chemical ionization mass spectroscopy/spectrometric
- CL – chemiluminescence
- CRDS – cavity ring-down spectroscopy
- 10 DF – discharge flow
- EPR – electron paramagnetic resonance
- F – flow system
- FP – flash photolysis
- FTIR – Fourier transform infrared
- 15 FTS – Fourier transform spectroscopy
- GC – gas chromatography/gas chromatographic
- HPLC – high-performance liquid chromatography
- IR – infrared
- LIF – laser induced fluorescence
- 20 LMR – laser magnetic resonance
- LP – laser photolysis
- MM – molecular modulation
- MS – mass spectrometry/mass spectrometric
- P – steady state photolysis
- 25 PLP – pulsed laser photolysis
- PR – pulse radiolysis
- RA – resonance absorption
- RF – resonance fluorescence
- RR – relative rate

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- S – static system
- TDLS – tunable diode laser spectroscopy
- UV – ultraviolet
- UVA – ultraviolet absorption
- 5 VUVA – vacuum ultraviolet absorption

For measurements of relative rate coefficients, wherever possible the comments contain the actual measured ratio of rate coefficients together with the rate coefficient of the reference reaction used to calculate the absolute rate coefficient listed in the data table. The absolute value of the rate coefficient given in the table may be different from that reported by the original author owing to a different choice of rate coefficient of the reference reaction. Whenever possible the reference rate data are those preferred in the present evaluation.

The preferred rate coefficients are presented (i) at a temperature of 298 K and (ii) in temperature dependent form over a stated temperature range. This is followed by a statement of the uncertainty limits in $\log k$ at 298 K and the uncertainty limits either in (E/R) or in n , for the mean temperature in the range. Some comments on the assignment of uncertainties are given later in this introduction.

The “Comments on Preferred Values” describe how the selection was made and give any other relevant information. The extent of the comments depends upon the present state of our knowledge of the particular reaction in question. The data sheets are concluded with a list of the relevant references.

3.2 Conventions concerning rate coefficients

All of the reactions in the table are elementary processes. Thus the rate expression is derived from a statement of the reaction, e.g.



$$-\frac{1}{2} \frac{d[A]}{dt} = \frac{d[B]}{dt} = \frac{d[C]}{dt} = k[A]^2.$$

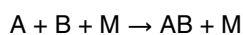
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Note that the stoichiometric coefficient for A, i.e. 2, appears in the denominator before the rate of change of [A] (which is equal to $2k[A]^2$) and as a power on the right-hand side.

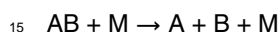
Representations of k as a function of temperature characterize simple “direct” bimolecular reactions. Sometimes it is found that k also depends on the pressure and the nature of the bath gas. This may be an indication of complex formation during the course of the bimolecular reaction, which is always the case in combination reactions. In the following sections the representations of k which are adopted in these cases are explained.

3.3 Treatment of combination and dissociation reactions

Unlike simple bimolecular reactions such as those considered in Sect. 1.2, combination reactions



and the reverse dissociation reactions



are composed of sequences of different types of physical and chemical elementary processes. Their rate coefficients reflect the more complicated sequential mechanism and depend on the temperature, T , and the nature and concentration of the third body, [M]. In this evaluation, the combination reactions are described by a formal second order rate law:

$$\frac{d[AB]}{dt} = k[A][B]$$

while dissociation reactions are described by a formal first-order rate law:

$$-\frac{d[AB]}{dt} = k[AB]$$

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In both cases, k depends on the temperature and on [M].

In order to rationalize the representations of the rate coefficients used in this evaluation, we first consider the Lindemann-Hinshelwood reaction scheme. The combination reactions follow an elementary mechanism of the form,



while the dissociation reactions are characterized by:



Assuming quasi-stationary concentrations for the highly excited unstable species AB^* (i.e. that $d[AB^*]/dt \sim 0$), it follows that the rate coefficient for the combination reaction is given by:

$$k = k_1 \left(\frac{k_2[M]}{k_{-1} + k_2[M]} \right)$$

while that for the dissociation reaction is given by:

$$k = k_{-2}[M] \left(\frac{k_{-1}}{k_{-1} + k_2[M]} \right)$$

In these equations the expressions before the parentheses represent the rate coefficients of the process initiating the reaction, whereas the expressions within the

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parentheses denote the fraction of reaction events which, after initiation, complete the reaction to products.

In the low pressure limit ($[M] \rightarrow 0$) the rate coefficients are proportional to $[M]$; in the high pressure limit ($[M] \rightarrow \infty$) they are independent of $[M]$. It is useful to express k in terms of the limiting low pressure and high pressure rate coefficients,

$$k_0 = \lim_{[M] \rightarrow 0} k([M]) \quad \text{and,} \quad k_\infty = \lim_{[M] \rightarrow \infty} k([M])$$

respectively. From this convention, the Lindemann-Hinshelwood equation is obtained

$$k = \frac{k_0 k_\infty}{k_0 + k_\infty}$$

It follows that for combination reactions, $k_0 = k_1 k_2 [M] / k_{-1}$ and $k_\infty = k_1$, while for dissociation reactions, $k_0 = k_{-2} [M]$ and $k_\infty = k_{-1} k_{-2} / k_2$. Since detailed balancing applies, the ratio of the rate coefficients for combination and dissociation at a fixed T and $[M]$ is given by the equilibrium constant $K_c = k_1 k_2 / k_{-1} k_{-2}$.

Starting from the high-pressure limit, the rate coefficients fall-off with decreasing third body concentration $[M]$ and the corresponding representation of k as a function of $[M]$ is termed the "falloff curve" of the reaction. In practice, the above Lindemann-Hinshelwood expressions do not suffice to characterize the falloff curves completely. Because of the multistep character of the collisional deactivation ($k_2[M]$) and activation ($k_{-2}[M]$) processes, and energy- and angular momentum-dependencies of the association (k_1) and dissociation (k_{-1}) steps, as well as other phenomena, the falloff expressions have to be modified. This can be done by including a broadening factor F to the Lindemann-Hinshelwood expression (Troe, 1979):

$$k = \frac{k_0 k_\infty}{k_0 + k_\infty} F = k_0 \left(\frac{1}{1 + \frac{k_0}{k_\infty}} \right) F = k_\infty \left(\frac{\frac{k_0}{k_\infty}}{1 + \frac{k_0}{k_\infty}} \right) F$$

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The broadening factor F depends on the ratio k_0/k_∞ , which is proportional to $[M]$, and can be used as a measure of "reduced pressure". The first factors on the right-hand side represent the Lindemann-Hinshelwood expression and the additional broadening factor F , at not too high temperatures, is approximately given by (Troe, 1979):

$$\log F \cong \frac{\log F_c}{1 + [\log(k_0/k_\infty)/N]^2}$$

where $\log = \log_{10}$ and $N = [0.75 - 1.27 \log F_c]$. In this way the three quantities k_0 , k_∞ , and F_c characterise the falloff curve for the present application.

The given approximate expression for the broadening factor F was obtained from statistical unimolecular rate theory in its simplest form (Troe, 1979). More rigorous representations require detailed information on the potential energy surfaces and on the collisional energy transfer step of the reaction. If this information is not available, one may assume typical behaviour and rely on the theoretical analysis given by Cobos and Troe (2003). For $T = 200 - 300$ K and the collider $M = N_2$ (with a collision efficiency $\beta_c \approx 0.3$), this treatment predicts $F_c \approx 0.49, 0.44, 0.39$, and 0.35 , if the reactants A and B in total have $r = 3, 4, 5$, or 6 rotational degrees of freedom, respectively (e.g. for the reaction $HO + NO_2$, one would have $r = 5$ and hence $F_c \approx 0.39$). It is also predicted that F_c , for the present applications, should be nearly temperature independent. Finally, more rigorous expressions for the broadening factors F are given in Cobos and Troe (2003) which, in general do not differ from the above formula by more than about 10 percent. Since the special properties of each reaction system may lead to some deviations from the given values of F_c , these should only be used for a first orientation. Larger deviations of experimentally fitted F_c -values from the given "standard values", however, may be an indication for inadequate falloff extrapolations to k_0 and k_∞ . In this case, the apparent values for F_c , k_0 , and k_∞ obtained by fitting still can provide a satisfactory representation of the considered experimental data, in spite of the fact that inadequate values of k_0 and k_∞ are obtained by extrapolation.

If a given falloff curve is fitted in different ways, changes in F_c require changes in the limiting k_0 and k_∞ values. For the purpose of this evaluation, this is irrelevant if

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the preferred k_0 and k_∞ are used consistently together with the preferred F_c values. If the selected F_c value is too large, the values of k_0 and k_∞ obtained by fitting the falloff expression to the experimental data are underestimated. If F_c is too small, k_0 and k_∞ are overestimated. However uncertainties in F_c influence the fitted k_0 and k_∞ in different ways. A simpler policy of fitting falloff was chosen by the NASA/JPL panel (Sander et al., 2003) in putting $F=0.6$ and $N=1$. This generally leads to different values of the fitted k_0 and k_∞ and their temperature dependencies than derived here, although experimental data over the range of atmospheric interest can generally be reproduced equally well. However the derived k_0 and k_∞ may differ from the true limiting rate coefficients and thus should be interpreted by theory only with caution.

In the present evaluation, we generally follow the experimentally fitted values for F_c , k_0 , and k_∞ , provided F_c does not differ too much from the values given above. If large deviations are encountered, the experimental data are re-evaluated using the given F_c -values given above.

Besides the energy-transfer mechanism, i.e. Reactions (1), (-1), and (2), a second mechanism appears to be relevant for some reactions considered here. This is the radical-complex (or chaperon) mechanism



which, in the low pressure range, leads to

$$k_0 = (k_3/k_{-3})k_4[M].$$

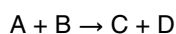
For some tri- and tetra-atomic adducts AB, this value of k_0 may exceed that from the energy-transfer mechanism and show stronger temperature dependencies. This mechanism may also influence high pressure experiments when k_0 from the radical-complex mechanism exceeds k_∞ from the energy-transfer mechanism (Oum et al., 6321

2003). In this case falloff over wide pressure ranges cannot be represented by contributions from the energy-transfer mechanism alone, in particular when measurements at pressures above about 10 bar are taken into consideration.

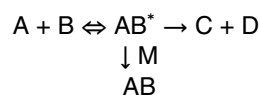
The dependence of k_0 and k_∞ on the temperature T is represented in the form $k \propto T^{-n}$ except for cases with an established energy barrier in the potential. We have used this form of temperature dependence because it usually gives a better fit to the data over a wider range of temperature than does the Arrhenius expression. It should be emphasised that the chosen form of the temperature dependence is often only adequate over limited temperature ranges such as 200–300 K. Obviously, the relevant values of n are different for k_0 and k_∞ . In this evaluation, values of k_0 are given for selected examples of third bodies M, and if possible for $M=N_2$, O_2 or air.

3.4 Treatment of complex-forming bimolecular reactions

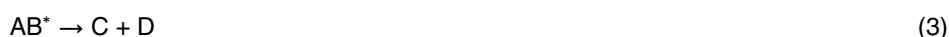
Bimolecular reactions may follow the “direct” pathway



and/or involve complex formation,



We designate the rate coefficients of the individual steps as in Sect. 1.3, above:



Assuming quasi-stationary concentrations of AB^* (i.e. $d[AB^*]/dt \sim 0$), a Lindemann-Hinshelwood type of analysis leads to,

$$\frac{d[AB]}{dt} = k_S[A][B]$$

$$\frac{d[C]}{dt} = k_D[A][B]$$

$$5 \quad \frac{d[A]}{dt} = (k_S + k_D)[A][B]$$

where

$$k_S = k_1 \left(\frac{k_2}{k_{-1} + k_2 + k_3} \right)$$

$$k_D = k_1 \left(\frac{k_3}{k_{-1} + k_2 + k_3} \right)$$

10 Note that since k_2 is proportional to $[M]$, k_S and k_D are dependent on the nature and concentration of the third body M , in addition to their temperature dependence. In reality, as for the combination and dissociation reactions, the given expressions for k_S and k_D have to be extended by suitable broadening factors F in order to account for the multistep character of process (2) and the energy dependencies of processes (1), (-1) and (3). These broadening factors, however, differ from those for combination and
15 dissociation reactions. For simplicity, they are ignored in this evaluation such that k_D at high pressure approaches

$$k_D \rightarrow k_1 k_3 / k_2$$

which is inversely proportional to $[M]$. k_D may also be expressed by

$$k_D \approx k_{D0} k_S / k_{S0}$$

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where k_{D0} and k_{S0} are the respective limiting low-pressure rate coefficients for the formation of $C+D$ or $A+B$ at the considered $[M]$. When it is established that complex-formation is involved, this equation is used to characterize the increasing suppression of $C+D$ formation with increasing $[M]$.

5 3.5 Photochemical reactions

The data sheets begin with a list of feasible primary photochemical transitions for wavelengths usually down to 170 nm, along with the corresponding enthalpy changes at 0 K where possible or alternatively at 298 K, calculated from the data in the Thermodynamic Data summary. Calculated threshold wavelengths corresponding to these
10 enthalpy changes are also listed, bearing in mind that the values calculated from the enthalpy changes at 298 K are not true "threshold values".

This is followed by tables which summarise the available experimental data for: (i) absorption cross-sections and (ii) quantum yields. These data are supplemented by a series of comments.

15 The next table lists the preferred absorption cross-section data and the preferred quantum yields at appropriate wavelength intervals. For absorption cross-sections the intervals are usually 1 nm, 5 nm or 10 nm. Any temperature dependence of the absorption cross-sections is also given where possible. The aim in presenting these preferred data is to provide a basis for calculating atmospheric photolysis rates. For absorption
20 continua the temperature dependence is often represented by Sulzer-Wieland type expressions (Astholz et al., 1981). Alternately a simple empirical expression of the form: $\log_{10}(\sigma_{T1}/\sigma_{T2}) = B(T_1 - T_2)$ is used.

The comments again describe how the preferred data were selected and include other relevant points. The photochemical data sheets are also concluded with a list of
25 references.

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3.6 Conventions concerning absorption cross-sections

These are presented in the data sheets as "absorption cross-sections per molecule, base e". They are defined according to the equations:

$$I/I_0 = \exp(-\sigma[N]l),$$

$$\sigma = \{1/([N]l)\} \ln(I_0/I),$$

where I_0 and I are the incident and transmitted light intensities, σ is the absorption cross-section per molecule (expressed in this paper in units of cm^2), $[N]$ is the number concentration of absorber (expressed in molecule cm^{-3}), and l is the path length (expressed in cm). Other definitions and units are frequently quoted. The closely related quantities "absorption coefficient" and "extinction coefficient" are often used, but care must be taken to avoid confusion in their definition. It is always necessary to know the units of concentration and of path length and the type of logarithm (base e or base 10) corresponding to the definition. To convert an absorption cross-section to the equivalent Napierian (base e) absorption coefficient (expressed in cm^{-1}) of a gas at a pressure of one standard atmosphere and temperature of 273 K, multiply the value of σ in cm^2 by 2.69×10^{19} .

3.7 Assignment of uncertainties

Under the heading "reliability," estimates have been made of the absolute accuracies of the preferred values of k at 298 K and of the preferred values of E/R over the quoted temperature range. The accuracy of the preferred rate coefficient at 298 K is quoted as the term $\Delta \log k$, where $\Delta \log k = D$ and D is defined by the equation, $\log_{10} k = C \pm D$. This is equivalent to the statement that k is uncertain to a factor of F , where $D = \log_{10} F$. The accuracy of the preferred value of E/R is quoted as the term $\Delta(E/R)$, where $\Delta(E/R) = G$ and G is defined by the equation $E/R = H \pm G$. D and G are expanded uncertainties corresponding approximately to a 95% confidence limit.

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For second-order rate coefficients listed in this evaluation, an estimate of the uncertainty at any given temperature within the recommended temperature range may be obtained from the equation:

$$\Delta \log k(T) = \Delta \log k(298 \text{ K}) + 0.4343\{\Delta E/R(1/T - 1/298)\}$$

The assignment of these absolute uncertainties in k and E/R is a subjective assessment of the evaluators. They are not determined by a rigorous, statistical analysis of the database, which is generally too limited to permit such an analysis. Rather, the uncertainties are based on a knowledge of the techniques, the difficulties of the experimental measurements, the potential for systematic errors, and the number of studies conducted and their agreement or lack thereof. Experience shows that for rate measurements of atomic and free radical reactions in the gas phase, the precision of the measurement, i.e. the reproducibility, is usually good. Thus, for single studies of a particular reaction involving one technique, standard deviations, or even 90% confidence limits, of $\pm 10\%$ or less are frequently reported in the literature. Unfortunately, when evaluators come to compare data for the same reaction studied by more than one group of investigators and involving different techniques, the rate coefficients often differ by a factor of 2 or even more. This can only mean that one or more of the studies has involved large systematic uncertainty which is difficult to detect. This is hardly surprising since, unlike molecular reactions, it is not always possible to study atomic and free radical reactions in isolation, and consequently mechanistic and other difficulties frequently arise.

The arbitrary assignment of uncertainties made here is based mainly on our state of knowledge of a particular reaction which is dependent upon factors such as the number of independent investigations carried out and the number of different techniques used. On the whole, our assessment of uncertainty limits tends towards the cautious side. Thus, in the case where a rate coefficient has been measured by a single investigation using one particular technique and is unconfirmed by independent work, we suggest that minimum uncertainty limits of a factor of 2 are appropriate.

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In contrast to the usual situation for the rate coefficients of thermal reactions, where intercomparison of results of a number of independent studies permits a realistic assessment of reliability, for many photochemical processes there is a scarcity of apparently reliable data. Thus, we do not feel justified at present in assigning uncertainty limits to the parameters reported for the photochemical reactions.

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APPENDIX 1

Data Sheets for O(³P) and O(¹D) atom, and O₃ reactions

5 APPENDIX 2

Data Sheets for HO and HO₂ radical reactions

APPENDIX 3

10 Data Sheets for NO₃ reactions

APPENDIX 4

15 Carbon radical reactions

APPENDIX 5

Data sheets for RO radical reactions

20 APPENDIX 6

Data Sheets for RO₂ reactions

25 APPENDIX 7

Halogen atom reactions

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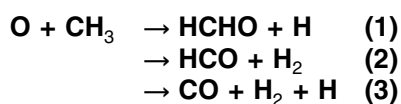
APPENDIX 8

Photochemical reactions

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Appendix 1: O_x + VOC reactions

II.A1.1



$$\Delta H^\circ(1) = -286.2 \text{ kJ}\cdot\text{mol}^{-1}$$

$$5 \quad \Delta H^\circ(2) = -352.5 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(3) = -288.1 \text{ kJ}\cdot\text{mol}^{-1}$$

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Rate coefficient data ($k = k_1 + k_2 + k_3$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.2 \pm 0.17) \times 10^{-10}$	1700–2300	Bhaskaran et al., 1979	SH-RA (a)
$(1.14 \pm 0.29) \times 10^{-10}$	295	Plumb and Ryan, 1982	DF-MS (b)
$(1.4 \pm 0.3) \times 10^{-10}$	294–900	Slagle et al., 1987	F-MS (c)
$k_1 = (1.1 \pm 0.4) \times 10^{-10}$	298	Zellner et al., 1988	LP-LIF (d)
$(1.3 \pm 0.2) \times 10^{-10}$	300	Oser et al., 1991	DF-MS (e)
$(9.4 \pm 3.0) \times 10^{-10}$	~298	Seakins and Leone, 1992	PLP-FTIR (f)
$(1.4 \pm 0.3) \times 10^{-10}$	1609–2002	Lim and Michael, 1993	SH-RA (g)
$(1.7 \pm 0.3) \times 10^{-10}$	299	Fockenberg et al., 1999	PLP-MS (h)
<i>Branching Ratios</i>			
$k_1/k > 0.85$	300	Niki et al., 1968	DF-MS (i)
$k_2/k \leq 0.2$	300	Hoyermann and Sievert, 1979	F-MS (j)
$k_1/k = 0.84 \pm 0.15$	299	Fockenberg et al., 1999	PLP-MS (h)
$k_3/k = 0.17 \pm 0.11$	299		
$k_3/k = 0.18 \pm 0.04$	296	Preses et al., 2000	PLP-IRA (k)

Comments

5 (a) Decomposition of C₂H₆-O₂ mixtures in a shock tube. k was derived from computer simulation of [O] and [H] profiles determined by RA.

(b) Discharge flow system with MS detection of O and CH₃, k was determined

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from the decay of $[\text{CH}_3]$ with $[\text{O}] \gg [\text{CH}_3]$.

- (c) Flow system with generation of CH_3 radicals and $\text{O}(^3\text{P})$ atoms from simultaneous in situ photolysis of $\text{CH}_3\text{C}(\text{O})\text{CH}_3$ and SO_2 , and determination of $[\text{CH}_3]$ and $[\text{O}]$ by photoionization MS. Experiments were performed under conditions such that $[\text{O}]/[\text{CH}_3] > 20$, and rate coefficients were determined from the decay of CH_3 radicals. The rate coefficient k was found to be independent of pressure over the range 1.3 mbar to 15 mbar (1 Torr to 11 Torr), and its value was confirmed by measurement of the rate of formation of HCHO. HCO and CH_2 were not detected as products but the analytical system could not detect CO or H_2 .
- (d) Laser photolysis at 193 nm of flowing mixtures of $\text{N}_2\text{-N}_2\text{O-(CH}_3)_2\text{N}_2$. k was determined from the rate of formation of HCHO (using LIF) with $[\text{O}] > [\text{CH}_3]$. Mass balance estimates indicated that channel (1) predominates.
- (e) Discharge flow system with generation of CH_3 from F+CH_4 in He-O_2 mixtures at pressures of 0.25 mbar to 1.0 mbar (0.17 Torr to 0.78 Torr). k was determined from the decay of $[\text{CH}_3]$ by MS with $[\text{O}]/[\text{CH}_3] > 10$.
- (f) Obtained from the rate of formation of HCHO product by monitoring the C-H stretch emission by FTIR spectroscopy.
- (g) Shock heating of CH_3Cl in Ar coupled with laser photolysis of SO_2 . k was determined from computer simulation of $[\text{O}]$ profiles measured by RA.
- (h) Pulsed laser photolysis at 193 nm of mixtures of $\text{CH}_3\text{C}(\text{O})\text{CH}_3$, CH_3Br and SO_2 at 1.3 mbar pressure. Product analysis by time-of-flight mass spectrometry.
- (i) DF-MS study of $\text{O+C}_2\text{H}_4$ reaction in which CH_3 is a product. HCHO assumed to arise from channel (1).

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- (j) Discharge flow system with CH_3 being generated from F+CH_4 and O from a microwave discharge. Electron impact MS analysis of HCO and HCHO. No evidence found for channel (2).
- (k) Pulsed laser photolysis at 193 nm of mixtures of CH_3COCH_3 , SO_2 , and Ar at 6.6 mbar pressure. Product analysis by tunable infrared diode laser absorption.

Preferred Values

- $k = 1.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 290–900 K.
- $k_1/k = 0.83$ at 298 K.
- $k_3/k = 0.17$ at 298 K.

Reliability

- $\Delta \log k = \pm 0.1$ at 298 K.
- $\Delta (E/R) = \pm 100$ K.
- $\Delta k_1/k = \pm 0.15$ at 298 K.
- $\Delta k_3/k = \pm 0.11$ at 298 K.

Comments on Preferred Values

The recommended value of k is the mean of the results of Plumb and Ryan (1982), Slagle et al. (1987), Zellner et al. (1988), Oser et al. (1991), Seakins and Leone (1992) and Fockenberg et al. (1999) which are in good agreement. The data of Bhaskaran et al. (1980) and Lim and Michael (1993)

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indicate that the rate coefficient is independent of temperature up to at least 2300 K.

The preferred branching ratios are based on the studies of Fockenberg et al. (1999) and Preses et al. (2000). The values of the branching ratio k_3/k reported in these studies, using completely different detection methods, are in excellent agreement. These results are consistent with earlier results reported in Niki et al. (1968), Hoyermann and Sievert (1979) and Seakins and Leone (1992). Seakins and Leone (1992) found CO to be a primary product, and they also estimated the overall branching ratio for CO formation to be 0.40 ± 0.10 . Fockenberg et al. (1999) and Preses et al. (2000) suggest that the overall branching ratio for CO formation estimated in Seakins and Leone (1992) includes CO formed in an oxidation chain beginning with HCHO.

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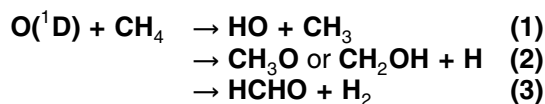
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II.A1.2



$$\Delta H^\circ(1) = -180.5 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -128.9 \text{ or } -163.0 \text{ kJ}\cdot\text{mol}^{-1}$$

$$^5 \Delta H^\circ(3) = -472.7 \text{ kJ}\cdot\text{mol}^{-1}$$

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Rate coefficient data ($k = k_1 + k_2 + k_3$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.3 \pm 0.2) \times 10^{-10}$	298	Davidson et al., 1976	PLP (a)
$(1.4 \pm 0.4) \times 10^{-10}$	200–350	Davidson et al., 1977	PLP (a)
$(1.57 \pm 0.13) \times 10^{-10}$	295	Amimoto et al., 1979	PLP-RA (b)
<i>Branching Ratios</i>			
$k_1/k = 0.9$	295	Lin and DeMore, 1973	P-GC (c)
$k_3/k = 0.09$	295		
$k_1/k = 0.90 \pm 0.02$	298	Jayanty et al., 1976	P-GC (d)
$k_3/k = 0.11 \pm 0.02$	298		
$k_1/k = 0.8$	293	Addison et al., 1979	FP-AS (e)
$k_3/k_2 < 0.25$	–	Casavecchia et al., 1980	(f)
$k_1/k = 0.75 \pm 0.08$	–	Sataypal et al., 1989	PLP-LIF (g)
$k_2/k = 0.25 \pm 0.08$	–		
$k_2/k = 0.15 \pm 0.03$	–	Matsumi et al., 1993	PLP-LIF
$k_1/k = 0.90^{+0.1}_{-0.2}$	298	Hack and Thiesemann, 1995	PLP-LIF
$k_2/k = 0.30 \pm 0.11$	298	Brownsword et al., 1998	PLP-LIF
$k_1/k = 0.71 \pm 0.05$	298	Ausfelder et al., 2000	PLP-LIF

Comments

- ⁵ (a) Pulsed laser photolysis of O₂ at 266 nm. O(¹D) atoms were monitored by time-resolved emission from the transition O(¹D) → O(³P) at 630 nm.

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- (b) Pulsed laser photolysis at 248 nm of O₃-CH₄-He mixtures with time-resolved measurement of O(³P) atoms by resonance absorption.
- (c) Photolysis of N₂O-CH₄ mixtures at 184.9 nm with end-product analysis by GC.
- 5 (d) Photolysis of N₂O-CH₄-O₂ mixtures at 216 nm with measurement of H₂ by GC.
- (e) Flash photolysis of O₃ at 200 nm to 300 nm with [OH] monitored by absorption at 308.15 nm.
- (f) Molecular beam study with MS detection of CH₃O or CH₂OH. Experimental
10 temperature not stated.
- (g) Pulsed laser photolysis of O₃ at 248.4 nm with LIF determination of [H]. Experimental temperature not stated.

Preferred Values ($k=k_1+k_2+k_3$)

$k = 1.5 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ independent of temperature over the range
15 200–350 K.

$k_1/k = 0.70$ at 298 K.

$k_2/k = 0.23$ at 298 K.

$k_3/k = 0.05$ at 298 K.

Reliability

20 $\Delta \log k = \pm 0.10$ at 298 K.

$\Delta k_1/k = \pm 0.15$ at 298 K.

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$\Delta k_2/k = \pm 0.07$ at 298 K.

$\Delta k_3/k = \pm 0.05$ at 298 K.

$\Delta (E/R) = \pm 100$ K.

Comments on Preferred Values

5 The preferred value of k at 298 K is the mean of the results of Davidson et al. (1977) and Amimoto et al. (1979), and the temperature dependence is that from Davidson et al. (1977).

The preferred branching ratios are based on the critical review by Lee and co-workers (1999) of the results of Hack and Thiesemann (1995), Brownsword
10 et al. (1998), Satayapal et al. (1989) and their own crossed-beam experiments (Casavecchia et al., 1980; Lin et al., 1998, 1999). Reaction channel (2) has been shown by Lee and co-workers (Lin et al., 1998, 1999, 2000) to produce mainly CH₂OH+H, and the production of CH₃O+H is at most a minor channel. In addition, the experiments of Wine and Ravishankara (1982), Matsumi et
15 al. (1993) and Takahashi et al. (1996) have shown that the yield of O(³P) atoms is small or zero. The 248 nm pulsed laser photolysis study of Aker et al. (1986), of O₃-CH₄ mixtures with low-pressure FTIR emission spectroscopy to monitor the HO* product, has provided evidence that the partitioning of energy in the vibrationally excited HO radical (up to $n=4$, the maximum allowable based on
20 the energetics of the reaction) is non-statistical.

A discussion of kinetic isotope effects in this reaction can be found in the publication of Saueressig et al. (2001) and references cited therein.

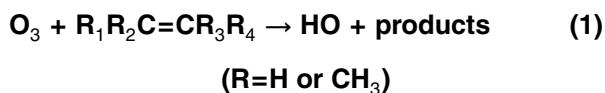
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O₃ Reactions – Appendix 1

II.A1.153



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Product yield data

Alkene	Criegee Intermediate(s)	HO Yield (1 bar) ($\Delta[\text{HO}]/\Delta[\text{R}_1\text{R}_2\text{C}=\text{CR}_3\text{R}_4]$)	Reference	Technique Comments
Ethene	CH ₂ OO	0.18 ± 0.06	Paulson et al., 1999a	Tracer (a)
Ethene	CH ₂ OO	0.14 ± 0.07	Rickard et al., 1999	Tracer (b)
Ethene	CH ₂ OO	0.20 ± 0.02	Mihelcic et al., 1999	MI-ESR (c)
Ethene	CH ₂ OO	(ca. 0.14)	Kroll et al., 2001a	Low pressure LIF see comment (d)
Propene	CH ₂ OO, CH ₃ CHOO	0.35 ± 0.07	Paulson et al., 1999a	Tracer (a)
Propene	CH ₂ OO, CH ₃ CHOO	0.32 ± 0.08	Richard et al., 1999	Tracer (b)
Propene	CH ₂ OO, CH ₃ CHOO	0.34 ^{+0.03} _{-0.06}	Neeb and Moorgat, 1999	Kinetic/ Scavenger (e)
Z-2-butene	CH ₃ CHOO	0.33 ± 0.07	McGill et al., 1999	Tracer (b)
Z-2-butene	CH ₃ CHOO	0.33 ± 0.05	Orzechowska and Paulson, 2002	Tracer (a)
E-2-butene	CH ₃ CHOO	0.61 ± 0.28	Fenske et al., 2000	Tracer (a)
E-2-butene	CH ₃ CHOO	0.64 ± 0.12	Orzechowska and Paulson, 2002	Tracer (a)
E-2-butene	CH ₃ CHOO	0.54 ± 0.11	McGill et al., 2000	Tracer (b)
E-2-butene	CH ₃ CHOO	ca. 0.60	Kroll et al., 2001a	Low pressure LIF see comment (d)
E-2-butene	CH ₃ CHOO	0.75 ± 0.19	Siese et al., 2001	LIF (f)
2-Methyl -propene	CH ₂ OO, (CH ₃) ₂ COO	0.72 ± 0.12	Paulson et al., 1999b	Tracer (a)

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Alkene	Criegee Intermediate(s)	HO Yield (1 bar) ($\Delta[\text{HO}]/\Delta$ [$\text{R}_1\text{R}_2\text{C}=\text{CR}_3\text{R}_4$])	Reference	Technique Comments
2-Methylpropene	CH_2OO , $(\text{CH}_3)_2\text{COO}$	0.60 ± 0.15	Rickard et al., 1999	Tracer (b)
2-Methylpropene	CH_2OO , $(\text{CH}_3)_2\text{COO}$	$0.60^{+0.05}_{-0.02}$	Neeb and Moortgat, 1999	Kinetic/ Scavenger (e)
Z-2-Pentene	CH_3CHOO , CH_3CHOO	0.29 ± 0.06	Orzechowska and Paulson, 2002	Tracer (a)
Z-2-Pentene	CH_3CHOO , $\text{CH}_3\text{CH}_2\text{CHOO}$	0.27 ± 0.07	Orzechowska and Paulson, 2002	Scavenger (g)
E-2-Pentene	CH_3CHOO , $\text{CH}_3\text{CH}_2\text{CHOO}$	0.46 ± 0.08	Orzechowska and Paulson, 2002	Tracer (a)
2-Methyl-2-butene	CH_3CHOO , $(\text{CH}_3)_2\text{COO}$	0.93 ± 0.14	Chew and Atkinson, 1996	Scavenger (g)
2-Methyl-2-butene	CH_3CHOO , $(\text{CH}_3)_2\text{COO}$	0.81 ± 0.16	McGill et al., 1999	Tracer (b)
2-Methyl-2-butene	CH_3CHOO , $(\text{CH}_3)_2\text{COO}$	(ca. 0.6)	Kroll et al., 2001a	Low pressure LIF see comment (d)
2-Methyl-2-butene	CH_3CHOO , $(\text{CH}_3)_2\text{COO}$	0.89 ± 0.22	Siese et al., 2001	LIF (f)
2-Methyl-2-butene	CH_3CHOO , $(\text{CH}_3)_2\text{COO}$	0.98 ± 0.24	Orzechowska and Paulson, 2002	Tracer (a)
2-Methyl-2-butene	CH_3CHOO , $(\text{CH}_3)_2\text{COO}$	0.80 ± 0.12	Orzechowska and Paulson, 2002	Scavenger (a)
2,3-Dimethyl-2-butene	$(\text{CH}_3)_2\text{COO}$	0.80 ± 0.12	Chew and Atkinson, 1996	Scavenger (g)

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Alkene	Criegee Intermediate(s)	HO Yield (1 bar) ($\Delta[\text{HO}]/\Delta$ [$\text{R}_1\text{R}_2\text{C}=\text{CR}_3\text{R}_4$])	Reference	Technique Comments
2,3-Dimethyl-2-butene	$(\text{CH}_3)_2\text{COO}$	0.89 ± 0.22	Rickard et al., 1999	Tracer (b)
2,3-Dimethyl-2-butene	$(\text{CH}_3)_2\text{COO}$	(ca. 1.00)	Kroll et al., 2001	Low pressure LIF see comment (d)
2,3-Dimethyl-2-butene	$(\text{CH}_3)_2\text{COO}$	1.00 ± 0.25	Siese et al., 2001	LIF (f)
2,3-Dimethyl-2-butene	$(\text{CH}_3)_2\text{COO}$	0.91 ± 0.14	Orzechowska and Paulson, 2002	Scavenger (a)
Isoprene (2-methyl-1,3-butadiene)	H_2COO , $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CHOO}$, $\text{OOC}(\text{CH}_3)\text{CH}=\text{CH}_2$	0.25 ± 0.06	Paulson et al., 1998	Tracer (a)
Isoprene (2-methyl-1,3-butadiene)	H_2COO , $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CHOO}$, $\text{OOC}(\text{CH}_3)\text{CH}=\text{CH}_2$	$0.26^{+0.03}_{-0.06}$	Neeb and Moortgat, 1999	Kinetic/ Scavenger (e)
Isoprene (2-methyl-1,3-butadiene)	H_2COO , $\text{H}_2\text{C}=\text{C}(\text{CH}_3)\text{CHOO}$, $\text{OOC}(\text{CH}_3)\text{CH}=\text{CH}_2$	(ca. 0.25)	Kroll et al., 2001a	Low pressure LIF see comment (d)
Methylvinyl ketone	H_2COO , $\text{CH}_3\text{C}(\text{O})\text{CHOO}$	0.16 ± 0.08	Aschmann et al., 1996	Scavenger (g)
Methylvinyl ketone	H_2COO , $\text{CH}_3\text{C}(\text{O})\text{CHOO}$	0.16 ± 0.05	Paulson et al., 1998	Tracer (a)
Methacrolein	H_2COO , $\text{HC}(\text{O})\text{C}(\text{CH}_3)\text{OO}$	$0.20^{+0.10}_{-0.13}$	Aschmann et al., 1996	Scavenger (g)
α -Pinene	R_1CHOO , $\text{R}_2\text{R}_3\text{COO}$	0.76 ± 0.11	Chew and Atkinson, 1996	Scavenger (g)

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Alkene	Criegee Intermediate(s)	HO Yield (1 bar) ($\Delta[\text{HO}]/\Delta[\text{R}_1\text{R}_2\text{C}=\text{CR}_3\text{R}_4]$)	Reference	Technique Comments
α -Pinene	R ₁ CHOO, R ₂ R ₃ COO	0.70 ± 0.17	Paulson et al., 1998	Tracer (a)
α -Pinene	R ₁ CHOO, R ₂ R ₃ COO	1.00	Pfeiffer et al., 1998	Absorption detection of HO (h)
α -Pinene	R ₁ CHOO, R ₂ R ₃ COO	0.83 ± 0.21	Rickard et al., 1999	Tracer (b)
α -Pinene	R ₁ CHOO, R ₂ R ₃ COO	0.91 ± 0.23	Siese et al., 2001	LIF (f)
β -Pinene	H ₂ COO, R ₁ R ₂ COO	0.24 ± 0.06	Rickard et al., 1999	Tracer (b)
Sabinene	H ₂ COO, R ₁ R ₂ COO	0.33 ± 0.06	Chew and Atkinson, 1996	Scavenger (g)

Comments

- (a) Small quantities of a tracer compound (1,3,5-trimethylbenzene, *m*-xylene and di-*n*-butyl ether), that react rapidly with HO and very slowly with ozone, were added to the ozone/alkene reaction mixture. HO yields were determined from the diminution in concentration of the added tracer.
- (b) Similar study to comment (b) using 1,3,5-trimethylbenzene as an HO tracer compound.
- (c) Matrix Isolation Electron Spin Resonance (MI-ESR) study in which HO₂ was quantitatively detected. HO was converted to HO₂ by reaction with

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CO.

- (d) Steady-state HO concentrations in a flow-tube were measured directly by laser induced fluorescence (LIF). The reported HO yields correspond to prompt HO production over short time-scales (within ca. 30 ms) at total pressures of a few Torr. Although prompt HO yields were seen to decrease rapidly with increasing pressure, the HO yield for 2,3-dimethyl-2-butene at atmospheric pressure was seen to approach the prompt, low-pressure yield over much longer time-scales. Thus although the reported yields are for prompt HO production, it is assumed that the long-time-scale yields of HO due to thermal decomposition of the carbonyl oxide are the same.
- (e) The rate of alkene consumption was observed under pseudo-first order conditions with an excess concentration of ozone. The decrease in observed rate in the presence of excess cyclohexane (to scavenge any HO formed) was used to derive HO formation yields.
- (f) HO detected by LIF in the EUPHORE outdoor simulation chamber in Valencia. Time-dependent HO and O₃ concentration data were numerically simulated to obtain HO yields.
- (g) Ozonolysis reactions carried out in the presence of sufficient 2-butanol to scavenge ≥95% of all adventitiously formed HO. HO yields derived from the amount of 2-butanone formed. This method superseded earlier experiments in the laboratory of Atkinson and co-workers (Atkinson et al., 1992; Atkinson and Aschmann, 1993) in which ozonolysis reactions were carried out in the presence of excess cyclohexane, and from which HO formation efficiencies were derived from measured yields of cyclohexanol and cyclohexanone. However, due to the complex peroxy radical chemistry giving rise to these observed products, an uncertainty of around a factor of 1.5

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was estimated for the HO yields determined from these studies.

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Preferred Values

Alkene	$k_{\text{ozone+alkene}}$ (298 K) /cm ³ molecule ⁻¹ s ⁻¹	Preferred HO Yield	References
Ethene	1.6×10^{-18}	0.16	Paulson et al., 1999a Rickard et al., 1999
Propene	1.0×10^{-17}	0.34	Paulson et al., 1999a Rickard et al., 1999 Neeb and Moortgat, 1999
Z-2-butene	1.3×10^{-16}	0.33	McGill et al., 1999 Orzechowska and Paulson, 2002
E-2-butene	1.9×10^{-16}	0.64	McGill et al., 1999 Orzechowska and Paulson, 2002 Fenske et al., 2000 Siese et al., 2001
2-Methylpropene	1.1×10^{-17}	0.62	Rickard et al., 1999 Neeb and Moortgat, 1999 Paulson et al., 1999
2-Methyl-2-butene	4.1×10^{-16}	0.88	McGill et al., 1999 Orzechowska and Paulson, 2002 Siese et al., 2001 Chew and Atkinson, 1996
2,3-Dimethyl-2-butene	1.1×10^{-15}	0.90	Rickard et al., 1999 Orzechowska and Paulson, 2002 Siese et al., 2001 Chew and Atkinson, 1996

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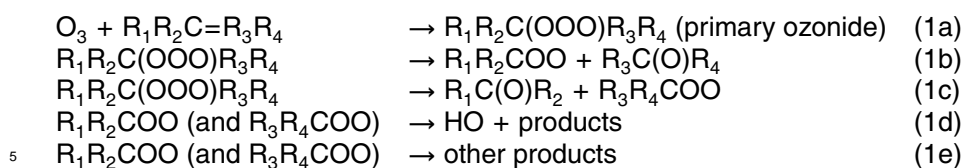
Alkene	$k_{\text{ozone+alkene}}$ (298 K) /cm ³ molecule ⁻¹ s ⁻¹	Preferred HO Yield	References
Isoprene	1.27×10^{-17}	0.25	Neeb and Moortgat, 1999 Paulson et al., 1998
α -Pinene	9.0×10^{-17}	0.80	Rickard et al., 1999 Siese et al., 2001 Chew and Atkinson, 1996 Paulson et al., 1998

$\Delta \log(\text{yield}) = 0.15$

^aRate coefficients taken from Atkinson (1997)

Comments on Preferred Values

The currently accepted mechanism of HO production from ozone-alkene reactions involves the following steps:



Until recently it was generally accepted that HO radicals were produced as a decomposition product of vibrationally excited carbonyl oxide (Criegee) intermediates. In the case of methyl-substituted Criegee intermediates (methylcarbonyl oxide and dimethylcarbonyl oxide) the HO yield varies with the number of methyl-groups in a manner that is consistent with isomerisation of the Criegee

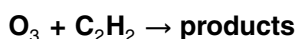
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intermediate to a hydroperoxide intermediate followed by decomposition and HO release (Rickard et al., 1999; Martinez et al., 1981; Niki et al., 1987; Martinez and Herron, 1988). However, experimental studies by Kroll et al. (2001a) looked directly at the formation of HO by LIF over short-timescales, as a function of pressure. As the pressure was increased from a few Torr to around atmospheric pressure, the yields of prompt HO (i.e. that formed within 30 ms or so) were seen to decrease to essentially zero. It was concluded that the majority of HO production reported in previous experimental studies of ozone-alkene reactions was due to the thermal decomposition of stabilised Criegee intermediates. This assertion was supported by further LIF studies in which HO production in the ozonolysis of 2,3-dimethyl-2-butene, at one atmosphere of pressure, was seen to increase over significantly longer time-scales (Kroll et al., 2001b). A study by Johnson et al. (2001) looked at the HO production efficiency of the reaction of ozone with 2-methyl-2-butene in the presence of relatively high concentrations of scavenger species believed to react with Criegee intermediates. Under the conditions of these latter experiments (with concentrations of scavenger species in excess of those that would be encountered in the troposphere), no effect upon the yield of HO was observed. Thus, it is concluded that, the bimolecular reactions of stabilised Criegee intermediates produced in the ozonolysis of 2-methyl-2-butene (methylcarbonyl oxide and dimethylcarbonyl oxide) will not under atmospheric conditions compete with the formation of HO due to their thermal decomposition. It is further concluded that the HO yield measurements summarised above are applicable to the chemistry of the troposphere. The preferred HO yield data listed above are the average values of the measurements for each individual compound.

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II.A1.154



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(7.8 \pm 1.2) \times 10^{-21}$	294	Atkinson and Aschmann, 1984	S-CL (a)

5 Comments

(a) Static system, with $[\text{O}_3]$ being monitored by chemiluminescence in large excess of C_2H_2 at a total pressure of 980 mbar.

Preferred Values

$k = 1 \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

10 Reliability

$\Delta \log k = \pm 1.0$ at 298 K.

Comments on Preferred Values

The literature data at room temperature (Atkinson and Aschmann, 1984; Cadle and Schadt, 1953; DeMore, 1969, 1971; Pate et al., 1976; Stedman
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and Niki, 1973) exhibit a large degree of scatter covering the range $k = (0.78\text{--}7.8) \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K. The preferred value at 298 K is based upon the value obtained by Atkinson and Aschmann (1984). This is the most recent study; it gives the lowest of the values so far obtained and is likely to be
5 the most accurate (any impurities are likely to lead to higher values).

There has been one study of the temperature dependence of the rate coefficient (DeMore, 1969) giving a value of $E/R=5435$ K over the temperature range 243–283 K. However, in view of the difficulties in studying this reaction and the
10 small temperature range covered, no recommendation is made concerning the temperature dependence of this rate coefficient. A large uncertainty is assigned to the preferred value at 298 K to encompass the wide scatter in the results.

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II.A1.155

 $\text{O}_3 + \text{C}_2\text{H}_4 \rightarrow \text{products}$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$3.3 \times 10^{-15} \exp[-(2365 \pm 101)/T]$	178–233	DeMore, 1969	S-UVA (a)
1.18×10^{-18}	298*		
$(1.55 \pm 0.15) \times 10^{-18}$	299	Stedman et al., 1973	S-CL (b)
$9.00 \times 10^{-15} \exp[-(2557 \pm 167)/T]$	235–362	Herron and Huie, 1974	(c)
1.69×10^{-18}	298		
$(1.9 \pm 0.1) \times 10^{-18}$	299	Japar et al., 1974	S-CL (b)
$(1.9 \pm 0.1) \times 10^{-18}$	299	Japar et al., 1976	S-CL (b)
$(1.69 \pm 0.13) \times 10^{-18}$	303	Toby et al., 1976	S-UVA (a)
$(1.43 \pm 0.19) \times 10^{-18}$	296	Atkinson et al., 1982	S-CL (b)
$7.72 \times 10^{-15} \exp[-(2557 \pm 30)/T]$	232–298	Bahta et al., 1984	S-UVA (a)
$(1.45 \pm 0.10) \times 10^{-18}$	298		
$5.1 \times 10^{-15} \exp[-(2446 \pm 91)/T]$	240–324	Treacy et al., 1992	S-CL (b)
$(1.37 \pm 0.08) \times 10^{-18}$	298		

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Comments

- (a) Static system, with UV absorption detection of O_3 at 253.7 nm.
- (b) Static system with chemiluminescence detection of O_3 .
- (c) Stopped flow system with MS detection of O_3 . Carried out at a total pressure of ~ 5 mbar but with sufficient O_2 present to minimize the occurrence of secondary reactions removing O_3 .

Preferred Values

$k = 1.6 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 9.1 \times 10^{-15} \exp(-2580/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 180–360 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.
 $\Delta (E/R) = \pm 100$ K.

Comments on Preferred Values

The temperature dependent kinetic studies of Bahta et al. (1984) and Treacy et al. (1992) are in good agreement. These two studies result in rate coefficients (Bahta et al., 1984; Treacy et al., 1992) which are somewhat lower than many of the previous determinations, including those of Su et al. (1980) and Kan et al. (1981) which are not used in this evaluation. Since Treacy et al. (1992) did not tabulate the individual rate coefficients at the various temperatures studied, only their 298 K value can be used in the evaluation of the rate coefficient for

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this reaction. The preferred values are obtained from a least-squares analysis of the rate coefficients of DeMore (1969), Stedman et al. (1973), Herron and Huie (1974), Japar et al. (1974, 1976), Toby et al. (1976), Atkinson et al. (1982), Bahta et al. (1984) (averaging the rate coefficients at each of the four temperatures studied) and the 298 K rate coefficient of Treacy et al. (1992).

As discussed by Atkinson (1997), the initial reaction forms the energy-rich 'primary ozonide' which rapidly decomposes (see Fig. 1a) to yield HCHO and the energy-rich Criegee intermediate $[\text{CH}_2\text{OO}]^*$. Grosjean and Grosjean (1996) and Grosjean et al. (1996) have measured a formation yield of HCHO of unity at atmospheric pressure of air.

The energy-rich Criegee intermediate can either be stabilized or decompose, with the decomposition channels (b) through (e) having been postulated (see Fig. 1b).

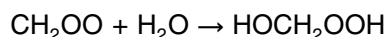
There have been a number of determinations of the yield of the stabilized Criegee intermediate. The values obtained at room temperature and atmospheric pressure by Su et al. (1980) ($35\pm 5\%$), Kan et al. (1981) ($37\pm 2\%$), Niki et al. (1981) ($35\pm 5\%$), Hatakeyama et al. (1984, 1986) ($39.0\pm 5.3\%$) and Hasson et al. (2001) ($39\pm 11\%$) are in good agreement (with an average yield of 37%) and are preferred to the slightly higher value of 47% obtained by Horie and Moortgat (1991). The yield of stabilized Criegee intermediate appears to be pressure dependent although a significant fraction have been reported to be formed thermally "cold" at low pressures; by extrapolation of measurements over the range 13 mbar to 1.5 bar, Hatakeyama et al. (1986) found this fraction to be $20\pm 3\%$ at zero pressure.

The formation of HO radicals has been observed from the reaction of O_3 with ethene at atmospheric pressure of air, with the measured HO radical yield being in the range 12–18% (Atkinson et al., 1992; Paulson et al., 1999; Rickard et al., 1999) (see the data sheet in this article on the reactions of

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$\text{O}_3 + \text{R}_1\text{R}_2\text{C}=\text{CR}_3\text{R}_4 \rightarrow \text{HO} + \text{products}$). This observed formation of HO radicals (Atkinson et al., 1992; Paulson et al., 1999; Rickard et al., 1999), presumably via pathway (e), suggests that pathway (d) does not occur, since the low pressure study of Herron and Huie (1977) which invoked pathway (d) could not differentiate between formation of H atoms and HO radicals (any H atoms formed would rapidly react with O_3 in the reaction system used by Herron and Huie (1977) to produce HO radicals). Hence a possible reaction sequence at atmospheric pressure of air is depicted in Fig. 1c.

Under typical lower tropospheric conditions, the stabilized Criegee intermediate CH_2OO is expected to react with water vapor to form hydroxymethyl hydroperoxide, HOCH_2OOH (Neeb et al., 1996; Hasson et al., 2001),



which may decompose on surfaces to formic acid plus water vapor (Neeb et al., 1996; Hasson et al., 2001).

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$\text{O}_3 + \text{C}_3\text{H}_6 \rightarrow \text{products}$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$6.14 \times 10^{-15} \exp[-(1897 \pm 109)/T]$	235–362	Herron and Huie, 1974	(a)
1.06×10^{-17}	298		
$4.9 \times 10^{-15} \exp[-(1858 \pm 70)/T]$	240–324	Treacy et al., 1992	S-CL (b)
$(9.4 \pm 0.4) \times 10^{-18}$	298		

5 **Comments**

(a) Stopped flow system, with MS detection of O_3 . Carried out at a total pressure of ~ 5 mbar, but with sufficient O_2 present to minimize the occurrence of secondary reactions removing O_3 . Due to a typographical error, the lowest temperature studied was 235.0 K and not 250.0 K as originally stated (Herron and Huie, 1974).

(b) Static system, with chemiluminescence detection of O_3 . C_3H_6 in large excess over O_3 .

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Preferred Values

$k = 1.0 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 5.5 \times 10^{-15} \exp(-1880/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 230–370 K.

5 *Reliability*

$\Delta \log k = \pm 0.10$ at 298 K.

$\Delta (E/R) = \pm 200$ K.

Comments on Preferred Values

The absolute rate coefficients of Herron and Huie (1974) (note that the lowest temperature studied was 235.0 K and not 250.0 K as given by Herron and Huie, 1974) and Treacy et al. (1992) are in excellent agreement for propene, 1-butene, *cis*- and *trans*-2-butene, 2-methylpropene and 2-methyl-2-butene over the temperature ranges common to both studies. Accordingly, the 298 K rate coefficients and temperature dependencies of Herron and Huie (1974) and Treacy et al. (1992) have been averaged to yield the preferred Arrhenius expression (note that the individual rate coefficients at the various temperatures studied by Treacy et al. (1992) were not tabulated).

The reaction proceeds via the initial formation of the 'primary ozonide' (Atkinson, 1997), which rapidly decomposes to two sets of 'primary' carbonyl plus Criegee intermediate (see Fig. 2a).

For 1-alkenes measured product yields suggest that the rate coefficient ratio $k_b/(k_a+k_b)$ is in the range 0.65–0.50 at room temperature (Atkinson, 1997; Grosjean et al., 1996; Tuazon et al., 1997; Rickard et al., 1999). For propene, yields of CH_3CHO have been measured in the presence of an HO radical scav-

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enger (see below) by Grosjean et al. (1996) (0.520 ± 0.026 at $55 \pm 10\%$ relative humidity), Tuazon et al. (1997) (0.446 ± 0.092 at $\sim 5\%$ relative humidity) and Rickard et al. (1999) (0.34 ± 0.01 in dry air). Higher yields of HCHO were obtained by Grosjean et al. (1996) and Tuazon et al. (1997), but these include
5 any formation of HCHO from subsequent reactions of the $[\text{CH}_3\text{CHOO}]^*$ intermediates. The energy-rich Criegee intermediates are believed to be carbonyl oxides, and the Criegee intermediate $[\text{CH}_3\text{CHOO}]^*$ can exist in the *anti*- or *syn*-configuration (Fenske et al., 2000a) (see Fig. 2b).

It is assumed (in the absence of other information; Rickard et al., 1999) that
10 the reactions of the energy-rich Criegee intermediate $[\text{CH}_2\text{OO}]^*$ formed from propene are similar to those for $[\text{CH}_2\text{OO}]^*$ formed from ethene. Hence, as for the $\text{O}_3 + \text{C}_2\text{H}_4$ reaction at room temperature and 1 bar of air, the reactions are as shown in Fig. 2c.

Less data are available concerning the stabilization and decomposition reactions of the $[\text{CH}_3\text{CHOO}]^*$ intermediate. Based upon the SO_2 to H_2SO_4 conversion yield in an $\text{O}_3 + \text{propene}$ reaction system, Hatakeyama et al. (1984) determined an overall stabilized Criegee intermediate $[\text{CH}_2\text{OO} + \text{CH}_3\text{CHOO}]$ yield of 0.254 ± 0.023 at room temperature and atmospheric pressure, while Horie and Moortgat (1991) obtained a stabilized Criegee intermediate yield of 0.44.
20 Rickard et al. (1999) measured the acetaldehyde yield in the presence and absence of 0.002 bar SO_2 and ascribed the observed increase in the acetaldehyde yield to the reaction $\text{SO}_2 + \text{CH}_3\text{CHOO} \rightarrow \text{SO}_3 + \text{CH}_3\text{CHO}$ (similar to the assumptions made by Hatakeyama et al., 1984) which corresponds to a yield of stabilized CH_3CHOO of 0.12–0.16 for rate coefficient ratios $k_b/(k_a + k_b)$ of 0.65–
25 0.50. For rate coefficient ratios $k_b/(k_a + k_b)$ of 0.65–0.50 and assuming that the $[\text{CH}_2\text{OO}]^*$ stabilization yield is 0.37, the data of Hatakeyama et al. (1984) lead to a fraction of the $[\text{CH}_3\text{CHOO}]^*$ intermediate which is stabilized at ~ 298 K and 1 bar of air of 0.14–0.19, reasonably consistent with the study of Rickard et

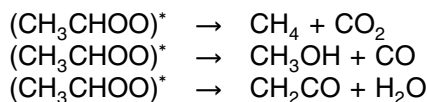
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al. (1999). While the stabilization/decomposition yields are expected to depend on the individual alkene reacting with O_3 (and on the total pressure and temperature), this fraction of $[\text{CH}_3\text{CHOO}]^*$ biradicals which are stabilized at 298 K and 1 bar of air (0.12–0.19) is similar to the measured yields of stabilized CH_3CHOO
5 from *trans*-2-butene of 0.185 (Hatakeyama et al., 1984) and 0.13 (Rickard et al., 1999) and from *cis*-2-butene of 0.18 (Niki et al., 1977) and 0.19 (Rickard et al., 1999). A yield of stabilized CH_3CHOO from $[\text{CH}_3\text{CHOO}]^*$ of 0.16 at 298 K and 1 bar of air is recommended, with it being likely that this stabilized CH_3CHOO intermediate is *anti*- CH_3CHOO .

10 The $[\text{CH}_3\text{CHOO}]^*$ decomposition pathways include the formation of HO radicals through the 'hydroperoxide' channel (see the data sheet on the reactions of $\text{O}_3 + \text{R}_1\text{R}_2\text{C}=\text{CR}_3\text{R}_4 \rightarrow \text{HO} + \text{products}$).



and this reaction pathway is believed to occur for the initially energy-rich
15 Criegee intermediate and possibly for the stabilized *syn*- CH_3CHOO intermediate (Fenske et al., 2000a; Kroll et al., 2001). At atmospheric pressure, the measured HO radical formation yield is in the range 0.32–0.37 (Atkinson and Aschmann, 1993; Neeb and Moortgat, 1999; Paulson et al., 1999; Rickard et al., 1999; Fenske et al., 2000b). Other decomposition pathways include (Atkinson,
20 son, 1997; Tuazon et al., 1997):



with measured methane, methanol and ketene yields at atmospheric pressure (in the presence of an HO radical scavenger) of 0.096 ± 0.010 (Tuazon et al., 1997), 0.055 ± 0.007 (Tuazon et al., 1997) and 0.036 ± 0.008 (Tuazon et

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al., 1997), respectively. Considering that subsequent reaction of the vinoxy (CH_2CHO) radical in air may lead to the formation of HO radicals (Atkinson, 1997), then a possible overall reaction sequence involves the initial formation of 35–40% ($[\text{CH}_2\text{OO}]^* + \text{CH}_3\text{CHO}$) and 65–60% ($[\text{CH}_3\text{CHOO}]^* + \text{HCHO}$), followed by the reactions of the $[\text{CH}_2\text{OO}]^*$ intermediate shown above (leading to an HO radical yield, relative to the propene reacted, of ~ 0.05) and the following reactions of the $[\text{CH}_3\text{CHOO}]^*$ intermediate (the yields are given relative to the propene reacted, and that for the $\text{HO} + \text{CH}_2\text{CHO}$ pathway depends on the amount of HO radicals formed from subsequent reactions of the vinoxy radical) (see Fig. 3).

Under lower tropospheric conditions, the stabilized Criegee intermediate CH_3CHOO (expected to be in the *anti*-configuration) is anticipated to react with water vapor to form the hydroxyhydroperoxide (Neeb et al., 1999; Sauer et al., 1999; Baker et al., 2002).



This hydroxyhydroperoxide may decompose (possibly heterogeneously) to $\text{CH}_3\text{C}(\text{O})\text{OH} + \text{H}_2\text{O}$ or to $\text{CH}_3\text{CHO} + \text{H}_2\text{O}_2$ (Neeb et al., 1999; Sauer et al., 1999).

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Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
1.27×10^{-17}	295 ± 1	Arnts and Gay, 1979	S-CL/GC (a)
7.0×10^{-18}	260 ± 2	Adeniji et al., 1981	S-CL
1.65×10^{-17}	294 ± 2		
1.1×10^{-17}	291	Kamens et al., 1982	(b)
$1.54 \times 10^{-14} \exp[-(2153 \pm 430)/T]$	278–323	Atkinson, et al., 1982	S-CL
$(1.17 \pm 0.19) \times 10^{-17}$	296 ± 2		
$7.8 \times 10^{-15} \exp[-(1913 \pm 139)/T]$	242–323	Treacy et al., 1992	S-UVA
$(1.28 \pm 0.12) \times 10^{-17}$	298		
$(8.95 \pm 0.25) \times 10^{-18}$	293 ± 2	Grosjean et al., 1993	S-UVA
$(1.13 \pm 0.32) \times 10^{-17}$	291 ± 2	Grosjean and Grosjean, 1996	S-UVA
<i>Relative Rate Coefficients</i>			
$(1.16 \pm 0.02) \times 10^{-17}$	296 ± 2	Greene and Atkinson, 1992	RR (c)
$9.21 \times 10^{-15} \exp[-(1955 \pm 42)/T]$	242–324	Khamaganov and Hites, 2001	RR (d,e)
$(1.29 \pm 0.08) \times 10^{-17}$	298		
$1.62 \times 10^{-14} \exp[-(2078 \pm 120)/T]$	242–324	Khamaganov and Hites, 2001	RR (d,f)
$(1.50 \pm 0.13) \times 10^{-17}$	298		
$1.24 \times 10^{-14} \exp[-(2050 \pm 87)/T]$	257–324	Khamaganov and Hites, 2001	RR (d,g)
$(1.26 \pm 0.07) \times 10^{-17}$	298		
$9.45 \times 10^{-15} \exp[-(1963 \pm 72)/T]$	258–324	Khamaganov and Hites, 2001	RR (d,h)
$(1.35 \pm 0.08) \times 10^{-17}$	298		
$1.36 \times 10^{-14} \exp[-(2015 \pm 149)/T]$	278–353	Avzianova and Ariya, 2002	RR (i)
$(1.22 \pm 0.03) \times 10^{-17}$	298		

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Comments

- (a) Carried out in one atmosphere of air in 330 liter volume reaction chambers. The O_3 and isoprene concentrations were measured by chemiluminescence and GC, respectively.
- 5 (b) Carried out at atmospheric pressure of air in a large outdoor chamber at night. O_3 was introduced continually over a period of 1.4 h to an isoprene-air mixture. The isoprene and O_3 concentrations were monitored by GC and chemiluminescence, respectively, and the rate coefficient obtained by fitting the measured isoprene and O_3 concentrations to a computer model.
- 10 (c) Relative rate study, with *n*-octane being present to scavenge the OH radicals formed from the O_3 reactions. The concentrations of isoprene and propene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(\text{O}_3+\text{isoprene})/k(\text{O}_3+\text{propene})=1.21\pm 0.02$ is placed on an absolute basis by use of a rate coefficient of
- 15 $k(\text{O}_3+\text{propene})=9.6\times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (IUPAC, current recommendation).
- (d) Relative rate method carried out at 760 Torr (1.013 bar) of helium diluent in a 192 cm^3 volume cylindrical quartz reactor, with ethanol or acetaldehyde being present to scavenge the OH radicals formed. The concentrations of
- 20 isoprene and the reference compound were monitored by MS.
- (e) With 2-methylpropene as the reference compound. The measured rate coefficient ratios $k(\text{O}_3+\text{isoprene})/k(\text{O}_3+2\text{-methylpropene})$ are placed on an absolute basis by use of a rate coefficient of $k(\text{O}_3+2\text{-methylpropene})=2.70\times 10^{-15} \exp(-1632/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson,
- 25 1997).

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- (f) With *cis*-2-butene as the reference compound. The measured rate coefficient ratios $k(\text{O}_3+\text{isoprene})/k(\text{O}_3+\textit{cis}\text{-2-butene})$ are placed on an absolute basis by use of a rate coefficient of $k(\text{O}_3+\textit{cis}\text{-2-butene})=3.22\times 10^{-15} \exp(-968/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson, 1997).
- 5 (g) With 1-butene as the reference compound. The measured rate coefficient ratios $k(\text{O}_3+\text{isoprene})/k(\text{O}_3+1\text{-butene})$ are placed on an absolute basis by use of a rate coefficient of $k(\text{O}_3+1\text{-butene})=3.36\times 10^{-15} \exp(-1744/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson, 1997).
- 10 (h) With 2,3-dimethyl-1,3-butadiene as the reference compound. The measured rate coefficient ratios $k(\text{O}_3+\text{isoprene})/k(\text{O}_3+2,3\text{-dimethyl-1,3-butadiene})$ are placed on an absolute basis by use of a rate coefficient of $k(\text{O}_3+2,3\text{-dimethyl-1,3-butadiene})=6.9\times 10^{-15} \exp(-1668/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson, 1997).
- 15 (i) Relative rate method carried out at 760 Torr (1.013 bar) of air diluent in a 3 liter volume Pyrex reactor, with 1,3,5-trimethylbenzene being present to scavenge the OH radicals formed. The concentrations of isoprene and propene (the reference compound) were monitored by GC. The measured rate coefficient ratios $k(\text{O}_3+\text{isoprene})/k(\text{O}_3+\text{propene})$ are placed on an absolute basis by use of a rate coefficient of $k(\text{O}_3+\text{propene})=5.5\times 10^{-15} \exp(-1880/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation). Note that the 298 K rate coefficient calculated from the Arrhenius expression is $1.57\times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, 29% higher than the measured value (see table).
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Preferred Values

$k = 1.27 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 1.03 \times 10^{-14} \exp(-1995/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 240–360 K.

5 Reliability

$\Delta \log k = \pm 0.10$ at 298 K.

$\Delta (E/R) = \pm 200 \text{ K}$.

Comments on Preferred Values

The measured room temperature rate coefficients (Arnts and Gay, 1979; Adeniji et al., 1981; Atkinson et al., 1982; Kamens et al., 1982; Greene and Atkinson, 1992; Treacy et al., 1992; Grosjean et al., 1993; Grosjean and Grosjean, 1996; Khamaganov and Hites, 2001; Avzianova and Ariya, 2002) and temperature dependencies (Atkinson et al., 1982; Treacy et al., 1992; Khamaganov and Hites, 2001; Avzianova and Ariya, 2002) are in good agreement.

15 The preferred temperature dependence is the average of those determined by Treacy et al. (1992); Khamaganov and Hites (2001) and Avzianova and Ariya (2002). The preferred 298 K rate coefficient is the average of the rate coefficients of Atkinson et al. (1982), Greene and Atkinson (1992), Treacy et al. (1992), Grosjean et al. (1993), Grosjean and Grosjean (1996); Khamaganov and Hites (2001) and Avzianova and Ariya (2002) adjusted to 298 K where necessary (Atkinson et al., 1982; Greene and Atkinson, 1992; Grosjean et al., 1993; Grosjean and Grosjean, 1996) using the preferred temperature dependence.

20 The preferred temperature dependence is combined with the preferred rate coefficient at 298 K to obtain the pre-exponential factor.

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The reaction proceeds by initial addition of O₃ to the C=C bonds to form one of two primary ozonides, which rapidly decompose to form four possible sets of carbonyl + Criegee intermediate (see data sheets on the reactions of O₃ with ethene and propene. Methacrolein, methyl vinyl ketone and formaldehyde are significant products of this reaction, with measured formation yields of 39–44%, 16–17%, and 90%, respectively (Atkinson, 1997). HO radicals are also formed from the reaction of O₃ with isoprene, in 25% yield (see the data sheet on the O₃+R₁R₂C=CR₃R₄±HO + products reaction).

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$O_3 + \alpha\text{-Pinene} \rightarrow \text{products}$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
1.6×10^{-16}	294	Ripperton et al., 1972	S-CL
1.45×10^{-16}	295 ± 1	Grimsrud et al., 1975	F-CL
$(3.3 \pm 0.3) \times 10^{-16}$	298	Japar et al., 1974	S-CL
$9.4 \times 10^{-16} \exp[-(731 \pm 173)/T]$	276–324	Atkinson et al., 1982	S-CL
$(8.4 \pm 1.9) \times 10^{-17}$	296 ± 2		
$(9.71 \pm 1.06) \times 10^{-17}$	296 ± 2	Atkinson et al., 1990	S-CL (a)
<i>Relative Rate Coefficients</i>			
$(8.20 \pm 1.24) \times 10^{-17}$	297 ± 2	Nolting et al., 1988	RR (b)
$5.7 \times 10^{-16} \exp[-(584 \pm 87)/T]$	288–363	Khamaganov and Hites, 2001	RR (c,d)
$(9.05 \pm 0.45) \times 10^{-17}$	298		
$3.5 \times 10^{-16} \exp[-(429 \pm 303)/T]$	288–343	Khamaganov and Hites, 2001	RR (c,e)
$(8.11 \pm 0.33) \times 10^{-17}$	298		
$(1.06 \pm 0.09) \times 10^{-16}$	295 ± 0.5	Witter et al., 2002	RR (f)

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Comments

- (a) From measurements of the absolute rate coefficient for the reaction of O_3 with sabinene and the rate coefficient ratio $k(O_3 + \alpha\text{-pinene})/k(O_3 + \text{sabinene})$, a rate coefficient of $k(O_3 + \alpha\text{-pinene}) = (7.99 \pm 1.20) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was also derived.
- (b) The concentrations of a series of alkenes (including α -pinene and *cis*-2-butene, the reference compound) were monitored by GC in a 520 L Pyrex chamber at ~ 1 bar pressure of purified air in the presence of O_3 . The measured rate coefficient ratio $k(O_3 + \alpha\text{-pinene})/k(O_3 + \text{cis-2-butene})$ is placed on an absolute basis by use of a rate coefficient at 297 K of $k(O_3 + \text{cis-2-butene}) = 1.24 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Arey, 2003a). Details concerning the reactant mixtures and the presence or absence of an OH radical scavenger were not reported.
- (c) The concentrations of α -pinene and 1-butene or 2-methylpropene (the reference compounds) were monitored by MS in reacting O_3 – α -pinene – 1-butene (or 2-methylpropene) – acetaldehyde (or ethanol) [OH radical scavengers] – He mixtures in a 192 cm^3 volume quartz vessel at ~ 1 bar pressure. The measured rate coefficient ratios $k(O_3 + \alpha\text{-pinene})/k(O_3 + 1\text{-butene}) = 0.17 \exp[(1190 \pm 87)/T]$ and $k(O_3 + \alpha\text{-pinene})/k(O_3 + 2\text{-methylpropene}) = 0.13 \exp[(1203 \pm 303)/T]$ are placed on an absolute basis by use of rate coefficients of $k(O_3 + 1\text{-butene}) = 3.36 \times 10^{-15} \exp(-1774/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k(O_3 + 2\text{-methylpropene}) = 2.70 \times 10^{-15} \exp(-1632/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Arey, 2003a). The combined data lead to the Arrhenius expression $k(O_3 + \alpha\text{-pinene}) = 4.8 \times 10^{-16} \exp[-(530 \pm 150)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 288–363 K and $k(O_3 + \alpha$

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pinene) $= (8.41 \pm 0.74) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Khamaganov and Hites, 2001).

(d) Relative to $k(\text{O}_3 + 1\text{-butene})$.

(e) Relative to $k(\text{O}_3 + 2\text{-methylpropene})$.

5 (f) The concentrations of α -pinene and 2-methyl-2-butene (the reference compounds) were monitored by GC in reacting O_3 – α -pinene – 2-methyl-2-butene – m -xylene (the OH radical scavenger) – air mixtures in a flow system at 1.00 bar pressure. The measured rate coefficient ratio of $k(\text{O}_3 + \alpha\text{-pinene})/k(\text{O}_3 + 2\text{-methyl-2-butene}) = 0.270 \pm 0.022$ is placed on an absolute basis by use of a rate coefficient at 295 K of $k(\text{O}_3 + 2\text{-methyl-2-butene}) = 3.92 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Arey, 2003a).

Preferred Values

$k = 9.0 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
15 $k = 6.3 \times 10^{-16} \exp(-580/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 270–370 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

$\Delta (E/R) = \pm 300 \text{ K}$.

Comments on Preferred Values

20 The room temperature rate coefficients reported by Ripperton et al. (1972), Grimsrud et al. (1975) and Japar et al. (1974) are significantly higher than
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the more recent measurements of Atkinson et al. (1982, 1990), Nolting et al. (1988), Khamaganov and Hites (2001) and Witter et al. (2002), although there is still a significant amount of scatter between the room temperature rate coefficients of Atkinson et al. (1982, 1990), Nolting et al. (1988), Khamaganov and Hites (2001) and Witter et al. (2002). The preferred temperature dependence is obtained from a simple average of the temperature dependencies obtained by Atkinson et al. (1982) and Khamaganov and Hites (2001). The preferred 298 K rate coefficient is an average of those of Atkinson et al. (1982, 1990), Nolting et al. (1988), Khamaganov and Hites (2001) and Witter et al. (2002), corrected to 298 K where necessary using the preferred temperature dependence. The pre-exponential factor is adjusted to fit the 298 K preferred value.

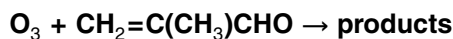
15 The reaction proceeds by initial addition of O_3 to the C=C bond to form a 'primary ozonide' which rapidly decomposes to two Criegee intermediates. Subsequent reactions of these lead to pinonaldehyde, HO radicals, formaldehyde, acetone, α -pinene oxide and a number of other products. A schematic reaction scheme is shown below (Fig. 4), noting that the pinonaldehyde yield shown is derived from product studies employing GC analyses (see Atkinson and Arey, 2003a, b).

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Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.12 \pm 0.13) \times 10^{-18}$	296 ± 2	Atkinson et al., 1981	S-CL
1.1×10^{-18}	~ 294	Kamens et al., 1982	S-CL/GC (a)
$1.3 \times 10^{-15} \exp[-(2112 \pm 131)/T]$	240–324	Treacy et al., 1992	S-UVA
$(1.1 \pm 0.2) \times 10^{-18}$	298		
$(1.02 \pm 0.05) \times 10^{-18}$	291 ± 2	Grosjean et al., 1993	S-UVA
$(1.08 \pm 0.20) \times 10^{-18}$	290 ± 1	Grosjean and Grosjean, 1998	S-UVA
5 $(1.3 \pm 0.14) \times 10^{-18}$	296 ± 2	Neeb et al., 1998	S-FTIR (b)

Comments

- (a) Carried out at atmospheric pressure of air in a large outdoor chamber at night. O_3 was introduced continually over a period of ~ 5 h to a methacrolein-air mixture. The methacrolein and O_3 concentrations were monitored by GC and chemiluminescence, respectively, and the rate coefficient obtained by fitting the measured methacrolein and O_3 concentrations to a computer model.
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- (b) The decays of methacrolein were measured in the presence of excess concentrations of O₃, with cyclohexane also being present as an HO radical scavenger.

Preferred Values

- 5 $k = 1.2 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 1.4 \times 10^{-15} \exp(-2100/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 240–330 K.

Reliability

- $\Delta \log k = \pm 0.2$ at 298 K.
10 $\Delta (E/R) = \pm 300$ K.

Comments on Preferred Values

- The measured room temperature rate coefficients (Atkinson et al., 1981; Kamens et al., 1982; Treacy et al., 1992; Grosjean et al., 1993; Grosjean and Grosjean, 1998; Neeb et al., 1998) are in good agreement. The preferred
15 298 K rate coefficient is the average of all of the measured rate coefficients (Atkinson et al., 1981; Kamens et al., 1982; Treacy et al., 1992; Grosjean et al., 1993; Grosjean and Grosjean, 1998; Neeb et al., 1998), adjusted to 298 K where necessary (Atkinson et al., 1981; Kamens et al., 1982; Grosjean et al., 1993; Grosjean and Grosjean, 1998; Neeb et al., 1998) using the temperature
20 dependence of Treacy et al. (1992). The temperature dependence measured by Treacy et al. (1992) is accepted, and is combined with the 298 K preferred value to obtain the pre-exponential factor.

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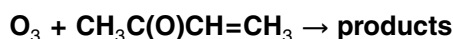
- The reaction proceeds by initial addition of O₃ to the C=C bond to form a primary ozonide which rapidly decomposes to methylglyoxal + [CH₂OO]^{*} or to formaldehyde + [CH₃C(OO)CHO]^{*} (see data sheets on the reactions of O₃ with ethene and propene). Methylglyoxal and formaldehyde have been observed as
5 significant products of this reaction, with formation yields of 52–64% and 9–15%, respectively (Grosjean et al., 1993), indicating that formation of methylglyoxal + [CH₂OO]^{*} dominates. HO radicals are also formed, with a reported yield of 20⁺¹⁰₋₁₃% (Aschmann et al., 1996).

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Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(4.77 \pm 0.59) \times 10^{-18}$	296 ± 2	Atkinson et al., 1981	S-CL
4.0×10^{-18}	~ 294	Kamens et al., 1982	S-CL/GC (a)
$6.9 \times 10^{-16} \exp[-(1521 \pm 78)/T]$	240–324	Treacy et al., 1992	S-UVA
$(4.2 \pm 0.4) \times 10^{-18}$	298		
$(4.72 \pm 0.09) \times 10^{-18}$	291 ± 2	Grosjean et al., 1993	S-UVA
$(5.84 \pm 0.39) \times 10^{-18}$	291 ± 1	Grosjean and Grosjean, 1998	S-UVA
$(5.4 \pm 0.6) \times 10^{-18}$	296 ± 2	Neeb et al., 1998	S-FTIR (b)

5 Comments

(a) Carried out at atmospheric pressure of air in a large outdoor chamber at night. O_3 was introduced continually over a period of ~ 5 h to a methyl vinyl ketone-air mixture. The methyl vinyl ketone and O_3 concentrations were monitored by GC and chemiluminescence, respectively, and the rate coefficient obtained by fitting the measured methyl vinyl ketone and O_3 concentrations to a computer model.

(b) The decays of methyl vinyl ketone were measured in the presence of excess concentrations of O_3 , with cyclohexane also being present as an HO
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radical scavenger.

Preferred Values

$k = 5.2 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 8.5 \times 10^{-16} \exp(-1520/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range
 5 240–330 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

$\Delta (E/R) = \pm 200$ K.

Comments on Preferred Values

10 The measured room temperature rate coefficients (Atkinson et al., 1981; Kamens et al., 1982; Treacy et al., 1992; Grosjean et al., 1993; Grosjean and Grosjean, 1998; Neeb et al., 1998) range over a factor of 1.5, with the temperature dependent study of Treacy et al. (1992) having the lowest measured rate coefficient (taking into account the actual value of room temperature in the
 15 various studies). The preferred 298 K rate coefficient is the average of all of the measured rate coefficients (Atkinson et al., 1981; Kamens et al., 1982; Treacy et al., 1992; Grosjean et al., 1993; Grosjean and Grosjean, 1998; Neeb et al., 1998), adjusted to 298 K where necessary (Atkinson et al., 1981; Kamens et al., 1982; Grosjean et al., 1993; Grosjean and Grosjean, 1998; Neeb et al., 1998) using the temperature dependence of Treacy et al. (1992). The temperature
 20 dependence measured by Treacy et al. (1992) is accepted, and is combined with the 298 K preferred value to obtain the pre-exponential factor.

The reaction proceeds by initial addition of O₃ to the C=C bond to form a primary ozonide which rapidly decomposes to methylglyoxal + [CH₂OO]^{*} or to formaldehyde + [CH₃C(O)CHOO]^{*} (see data sheets on the reactions of O₃ with ethene and propene). Methylglyoxal has been observed as a major product of this reaction, with a formation yield of 82–92% (Grosjean et al., 1993), indicating that formation of methylglyoxal + [CH₂OO]^{*} dominates. HO radicals are also formed, with measured yields of 16±8% (Aschmann et al, 1996) and 16±5% (Paulson et al., 1998).

References

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II.A1.161

O₃ + 3 methyl furan → products

Rate coefficient data

<i>k</i> /cm ³ molecule ⁻¹ s ⁻¹	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
(2.04 ± 0.08) × 10 ⁻¹⁷	296 ± 2	Alvarado et al., 1996	RR (a)

5 Comments

- (a) Relative rate method carried out at atmospheric pressure of air. The concentrations of 3-methylfuran and propene (the reference compound) were measured by GC, and cyclohexane was added to the reactant mixtures to scavenge the HO radicals formed (Atkinson, 1997). The measured rate coefficient ratio of $k(\text{O}_3 + 3\text{-methylfuran})/k(\text{O}_3 + \text{propene}) = 2.12 \pm 0.08$ is placed on an absolute basis by use of a rate coefficient of $k(\text{O}_3 + \text{propene}) = 9.6 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (IUPAC, current recommendation).

Preferred Values

- 15 $k = 2.0 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

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Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

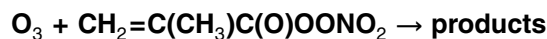
The preferred value is based on the sole study of this reaction by Alvarado et al. (1996). The reaction proceeds by initial addition of O₃ to the C=C bonds. HO radicals were observed to be formed from the reaction of O₃ with 3-methylfuran, in ~60% yield (Alvarado et al., 1996).

References

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Atkinson, R.: *J. Phys. Chem. Ref. Data*, 26, 215, 1997.
IUPAC: <http://www.iupac-kinetic.ch.cam.ac.uk/>, 2004.

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II.A1.162



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(8.2 \pm 2.0) \times 10^{-18}$	295 ± 5	Grosjean et al., 1993	(a)

Comments

- (a) Experiments were carried out at atmospheric pressure of air, by monitoring the decay rates of CH₂=C(CH₃)C(O)OONO₂ (MPAN) in the presence of known excess concentrations of O₃. Cyclohexane was added to the reactant mixtures to scavenge any OH radicals present. MPAN concentrations were measured by GC with electron capture detection.

Preferred Values

$k = 8.2 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

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Comments on Preferred Values

The preferred value is based on the sole study of this reaction by Grosjean et al. (1993). The rate coefficient for this reaction is similar in magnitude to those for the reactions of O₃ with propene (Atkinson, 1997; IUPAC, current recommendation) and 2-methylpropene (Atkinson, 1997) and a factor of 5 higher than that for the reaction of O₃ with ethene (Atkinson, 1997; IUPAC, current recommendation). This reactivity of MPAN towards O₃ is consistent with the recommended rate coefficient for the reaction of MPAN with HO radicals (IUPAC, current recommendation). The reaction of O₃ with MPAN proceeds by initial addition of O₃ to the C=C bond, and formaldehyde has been observed as a reaction product with a formation yield of 60 ± 10% (Grosjean et al., 1993).

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IUPAC: <http://www.iupac-kinetic.ch.cam.ac.uk/>, 2004.

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II.A1.163

O₃ + Pinonaldehyde → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(8.9 \pm 1.3) \times 10^{-20}$	300 ± 5	Gladius et al., 1997	S-FTIR (a,b)
$<2 \times 10^{-20}$	296 ± 2	Alvarado et al., 1998	S-GC (a,c)

5 Comments

- (a) Decays of pinonaldehyde monitored in the presence of an excess concentration of O₃ in the presence of ~1 bar of air.
- (b) Pinonaldehyde was observed to decay to the 480 L reaction chamber walls in the absence of O₃, and these measured dark decays were taken into account in the data analysis.
- 10 (c) No decays of pinonaldehyde (<5%) were observed in the 7000 L Teflon chamber used.

Preferred Values

$k = <2 \times 10^{-20} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

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The preferred upper limit to the 298 K rate coefficient is based on the study of Alvarado et al. (1998) carried out in a large volume Teflon chamber in which no wall losses of pinonaldehyde were observed.

5 **References**

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 Glasius, M., Calogirou, A., Jensen, N. R., Hjorth, J., and Nielsen, C. J.: Int. J. Chem. Kinet., 29, 527, 1997.

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II.A1.164



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.00 \pm 0.3) \times 10^{-17}$	291 ± 1	Grosjean and Grosjean, 1994	S-UV
<i>Relative Rate Coefficients</i>			
9×10^{-18}	298 ± 2	Fantechi et al., 1998a	RR (a)

5 **Comments**

(a) O_3 was reacted with 2-methyl-3-buten-2-ol and propene or 2-methylpropene (the reference compounds) in the presence of propane as an OH radical scavenger. The concentrations of 2-methyl-3-buten-2-ol and propene or 2-methylpropene were monitored by FTIR spectroscopy. The measured rate coefficient ratios (which were not reported) were placed on an absolute basis by use of rate coefficients at 298 K of $k(\text{O}_3 + \text{propene}) = 1.2 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson et al., 1992) and $k(\text{O}_3 + 2\text{-methylpropene}) = 1.13 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson, 1997). The reference compound corresponding to each of the two reported rate coefficients of $k(\text{O}_3 + 2\text{-methyl-3-buten-2-ol}) = (1.15 \pm 0.22) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $(8.0 \pm 1.0) \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was not reported; however, using the currently recommended rate coefficients at

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298 K of $k(\text{O}_3 + \text{propene}) = 1.01 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Arey, 2003a; IUPAC, current recommendation) and $k(\text{O}_3 + 2\text{-methylpropene}) = 1.13 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Arey, 2003a) results in the approximate average rate coefficient cited in the table.

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Preferred Values

$k = 1.0 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

10 Comments on Preferred Values

The rate coefficients of Grosjean and Grosjean (1994) at $291 \pm 1 \text{ K}$ and of Fantechi et al. (1998a) at $298 \pm 2 \text{ K}$ are in reasonable agreement. However, as noted in comment (a), the lack of detail in the Fantechi et al. (1998a) publication makes re-evaluation of their data somewhat uncertain, especially the derivation of the associated uncertainty. Assuming that the reaction of O_3 with 2-methyl-3-buten-2-ol has a similar temperature dependence to the reactions of O_3 with propene and 2-methylpropene (which have similar room temperature rate coefficients as noted in comment (a)), then the Grosjean and Grosjean (1994) rate coefficient corresponds to a 298 K rate coefficient of $\sim 1.16 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The preferred value is an average of the 298 K rate coefficients obtained from the studies of Grosjean and Grosjean (1994) and Fantechi et al. (1998a).

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The reaction proceeds by initial addition of O_3 across the $\text{C}=\text{C}$ bond to form a 'primary ozonide' which rapidly decomposes to $(\text{CH}_3)_2\text{C}(\text{OH})\text{CHO} + [\text{CH}_2\text{OO}]^*$ and to $\text{HCHO} + [(\text{CH}_3)_2\text{C}(\text{OH})\text{CHOO}]^*$ (Grosjean and Grosjean, 1995; Fantechi et al., 1998b; Alvarado et al., 1999). Product studies of this reaction have been carried out by Grosjean and Grosjean (1995), Fantechi et al. (1998b) and Alvarado et al. (1999) (see also Atkinson and Arey, 2003b), and the observed products are HCHO , $(\text{CH}_3)_2\text{C}(\text{OH})\text{CHO}$ (2-hydroxy-2-methylpropanal), acetone, formic acid, and OH radicals. There are significant discrepancies in the measured yields of formaldehyde, 2-hydroxy-2-methylpropanal and acetone (Grosjean and Grosjean, 1995; Fantechi et al., 1998b; Alvarado et al., 1999; Atkinson and Arey, 2003b), with the most recent and extensive study of Alvarado et al. (1999) reporting molar formation yields of: HCHO , $29 \pm 3\%$; $(\text{CH}_3)_2\text{C}(\text{OH})\text{CHO}$, $\sim 47\%$; acetone, initially $\sim 15\%$ and apparently increasing with the extent of reaction; and OH radicals, $19_{-7}^{+10}\%$. As discussed by Grosjean and Grosjean (1995) and Alvarado et al. (1999), acetone is presumably formed from the $[(\text{CH}_3)_2\text{C}(\text{OH})\text{CHOO}]^*$ Criegee intermediate, and this may account for the variable yields reported (Grosjean and Grosjean, 1995; Fantechi et al., 1998b; Alvarado et al., 1999; Atkinson and Arey, 2003b) and for the observation of Alvarado et al. (1999) of an increasing yield with extent of reaction. Note that the reported yields of 2-hydroxy-2-methylpropanal (Grosjean and Grosjean, 1995; Alvarado et al., 1999) are likely to be lower limits because of the difficulties in quantitatively analyzing this hydroxyaldehyde, which is not commercially available and does not elute from GC columns without prior derivatization.

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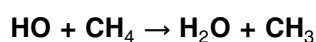
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- 15 IUPAC: <http://www.iupac-kinetic.ch.cam.ac.uk/>, 2004.

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Appendix 2: HO_x + VOC reactions

II.A2.3



$$\Delta H^\circ = -57.8 \text{ kJ} \cdot \text{mol}^{-1}$$

5 Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(4.3 \pm 0.9) \times 10^{-12}$	1234 ± 15	Bott and Cohen, 1989	SH-RA
$1.59 \times 10^{-20} T^{2.84} \exp(-978/T)$	223–420	Vaghjiana and	PLP-LIF
6.35×10^{-15}	298	Ravishankara, 1991	
$4.0 \times 10^{-12} \exp[-(1994 \pm 114)/T]$	278–378	Findlayson-Pitts et al., 1992	DF-RF
5.87×10^{-15}	298		
$9.65 \times 10^{-20} T^{2.58} \exp(-1082/T)$	293–800	Dunlop and Tully, 1993	PLP-LIF (a)
$(5.62 \pm 0.43) \times 10^{-15}$	293		
$2.56 \times 10^{-12} \exp[-(1765 \pm 146)/T]$	233–343	Mellouki et al., 1994	PLP-LIF
$(6.34 \pm 0.88) \times 10^{-15}$	298		
$1.85 \times 10^{-20} T^{-2.82} \exp[-(987 \pm 6)/T]$	195–296	Gierczak et al., 1997	PLP-LIF
$(6.40 \pm 0.38) \times 10^{-15}$	298		FP-LIF (b)
$5.65 \times 10^{-21} T^{3.01} \exp[-(959 \pm 36)/T]$	295–668	Bonard et al., 2002	PLP-LIF
$(6.23 \pm 0.20) \times 10^{-15}$	295		

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Comments

(a) The temperature-dependent expression cited is that for the rate coefficients of Dunlop and Tully (1993) ($T=293\text{--}800\text{ K}$) combined with those of Vaghjiani and Ravishankara (1991) ($T=223\text{--}420\text{ K}$) and as such covers the temperature range 223–800 K.

(b) The temperature-dependent expression cited is that for the rate coefficients of Gierczak et al. (1997) ($T=195\text{--}296\text{ K}$) combined with those of Vaghjiani and Ravishankara (1991) ($T=223\text{--}420\text{ K}$) obtained using a similar technique, and therefore covers the temperature range 195–420 K.

Preferred Values

$k = 6.4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 1.85 \times 10^{-12} \exp(-1690/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–300 K.

Reliability

$\Delta \log k = \pm 0.08$ at 298 K.
 $\Delta (E/R) = \pm 100\text{ K}$.

Comments on Preferred Values

The absolute rate coefficients of Vaghjiani and Ravishankara (1991), Finlayson-Pitts et al. (1992), Dunlop and Tully (1993), Mellouki et al. (1994), Gierczak et al. (1997) and Bonard et al. (2002) are in good agreement. However, over the temperature range $\sim 250\text{--}420\text{ K}$ these rate coefficients of

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Vaghjiani and Ravishankara (1991), Finlayson-Pitts et al. (1992), Dunlop and Tully (1993), Mellouki et al. (1994), Gierczak et al. (1997) and Bonard et al. (2002) are $\sim 20\%$ lower than most of the previously reported absolute rate coefficients (Atkinson, 1994).

The preferred values are derived from the absolute rate coefficient data of Vaghjiani and Ravishankara (1991) and Gierczak et al. (1997), both conducted over significant and overlapping temperature ranges. The temperature-dependent expression obtained by Gierczak et al. (1997) from a fit of their data and those of Vaghjiani and Ravishankara (1991) to the three-parameter equation $k = CT^n \exp(-D/T)$ is accepted, of $k = 1.85 \times 10^{-20} T^{2.82} \exp(-987/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 195–420 K (Gierczak et al., 1997). The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 250 K and is derived from the three-parameter equation with $A = Ce^n T^n$ and $B = D + nT$. The recommended three-parameter expression leads to calculated rate coefficients at 800 K and 1234 K which are within 12% and 3%, respectively of the values measured by Dunlop and Tully (1993) at 800 K and Bott and Cohen (1989) at 1234 K, and agrees to within 8% with the rate coefficients measured by Bonard et al. (2002) over the temperature range 295–668 K.

References

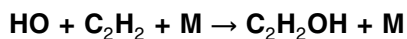
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 Mellouki, A., Téton, S., Laverdet, G., Quilgars, A., and Le Bras, G.: J. Chim. Phys., 91, 473, 1994.
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II.A2.4



$$\Delta H^\circ = -147 \text{kJ} \cdot \text{mol}^{-1}$$

Low-pressure Rate coefficients

5 Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(3 \pm 1) \times 10^{-30} (T/300)^{1.0} [\text{Ar}]$	297–429	Perry and Williamson, 1982	FP-RF (a)
$(6 \pm 3) \times 10^{-30} [\text{He}]$	298	Hack et al., 1983	DF-EPR (b)
$(2.5 \pm 0.3) \times 10^{-30} [\text{Ar}]$	295	Schmidt et al., 1985	PLP-LIF (c)
$5 \times 10^{-30} [\text{N}_2]$	298	Wahner and Zetzsch, 1985	PLP-A (d)
$(4.1 \pm 1.6) \times 10^{-30} [\text{N}_2]$	298	Bohn et al., 1996	PLP-A (e)
$4.3 \times 10^{-29} (T/300)^{-3.1} \exp(-910/T) [\text{He}]$	300–814	Fulle et al., 1997	PLP-LIF (f)
$2.1 \times 10^{-30} [\text{He}]$	298		

Comments

- (a) Photolysis of $\text{H}_2\text{O}-\text{C}_2\text{H}_2$ mixtures with Ar diluent at between 26 mbar and 530 mbar. Pressure dependence observed is in agreement with earlier work (Perry et al., 1977; Michael et al., 1980). Evaluation of the falloff curve with $F_c=0.5$.
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- (b) Pressures around 2.6 mbar were used. By the use of data from Perry and Williamson (1982) and $F_c=0.5$, a falloff analysis of the measured k leads to the given k_0 value.
- (c) Experiments in He, Ar and N_2 at pressures between 1 mbar and 1000 mbar (in Ar). Construction of falloff curve with $F_c=0.6$ leading to $k_\infty=(8.3\pm 0.8) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- (d) Experiments in N_2 over the range 20 mbar to 1000 mbar. Falloff curve constructed with $F_c=0.6$ leading to $k_\infty=9 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- (e) Experiments with $M=N_2, O_2$, and synthetic air at pressures from 15 mbar to 1 bar. Falloff extrapolation with $F_c=0.6$. Effective rate coefficients for HO radical removal in O_2 and synthetic air were markedly lower than in N_2 due to HO radical regeneration by the reaction $C_2H_2OH+O_2 \rightarrow HO + \text{products}$, which shows evidence for an influence of the extent of vibrational de-excitation of C_2H_2OH .
- (f) Pressure range 2 mbar to 130 bar of He. Falloff curves were constructed with the present and earlier data (Schmidt et al., 1985) using a calculated $F_c=[0.17 \exp(-51/T)+\exp(-T/204)]$, i.e., $F_c(298 \text{ K})=0.37$. From a third-law analysis of the equilibrium constant, the value $\Delta H^\circ(0 \text{ K})=-(146\pm 10) \text{ kJ mol}^{-1}$ was derived. The equilibrium constant obtained at temperatures above 700 K is given by $K_c=5.4 \times 10^{-2} T^{-1.7} \exp(17560/T) \text{ bar}^{-1}$.

Preferred Values

$k_0 = 5 \times 10^{-30} (T/300)^{-1.5} [N_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 300–800 K.

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Reliability

$\Delta \log k_0 = \pm 0.1$ at 298 K.

$\Delta n = \pm 1.5$.

Comments on Preferred Values

- The preferred rate coefficient at 298 K is based on the experimental data of Schmidt et al. (1985), Wahner and Zetzsch (1985) and Bohn et al. (1996) and the theoretical analysis of Smith et al. (1984). The temperature dependence is based on the data of Perry et al. (1977), Michael et al. (1980) and Perry and Williamson (1982) as discussed and evaluated by Atkinson (1989). At temperatures above ~ 500 K another component of the rate coefficient with a much stronger temperature dependence also has to be taken into account (Atkinson, 1989). The preferred values should be used in connection with the calculated F_c values from Fulle et al. (1997) such as given in comment (f) of k_0 . Fulle et al. (1997) provide a set of falloff curves from 250 K to 1200 K and from 0.26 bar to 80 bar which relate the low temperature-low activation energy regime with the high temperature-high activation energy regime. A comparison of earlier data at pressures between 0.01 bar and 1 bar with the results from Fulle et al. (1997) at 2 bar to 80 bar shows considerable discrepancies. Earlier measurements appeared to level off below 1 bar while Fulle et al. (1997) find falloff curves leading to k_∞ considerably higher than previous extrapolations. This influences the construction of falloff curves and the extrapolation to k_0 .

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High-pressure Rate coefficients

Rate coefficient data

$k_{\infty}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(6.91 \pm 0.90) \times 10^{-13}$	297	Perry and Williamson, 1982	FP-RF (a)
$(8.3 \pm 0.8) \times 10^{-13}$	295	Schmidt et al., 1985	PLP-LIF (b)
9×10^{-13}	298	Wahner and Zetzsch, 1985	PLP-A (c)
$(8.5 \pm 0.6) \times 10^{-13}$	298	Bohn et al., 1996	PLP-A (d)
$8.5 \times 10^{-12} \exp(-705/T)$	333–1273	Liu et al., 1988	PR-RA(e)
8.0×10^{-13}	298*		
$3.8 \times 10^{-11} \exp(-910/T)$	300–814	Fulle et al., 1997	PLP-LIF (f)
1.8×10^{-12}	298*		
<i>Relative Rate Coefficients</i>			
$(8.4 \pm 1.4) \times 10^{-13}$	298	Atkinson and Aschmann, 1984	RR (g)
$(8.3 \pm 1.8) \times 10^{-13}$	297 ± 2	Hatakeyama et al., 1986	RR (h)
$(7.0 \pm 0.7) \times 10^{-13}$	297 ± 2	Arnts et al., 1989	RR (i)

Comments

- 5 (a) See comment (a) for k_0 .
(b) See comment (c) for k_0 .
(c) See comment (d) for k_0 .

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- (d) See comment (e) for k_0 .
(e) Pulsed radiolysis technique with resonance absorption measurement of HO radicals. Measurements were conducted at 1 bar of Ar.
(f) See comment (f) for k_0 .
5 (g) HO radicals were generated by the photolysis of CH_3ONO in CH_3ONO - NO - C_2H_2 -cyclohexane-air mixtures at 1 bar total pressure. The concentrations of acetylene and cyclohexane were measured by GC. The measured rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{cyclohexane}) = 7.21 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson, 1997).
10 (h) HO radicals were generated by photolysis of H_2O_2 in air at 254 nm. The concentrations of acetylene and cyclohexane (the reference compound) were monitored by FTIR spectrometry. Measurements were carried out at 1 bar pressure in air. The measured rate coefficient ratio $k(\text{HO} + \text{C}_2\text{H}_2)/k(\text{HO} + \text{cyclohexane}) = 0.116 \pm 0.025$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{cyclohexane}) = 7.19 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson, 1997).
15 (i) HO radicals were generated by the photolysis of CH_3ONO in air at 1 bar pressure. The concentrations of acetylene and ethane (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(\text{HO} + \text{C}_2\text{H}_2)/k(\text{HO} + \text{ethane}) = 2.84 \pm 0.26$ (two standard deviations) is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{ethane}) = 2.46 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current evaluation).
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Preferred Values

no recommendation

Comments on Preferred Values

The measurements of Fulle et al. (1997), carried out at total pressures of He diluent of 2 bar to 130 bar, show that the rate coefficient k continues to increase markedly with increasing pressure for pressures above 1 bar. Fulle et al. (1997) obtained $k_{\infty} = 3.8 \times 10^{-11} \exp(-910/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, with $k_{\infty} = 1.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and $k = 1.4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and 1 bar of He, with $F_c = [0.17 \exp(-51/T) + \exp(-T/204)]$ for $M = \text{He}$ ($F_c = 0.37$ at 298 K). The results of this study of Fulle et al. (1997) at 1 bar, however, are considerably higher than several previous absolute rate coefficient studies (Perry and Williamson, 1982; Schmidt et al., 1985; Wahner and Zetzsch, 1985; Bohn et al., 1996; Perry et al., 1977; Michael et al., 1980; Liu et al., 1988; Pastrana and Carr, 1974) and relative rate coefficient studies (Atkinson and Aschmann, 1984; Hatakeyama et al., 1986; Arnts et al., 1989), which indicate a rate coefficient at room temperature and 1 bar of air or N_2 of $(8-9) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The relative rate studies of Atkinson and Aschmann (1984) Hatakeyama et al. (1986) and Arnts et al. (1989) measured the disappearance rate of acetylene in ~ 1 bar of air; however, the HO radical reaction with acetylene is slow and measurements of this rate coefficient using relative rate methods may be subject to significant uncertainty.

Clearly, relative rate studies (Atkinson and Aschmann, 1984; Hatakeyama et al., 1986; Arnts et al., 1989) and absolute rate studies conducted up to ≤ 1 bar total pressure (Perry et al., 1977; Michael et al., 1980; Perry and Williamson, 1982; Schmidt et al., 1985; Wahner and Zetzsch, 1985; Liu et al., 1988; Bohn

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et al., 1996) lead to a rate coefficient at ~ 1 bar pressure of air or N_2 markedly lower (by $\sim 40\%$) than that calculated from the study of Fulle et al. (1997) with the earlier absolute studies (Perry et al., 1977; Michael et al., 1980; Perry and Williamson, 1982; Schmidt et al., 1985; Wahner and Zetzsch, 1985; Liu et al., 1988; Bohn et al., 1996) also leading to a markedly lower value of k_{∞} at room temperature. In view of these inconsistencies, we make no recommendation concerning either the rate coefficient k_{∞} or the rate coefficient k at 298 K and 1 bar of air. Further absolute (and relative) rate studies are urgently needed to resolve the above noted discrepancies.

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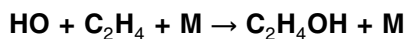
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II.A2.5



$$\Delta H^\circ = -23 \text{kJ} \cdot \text{mol}^{-1}$$

Low-pressure Rate coefficients

5 Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$5.5 \times 10^{-29} [\text{Ar}]$	296	Zellner and Lorenz, 1984	PLP-RF (a)
$(6.1 \pm 1.2) \times 10^{-29} [\text{N}_2]$	300	Kuo and Lee, 1991	DF-RF (b)
$(5.2 \pm 1.1) \times 10^{-29} [\text{O}_2]$	300		
$4.1 \times 10^{-29} (T/300)^{-3.4} [\text{He}]$	300–800	Fulle et al., 1997	PLP-LIF (c)
$(2.8 \pm 0.1) \times 10^{-29} (T/300)^{-3.5} [\text{He}]$	300–423	Chuong and Stevens, 2000	DF-LIF (d)
<i>Relative Rate Coefficients</i>			
$(9.5^{+3.2}_{-2.4}) \times 10^{-29} [\text{air}]$	295	Klein et al., 1984	RR (e)
$(5.9^{+3.0}_{-1.0}) \times 10^{-29} [\text{Ar}]$	295		

Comments

- (a) Pressure range 4 mbar to 130 mbar, temperature range 296 K to 524 K. Falloff extrapolation using $F_c=0.8$.

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- (b) Pressure range 0.4 mbar to 66 mbar. HO radicals were generated by reaction of H atoms with excess NO₂. Data extrapolated using $F_c=0.7$.
- (c) The pressure was varied between 1 mbar and 150 bar. Falloff curves were also constructed using earlier rate data with a calculated $F_c=0.21 \exp(-220/T)+\exp(-T/305)$ and $F_c(300)=0.47$. The value $\Delta H^\circ(0\text{ K})=-(123\pm 6)\text{ kJ mol}^{-1}$ was derived from a third-law analysis of the equilibrium constant K_c for which $K_c=2.1\times 10^{-2} T^{-0.95} \exp(14\,780/T)\text{ bar}^{-1}$ was obtained from measurements performed at 646 K to 803 K and He pressures up to 140 bar.
- (d) Pressure range 2.6 mbar to 8 mbar. Falloff extrapolation using $F_c=0.6$ and $k_\infty=1.96\times 10^{-12} \exp(438/T)\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ from Klein et al. (1984). Differences to the results from Fulle et al. (1997) due to the use of a larger F_c .
- (e) HO₂NO₂-NO system used as source of HO radicals. Reaction of HO radicals with C₂H₄ was studied in 420 L glass reactor relative to HO + *n*-hexane where the latter reaction was calibrated against absolute measurements of the reaction HO + *n*-butane [$k(295\text{ K})=2.53\times 10^{-12}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$]. Pressure range 1.3 mbar to 1000 mbar, falloff curves constructed with $F_c=0.7$.

Preferred Values

- $k = 7 \times 10^{-29} (T/300)^{-3.1} [\text{N}_2]\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ over the temperature range 200–300 K.

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Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.
 $\Delta n = \pm 2$.

Comments on Preferred Values

- Preferred values are based on an average of the data from Zellner and Lorenz (1984), Kuo and Lee (1991), Fulle et al. (1997), Chuong and Stevens (2000), Klein et al. (1984), Atkinson (1994), Tully (1983), Davis et al. (1975), Howard (1976), Greiner (1970), Morris et al. (1971), Overend and Paraskevopoulos (1977), Atkinson et al. (1977), Lloyd et al. (1976) and Cox (1975). Falloff curves are constructed with the calculated $F_c=0.48$ from Fulle et al. (1997).

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High-pressure Rate coefficients

Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(8.47 \pm 0.24) \times 10^{-12}$	291	Tully, 1993	PLP-LIF (a)
$3.3 \times 10^{-12} \exp[(320 \pm 150)/T]$	296–524	Zellner and Lorenz, 1984	PLP-RF (b)
9.7×10^{-12}	298		
$(9.4 \pm 1.6) \times 10^{-12}$	298	Nielsen et al., 1990	PR-RA (c)
$(7.7 \pm 1.0) \times 10^{-12}$	298	Becker et al., 1991	PLP-LIF (d)
1.0×10^{-11}	300–800	Fulle et al., 1997	PLP-LIF (e)
<i>Relative Rate Coefficients</i>			
$(8.11 \pm 0.37) \times 10^{-12}$	299 ± 2	Atkinson et al., 1982	RR (f)
$(8.5 \pm 0.6) \times 10^{-12}$	295	Klein et al., 1984	RR (g)

Comments

- 5 (a) Higher end of falloff curve at 66 mbar to 790 mbar; temperature range 291 K to 591 K.
- (b) See comment (a) for k_0 .
- (c) Pulse radiolysis of H_2O -Ar mixtures. HO monitored by UV absorption at 309 nm. Rate coefficient determined at a total pressure of 1 bar.

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- (d) Experiments were carried out at a total pressure of 1 bar of synthetic air. Numerical simulation with a mechanism of 12 reactions.
- (e) See comment (c) for k_0 .
- 5 (f) HO radicals were generated by photolysis of CH_3ONO in presence of air containing NO. Concentrations of ethene and cyclohexane (the reference compound) were measured by GC. The rate coefficient ratio of $k(\text{HO} + \text{ethene})/k(\text{HO} + \text{cyclohexane}) = 1.12 \pm 0.05$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{cyclohexane}) = 7.24 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson, 1997).
- 10 (g) See comment (e) for k_0 .

Preferred Values

$k = 7.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and 1 bar of air.
 $k = 9.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 200–300 K.

15 Reliability

$\Delta \log k_\infty = \pm 0.3$ at 298 K.
 $\Delta n = \pm 0.5$.

Comments on Preferred Values

- 20 The preferred value is similar to those selected in Fulle et al. (1997), Lloyd et al. (1976) and Nielsen et al. (1990). The recent experiments by Fulle et al. (1997) confirm temperature independent k values. Falloff curves should be

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calculated with the theoretical expression for $F_c=0.48$ which probably applies to $M = \text{He}$ as well as N_2 and is practically constant over the indicated temperature range.

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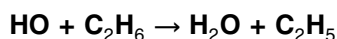
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II.A2.6



$$\Delta H^\circ = -74 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.90 \pm 0.60) \times 10^{-13}$	296	Howard and Evenson, 1976	DF-LMR
$(2.6 \pm 0.4) \times 10^{-13}$	298	Leu, 1979	DF-RF
8.0×10^{-14}	238	Margitan and Watson, 1982	PLP-RF
$1.43 \times 10^{-14} T^{1.05} \exp(-911/T)$	297–800	Tully et al., 1983	FP-RF
$(2.59 \pm 0.21) \times 10^{-13}$	297		
$1.80 \times 10^{-11} \exp[-(1240 \pm 110)/T]$	240–295	Smith et al., 1984	FP-RF
$(2.63 \pm 0.10) \times 10^{-13}$	295		
2.75×10^{-13}	295	Devolder et al., 1984	DF-RF
$(2.67 \pm 0.40) \times 10^{-13}$	295 ± 2	Baulch et al., 1985	DF-RF
$8.51 \times 10^{-18} T^{2.06} \exp(-430/T)$	293–705	Tully et al., 1986	PLP-LIF
$(2.39 \pm 0.10) \times 10^{-13}$	292.5		
$(1.27 \pm 0.08) \times 10^{-13}$	248	Stachnik et al., 1986	PLP-RA
$(1.29 \pm 0.09) \times 10^{-13}$	248		
$(2.51 \pm 0.06) \times 10^{-13}$	297		
$(2.50 \pm 0.06) \times 10^{-13}$	297		
$(2.77 \pm 0.3) \times 10^{-13}$	296 ± 2	Bourmada et al., 1987	DF-RF
$8.4 \times 10^{-12} \exp[-(1050 \pm 100)/T]$	226–363	Wallington et al., 1987	FP-RF
$(2.30 \pm 0.26) \times 10^{-13}$	296		
$(2.61 \pm 0.13) \times 10^{-13}$	296	Zabarnick et al., 1988	PLP-LIF

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$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
$(2.38 \pm 0.16) \times 10^{-13}$	297 ± 2	Abbatt et al., 1990	DF-LIF
$(1.54 \pm 0.24) \times 10^{-11}$	1225 ± 16	Bolt and Cohen, 1991	SH-RA
$1.03 \times 10^{-11} \exp[-(1108 \pm 40)/T]$	231–377	Talukdar et al., 1994	PLP-LIF
$(2.43 \pm 0.13) \times 10^{-13}$	298		
8.37×10^{-12}	974 ± 16	Koffend and Cohen, 1996	SH-RA
$(2.55 \pm 0.3) \times 10^{-13}$	300	Donahue et al., 1996	DF-LIF
$(2.59 \pm 0.08) \times 10^{-13}$	300	Donahue et al., 1998	DF-LIF
$(3.55 \pm 0.11) \times 10^{-13}$	325		
$(3.90 \pm 0.12) \times 10^{-13}$	340		
$(4.38 \pm 0.23) \times 10^{-13}$	360		
$(5.61 \pm 0.17) \times 10^{-13}$	375		
$(6.04 \pm 0.18) \times 10^{-13}$	390		
$(2.69 \pm 0.27) \times 10^{-14}$	180	Clark et al., 1998	DF-LIF
$(3.77 \pm 0.04) \times 10^{-14}$	190		
$(4.54 \pm 0.25) \times 10^{-14}$	200		
$(6.51 \pm 0.07) \times 10^{-14}$	213		
$(8.08 \pm 0.12) \times 10^{-14}$	225		
$(9.67 \pm 0.18) \times 10^{-14}$	238		
$(1.251 \pm 0.014) \times 10^{-13}$	250		
$(1.640 \pm 0.018) \times 10^{-13}$	265		
$(2.081 \pm 0.016) \times 10^{-13}$	280		
$(2.515 \pm 0.021) \times 10^{-13}$	295		
$(2.953 \pm 0.050) \times 10^{-13}$	310		
$(3.464 \pm 0.037) \times 10^{-13}$	325		
$(3.744 \pm 0.038) \times 10^{-13}$	340		
$(4.637 \pm 0.164) \times 10^{-13}$	360		

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Preferred Values

$k = 2.4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 6.9 \times 10^{-12} \exp(-1000/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–300 K.

5 Reliability

$\Delta \log k = \pm 0.08$ at 298 K.

$\Delta (E/R) = \pm 100$ K.

Comments on Preferred Values

The preferred values were obtained by using the absolute rate coefficient data of Smith et al. (1984), Tully et al. (1986) (this study being judged to supersede that of Tully et al., 1983), Stachnick et al. (1986), Wallington et al. (1987), Abbatt et al. (1990), Bott and Cohen (1991), Talukdar et al. (1994), Koffend and Cohen (1996), Donahue et al. (1996, 1998) and Clarke et al. (1998). The absolute rate coefficients used in the evaluation (Smith et al., 1984; Tully et al., 1986; Stachnick et al., 1986; Wallington et al., 1987; Abbatt et al., 1990; Bott and Cohen, 1991; Talukdar et al., 1994; Koffend and Cohen, 1996; Donahue et al., 1996, 1998; Clarke et al., 1998) were fitted to the three-parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 1.49 \times 10^{-17} T^2 \exp(-499/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 180–1230 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 250 K and is derived from the three-parameter equation with $A = Ce^{2T^2}$ and $B = D + 2T$. The preferred Arrhenius expression predicts rate coefficients at 180 K and 190 K which agree to within 6% with those measured by Clarke et al. (1998).

The absolute rate coefficients of Howard and Evenson (1976), Leu (1979),

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Margitan and Watson (1982), Devolder et al. (1984), Baulch et al. (1985), Bourmada et al. (1987), Zabarnick et al. (1988) and Schiffman et al. (1991) (at room temperature, the precise temperature not being specified), which are not used in the evaluation of the rate coefficient, are in good agreement with the preferred values, as are the relative rate coefficients of Baulch et al. (1983), Edney et al. (1986) and Finlayson-Pitts et al. (1993).

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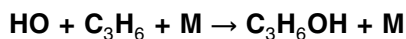
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II.A1.7



$$\Delta H^\circ = -134 \text{ kJ} \cdot \text{mol}^{-1}$$

Low-pressure Rate coefficients

5 Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$8 \times 10^{-28}[\text{Ar}]$	298	Zellner and Lorenz, 1983	PLP-RF (a)
<i>Relative Rate Coefficients</i>			
$8 \times 10^{-27}[\text{Ar}]$	298	Klein et al., 1984	(b)
$8 \times 10^{-27}[\text{air}]$			

Comments

- (a) Pressure range 1.3 mbar to 170 mbar. Falloff behavior detected, and evaluated with $F_c=0.8$. Rough estimate of k_0 because of the only limited extent of observed falloff.
 10 (b) $\text{HO}_2\text{-NO}_2\text{-NO}$ system used as source of HO radicals. Reaction studied relative to $\text{HO} + n\text{-hexane}$, with the latter reaction calibrated against absolute measurements of the reaction $\text{HO} + n\text{-butane}$ ($k=2.53 \times 10^{-12} \text{ cm}^3$

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molecule⁻¹ s⁻¹ at 295 K). Pressure range 1.3 mbar to 1000 mbar; falloff effects could be detected. Evaluation with $F_c=0.5$ gives the present k_0 value. Rough estimate of k_0 because of the only limited extent of observed falloff.

Preferred Values

- 5 $k_0 = 8 \times 10^{-27} (T/300)^{-3.5} [\text{N}_2] \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 1.0$ at 298 K.

$\Delta n = \pm 1$.

- 10 *Comments on Preferred Values*

The uncertainty of the extrapolated k_0 is large, because the reaction is close to the high-pressure limit at the pressures studied. The preferred values follow the falloff extrapolation from Klein et al. (1984) which shows the smallest scatter. Falloff extrapolations are made using $F_c=0.5$ at 300 K.

- 15 The temperature coefficient of k_0 is estimated by analogy to the reaction $\text{HO} + \text{C}_2\text{H}_4 + \text{M} \rightarrow \text{C}_2\text{H}_4\text{OH} + \text{M}$.

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High-pressure Rate coefficients

Rate coefficient data

$k_\infty/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(3.0 \pm 0.5) \times 10^{-11}$	298	Zellner and Lorenz, 1984	PLP-RF (a)
<i>Relative Rate Coefficients</i>			
$(3.0 \pm 0.2) \times 10^{-11}$	295	Klein et al., 1984	(b)
$(8.1 \pm 1.8) \times 10^{-11}$	103	Vakhtin et al., 2001	(c)

Comments

- 5 (a) See comment (a) for k_0 .
 (b) See comment (b) for k_0 .
 (c) Pulsed Laval nozzle supersonic expansion of nitrogen with admixed reactants. HO generated by photolysis of H_2O_2 or reaction of $\text{O}(^1\text{D})$ with *n*-butane after photolysis of N_2O . $[\text{N}_2]=2.1 \times 10^{16} \text{ molecule cm}^{-3}$. Reaction
 10 observed very close to the high pressure limit.

Preferred Values

$k = 2.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and 1 bar of air.

$k_\infty = 3.0 \times 10^{-11} (T/300)^{-1} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the range 200–300 K.

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Reliability

$\Delta \log k_{\infty} = \pm 0.1$ over the temperature range 200–300 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

- 5 The preferred values are based on Zellner and Lorenz (1984), Klein et al. (1984), Vakhtin et al. (2001), Nielsen et al. (1990) and Tully and Goldsmith (1985). There is an uncertainty about the extent of falloff at temperatures above 300 K and there is the possibility of a small activation barrier, such as observed in the reaction $\text{HO} + \text{C}_2\text{H}_2 + \text{M} \rightarrow \text{C}_2\text{H}_2\text{OH} + \text{M}$. The preferred
- 10 temperature dependence is derived by combining the results from Zellner and Lorenz (1984), Klein et al. (1984) and Vakhtin et al. (2001), confirming the suggestions from Atkinson (1994) and Tsang (1991). $F_c = 0.5$ serves for estimating the extent of falloff.

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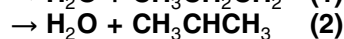
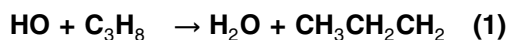
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II.A2.8



$$\Delta H^0 (1) = -73.7 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H^0 (2) = -87.9 \text{ kJ} \cdot \text{mol}^{-1}$$

5 Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.62 \pm 0.67) \times 10^{-11}$	1220 ± 15	Bott and Cohen, 1984	SH-RA
$(2.19 \pm 0.60) \times 10^{-11}$	1074	Smith et al., 1985	LH-LIF
$(1.20 \pm 0.18) \times 10^{-12}$	295 ± 2	Baulch et al., 1985	DF-RF
$1.04 \times 10^{-16} T^{-1.72} \exp(-145/T)$	293–854	Droege and Tully, 1986	PLP-LIF
$(1.10 \pm 0.04) \times 10^{-12}$	293		
$(1.21 \pm 0.10) \times 10^{-12}$	297 ± 2	Abbatt et al., 1990	DF-LIF
$(1.22 \pm 0.08) \times 10^{-12}$	298	Mac Leod et al., 1990	PLP-LIF
$9.81 \times 10^{-12} \exp[-(650 \pm 30)/T]$	233–363	Mellouki et al., 1994	PLP-LIF
$(1.05 \pm 0.09) \times 10^{-12}$	295		
$1.01 \times 10^{-11} \exp[-(657 \pm 46)/T]$	233–376	Talukdar et al., 1994	PLP-LIF
$(1.11 \pm 0.04) \times 10^{-12}$	298		
$(1.09 \pm 0.03) \times 10^{-12}$	300	Donahue et al., 1998	DF-LIF
$(1.37 \pm 0.04) \times 10^{-12}$	325		
$(1.46 \pm 0.04) \times 10^{-12}$	340		
$(1.60 \pm 0.09) \times 10^{-12}$	360		
$(1.85 \pm 0.06) \times 10^{-12}$	375		
$(1.83 \pm 0.10) \times 10^{-12}$	390		
$(3.626 \pm 0.247) \times 10^{-13}$	190	Clarke et al., 1998	DF-LIF

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$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
$(4.136 \pm 0.127) \times 10^{-13}$	200		
$(4.864 \pm 0.095) \times 10^{-13}$	213		
$(5.602 \pm 0.063) \times 10^{-13}$	225		
$(6.475 \pm 0.053) \times 10^{-13}$	238		
$(7.532 \pm 0.051) \times 10^{-13}$	250		
$(8.691 \pm 0.147) \times 10^{-13}$	265		
$(1.129 \pm 0.0159) \times 10^{-12}$	295		
$(1.276 \pm 0.0182) \times 10^{-12}$	310		
$(1.356 \pm 0.0140) \times 10^{-12}$	325		
$(1.480 \pm 0.0136) \times 10^{-12}$	340		
$(1.640 \pm 0.0229) \times 10^{-12}$	360		
$(1.15 \pm 0.1) \times 10^{-12}$	298	Carl and Crowley, 2001	PLP-RF
$(1.17 \pm 0.1) \times 10^{-12}$	298		
$5.81 \times 10^{-12} T^{-1.83} \exp(-167/T)$	210–480	Kozlov et al., 2003	FP-RF
$(1.13 \pm 0.02) \times 10^{-12}$	298		

Preferred Values

$$k = 1.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 7.6 \times 10^{-12} \exp(-585/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range}$$

5 200–300 K.

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Reliability

$\Delta \log k = \pm 0.08$ at 298 K.

$\Delta (E/R) = \pm 100$ K.

Comments on Preferred Values

5 The absolute rate coefficient data of Bott and Cohen (1984), Smith et al. (1985), Droege and Tully (1986), Abbatt et al. (1990), Mac Leod et al. (1990), Mellouki et al. (1994), Talukdar et al. (1994), Donahue et al. (1998) and Clarke et al. (1998) were used to derive the preferred value. These data were fitted to the three-parameter equation $k = CT^2 \exp(-D/T)$, resulting in $k = 1.65 \times 10^{-17} T^2$
10 $\exp(-87/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 190–1220 K. The rate coefficients recently measured by Kozlov et al. (2003) are in agreement with the preferred value to within 5% over the entire temperature range studied (210–480 K). The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 250 K, and is derived from the three-parameter equation with $A = Ce^2 T^2$ and
15 $B = D + 2T$. The preferred Arrhenius expression predicts a rate coefficient at 190 K which is within 4% of that measured by Clarke et al. (1998). The relative rate coefficients of Atkinson et al. (1982), Baulch et al. (1983), Edney et al. (1986), Nielsen et al. (1991), Finlayson-Pitts et al. (1993) and DeMore and Bayes (1999) are in good agreement with the recommended expression, as
20 are the absolute rate coefficients of Tully et al. (1983) (judged to be superseded by the study of Droege and Tully, 1986), Baulch et al. (1985), Schiffman et al. (1991) and Carl and Crowley (2001).

Droege and Tully (1986) also measured rate coefficients for the reaction of the HO radical with fully and partially deuterated propanes, and derived a value
25 of $k_1/k_2 = 226 T^{-0.64} \exp(-816/T)$, leading to $k_1 = 3.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

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at 298 K and $k_2 = 8.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

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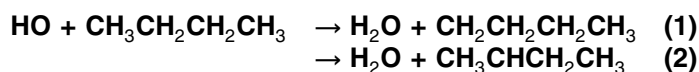
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II.A2.9



$$\Delta H^0 (1) = -72.4 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H^0 (2) = -86.6 \text{ kJ} \cdot \text{mol}^{-1}$$

5 Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.41 \times 10^{-11} \exp[-(524 \pm 93)/T]$	298–495	Greiner, 1970	FP-KS
$(2.56 \pm 0.08) \times 10^{-12}$	298		
$(2.35 \pm 0.35) \times 10^{-12}$	298	Stuhl, 1973	FP-RF
$(4.22 \pm 0.17) \times 10^{-12}$	298	Gordon and Mulac, 1975	PR-RA
$(4.15 \pm 0.17) \times 10^{-12}$	381		
$(4.98 \pm 0.17) \times 10^{-12}$	416		
$1.76 \times 10^{-11} \exp[-(559 \pm 151)/T]$	298–420	Perry et al., 1976	FP-RF
$(2.72 \pm 0.27) \times 10^{-12}$	298		
$(2.67 \pm 0.22) \times 10^{-12}$	297 ± 2	Paraskevopoulos and Nip, 1980	FP-RA
$(2.3 \pm 0.3) \times 10^{-12}$	295	Schmidt et al., 1985	PLP-LIF
$2.34 \times 10^{-17} T^{1.95} \exp(134/T)$	294–509	Droege and Tully, 1986	PLP-LIF
$(2.42 \pm 0.10) \times 10^{-12}$	294		
$(2.25 \pm 0.10) \times 10^{-12}$	297 ± 2	Abbatt et al., 1990	DF-LIF
$(2.32 \pm 0.08) \times 10^{-12}$	~298	Schiffman et al., 1991	PLP-IR

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$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
$2.04 \times 10^{-17} T^2 \exp[(85 \pm 8)/T]$	231–378	Talukdar et al., 1994	PLP-LIF
$(2.459 \pm 0.018) \times 10^{-12}$	299		
$(2.43 \pm 0.07) \times 10^{-12}$	300	Donahue et al., 1998	DF-LIF
$(2.74 \pm 0.08) \times 10^{-12}$	325		
$(2.87 \pm 0.09) \times 10^{-12}$	340		
$(3.48 \pm 0.10) \times 10^{-12}$	375		
$(3.54 \pm 0.11) \times 10^{-12}$	390		
$(2.6 \pm 0.5) \times 10^{-12}$	300	Chuong and Stevens, 2002	DF-LIF
$(2.6 \pm 0.2) \times 10^{-12}$	300		
<i>Relative Rate Coefficients</i>			
9.9×10^{-12}	753	Baker et al., 1970; Baldwin and Walker, 1979	RR (a)
$(9.3 \pm 0.8) \times 10^{-12}$	653	Hucknell et al., 1975	RR (b)
$(2.52 \pm 0.25) \times 10^{-12}$	299 ± 2	Atkinson et al., 1981	RR (c)
$(2.71 \pm 0.32) \times 10^{-12}$	295 ± 1	Atkinson and Aschmann, 1984	RR (c)
$(2.70 \pm 0.34) \times 10^{-12}$	300 ± 2	Barnes et al., 1986	RR (d)
$(2.36 \pm 0.04) \times 10^{-12}$	300 ± 2	Behnke et al., 1988	RR (e)
$1.39 \times 10^{-11} \exp(-526/T)$	235–361	DeMore and Bayes, 1999	RR (f)
2.33×10^{-12}	298		

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Comments

- 5 (a) Derived from the effects of the addition of small amounts of *n*-butane to slowly reacting mixtures of $\text{H}_2 + \text{O}_2$. The loss of H_2 was followed by monitoring the pressure change due to the reaction $2\text{H}_2 + \text{O}_2 \rightarrow 2\text{H}_2\text{O}$, and the loss of *n*-butane was measured by GC. The rate coefficient ratio $k(\text{HO} + n\text{-butane})/k(\text{HO} + \text{H}_2) = 13.2$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{H}_2) = 7.87 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 753 K (Atkinson, 2003).
- 10 (b) HO radicals were generated by the decomposition of H_2O_2 in a boric acid-coated reaction vessel, and the concentrations of *n*-butane and propane (the reference compound) were measured by GC. The measured rate coefficient ratios of $k(\text{HO} + n\text{-butane})/k(\text{HO} + \text{propane}) = 1.54 \pm 0.13$ is placed on an absolute value using a rate coefficient of $k(\text{HO} + \text{propane}) = 6.16 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 653 K (IUPAC, current recommendation).
- 15 (c) HO radicals were generated by the photolysis of CH_3ONO in one atmosphere of air. The concentrations of *n*-butane and propene (the reference compound) were measured by GC. The measured rate coefficient ratios of $k(\text{HO} + n\text{-butane})/k(\text{HO} + \text{propene}) = 0.0962 \pm 0.0093$ at 299 ± 2 K (Atkinson et al., 1981) and 0.101 ± 0.012 at 295 ± 1 K (Atkinson and Aschmann, 1984) are placed on an absolute value using a rate coefficient of $k(\text{HO} + \text{propene}) = 4.85 \times 10^{-12} \exp(504/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at atmospheric pressure of air (Atkinson, 1997).
- 20 (d) HO radicals were generated by the photolysis of H_2O_2 in air at atmospheric pressure, and the concentrations of *n*-butane and ethene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(\text{HO} + n\text{-butane})/k(\text{HO} + \text{ethene}) = 0.32 \pm 0.04$ is placed on an absolute
- 25

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basis by use of a rate coefficient of $k(\text{HO} + \text{ethene}) = 8.44 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 300 K and atmospheric pressure of air (Atkinson, 1997).

- (e) HO radicals were generated by the photolysis of NO_x -organic-air mixtures at atmospheric pressure. The concentrations of *n*-butane and *n*-octane (the reference compound) were measured by GC, and the measured rate coefficient ratio of $k(\text{HO} + n\text{-butane})/k(\text{HO} + n\text{-octane})$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + n\text{-octane}) = 8.15 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 300 K (Atkinson, 2003).
- (f) HO radicals were generated by the photolysis of H_2O at 185 nm or, at low temperatures, by the photolysis of N_2O at 185 nm in the presence of H_2 . The concentrations of *n*-butane and propane (the reference compound) were measured by GC. The measured rate coefficient ratios $k(\text{HO} + n\text{-butane})/k(\text{HO} + \text{propane})$ are placed on an absolute basis using a rate coefficient of $k(\text{HO} + \text{propane}) = 1.65 \times 10^{-17} T^2 \exp(87/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-10}$ (IUPAC, current recommendation).

Preferred Values

$k = 2.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 9.1 \times 10^{-12} \exp(-405/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 230–300 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.

$\Delta (E/R) = \pm 150 \text{ K}$.

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Comments on Preferred Values

The preferred values are based on the absolute rate coefficients of Droege and Tully (1986), Abbatt et al. (1990), Talukdar et al. (1994) and Donahue et al. (1998) and the relative rate coefficients of Baker et al. (1970) (as re-evaluated by Baldwin and Walker, 1979), Hucknall et al. (1975) and DeMore and Bayes (1999). The rate coefficients from these studies are fitted to the three parameter expression, $k = CT^2 \exp(-D/T)$, resulting in $k = 1.81 \times 10^{-17} T^2 \exp(114/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 230–760 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 260 K and is derived from the three parameter expression with $A = Ce^2T^2$ and $B = D + 2T$. The preferred values are in good agreement with the room temperature absolute and relative rate coefficients of Greiner (1970), Stuhl (1973), Perry et al. (1976), Paraskevopoulos and Nip (1980), Schmidt et al. (1985), Schiffman et al. (1991), Atkinson et al. (1981), Atkinson and Aschmann (1984), Barnes et al. (1986), Behnke et al. (1988) and Chuong and Stevens (2002), which were not used in the evaluation of the rate coefficient.

Droege and Tully (1986) also measured rate coefficients for the reaction of the HO radical with *n*-butane- d_{10} , and derived a value of $k_1/k_2 = 1.035 \exp(-536/T)$, leading to $k_1 = 3.4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and $k_2 = 2.00 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

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II.A2.10

HO + CH₂=C(CH₃)CH=CH₂ (isoprene) → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$2.36 \times 10^{-11} \exp[(409 \pm 28)/T]$	299–422	Kleindienst et al., 1982	FP-RF
$(9.26 \pm 1.5) \times 10^{-11}$	299		
$9.7 \times 10^{-11} (T/298)^{-1.36}$	249–348	Siese et al., 1994	FP-RF
9.7×10^{-11}	298		
$(1.10 \pm 0.05) \times 10^{-10}$	298	Stevens et al., 1999	DF-LIF
$2.70 \times 10^{-11} \exp[(336 \pm 74)/T]$	251–341	Campuzano-Jost et al., 2000	PLP-LIF (a)
$(8.56 \pm 0.26) \times 10^{-11}$	297		
$(1.10 \pm 0.04) \times 10^{-10}$	300	Chuong and Stevens, 2000	DF-LIF (b)
$(9.6 \pm 0.5) \times 10^{-11}$	295	McGivern et al., 2000	PLP-LIF (c)
$(1.01 \pm 0.08) \times 10^{-10}$	298 ± 2	Zhang et al., 2000	DF-CIMS (d)
9.1×10^{-11}	298 ± 2	Zhang et al., 2001	DF-CIMS (e)
$(1.08 \pm 0.05) \times 10^{-10}$	300	Chuong and Stevens, 2002	DF-LIF (f)
<i>Relative Rate Coefficients</i>			
7.8×10^{-11}	300	Cox et al., 1980	RR (g)
$(9.98 \pm 0.45) \times 10^{-11}$	299 ± 2	Atkinson et al., 1982	RR (h)
$(9.90 \pm 0.27) \times 10^{-11}$	297 ± 2	Ohta, 1983	RR (i)
$(1.02 \pm 0.04) \times 10^{-10}$	295 ± 1	Atkinson and Aschmann, 1984	RR (j)
$(1.01 \pm 0.02) \times 10^{-10}$	297 ± 1	Edney et al., 1986	RR (k)
$(1.11 \pm 0.23) \times 10^{-10}$	298	McQuaid et al., 2002	RR (l)
$2.56 \times 10^{-11} \exp[(408 \pm 42)/T]$	298–363	Gill and Hites, 2002	RR (m)
$(1.01 \pm 0.05) \times 10^{-10}$	298		

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Comments

- (a) Rate coefficients for the reactions of HO radicals with isoprene-d₆ and DO radicals with isoprene were also measured at 297 K, these being $(8.31 \pm 0.10) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $(8.27 \pm 0.10) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively.
- (b) Carried out at total pressures of 2–6 Torr (2.7–8.0 mbar) of helium diluent. No pressure dependence of the rate coefficient was observed at 300 K. However, at higher temperatures (321–423 K) the rate coefficient increased with increasing total pressure, with the effect being more pronounced at higher temperature.
- (c) Carried out at total pressures of 0.5–20 Torr (0.7–27 mbar) of argon diluent. The rate coefficient was observed to be pressure dependent below 10 Torr total pressure; the value cited in the table is that measured at 20 Torr total pressure.
- (d) Carried out at total pressures of 72.7–112.7 Torr (97–150 mbar) of N₂ diluent. The measured rate coefficient was independent of pressure over this range.
- (e) Based on a very limited kinetic study carried out at a total pressure of 1.9 Torr (2.5 mbar) of helium diluent (the focus of the study was on formation of HO-isoprene adducts and their subsequent reactions).
- (f) Carried out at total pressures of argon diluent of 100 Torr (133 mbar) and 150 Torr (200 mbar). The measured rate coefficient was independent of total pressure over this range.
- (g) Relative rate method carried out at atmospheric pressure of air. HO radicals were generated by photolysis of HONO at wavelengths >300 nm.

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The concentrations of isoprene and ethene (the reference compound) were measured by GC. The measured rate coefficient ratio $k(\text{HO} + \text{isoprene})/k(\text{HO} + \text{ethene})$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{ethene}) = 8.44 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 300 K and atmospheric pressure of air (Atkinson, 1997).

(h) Relative rate method carried out at atmospheric pressure of air. HO radicals were generated by photolysis of CH_3ONO at wavelengths $>300 \text{ nm}$. The concentrations of isoprene and propene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(\text{HO} + \text{isoprene})/k(\text{HO} + \text{propene}) = 3.81 \pm 0.17$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{propene}) = 2.62 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 299 K and atmospheric pressure of air (Atkinson, 1997).

(i) Relative rate method carried out at atmospheric pressure of $\text{N}_2 + \text{O}_2$. HO radicals were generated by photolysis of H_2O_2 at 253.7 nm. The concentrations of isoprene and 1,3-butadiene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(\text{HO} + \text{isoprene})/k(\text{HO} + 1,3\text{-butadiene}) = 1.48 \pm 0.04$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + 1,3\text{-butadiene}) = 6.69 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 297 K and atmospheric pressure of air (Atkinson, 1997).

(j) Relative rate method carried out at atmospheric pressure of air. HO radicals were generated by photolysis of CH_3ONO at wavelengths $>300 \text{ nm}$. The concentrations of isoprene and propene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(\text{HO} + \text{isoprene})/k(\text{HO} + \text{propene}) = 3.81 \pm 0.15$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{propene}) = 2.68 \times 10^{-11} \text{ cm}^3$

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$\text{ molecule}^{-1} \text{ s}^{-1}$ at 295 K and atmospheric pressure of air (Atkinson, 1997).

(k) Relative rate method carried out at atmospheric pressure of air. HO radicals were generated by photolysis of CH_3ONO at wavelengths $>300 \text{ nm}$. The concentrations of isoprene and propene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(\text{HO} + \text{isoprene})/k(\text{HO} + \text{propene})$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{propene}) = 2.65 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 297 K and atmospheric pressure of air (Atkinson, 1997).

(l) Relative rate method carried out at atmospheric pressure of air. HO radicals were generated by photolysis of CH_3ONO . The concentrations of isoprene and *trans*-2-butene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(\text{HO} + \text{isoprene})/k(\text{HO} + \textit{trans}\text{-butene}) = 1.74 \pm 0.14$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \textit{trans}\text{-2-butene}) = 6.40 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and atmospheric pressure of air (Atkinson, 1997). The cited error limits are the 95% confidence intervals (McQuaid et al., 2002).

(m) Relative rate method carried out in a 192 cm^3 volume quartz reaction vessel at atmospheric pressure of helium diluent. HO radicals were generated by photolysis of H_2O_2 . The concentrations of isoprene and 2-methylpropene (the reference compound) were measured by MS. The measured rate coefficient ratios of $k(\text{HO} + \text{isoprene})/k(\text{HO} + 2\text{-methylpropene})$ are placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + 2\text{-methylpropene}) = 9.47 \times 10^{-12} \exp(504/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson, 1997). The error limits for the 298 K rate coefficient cited in the table are based on those associated with the rate coefficient ratio (Gill and Hites, 2002).

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Preferred Values

$k = 1.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 2.7 \times 10^{-11} \exp(390/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 240–430 K.

5 Reliability

$\Delta \log k = \pm 0.10$ at 298 K.

$\Delta (E/R) = \pm 100$ K.

Comments on Preferred Values

The measured room temperature rate coefficients (Atkinson and Aschmann, 1984; Atkinson et al., 1982; Campuzano-Jost et al., 2000; Chuong and Stevens, 2000, 2002; Cox et al., 1980; Edney et al., 1986; Gill and Hites, 2002; Kleindienst et al., 1982; McGivern et al., 2000; McQuaid et al., 2002; Ohta, 1983; Siese et al., 1994; Stevens et al., 1999; Zhang et al., 2000, 2002) and temperature dependencies (Campuzano-Jost et al., 2000; Gill and Hites, 2002; Kleindienst et al., 1982; Siese et al., 1994) are in good agreement (the temperature dependence measured by Siese et al., 1994 corresponds to $E/R = -400$ K over the temperature range 249–349 K). The preferred 298 K rate coefficient is an average of the room temperature rate coefficients of Atkinson and Aschmann (1984), Atkinson et al. (1982), Campuzano-Jost et al. (2000), Chuong and Stevens (2000, 2002), Edney et al. (1986), Gill and Hites (2002), Kleindienst et al. (1982), McGivern et al. (2000), McQuaid et al. (2002), Ohta (1983), Siese et al. (1994), Stevens et al. (1999) and Zhang et al. (2000). The preferred temperature dependence is an average of those obtained from the four temperature dependent studies (Campuzano-Jost et al., 2000; Gill and Hites, 2002;

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Kleindienst et al., 1982; Siese et al., 1994). The pre-exponential factor is calculated from the preferred 298 K rate coefficient and the preferred temperature dependence.

The reaction proceeds by initial addition of the HO radical to the two C=C bonds, followed by addition of O₂ to form six possible hydroxyalkyl peroxy radicals (Atkinson, 1997). The subsequent chemistry of these radicals in the atmosphere and the products observed is discussed by Atkinson (1997) and Calvert et al. (2000). In the presence of NO (so that organic peroxy radicals react dominantly with NO) the products observed (Atkinson, 1997; Atkinson et al., 1989; Chen et al., 1998; Kwok et al., 1995; Miyoshi et al., 1994; Paulson et al., 1992; Tuazon and Atkinson, 1990) are methyl vinyl ketone (33%), methacrolein (23%), formaldehyde (60%), 3-methylfuran (4.8%), hydroxynitrates such as HOCH₂C(CH₃)=CHCH₂ONO₂ (and isomers) (4.4%), and the hydroxycarbonyls HOCH₂C(CH₃)=CHCHO and/or HOCH₂CH=C(CH₃)CHO.

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II.A2.11

HO + α -Pinene \rightarrow products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.37 \times 10^{-11} \exp[(446 \pm 76)/T]$	298–422	Kleindienst et al., 1982	FP-RF
$(6.01 \pm 0.82) \times 10^{-11}$	298		
$1.63 \times 10^{-12} \exp[(1080 \pm 50)/T]$	300–435	Choung et al., 2002	DF-RF (a)
$(6.08 \pm 0.24) \times 10^{-11}$	300		
<i>Relative Rate Coefficients</i>			
$(5.6 \pm 1.7) \times 10^{-11}$	305 ± 2	Winer et al., 1976	RR (b)
$(5.35 \pm 0.31) \times 10^{-11}$	294 ± 1	Atkinson et al., 1986	RR (c)
$1.17 \times 10^{-11} \exp[(436 \pm 53)/T]$	295–364	Gill and Hites, 2002	RR (d)
$(5.05 \pm 1.23) \times 10^{-11}$	298		

5 Comments

- (a) Experiments carried out at 5 Torr (6.7 mbar) of He or 90% He+10% O₂.
- (b) HO radicals were generated by the photolysis of NO_x-organic-air mixtures in a 5870 L chamber at ~1 bar pressure. The concentrations of α -pinene and 2-methylpropene (the reference compound) were analyzed by GC

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during the experiments. The measured rate coefficient ratio $k(\text{HO} + \alpha\text{-pinene})/k(\text{HO} + 2\text{-methylpropene}) = 1.14 (\pm 30\%)$ is placed on an absolute basis by use of a rate coefficient at 305 K of $k(\text{HO} + 2\text{-methylpropene}) = 4.94 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Arey, 2003a).

- 5 (c) HO radicals were generated by the photolysis of CH₃ONO in air at wavelengths >300 nm in a 6400 L Teflon chamber at ~980 mbar pressure. The concentrations of α -pinene and 2,3-dimethyl-2-butene (the reference compound) were analyzed by GC during the CH₃ONO-NO- α -pinene-2,3-dimethyl-2-butene-air irradiations. The measured rate coefficient ratio $k(\text{HO} + \alpha\text{-pinene})/k(\text{HO} + 2,3\text{-dimethyl-2-butene}) = 0.487 \pm 0.028$ is placed on an absolute basis by use of a rate coefficient at 294 K of $k(\text{HO} + 2,3\text{-dimethyl-2-butene}) = 1.10 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Arey, 2003a).
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- (d) HO radicals were generated by the photolysis of H₂O₂ in helium diluent in a 192 cm³ volume quartz vessel. The concentrations of α -pinene and 1-butene, 2-methylpropene or *trans*-2-butene (the reference compounds) were analyzed by MS during the experiments. The measured rate coefficient ratios $k(\text{HO} + \alpha\text{-pinene})/k(\text{HO} + 1\text{-butene})$, $k(\text{HO} + \alpha\text{-pinene})/k(\text{HO} + 2\text{-methylpropene})$ and $k(\text{HO} + \alpha\text{-pinene})/k(\text{HO} + \textit{trans}\text{-2-butene})$ are placed on an absolute basis by use of rate coefficients of $k(\text{HO} + 1\text{-butene}) = 6.55 \times 10^{-12} \exp(467/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k(\text{HO} + 2\text{-methylpropene}) = 9.47 \times 10^{-12} \exp(504/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k(\text{HO} + \textit{trans}\text{-2-butene}) = 1.01 \times 10^{-11} \exp(550/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Arey, 2003a).
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Preferred Values

$k = 1.2 \times 10^{-11} \exp(440/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 290–430 K.

$k = 5.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

5 Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

$\Delta (E/R) = \pm 200$ K.

Comments on Preferred Values

At room temperature, the rate coefficients of Winer et al. (1976), Kleindienst et al. (1982), Atkinson et al. (1986), Gill and Hites (2002) and Choung et al. (2002) are in good agreement, as are the temperature dependencies obtained by Kleindienst et al. (1982) and Gill and Hites (2002). The temperature dependence obtained by Chuong et al. (2002) at 6.7 mbar pressure is significantly higher than those of Kleindienst et al. (1982) and Gill and Hites (2002), possibly because of fall-off effects above 300 K (although no evidence was obtained to support this conclusion). The preferred temperature dependence is based on those obtained by Kleindienst et al. (1982) and Gill and Hites (2002), and the preferred 298 K rate coefficient is the average of the measurements of Kleindienst et al. (1982), Atkinson et al. (1986) (corrected to 298 K using the preferred temperature dependence) and Gill and Hites (2002). The pre-exponential factor is adjusted to fit the 298 K preferred value.

A number of product studies have been carried out at room temperature and atmospheric pressure of air (see Atkinson and Arey, 2003b, and references therein). The reaction proceeds mainly by initial addition of the HO radical to the

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C=C bond, resulting in two hydroxyalkyl radicals which then add O₂ to form two 1,2-hydroxyalkyl peroxy radicals. H-atom abstraction almost certainly occurs to a minor extent, with acetone (Aschmann et al., 1998; Reissell et al., 1999; Nozière et al., 1999; Orlando et al., 2000) being one of the likely products. Subsequent reactions of these 1,2-hydroxyalkyl peroxy radicals with NO, NO₂, HO₂ radicals, organic peroxy radicals and NO₃ radicals will lead to the products formed in the atmosphere. In the presence of NO such that organic peroxy radicals react dominantly with NO, the products observed (and their reported yields) are: pinonaldehyde, 28±5% to 87±20% (Arey et al., 1990; Hatakeyama et al., 1991; Hakola et al., 1994; Nozière et al., 1999; Wisthaler et al., 2001; Aschmann et al., 2002) with the lower yields being obtained by GC analyses (Arey et al., 1990; Hakola et al., 1994; Aschmann et al., 2002) and by proton-transfer mass spectrometry (Wisthaler et al., 2001) and the higher values by in situ FTIR spectroscopy (Hatakeyama et al., 1991; Nozière et al., 1999); acetone, 5–11% (Aschmann et al., 1998; Reissell et al., 1999; Nozière et al., 1999; Orlando et al., 2000), formic acid, 7% (Orlando et al., 2000); organic nitrates, 18±9% (Nozière et al., 1999); a molecular weight 184 (dihydroxycarbonyl), ~19% (Aschmann et al., 2002); a molecular weight 200 product, ~11% (Aschmann et al., 2002), and molecular weight 215 C₁₀-hydroxynitrates and molecular weight 231 C₁₀-dihydroxynitrates (Aschmann et al., 1998, 2002).

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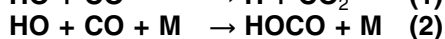
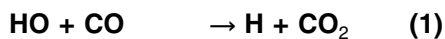
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II.A2.12



$$\Delta H^0 (1) = -102.3 \text{ kJ} \cdot \text{mol}^{-1}$$

$$\Delta H^0 (2) = -114.6 \text{ kJ} \cdot \text{mol}^{-1}$$

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Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$K(P \rightarrow 0)$			
1.37×10^{-13}	300	Greiner, 1969	FP-RA (a,c)
1.35×10^{-13}	300	Stuhl and Niki, 1972	FP-RF
1.66×10^{-13}	300	Mulcahy and Smith, 1971	DF-MS
1.33×10^{-13}	298	Westenberg and deHaas, 1973	DF-EPR
1.39×10^{-13}	298	Smith and Zellner, 1973	FP-RA (a,c)
1.58×10^{-13}	298	Davis et al., 1974	FP-RF
1.56×10^{-13}	296	Howard and Evenson, 1974	DF-LMR
1.20×10^{-13}	298	Trainor and von Rosenberg, 1974	FP-RA (a,c)
0.90×10^{-13}	298	Gordon and Mulac, 1975	PR-RA (b,d)
1.54×10^{-13}	299	Atkinson et al., 1977	FP-RF (e)
1.63×10^{-13}	296	Overend and Paraskevopoulos, 1977	FP-RA (d,f)
1.41×10^{-13}	299	Perry et al., 1977	FP-RF (g)
1.46×10^{-13}	300	Biermann et al., 1978	FP-RA (h)
1.50×10^{-13}	298	Dreier and Wolfrum, 1981	DF (i)
1.46×10^{-13}	298	Husain et al., 1982	FP-RF
1.28×10^{-13}	298	Ravishankara and Thompson, 1983	FP-RF (j)
1.50×10^{-13}	298	Paraskevopoulos and Irwin, 1984	FP-RA
1.58×10^{-13}	298	Hofzumahaus and Stuhl, 1984	FP-RA (k)
1.23×10^{-13}	298	Jonah et al., 1984	PR-RA (l)
0.88×10^{-13}	298	Beno et al., 1985	PR-RA (l)
1.47×10^{-13}	299	Hynes et al., 1986	PLP-LIF
1.50×10^{-13}	298	Stacknik and Molina, 1988	PLP-RA
1.26×10^{-13}	298	Wahner and Zetsch, 1988	PLP-A (m)
1.49×10^{-13}	298	Brunning et al., 1988	FP-LIF (n)
1.30×10^{-13}	298	Forster et al., 1995	PLP-LIF

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$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
1.53×10^{-13}	298	Golden et al., 1998	PLP-LIF
1.57×10^{-13}	220–400	McCabe et al., 2001	PLP-LIF
<i>$k/k(P \rightarrow 0)$ with $[\text{N}_2]$ in molecule cm^{-3}</i>			
$1 + [\text{N}_2]/5.4 \times 10^{-19}$	298	Paraskevopoulos and Irwin, 1984	FP-RA
$1 + [\text{N}_2]/4.1 \times 10^{-19}$	298	Hofzumahaus and Stuhl, 1984	FP-RA (o)
$1 + [\text{N}_2]/4.8 \times 10^{-19}$	298	Hynes et al., 1986	PLP-LIF
$1 + [\text{N}_2]/4.6 \times 10^{-19}$	298	Wahner and Zetsch, 1988	PLP-A (m)
$1 + [\text{N}_2]/4.4 \times 10^{-19}$	220–400	McCabe et al., 2001	PLP-LIF
$1 + [\text{N}_2]/4.0 \times 10^{-19}$	200–300	Fulle et al., 1996	PLP-LIF (p)

Comments

- (a) Extrapolation for $P \rightarrow 0$ with pressure dependence from Golden et al. (1998).
- 5 (b) Extrapolation for $P \rightarrow 0$ with pressure dependence from Paraskevopoulos and Irwin (1984).
- (c) Measurements at 100 Torr of He giving $k = 1.43 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- (d) Measurements at 760 Torr of Ar giving $k = 1.54 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- (e) No pressure dependence detected between 25 and 650 Torr of Ar. Value taken as indicated.
- 10 (f) Measurements at 50 Torr of He giving $k = 1.66 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- (g) Measurements at 25 Torr of SF_6 giving $k = 1.53 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

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- (h) Measurements at 25 Torr of N₂ giving $k=1.51 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- (i) Measurements of CO₂ yields accounting for loss of HO by other reactions.
- (j) Measurements at 100 Torr of Ar giving $k=1.4 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- (k) Measurements at 760 Torr of N₂ giving $k=2.3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- 5 (l) Measurements at 760 Torr of Ar giving $k=2.1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- (m) Measurements at 760 Torr of N₂ giving $k=2.15 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- (n) Measurements at 25 Torr of Ar giving $k=1.53 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- (o) Referred to $k_0=1.44 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.
- 10 (p) Measurements up to 700 bar of He with data representation between 90 and 3000 K. Conversion to the bath gas N₂ with efficiency relative to He at 298 K, see comments on preferred values. Temperature dependence from theoretical modelling of the experimental results, see Troe (1998).

Preferred Values

15 $k = 1.44 \times 10^{-13} (1 + [\text{N}_2]/4.2 \times \text{molecule cm}^{-3}) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–300 K and the pressure range 0–1 bar of N₂.

Reliability

$\Delta \log k = \pm 0.05$ at 298 K.

$\Delta (E/R) = \pm 1$ over the temperature range 200–300 K and the pressure range 0–1 bar.

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Comments on Preferred Values

5 The preferred values at $P \rightarrow 0$ represent a weighted average of all low pressure data excluding pulse radiolysis results which show larger scatter. The preferred values at $P=1$ bar of N₂ correspond to an average over those results for which $k/k(P \rightarrow 0)$ is given in the table (except the results from Fulle et al., 1996, which were obtained in the bath gas He).

The preferred values for k cannot be used over larger pressure and temperature ranges where more complicated expressions have to be employed. One may, e.g. take the representation $k_1=k_{1,0} [1 - [x/(x+1)]F_c^{1/[1+(\log x)^2]}]$, $k_2=k_{2,0} [1+y/(1+x)]F_c^{1/[1+(\log x)^2]}$ with $x=k_{2,0}/(k_{2,\infty}-k_{1,0})$ and $y=k_{1,0}/(k_{2,\infty}-k_{1,0})$, $F_c \approx 0.7$, $k_{1,0}=1.8 \times 10^{-12} \exp(-2720/T)+1.6 \times 10^{-13} \exp(-60/T)$, $k_{2,0}=[\text{He}] 2.0 \times 10^{-32} (T/300)^{-2.7} \exp(-490/T)$ and $k_{2,\infty}=1.8 \times 10^{-11} \exp(-1850/T)+1.5 \times 10^{-12} \exp(-130/T)$, see Fulle et al. (1996) and Troe (1998). For N₂ instead of He, $k_{2,0}$ should be increased by a factor of 1.6. These expressions also give the partitioning of k into k_1 and k_2 . For the limited temperature and pressure range of the present evaluation, the simplified model from the introduction for complex-forming bimolecular reactions can be used. At low pressures this gives a relative HOCO yield of approximately $[k-k(P \rightarrow 0)]/[k(P \rightarrow \infty)-k(P \rightarrow 0)]$ which at 298 K and 1 bar of N₂ corresponds to about 12% (Troe, 1998). As HOCO under excess of O₂ rapidly reacts to HO₂+CO₂ (Miyoshi et al., 1994) and as other reactions of HOCO presumably proceed similarly as reactions of H, k probably in effect can be used as if it would correspond to Reaction (1) alone. At higher temperatures, thermal decomposition of HOCO would occur which would lead to more complex kinetic rate laws, see Forster et al. (1996). This can be neglected at temperatures below 300 K.

25 The present evaluation was based on absolute rate coefficients only, neglect-

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ing relative rate measurements and measurements in other bath gases such as H₂O. Reference to this work is found in the given literature. Since the reaction has been studied very extensively, the present evaluation also cannot be exhaustive. The thermochemistry of HOCO is based on the new determination by Feller et al. (2003). There is extensive modelling of the reaction, see Golden et al. (1998) and Troe (1998), which provide excellent representations of the experimental data with empirically fitted potential parameters. Increasingly reliable quantum-chemical determinations of the HOCO potential (see e.g. Yu et al., 2001 and Lakin et al., 2003) allows also for more basic treatments of the dynamics, see e.g. Medvedev et al. (2004), He et al. (2004), Valero and Kroes (2002), Valero et al. (2004). However, this work does not yet replace the experiments on which this evaluation is based.

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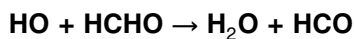
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II.A2.13



$$\Delta H^\circ = -127.3 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.25 \times 10^{-11} \exp[-(88 \pm 151)/T]$	299–426	Atkinson and Pitts, 1978	FP-RF
$(9.4 \pm 1.0) \times 10^{-12}$	299		
$(1.05 \pm 0.11) \times 10^{-11}$	228–362	Stief et al., 1980	FP-RF
$(9.86 \pm 1.13) \times 10^{-12}$	298		
$(8.1 \pm 1.7) \times 10^{-12}$	296	Temps and Wagner, 1984	DF-LMR
$1.66 \times 10^{-11} \exp[-(86 \pm 40)/T]$	296–576	Zabarnick et al., 1988	PLP-LIF
$(1.25 \pm 0.11) \times 10^{-11}$	298 ± 3		
$(7.95^{+2.04}_{-1.44}) \times 10^{-12}$	298	Yetter et al., 1989	DF-RF
$(1.94 \pm 0.30) \times 10^{-11}$	1205 ± 16	Bott and Cohen, 1991	SH-RA
$9.52 \times 10^{-18} T^{2.03} \exp(636/T)$	202–399	Sivakumaran et al., 2003	PLP-LIF (a)
$(8.46 \pm 0.5) \times 10^{-12}$	298		
<i>Relative Rate Coefficients</i>			
$(8.40 \pm 0.51) \times 10^{-12}$	299 ± 2	Niki et al., 1984	RR (b)

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Comments

- (a) The authors combined their data with previous room temperature data of Atkinson and Pitts (1978), Stief et al. (1980), Temps and Wagner (1984), Niki et al. (1984), Zabarnick et al. (1988) and Yetter et al. (1989) to obtain a 298 K rate coefficient of $k=8.6\times 10^{-12}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ and a temperature-dependent expression of $k=9.65\times 10^{-18} T^{2.03}\text{ exp}(636/T)\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ over the temperature range 200–400 K. Using resonance fluorescence detection of H atoms, an upper limit of 4% was determined for the production of H atoms at 298 K.
- (a) HO radicals were generated by the photolysis of methyl or ethyl nitrite in air, and the concentration of $^{13}\text{CH}_2\text{O}$ and ethene (the reference compound) were measured by FTIR absorption spectroscopy during the experiments. The measured rate coefficient ratio of $k(\text{HO}+^{13}\text{CH}_2\text{O})/k(\text{HO} + \text{ethene}) = 0.99\pm 0.06$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{ethene}) = 8.48\times 10^{-12}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ at 299 K and atmospheric pressure (Atkinson and Arey, 2003).

Preferred Values

- $k = 8.5 \times 10^{-12}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ at 298 K.
 $k = 5.4 \times 10^{-12}\text{ exp}(135/T)\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ over the temperature range 200–300 K.

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Reliability

- $\Delta \log k = \pm 0.08$ at 298 K.
 $\Delta (E/R) = \pm 100\text{ K}$.

Comments on Preferred Values

- The absolute rate coefficients of Atkinson and Pitts (1978), Stief et al. (1980), Temps and Wagner (1984), Yetter et al. (1989) and Sivakumaran et al. (2003) and the relative rate coefficient of Niki et al. (1984) at $299\pm 2\text{ K}$ are in good agreement (to within ~20% or better at any given temperature) over the temperature range common to two or more of these studies (228–399 K). The absolute rate coefficients of Zabarnick et al. (1988) over the temperature range 296–378 K are consistently higher than those of Atkinson and Pitts (1978), Stief et al. (1980), Temps and Wagner (1984), Niki et al. (1984), Yetter et al. (1989) and Sivakumaran et al. (2003), and are not used in the evaluation.
- The absolute rate coefficients of Atkinson and Pitts (1978), Stief et al. (1980), Temps and Wagner (1984), Yetter et al. (1989) and Sivakumaran et al. (2003), and the relative rate coefficient of Niki et al. (1984) for formaldehyde- ^{13}C , have been fitted to the three parameter expression $k=CT^2\text{ exp}(-D/T)$, resulting in $k=1.25\times 10^{-17} T^2\text{ exp}(615/T)\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ over the temperature range 202–426 K. This expression yields rate coefficients which are within 3% of those calculated from the three parameter expression recommended by Sivakumaran et al. (2003) for the temperature range 200–430 K (see comment (a) above) and predicts a rate coefficient at 1205 K a factor of 1.56 higher than that measured by Bott and Cohen (1991). The preferred Arrhenius expression, $k=A\text{ exp}(-B/T)$, is centered at 240 K and is derived from the three parameter expression with $A = C e^2 T^2$ and $B = D + 2T$. Note that the preferred Arrhenius expression should not be used outside of the specified temperature range

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(200–300 K); rather the full three parameter expression should be used.

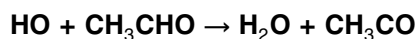
The product data of Temps and Wagner (1984), Niki et al. (1984) and Sivakumaran et al. (2003) and the kinetic/modeling results of Yetter et al. (1989) show that at 298 K this reaction yields H₂O+HCO, as also concluded by
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II.A2.14



$$\Delta H^\circ = -123.2 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.55 \pm 0.39) \times 10^{-11}$	300	Morris et al., 1971	DF-MS
$6.87 \times 10^{-12} \exp[(257 \pm 151)/T]$	299–426	Atkinson and Pitts, 1978	FP-RF
$(1.60 \pm 0.16) \times 10^{-11}$	299		
$7.1 \times 10^{-12} \exp[(165 \pm 91)/T]$	253–424	Semmes et al., 1985	FP-RF
$(1.22 \pm 0.27) \times 10^{-11}$	298		
$5.52 \times 10^{-12} \exp[(307 \pm 52)/T]$	244–528	Michael et al., 1985	DF-RF
$(1.47 \pm 0.28) \times 10^{-11}$	298		
$8.6 \times 10^{-12} \exp[(200 \pm 60)/T]$	297–517	Dóbe et al., 1989	DF-RF/LIF
$(1.69 \pm 0.34) \times 10^{-11}$	298 ± 2		
$(1.7 \pm 0.3) \times 10^{-11}$	298	Balestra-Garcia et al., 1992	PLP-RF
$(1.44 \pm 0.25) \times 10^{-11}$	298	Tyndall et al., 1995	DF-LIF
$4.31 \times 10^{-12} \exp[(309 \pm 19)/T]$	295–550	Taylor et al., 1996	PLP-LIF
1.23×10^{-11}	295		
$4.4 \times 10^{-12} \exp[(366 \pm 30)/T]$	202–348	Sivakumaran and Crowley, 2002	PLP-LIF
1.50×10^{-11}	298		
<i>Relative Rate Coefficients</i>			
$(1.62 \pm 0.18) \times 10^{-11}$	298 ± 2	Niki et al., 1978	RR (a)
$(1.28 \pm 0.43) \times 10^{-11}$	298 ± 4	Kerr and Sheppard, 1981	RR (b)
$(1.62 \pm 0.10) \times 10^{-11}$	298 ± 2	Scollard et al., 1993	RR (c)
5 $(1.44 \pm 0.08) \times 10^{-11}$	298 ± 2	D'Anna et al., 2001	RR (d)

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Comments

- (a) HO radicals were generated by the photolysis of HONO in air, and the concentrations of CH₃CHO and ethene (the reference compound) were measured by FTIR absorption spectroscopy. The measured rate coefficient ratio of $k(\text{HO} + \text{CH}_3\text{CHO})/k(\text{HO} + \text{ethene}) = 1.9 \pm 0.2$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{ethene}) = 8.52 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and atmospheric pressure (Atkinson, 1997).
- (b) HO radicals were generated by the photolysis of HONO in air, and the concentrations of CH₃CHO and ethene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(\text{HO} + \text{CH}_3\text{CHO})/k(\text{HO} + \text{ethene}) = 1.50 \pm 0.50$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{ethene}) = 8.52 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and atmospheric pressure (Atkinson, 1997).
- (c) HO radicals were generated from the photolysis of CH₃ONO in air, and the concentrations of CH₃CHO and ethene (the reference compound) were measured during the experiments by GC. The measured rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{ethene}) = 8.52 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and atmospheric pressure (Atkinson, 1997).
- (d) HO radicals were generated by the photolysis of an organic nitrite in air and the concentrations of acetaldehyde and 1-butene (the reference compound) were measured by FTIR spectroscopy. The measured rate coefficient ratio of $k(\text{HO} + \text{CH}_3\text{CHO})/k(\text{HO} + 1\text{-butene}) = 0.458 \pm 0.024$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + 1\text{-butene}) = 3.14 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and atmospheric pres-

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sure of air (Atkinson, 1997).

Preferred Values

$k = 1.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 4.4 \times 10^{-12} \exp(365/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–350 K.

Reliability

$\Delta \log k = \pm 0.08$ at 298 K.

$\Delta (E/R) = \pm 100 \text{ K}$.

Comments on Preferred Values

- The room temperature rate coefficients range from $(1.2\text{--}1.7) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, with the absolute rate coefficients of Atkinson and Pitts (1978), Michael et al. (1985), Tyndall et al. (1995) and Sivakumaran and Crowley (2002) being in reasonably good agreement. The temperature dependences of Michael et al. (1985), Taylor et al. (1996) and Sivakumaran and Crowley (2002) are in excellent agreement and also agree well with the temperature dependence measured over a smaller temperature range by Atkinson and Pitts (1978). The extensive study of Sivakumaran and Crowley (2002), which extends to significantly lower temperatures than the other temperature-dependent studies (Atkinson and Pitts, 1978; Semmes et al., 1985; Michael et al., 1985; Dóbé et al., 1989; Taylor et al., 1996), is used as the basis for the preferred values. The data of Semmes et al. (1985) are lower than the preferred values by up to ~20%, possibly because of the reported difficulties in accurately determining the acetaldehyde concentrations (Semmes et al., 1985). While the

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absolute rate coefficients measured by Dóbe et al. (1989) for CH_3CHO are in good agreement with the preferred values, their measured rate coefficients for the reactions of the HO radical with the higher aldehydes $(\text{CH}_3)_2\text{CHCHO}$ and $(\text{CH}_3)_3\text{CCHO}$ are significantly higher, by factors of ~ 1.5 to 2.3, than the rate coefficients of Kerr and Sheppard (1981) and Semmes et al. (1985) (which are in good agreement).

Cameron et al. (2002) have investigated the products of this reaction, using absorption spectroscopy to detect CH_3 and CH_3CO radicals and resonance fluorescence to detect H atoms. Upper limits for the formation of $\text{CH}_3+\text{HC(O)OH}$ ($<3\%$ at 296 K) and $\text{H}+\text{CH}_3\text{C(O)OH}$ ($<2\%$ over the temperature range 237–296 K) were obtained, and the major reaction pathway was determined to be formation of $\text{CH}_3\text{CO}+\text{H}_2\text{O}$, with a measured yield of $93\pm 18\%$ at 296 K (Cameron et al., 2002). H-atom abstraction from the CH_3 group therefore accounts for $<25\%$ of the overall reaction at room temperature.

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II.A2.15

HO + C₂H₅CHO → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.71 \pm 0.24) \times 10^{-11}$	298	Semmes et al., 1985	FP-RF
$5.3 \times 10^{-11} \exp[(405 \pm 30)/T]$	240–372	Thévenet et al., 2000	PLP-LIF
$(2.0 \pm 0.3) \times 10^{-11}$	298		
<i>Relative Rate Coefficients</i>			
$(2.22 \pm 0.09) \times 10^{-11}$	298 ± 2	Niki et al., 1978	RR (a)
$(1.94 \pm 0.15) \times 10^{-11}$	298 ± 4	Kerr and Sheppard, 1981	RR (b)
$(2.00 \pm 0.14) \times 10^{-11}$	296 ± 2	Papagni et al., 2000	RR (c)
$(1.89 \pm 0.16) \times 10^{-11}$	298 ± 2	D'Anna et al., 2001	RR (d)

5 Comments

(a) HO radicals were generated by the photolysis of HONO in air and the concentrations of propanal and ethene (the reference compound) were measured by FTIR absorption spectroscopy during the experiments. The measured rate coefficient ratio of $k(\text{HO} + \text{propanal})/k(\text{HO} + \text{ethene}) = 2.6 \pm 0.1$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} +$

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+ ethene) = $8.52 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and atmospheric pressure (Atkinson, 1997).

(b) HO radicals were generated by the photolysis of HONO in air and the concentrations of propanal and ethene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(\text{HO} + \text{propanal})/k(\text{HO} + \text{ethene}) = 2.28 \pm 0.17$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{ethene}) = 8.52 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and atmospheric pressure (Atkinson, 1997).

(c) HO radicals were generated by the photolysis of CH₃ONO in air and the concentrations of propanal and methyl vinyl ketone (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(\text{HO} + \text{propanal})/k(\text{HO} + \text{methyl vinyl ketone}) = 0.982 \pm 0.065$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{methyl vinyl ketone}) = 2.04 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (IUPAC, current recommendation).

(d) HO radicals were generated by the photolysis of an organic nitrite in air and the concentrations of propanal and propene (the reference compound) were measured by FTIR spectroscopy. The measured rate coefficient ratio of $k(\text{HO} + \text{propanal})/k(\text{HO} + \text{propene}) = 0.72 \pm 0.06$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{propene}) = 2.63 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and atmospheric pressure of air (Atkinson, 1997).

Preferred Values

$k = 2.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 5.1 \times 10^{-12} \exp(405/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 240–380 K.

5 Reliability

$\Delta \log k = \pm 0.10$ at 298 K.

$\Delta (E/R) = \pm 200 \text{ K}$.

Comments on Preferred Values

The preferred 298 K rate coefficient is derived from the mean of the room temperature absolute rate coefficients of Semmes et al. (1985) and Thévenet et al. (2000) and the relative rate coefficients of Niki et al. (1978), Kerr and Sheppard (1981), Papagni et al. (2000) and D'Anna et al. (2001). The temperature dependence is that measured by Thévenet et al. (2000) and the pre-exponential factor is adjusted to fit the 298 K preferred value. The relative rate coefficient of Audley et al. (1981) was not used in the evaluation, due to questions concerning the applicability of the experimental technique used (Semmes et al., 1985; Atkinson, 1989).

The major reaction channel is expected to be H-atom abstraction from the -CHO group to form $\text{H}_2\text{O} + \text{C}_2\text{H}_5\text{CO}$.

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II.A2.16

HO + CH₃CH₂CH₂CHO → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$5.7 \times 10^{-12} \exp[(411 \pm 164)/T]$	258–422	Semmes et al., 1985	FP-RF
$(2.06 \pm 0.30) \times 10^{-11}$	298		
<i>Relative Rate Coefficients</i>			
$(2.52 \pm 0.06) \times 10^{-11}$	298 ± 4	Kerr and Sheppard, 1981	RR (a)
$(2.45 \pm 0.15) \times 10^{-11}$	296 ± 2	Papagni et al., 2000	RR (b)
$(2.39 \pm 0.16) \times 10^{-11}$	298 ± 2	D'Anna et al., 2001	RR (c)

5 Comments

(a) HO radicals were generated by the photolysis of HONO in air and the concentrations of butanal and ethene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(\text{HO} + \text{butanal})/k(\text{HO} + \text{ethene}) = 2.96 \pm 0.07$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{ethene}) = 8.52 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and atmospheric pressure (Atkinson, 1997).

(b) HO radicals were generated by the photolysis of CH₃ONO in air and the concentrations of butanal and methyl vinyl ketone (the reference com-
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pound) were measured by GC. The measured rate coefficient ratio of $k(\text{HO} + \text{butanal})/k(\text{HO} + \text{methyl vinyl ketone}) = 1.20 \pm 0.07$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{methyl vinyl ketone}) = 2.04 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (IUPAC, current recommendation).

(c) HO radicals were generated by the photolysis of an organic nitrite in air and the concentrations of butanal and 1-butene (the reference compound) were measured by FTIR spectroscopy. The measured rate coefficient ratio of $k(\text{HO} + \text{butanal})/k(\text{HO} + 1\text{-butene}) = 0.76 \pm 0.05$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + 1\text{-butene}) = 3.14 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and atmospheric pressure of air (Atkinson, 1997).

Preferred Values

$k = 2.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
15 $k = 6.0 \times 10^{-12} \exp(410/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250–430 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.

$\Delta (E/R) = \pm 250 \text{ K}$.

20 Comments on Preferred Values

The preferred 298 K rate coefficient is the mean of the room temperature absolute rate coefficient of Semmes et al. (1985) and the relative rate coefficients

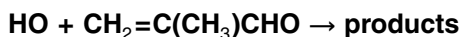
of Kerr and Sheppard (1981), Papagni et al. (2000) and D'Anna et al. (2001). The temperature dependence is that measured by Semmes et al. (1985), with the pre-exponential factor being adjusted to fit the 298 K preferred value. The relative rate coefficient of Audley et al. (1981) has not been used in the evaluation because, while it is in good agreement with the preferred 298 K rate coefficient, the rate coefficients of Audley et al. (1981) for 2-methyl-1-propanal, 1-pentanal and 2, 2-dimethyl-1-propanal are significantly lower than the values of Semmes et al. (1985) and Kerr and Sheppard (1981). At room temperature and below, the reaction is expected to proceed primarily by H-atom abstraction from the -CHO group.

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II.A2.17



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.77 \times 10^{-11} \exp[(175 \pm 52)/T]$	300–423	Kleindienst et al., 1982	FP-RF
$(3.14 \pm 0.49) \times 10^{-11}$	300		
$7.73 \times 10^{-12} \exp[(379 \pm 46)/T]$	234–373	Gierczak et al., 1997	PLP-LIF
$(2.79 \pm 0.12) \times 10^{-11}$	298		
<i>Relative Rate Coefficients</i>			
$(2.96 \pm 0.24) \times 10^{-11}$	299 ± 2	Atkinson et al., 1983	RR (a)
$(3.90 \pm 0.31) \times 10^{-11}$	298 ± 2	Edney et al., 1986	RR (b)

Comments

- (a) Relative rate study carried out at atmospheric pressure of air. The concentrations of methacrolein and propene (the reference compound) were measured by GC. The measured rate coefficient ratio $k(\text{HO} + \text{methacrolein})/k(\text{HO} + \text{propene}) = 1.13 \pm 0.09$ is placed on an absolute basis by using a rate coefficient of $k(\text{HO} + \text{propene}) = 2.62 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 299 K and atmospheric pressure of air (Atkinson, 1997).

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(b) Relative rate study carried out at atmospheric pressure of air. The concentrations of methacrolein and propene and *trans*-2-butene (the reference compounds) were measured by GC. The measured rate coefficient ratios are placed on an absolute basis by using rate coefficients of $k(\text{HO} + \text{propene}) = 2.63 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k(\text{HO} + \textit{trans}\text{-2-butene}) = 6.40 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and atmospheric pressure of air (Atkinson, 1997). The indicated uncertainty is one standard deviation (Edney et al., 1986).

Preferred Values

$k = 2.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 8.0 \times 10^{-12} \exp(380/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 230–380 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
 $\Delta (E/R) = \pm 200 \text{ K}$.

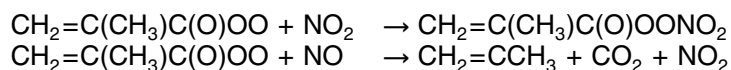
Comments on Preferred Values

The room temperature rate coefficients of Kleindienst et al. (1982), Atkinson et al. (1983) and Gierczak et al. (1997) are in good agreement, with the relative rate measurement of Edney et al. (1986) being ~30% higher. The temperature dependence obtained by Kleindienst et al. (1982) (300–423 K) is significantly lower than that determined by Gierczak et al. (1997) over a much wider temperature range (234–373 K), and accordingly the temperature dependence of

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Gierczak et al. (1997) is accepted. The preferred 298 K rate coefficient is based on the room temperature rate coefficients of Atkinson et al. (1983) and Gierczak et al. (1997), and the pre-exponential factor is calculated from the preferred 298 K rate coefficient and the temperature dependence.

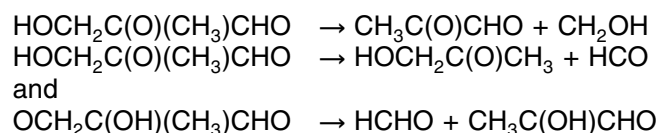
The products of the reaction of HO radicals with methacrolein in the presence of NO have been investigated by Tuazon and Atkinson (1990) and Orlando and Tyndall (1999). The reaction proceeds by two pathways: H-atom abstraction from the CHO group, and initial addition of the HO radical to the carbon atoms of the C=C bond. H-atom abstraction from the CHO group accounts for 50–55% of the overall reaction at room temperature (Tuazon and Atkinson, 1990; Orlando and Tyndall, 1999), forming the acyl radical $\text{CH}_2=\text{C}(\text{CH}_3)\text{CO}$ which then adds O_2 to form the acyl peroxy radical $\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OO}$. This acyl peroxy radical reacts with NO_2 , to form the peroxyacyl nitrate $\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OONO}_2$ (MPAN), or with NO (Tuazon and Atkinson, 1990; Orlando and Tyndall, 1999).



The $\text{CH}_2=\text{CCH}_3$ radical reacts to form HCHO, CO and CO_2 (Orlando and Tyndall, 1999).

Initial HO radical addition to the C=C bond leads (in the presence of NO) to the intermediate hydroxyalkoxy radicals $\text{HOCH}_2\text{C}(\text{O})(\text{CH}_3)\text{CHO}$ and $\text{OCH}_2\text{C}(\text{OH})(\text{CH}_3)\text{CHO}$, which decompose by the pathways (Tuazon and Atkinson, 1990; Orlando and Tyndall, 1999):

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followed by reactions of CH_2OH and $\text{CH}_3\text{C(OH)CHO}$ radicals with O_2 to form $\text{HCHO} + \text{HO}_2$ and $\text{CH}_3\text{C(O)CHO} + \text{HO}_2$, respectively. The first generation products from the HO radical addition pathways are therefore $\text{HCHO} + \text{CH}_3\text{C(O)CHO}$ and $\text{HOCH}_2\text{C(O)CH}_3 + \text{CO}$ (the CO arising from reaction of HCO with O_2). The studies of Tuazon and Atkinson (1990) and Orlando and Tyndall (1999) measured formation yields of methylglyoxal and hydroxyacetone of 8.4% and 44%, respectively, showing that initial HO radical addition occurs mainly at the terminal CH_2 group (Tuazon and Atkinson, 1990).

10 References

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II.A2.18

OH + Pinonaldehyde \rightarrow products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
$(8.72 \pm 1.14) \times 10^{-11}$	298 ± 2	Hallquist et al., 1997	RR (a)
$(8.9 \pm 2.6) \times 10^{-11}$	300 ± 5	Gladius et al., 1997	RR (b,c)
$(9.0 \pm 1.3) \times 10^{-11}$	300 ± 5	Gladius et al., 1997	RR (b,d)
$(4.5 \pm 0.8) \times 10^{-11}$	296 ± 2	Alvarado et al., 1998	RR (e,f)
$(4.9 \pm 1.1) \times 10^{-11}$	296 ± 2	Alvarado et al., 1998	RR (e,g)
$(5.4 \pm 0.9) \times 10^{-11}$	296 ± 2	Alvarado et al., 1998	RR (e,h)
$(3.0 \pm 0.8) \times 10^{-11}$	295 ± 3	Nozière et al., 1999	RR (c,i)
$(5.5 \pm 1.5) \times 10^{-11}$	295 ± 3	Nozière et al., 1999	RR (d,i)
$(4.7 \pm 0.6) \times 10^{-11}$	295 ± 3		
$(2.8 \pm 1.0) \times 10^{-11}$	295 ± 3		
$(2.7 \pm 0.6) \times 10^{-11}$	295 ± 3	Nozière et al., 1999	RR (i,j)
$(3.3 \pm 0.3) \times 10^{-11}$	295 ± 3		
$(2.8 \pm 0.3) \times 10^{-11}$	295 ± 3		
$(3.9 \pm 0.4) \times 10^{-11}$	295 ± 3		
$(3.7 \pm 1.1) \times 10^{-11}$	299 ± 2	Nozière et al., 1999	RR (j,k)
$(4.2 \pm 1.1) \times 10^{-11}$	290 ± 2		
$(3.8 \pm 1.5) \times 10^{-11}$	288 ± 1		
$(4.4 \pm 0.8) \times 10^{-11}$	287 ± 1		
$(4.4 \pm 1.0) \times 10^{-11}$	289 ± 2		

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Comments

- 5 (a) HO radicals were generated by the photolysis of CH₃ONO-NO-air mixtures at 1013±5 mbar pressure. The concentrations of pinonaldehyde and propene (the reference compound) were measured by FTIR spectroscopy. Wall losses of pinonaldehyde in the 153 L chamber were observed and measured in separate experiments and taken into account in the data analysis. The measured rate coefficient ratio of $k(\text{HO} + \text{pinonaldehyde})/k(\text{HO} + \text{propene})$ is placed on an absolute basis by use of a rate coefficient at 298 K and atmospheric pressure of air of $k(\text{HO} + \text{propene}) = 2.63 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Arey, 2003).
- 10 (b) HO radicals were generated by the photolysis of CH₃ONO-NO-air or H₂O₂-air mixtures at 987±7 mbar pressure. The concentrations of pinonaldehyde and isoprene or 1,3-butadiene (the reference compounds) were measured by FTIR spectroscopy. Decays of pinonaldehyde in the dark and due to photolysis were observed in the 480 L reaction chamber used and were taken into account in the data analysis. The measured rate coefficient ratios of $k(\text{HO} + \text{pinonaldehyde})/k(\text{HO} + \text{isoprene}) = 0.896 \pm 0.260$ and $k(\text{HO} + \text{pinonaldehyde})/k(\text{HO} + 1,3\text{-butadiene}) = 1.37 \pm 0.19$ are placed on an absolute basis by use of rate coefficients at 300 K of $k(\text{HO} + \text{isoprene}) = 9.91 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation) and $k(\text{HO} + 1,3\text{-butadiene}) = 6.59 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Arey, 2003).
- (c) Relative to $k(\text{HO} + \text{isoprene})$.
- (d) Relative to $k(\text{HO} + 1,3\text{-butadiene})$.
- 25 (e) HO radicals were generated by the photolysis of CH₃ONO-NO-air mixtures at 987 mbar pressure. The concentrations of pinonaldehyde and

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propene, 1-butene or *m*-xylene (the reference compounds) were measured by GC. No measurable decays (<5%) of pinonaldehyde were observed due to dark decays to the walls of the 7000 L Teflon chamber used or due to photolysis at wavelengths >300 nm. The measured rate coefficient ratios of $k(\text{HO} + \text{pinonaldehyde})/k(\text{HO} + \text{propene}) = 1.70 \pm 0.29$, $k(\text{HO} + \text{pinonaldehyde})/k(\text{HO} + 1\text{-butene}) = 1.56 \pm 0.33$ and $k(\text{HO} + \text{pinonaldehyde})/k(\text{HO} + m\text{-xylene}) = 2.35 \pm 0.35$ are placed on an absolute basis by use of rate coefficients at 296 K and atmospheric pressure of air of $k(\text{HO} + \text{propene}) = 2.66 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k(\text{HO} + 1\text{-butene}) = 3.17 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k(\text{HO} + m\text{-xylene}) = 2.31 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Arey, 2003).

- 5 (f) Relative to $k(\text{HO} + \text{propene})$.
- (g) Relative to $k(\text{HO} + 1\text{-butene})$.
- (h) Relative to $k(\text{HO} + m\text{-xylene})$.
- 15 (i) HO radicals were generated by the photolysis of CH₃ONO-NO-air or H₂O₂-air mixtures at 1013 mbar pressure. The concentrations of pinonaldehyde and reference compound (isoprene, 1,3-butadiene or cyclohexane) were measured by FTIR spectroscopy. Wall losses and photolysis was observed in the various chambers used (ranging from 405 to 1080 L volume) and were taken into account in the data analysis. The measured rate coefficient ratios of $k(\text{HO} + \text{pinonaldehyde})/k(\text{HO} + \text{isoprene})$, $k(\text{HO} + \text{pinonaldehyde})/k(\text{HO} + 1,3\text{-butadiene})$ and $k(\text{HO} + \text{pinonaldehyde})/k(\text{HO} + \text{cyclohexane})$ are placed on an absolute basis by use of rate coefficients at 295 K of $k(\text{HO} + \text{isoprene}) = 1.01 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation), $k(\text{HO} + 1,3\text{-butadiene}) = 6.76 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Arey,
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2003) and $k(\text{HO} + \text{cyclohexane}) = 6.90 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson, 2003; Atkinson and Arey, 2003).

(j) Relative to $k(\text{HO} + \text{cyclohexane})$.

(k) Experiments carried out in the $\sim 180\,000$ L volume EUPHORE chamber with HO radicals being generated by the dark reaction of ozone with 2,3-dimethyl-2-butene in air at ~ 1 bar pressure. The concentrations of pinonaldehyde and cyclohexane were monitored during the experiments by FTIR spectroscopy (pinonaldehyde and cyclohexane) and also by HPLC after derivatization for pinonaldehyde and by GC for cyclohexane. The measured rate coefficient ratios of $k(\text{HO} + \text{pinonaldehyde})/k(\text{HO} + \text{cyclohexane})$ are placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{cyclohexane}) = 3.26 \times 10^{-17} T^2 \exp(262/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson, 2003; Atkinson and Arey, 2003).

Preferred Values

$k = 4.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.25$ at 298 K.

Comments on Preferred Values

Pinonaldehyde is a low volatility product of the atmospheric reactions of α -pinene which is prone to wall losses, making measurement of its reaction rate coefficients difficult. The available rate coefficients are all from relative rate

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studies carried out at around room temperature, and range over a factor of ~ 3 (Hallquist et al., 1997; Glasius et al., 1997; Alvarado et al., 1998; Nozière et al., 1999). The rate coefficients measured by Hallquist et al. (1997) and Glasius et al. (1997) are a factor of ~ 2 higher than those of Alvarado et al. (1998) and Nozière et al. (1999), possibly because of unresolved wall adsorption problems. The preferred values are based on the study of Alvarado et al. (1998) carried out in a large volume Teflon chamber and the extensive study of Nozière et al. (1999) carried out in various chambers of volume ranging from 405 L to $\sim 180\,000$ L. The rate coefficients measured by Alvarado et al. (1998) have been aggregated into an average rate coefficient of $4.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and those measured by Nozière et al. (1999) have been aggregated into an average rate coefficient from the indoor chambers with photolytic production of HO radicals of $3.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and an average rate coefficient from the EUPHORE chamber study (with dark production of HO radicals) of $4.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. A simple average of these three rate coefficients, which are in agreement within their large experimental uncertainties, leads to the preferred 298 K rate coefficient.

The reaction proceeds by H-atom abstraction from the various C-H bonds, including from the -CHO group.

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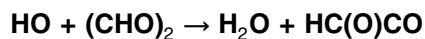
IUPAC: <http://www.iupac-kinetic.ch.cam.ac.uk/>.

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6485

II.A2.19



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.06 \pm 0.04) \times 10^{-11}$	298 ± 2	Plum et al., 1983	RR (a)

5 Comments

(a) HO radicals were generated by the photolysis of CH_3ONO in air, and the concentrations of glyoxal and cyclohexane (the reference compound) were measured by differential optical absorption spectroscopy and GC, respectively. The measured rate coefficient ratio of $k(\text{HO} + \text{glyoxal})/k(\text{HO} + \text{cyclohexane}) = 1.52 \pm 0.05$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{cyclohexane}) = 6.97 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Atkinson, 2003).

Preferred Values

$k = 1.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

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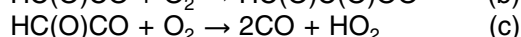
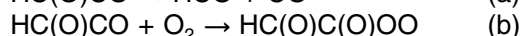
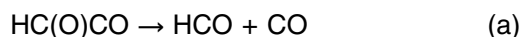
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Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

- 5 The preferred rate coefficient is based on the study of Plum et al. (1983), with increased uncertainty limits. The rate coefficient at 298 K is similar to those for other aldehydes. A close to zero temperature dependence is expected at around 298 K. The reaction is assumed to proceed via overall H-atom abstraction to yield $\text{H}_2\text{O} + \text{HC(O)CO}$. Niki et al. (1985) showed from a
10 study of the Cl atom-initiated reaction of glyoxal that at 298 K and 933 mbar (700 Torr) total pressure the HC(O)CO radical reacts by the pathways:



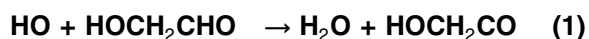
with $k_b \sim k_c$ and $k_a/k_b = 3.5 \times 10^{-18}$ molecule cm^{-3} .

15 References

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II.A2.20



Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
$(9.4 \pm 0.9) \times 10^{-12}$	298 ± 2	Niki et al., 1987	RR (a)
$(1.55 \pm 0.20) \times 10^{-11}$	298	Bacher et al., 2001	RR (a)
$(1.29 \pm 0.08) \times 10^{-11}$	298	Bacher et al., 2001	RR (b)
<i>Branching Ratios</i>			
$k_1/k = 0.80$	298 ± 2	Niki et al., 1987	(c)
$k_2/k = 0.20$	298 ± 2	Niki et al., 1987	(c)

5 Comments

- (a) HO radicals were generated by the photolysis of CH_3ONO in air and the concentrations of HOCH_2CHO and acetaldehyde (the reference compound) measured by FTIR absorption spectroscopy. The measured rate coefficient ratios of $k(\text{HO} + \text{CH}_3\text{CHO})/k(\text{HO} + \text{HOCH}_2\text{CHO}) = 1.6 \pm 0.15$ (Niki et al., 1987) and $k(\text{HO} + \text{HOCH}_2\text{CHO})/k(\text{HO} + \text{CH}_3\text{CHO}) = 1.03 \pm 0.13$ (Bacher et al., 2001) are placed on an absolute basis by use
10 of a rate constant of $k(\text{HO} + \text{CH}_3\text{CHO}) = 1.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (IUPAC, current recommendation).

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- (b) HO radicals were generated by the photolysis of CH₃ONO in air and the concentrations of HOCH₂CHO and propene (the reference compound) measured by FTIR absorption spectroscopy. The measured rate coefficient ratio of $k(\text{HO} + \text{HOCH}_2\text{CHO})/k(\text{HO} + \text{propene}) = 0.49 \pm 0.03$ is placed on an absolute basis by use of a rate constant of $k(\text{HO} + \text{propene}) = 2.63 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and atmospheric pressure of air (Atkinson, 1997).
- (c) HO radicals were generated by the photolysis of ethyl nitrite in air, and HOCH₂CHO and products [(CHO)₂, CO₂ and HCHO] were measured by FTIR absorption spectroscopy. Product formation yields of (CHO)₂, 0.211 ± 0.024; CO₂, 0.813 ± 0.032; and HCHO, 0.824 ± 0.046 were obtained, leading to rate coefficient ratios of $k_1/k = 0.80$ and $k_2/k = 0.20$.

Preferred Values

- $k = 1.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k_1/k = 0.80$ at 298 K.

Reliability

- $\Delta \log k = \pm 0.2$ at 298 K.
 $\Delta (k_1/k) = \pm 0.10$ at 298 K.

Comments on Preferred Values

- The preferred 298 K rate coefficient is a mean of the room temperature rate coefficients of Niki et al. (1987) and Bacher et al. (2001), which are not in par-

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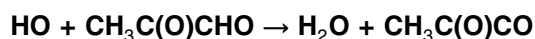
ticularly good agreement. The branching ratios k_1/k and k_2/k are taken from the study of Niki et al. (1987), with the error limits increased accordingly.

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6490

II.A2.21



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(7.1 \pm 1.6) \times 10^{-12}$	297 ± 2	Kleindienst et al., 1982	FP-RF
$8.4 \times 10^{-13} \exp[(830 \pm 300)/T]$	260–333	Tyndall et al., 1995	DF-LIF
$(1.32 \pm 0.30) \times 10^{-11}$	298		
<i>Relative Rate Coefficients</i>			
$(1.60 \pm 0.12) \times 10^{-11}$	298 ± 2	Plum et al., 1983	RR (a)

5 Comments

(a) HO radicals were generated by the photolysis of CH_3ONO in air. The concentrations of $\text{CH}_3\text{C}(\text{O})\text{CHO}$ and cyclohexane (the reference compound) were measured by differential optical absorption spectroscopy and GC, respectively. The measured rate coefficient ratio of $k(\text{HO} + \text{CH}_3\text{C}(\text{O})\text{CHO})/k(\text{HO} + \text{cyclohexane}) = 2.29 \pm 0.16$ is placed on an absolute basis by use of a rate coefficient $k(\text{HO} + \text{cyclohexane}) = 6.97 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Atkinson, 2003).

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Preferred Values

$k = 1.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

5 Comments on Preferred Values

The preferred 298 K rate coefficient is an average of the relative rate coefficient of Plum et al. (1983) and the absolute rate coefficient of Tyndall et al. (1995). The absolute rate coefficient measured by Kleindienst et al. (1982) may have been low due to the presence of significant levels of low reactivity impurities in the methylglyoxal samples used. The data of Tyndall et al. (1995) indicate a significant negative temperature dependence; while no recommendation is made concerning the temperature dependence of this reaction a negative temperature dependence is expected at around room temperature (see, for example, the $\text{HO} + \text{CH}_3\text{CHO}$ reaction (IUPAC, this evaluation). The reaction is assumed to proceed via H-atom abstraction to form $\text{H}_2\text{O} + \text{CH}_3\text{C}(\text{O})\text{CO}$. Green et al. (1990) have shown that the dominant fate of the $\text{CH}_3\text{C}(\text{O})\text{CO}$ radical under atmospheric conditions is decomposition to form $\text{CH}_3\text{CO} + \text{CO}$.

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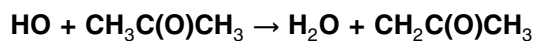
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II.A2.22



$$\Delta H^\circ = -87.8 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.7 \times 10^{-12} \exp[-(600 \pm 75)/T]$	240–440	Wallington and Kurylo, 1987	FP-RF
$(2.16 \pm 0.16) \times 10^{-13}$	296		
$(8.80 \pm 1.32) \times 10^{-12}$	1217	Bott and Cohen, 1991	SH-RA
$1.25 \times 10^{-12} \exp[-(561 \pm 57)/T]$	243–372	Le Calvé et al., 1998	PLP-LIF
$(1.84 \pm 0.24) \times 10^{-13}$	298		
$8.8 \times 10^{-12} \exp[-(1320 \pm 163)/T]$	202–395	Wollenhaupt et al., 2000	PLP-LIF/RF
$+ 1.7 \times 10^{-14} \exp[(423 \pm 109)/T]$			
$(1.73 \pm 0.09) \times 10^{-13}$	298		
$(1.73 \pm 0.05) \times 10^{-13}$	298	Vasvári et al., 2001	DF-RF
<i>Relative Rate Coefficients</i>			
$(2.7 \pm 0.1) \times 10^{-13}$	303 ± 2	Kerr and Stocker, 1986	RR (a)

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Comments

(a) HO radicals were generated by the photolysis of HONO in air, and the concentrations of acetone and ethene (the reference compound) were mea-

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sured by GC. The measured rate coefficient ratio of $k(\text{HO} + \text{acetone})/k(\text{HO} + \text{ethene}) = 0.032 \pm 0.001$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{ethene}) = 8.32 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 303 K and atmospheric pressure (Atkinson, 1997).

5 Preferred Values

$k = 1.7 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = \{8.8 \times 10^{-12} \exp(-1320/T) + 1.7 \times 10^{-14} \exp(420/T)\} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$
over the temperature range 200–400 K.

Reliability

10 $\Delta \log k = \pm 0.10$ over the temperature range 200–400 K.

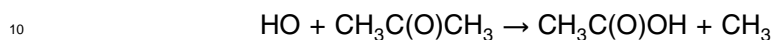
Comments on Preferred Values

The absolute rate studies of Wallington and Kurylo (1987), Le Calvé et al. (1998), Wollenhaupt et al. (2000) and Vasvári et al. (2001) are in generally excellent agreement. In particular, the rate coefficients of Le Calvé et al. (1998) and Wollenhaupt et al. (2000) are in excellent agreement over the temperature range common to both studies (243–372 K). The low temperature data of Wollenhaupt et al. (2000) have been confirmed by Gierczak et al. (2003), who also measured rate coefficients for the reactions of HO and DO radicals with acetone- d_6 and find that the H/D isotope effect, $k(\text{HO} + \text{CH}_3\text{C}(\text{O})\text{CH}_3)/k(\text{HO} + \text{CD}_3\text{C}(\text{O})\text{CD}_3)$, increases from ~ 6 at 298 K to ~ 10 at ~ 210 K (Gierczak et al., 2003). In the study of Wollenhaupt et al. (2000), the concentration of acetone in the flow stream was measured by UV absorp-

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tion, and measurements of the rate coefficient were extended to lower temperatures than in previous temperature-dependent studies (Wallington and Kurylo, 1987; Le Calvé et al., 1998). The rate expression reported by Wollenhaupt et al. (2000) is therefore accepted as the preferred value.

5 Products of this reaction have been investigated by Wollenhaupt and Crowley (2000), Vasvári et al. (2001), Vandenberg et al. (2002) and Talukdar et al. (2003) with conflicting results in some cases. Wollenhaupt and Crowley (2000) measured the amount of CH_3 radicals formed in the pathway



by converting methyl radicals to methoxy radicals by reaction with NO_2 and monitoring CH_3O by LIF, and concluded that the channel forming $\text{CH}_3\text{C}(\text{O})\text{OH} + \text{CH}_3$ accounted for $\sim 50\%$ of the overall reaction at 298 K and $\sim 30\%$ at 233 K (Wollenhaupt and Crowley, 2000). Vasvári et al. (2001) used a DF system with LIF detection of HO radicals and $\text{CH}_3\text{C}(\text{O})\text{CH}_2$ radicals to obtain a branching ratio for the H-atom abstraction pathway of 0.50 ± 0.04 at 298 K, apparently consistent with the data of Wollenhaupt and Crowley (2000). However, Vandenberg et al. (2002) and Talukdar et al. (2003) measured upper limits to acetic acid formation at room temperature, of $< 5\%$ (Vandenberg et al., 2002) and $< 1\%$ (Talukdar et al., 2003). These two studies (Vandenberg et al., 2002; Talukdar et al., 2003) measured a yield of $\text{CH}_3\text{C}(\text{O})\text{CH}_2$ radicals of $96 \pm 11\%$, independent of temperature (242–350 K), together with the large deuterium isotope effect observed by Talukdar et al. (2003) and the lack of a pressure dependence at 250 K (Talukdar et al., 2003), indicate that the reaction proceeds by H-atom abstraction at temperatures above 200 K.

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6497

II.A2.23

HO + CH₃C(O)CH₂CH₃ → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$2.3 \times 10^{-12} \exp[-(170 \pm 120)/T]$	240–440	Wallington and Kurylo, 1987	FP-RF
$(1.15 \pm 0.10) \times 10^{-12}$	296		
$1.51 \times 10^{-12} \exp[-(60 \pm 61)/T]$	243–372	Le Calvé et al., 1998	PLP-LIF
$(1.19 \pm 0.18) \times 10^{-12}$	298		
<i>Relative Rate Coefficients</i>			
$(3.5 \pm 1.0) \times 10^{-12}$	305 ± 2	Winer et al., 1976	RR (a)
2.74×10^{-12}	300	Cox et al., 1980	RR (b)
$(9.5 \pm 0.9) \times 10^{-13}$	295 ± 2	Cox et al., 1981	RR (b)
$(9.1 \pm 1.6) \times 10^{-13}$	297	Edney et al., 1986	RR (c)

5 Comments

- (a) HO radicals were generated by the photolysis of NO_x-organic-air mixtures, and the concentrations of 2-butanone and 2-methylpropene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(\text{HO} + 2\text{-butanone})/k(\text{HO} + 2\text{-methylpropene}) = 0.07 (\pm 30\%)$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} +$
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2-methylpropene) = $4.94 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 305 K (Atkinson, 1997).

- (b) HO radicals were generated by the photolysis of HONO in air, and the concentrations of 2-butanone and ethene (the reference compound) were measured by GC. The measured rate coefficient ratios $k(\text{HO} + 2\text{-butanone})/k(\text{HO} + \text{ethene})$ are placed on an absolute basis by use of rate coefficients at atmospheric pressure of $k(\text{HO} + \text{ethene}) = 8.44 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 300 K and $8.65 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 295 K (Atkinson, 1997).
- (c) HO radicals were generated from the photolysis of CH_3ONO in air, and the concentrations of 2-butanone and propane (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(\text{HO} + 2\text{-butanone})/k(\text{HO} + \text{propane})$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{propane}) = 1.07 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 297 K (IUPAC, current recommendation).

Preferred Values

$k = 1.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 1.3 \times 10^{-12} \exp(-25/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 240–300 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

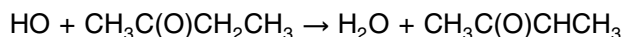
$\Delta (E/R) = \pm 200 \text{ K}$.

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Comments on Preferred Values

Photolysis of 2-butanone may have contributed to the measured 2-butanone loss rates in the relative rate studies of Winer et al. (1976) and Cox et al. (1980). A unit-weighted least-squares analysis of the absolute rate coefficients of Wallington et al. (1987) and Le Calvé et al. (1998), using the three-parameter expression $k = CT^2 \exp(-D/T)$, results in $k = 2.53 \times 10^{-18} T^2 \exp(503/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 240–440 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K and is derived from the above three-parameter expression with $A = C e^{2T^2}$ and $B = D + 2T$.

Cox et al. (1981) observed acetaldehyde as a product of the HO radical reaction with 2-butanone, with a formation yield of 0.62 ± 0.02 . Acetaldehyde is expected to arise from 2-butanone after H-atom abstraction from the CH_2 group, and hence the fraction of the overall HO radical reaction with 2-butanone proceeding via



is ~ 0.62 .

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6501

II.A2.24

HO + CH₃C(O)CH=CH₂ (methyl vinyl ketone) → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$3.85 \times 10^{-12} \exp[(456 \pm 73)/T]$	298–424	Kleindienst et al., 1982	FP-RF
$(1.79 \pm 0.28) \times 10^{-11}$	298		
$2.67 \times 10^{-12} \exp[(612 \pm 49)/T]$	232–378	Gierczak et al., 1997	PLP-LIF
$(2.03 \pm 0.17) \times 10^{-11}$	298		
<i>Relative Rate Coefficients</i>			
1.48×10^{-11}	300	Cox et al., 1980	RR (a)
$(1.96 \pm 0.15) \times 10^{-11}$	299 ± 2	Atkinson et al., 1983	RR (b)

5 Comments

- (a) Relative rate study carried out at atmospheric pressure of air. The concentrations of methyl vinyl ketone and ethene (the reference compound) were measured by GC. The measured rate coefficient ratio is placed on an absolute basis by using a rate coefficient of $k(\text{HO} + \text{ethene}) = 8.44 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 300 K and atmospheric pressure of air (Atkinson, 1997).
 10 (b) Relative rate study carried out at atmospheric pressure of air. The concentrations of methyl vinyl ketone and propene (the reference compound)

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were measured by GC. The measured rate coefficient ratio $k(\text{HO} + \text{methyl vinyl ketone})/k(\text{HO} + \text{propene}) = 0.747 \pm 0.055$ is placed on an absolute basis by using a rate coefficient of $k(\text{HO} + \text{propene}) = 2.62 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 299 K and atmospheric pressure of air (Atkinson, 1997).

5 Preferred Values

$k = 2.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 2.6 \times 10^{-12} \exp(610/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 230–380 K.

Reliability

10 $\Delta \log k = \pm 0.15$ at 298 K.
 $\Delta (E/R) = \pm 200 \text{ K}$.

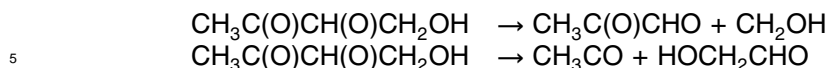
Comments on Preferred Values

The room temperature rate coefficients of Atkinson et al. (1983) and Gierczak et al. (1997) are in excellent agreement, but are higher by ~10% and 30–35% than the earlier absolute and relative rate measurements of Kleindienst et al. (1982) and Cox et al. (1980), respectively. The preferred 298 K rate coefficient is based on the room temperature rate coefficients of Atkinson et al. (1983) and Gierczak et al. (1997). The temperature dependence measured by Gierczak et al. (1997) is accepted and the pre-exponential factor is calculated from the preferred 298 K rate coefficient and temperature dependence.

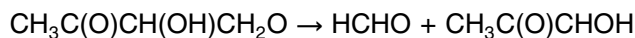
20 The products of the reaction of HO radicals with methyl vinyl ketone in the presence of NO have been investigated by Tuazon and Atkinson (1989). The

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reaction proceeds by initial addition of the HO radical to the carbon atoms of the C=C bond, forming (in the presence of NO) the intermediate hydroxyalkoxy radicals $\text{CH}_3\text{C}(\text{O})\text{CH}(\text{O})\text{CH}_2\text{OH}$ and $\text{CH}_3\text{C}(\text{O})\text{CH}(\text{OH})\text{CH}_2\text{O}$, which decompose by the pathways:



and



followed by reactions of CH_2OH and $\text{CH}_3\text{C}(\text{O})\text{CHOH}$ radicals with O_2 to form $\text{HCHO} + \text{HO}_2$ and $\text{CH}_3\text{C}(\text{O})\text{CHO} + \text{HO}_2$, respectively. The first generation products are therefore $\text{HCHO} + \text{CH}_3\text{C}(\text{O})\text{CHO}$ and $\text{HOCH}_2\text{CHO} + \text{CH}_3\text{CO}$ (with the acetyl radical reacting to form peroxyacetyl nitrate [$\text{CH}_3\text{C}(\text{O})\text{OONO}_2$; PAN] or HCHO (Tuazon and Atkinson, 1989; IUPAC, current recommendation). Tuazon and Atkinson (1989) measured formation yields of methylglyoxal and glycolaldehyde of $25 \pm 8\%$ and $64 \pm 16\%$, respectively, showing that initial HO radical addition occurs mainly at the terminal CH_2 group (Tuazon and Atkinson, 1989).

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IUPAC: <http://www.iupac-kinetic.ch.cam.ac.uk/>.

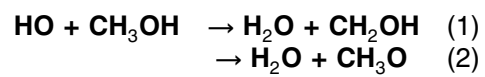
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II.A2.25



$$\Delta H^\circ(1) = -95.2 \text{kJ} \cdot \text{mol}^{-1}$$

$$\Delta H^\circ(2) = -60.2 \text{kJ} \cdot \text{mol}^{-1}$$

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Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.06 \pm 0.10) \times 10^{-12}$	296 ± 2	Overend and Paraskevopoulos, 1978	FP-RA
$(1.00 \pm 0.10) \times 10^{-12}$	298	Ravishankara and Davis, 1978	FP-RF
$4.8 \times 10^{-12} \exp[-(480 \pm 70)/T]$	240–440	Wallington and Kurylo, 1987	FP-RF
$(8.61 \pm 0.47) \times 10^{-13}$	296		
$(1.01 \pm 0.10) \times 10^{-12}$	298 ± 2	McCaulley et al., 1989	DF-LIF
$5.89 \times 10^{-20} T^{2.65} \exp(444/T)$	294–866	Hess and Tully, 1989	PLP-LIF
$(9.34 \pm 0.41) \times 10^{-13}$	294		
$(9.0 \pm 0.9) \times 10^{-13}$	298 ± 2	Nelson et al., 1990	PR-RA
$(8.64 \pm 1.30) \times 10^{-12}$	1205 ± 16	Bott and Cohen, 1991	SH-RA
<i>Relative Rate Coefficients</i>			
$(9.0 \pm 0.7) \times 10^{-13}$	300 ± 3	Tuazon et al., 1983	RR (a)
$(9.3 \pm 2.2) \times 10^{-13}$	298 ± 2	Nelson et al., 1990	RR (b)
$(8.6 \pm 0.8) \times 10^{-13}$	298 ± 4	Picquet et al., 1998	RR (c)
$(9.6 \pm 1.0) \times 10^{-13}$	298 ± 2	Oh and Andino, 2001	RR (d)
$(8.4 \pm 0.7) \times 10^{-13}$	298 ± 2	Oh and Andino, 2001	RR (b)
<i>Branching Ratios</i>			
$k_2/k = 0.15 \pm 0.08$	298 ± 2	McCaulley et al., 1989	(e)

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Comments

- 5 (a) HO radicals were generated by the dark reaction of hydrazine with O₃ in air. The concentrations of methanol and dimethyl ether (the reference compound) were measured by FTIR spectroscopy. The measured rate coefficient ratio of $k(\text{HO} + \text{methanol})/k(\text{HO} + \text{dimethyl ether}) = 0.314 \pm 0.024$ is placed on an absolute basis using the rate coefficient $k(\text{HO} + \text{dimethyl ether}) = 2.86 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 300 K (IUPAC, current recommendation).
- 10 (b) HO radicals were generated by the photolysis of CH₃ONO in air at >300 nm. The concentrations of methanol and cyclohexane (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(\text{HO} + \text{methanol})/k(\text{HO} + \text{cyclohexane})$ is placed on an absolute basis using a rate coefficient of $k(\text{HO} + \text{cyclohexane}) = 6.97 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Atkinson, 2003).
- 15 (c) HO radicals were generated by the photolysis of H₂O₂ in air at 254 and 310 nm. The concentrations of methanol and *n*-pentane (the reference compound) were measured by GC. The measured rate coefficient ratio, $k(\text{HO} + \text{methanol})/k(\text{HO} + n\text{-pentane})$, is placed on an absolute basis using a rate coefficient of $k(\text{HO} + n\text{-pentane}) = 3.80 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Atkinson, 2003).
- 20 (d) HO radicals were generated by the photolysis of CH₃ONO in air at >300 nm. The concentrations of methanol and ethanol (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(\text{HO} + \text{methanol})/k(\text{HO} + \text{ethanol}) = 0.30 \pm 0.03$ is placed on an absolute basis using a rate coefficient of $k(\text{HO} + \text{ethanol}) = 3.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1}$
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s⁻¹ at 298 K (IUPAC, current recommendation).

(e) Derived from measurements of the rate coefficients for the reactions of the HO radical with CH₃OH, CD₃OH and CD₃OD and of the DO radical with CH₃OH, CH₃OD, CD₃OH and CD₃OD, assuming that secondary kinetic isotope effects are negligible.

Preferred Values

$k = 9.3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 3.1 \times 10^{-12} \exp(-360/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 240–300 K.

$k_2/k = 0.15$ at 298 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

$\Delta (E/R) = \pm 200$ K.

$\Delta k_2/k = \pm 0.10$ at 298 K.

Comments on Preferred Values

The preferred rate coefficient is obtained by fitting the absolute rate coefficients of Overend and Paraskevopoulos (1978), Ravishankara and Davis (1978), Wallington and Kurylo (1987), McCaulley et al. (1989), Hess and Tully (1989), Nelson et al. (1990) and Bott and Cohen (1991) to the three parameter expression $k = CT^2 \exp(-D/T)$. This results in $k = 6.01 \times 10^{-18} T^2 \exp(170/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 240–1205 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 265 K, and is derived from the

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three parameter equation with $A = Ce^{2T^2}$ and $B = D + 2T$. The kinetic (McCaulley et al., 1989) and product (Hägele et al., 1983; Meier et al., 1984) studies show that the reaction proceeds mainly by channel (1) at room temperature, as expected from the thermochemistry of the reaction pathways (1) and (2).

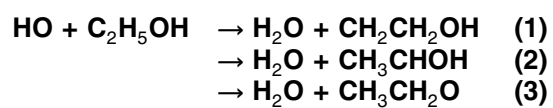
The room temperature relative rate coefficients of Tuazon et al. (1983), Nelson et al. (1990), Picquet et al. (1998) and Oh and Andino (2001) are in agreement with the preferred value.

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II.A2.26



$$\Delta H^\circ(1) = -67\text{kJ} \cdot \text{mol}^{-1}$$

$$\Delta H^\circ(2) = -95.8\text{kJ} \cdot \text{mol}^{-1}$$

$$5 \quad \Delta H^\circ(3) = -59.7\text{kJ} \cdot \text{mol}^{-1}$$

6512

Rate coefficient data ($k=k_1+k_2+k_3$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.25 \times 10^{-11} \exp[-(360 \pm 52)/T]$	255–459	Greenhill and O'Grady, 1986	FP-RA
$(3.40 \pm 0.17) \times 10^{-12}$	293		
$7.4 \times 10^{-12} \exp[-(240 \pm 110)/T]$	240–440	Wallington and Kurylo, 1987	FP-RF
$(3.33 \pm 0.23) \times 10^{-12}$	296		
$(3.26 \pm 0.14) \times 10^{-12}$	293	Hess and Tully, 1988	PLP-LIF (a,b)
$(3.33 \pm 0.14) \times 10^{-12}$	326.5		
$(3.63 \pm 0.15) \times 10^{-12}$	380		
$(3.94 \pm 0.16) \times 10^{-12}$	441		
$(3.32 \pm 0.16) \times 10^{-12}$	295	Hess and Tully, 1988	PLP-LIF (b,c)
$(5.47 \pm 0.34) \times 10^{-12}$	599		
$(3.04 \pm 0.25) \times 10^{-12}$	298 ± 2	Nelson et al., 1990	PR-RA
$k_2 + k_3 = (8.80 \pm 1.32) \times 10^{-12}$	1204 ± 16	Bott and Cohen, 1991	SH-RA (d)
<i>Relative Rate Coefficients</i>			
$(3.22 \pm 0.49) \times 10^{-12}$	298 ± 2	Nelson et al., 1990	RR (e)
$(3.64 \pm 0.11) \times 10^{-12}$	298 ± 4	Picquet et al., 1998	RR (f)
$(2.79 \pm 0.28) \times 10^{-12}$	298 ± 2	Oh and Andino, 2001	RR (e)
$(2.72 \pm 0.25) \times 10^{-12}$	298 ± 2	Oh and Andino, 2001	RR (g)

6513

Comments

- (a) Reaction of H^{16}O radicals.
- (b) Thermal decomposition of the $\text{H}^{16}\text{OCH}_2\text{CH}_2$ radical formed by H-atom abstraction from the $-\text{CH}_3$ group to regenerate H^{16}O radicals occurs at temperatures >500 K, and hence the H^{16}O rate coefficient data do not yield the rate coefficient $k=(k_1+k_2+k_3)$ above ~ 500 K. Since thermal decomposition of the $\text{H}^{16}\text{OCH}_2\text{CH}_2$ radical does not lead to regeneration of the H^{18}O radical, the H^{18}O rate coefficient data yield the overall reaction rate coefficient, $k=(k_1+k_2+k_3)$.
- (c) Rate coefficients for reaction of the H^{18}O radical. H^{18}O radicals were generated from pulsed laser photolysis of H_2^{18}O , with H^{18}O radicals being detected by LIF.
- (d) HO radicals were generated by the thermal decomposition of *t*-butyl hydroperoxide in a shock tube, with detection by resonance absorption at 309 nm. The measured rate coefficient corresponds to (k_2+k_3) because of the rapid thermal decomposition of the $\text{CH}_2\text{CH}_2\text{OH}$ radical formed in reaction channel (1) [this is the same radical as formed from the addition of HO radicals to ethene].
- (e) HO radicals were generated by photolysis of CH_3ONO in air. The ethanol and cyclohexane (the reference organic) concentrations were measured by GC. The measured rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{cyclohexane}) = 6.97 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson, 2003).

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- (f) HO radicals were generated by the photolysis of H₂O₂ in air at 254 and 310 nm. The concentrations of ethanol and *n*-hexane (the reference compound) were measured by GC. The measured rate coefficient ratio, $k(\text{HO} + \text{ethanol})/k(\text{HO} + n\text{-hexane})$, is placed on an absolute basis using a rate coefficient of $k(\text{HO} + n\text{-hexane}) = 5.20 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Atkinson, 2003).
- (g) HO radicals were generated by photolysis of CH₃ONO in air. The ethanol and *p*-xylene (the reference organic) concentrations were measured by GC. The measured rate coefficient ratio of $k(\text{HO} + \text{ethanol})/k(\text{HO} + p\text{-xylene}) = 0.19 \pm 0.01$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + p\text{-xylene}) = 1.43 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Calvert et al., 2002).

Preferred Values

- $k = 3.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 4.1 \times 10^{-12} \exp(-70/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 270–340 K.
 $k_1/k = 0.05$ at 298 K.
 $k_3/k = 0.05$ at 298 K.

Reliability

- $\Delta \log k = \pm 0.15$ at 298 K.
 $\Delta (E/R) = \pm 200 \text{ K}$.
 $\Delta k_1/k = \begin{matrix} +0.10 \\ -0.05 \end{matrix}$ at 298 K.
 $\Delta k_3/k = \begin{matrix} +0.10 \\ -0.05 \end{matrix}$ at 298 K.

6515

Comments on Preferred Values

- There is substantial scatter in the room temperature rate coefficients measured to date. The most definite study to date is that of Hess and Tully (1988). The preferred rate coefficient is derived from fitting the H¹⁸O and (for temperatures <500 K) the H¹⁶O rate coefficients of Hess and Tully (1988) to the three parameter expression $k = CT^2 \exp(-D/T)$. This results in $k = 6.18 \times 10^{-18} T^2 \exp(532/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 293–599 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$ is centered at 300 K and is derived from this three parameter expression with $A = Ce^2T^2$ and $B = D + 2T$.
- The rate coefficients calculated from the preferred Arrhenius expression are ~10% higher than the lowest temperature rate coefficients reported by Greenhill and O'Grady (1986) (at 255 K) and Wallington and Kurylo (1987) (at 240 K). The preferred 298 K rate coefficient is in good agreement with the absolute and relative rate coefficients of Nelson et al. (1990) and Picquet et al. (1998), but is ~15% higher than the relative rate data of Oh and Andino (2001). The rate coefficient measured by Bott and Cohen (1991) at 1204 K, and ascribed to $(k_2 + k_3)$, is consistent with the value of $(k_1 + k_2 + k_3)$ calculated from the recommended three parameter expression and with the rate coefficient k_1 at 1204 K estimated using the procedure of Atkinson (1987).
- Meier et al. (1985) determined that at room temperature the reaction proceeds mainly (75±15%) via formation of the CH₃CHOH radical, consistent with the thermochemistry of the reaction steps. The kinetic data of Hess and Tully (1988) for the reactions of the H¹⁶O and H¹⁸O radicals with ethanol indicate that channel (1) accounts for ~15% of the overall reaction at 600 K, in agreement with the calculated value of ~20% from the estimation procedure of Atkinson (1987). This agreement allows a rate coefficient ratio of $k_1/k = 0.05$ at 298 K to be estimated. Assuming that H-atom abstraction from the -OH group in

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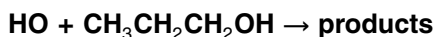
ethanol [channel (3)] has a similar rate coefficient to the analogous channel for methanol (IUPAC, this evaluation) allows $k_3/k=0.05$ at 298 K to be estimated. The resulting value of $k_2/k=0.90$ at 298 K is just consistent with the product data of Meier et al. (1985).

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II.A2.27



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(5.33 \pm 0.54) \times 10^{-12}$	296 ± 2	Overend and Paraskevopoulos, 1978	FP-RA
$(5.34 \pm 0.39) \times 10^{-12}$	296	Wallington and Kurylo, 1987	FP-RF
$(5.64 \pm 0.48) \times 10^{-12}$	298 ± 2	Nelson et al., 1990	PR-RA
$4.68 \times 10^{-12} \exp[(68 \pm 41)/T]$	263–372	Yujing and Mellouki, 2001	PLP-LIF
$(5.83 \pm 0.18) \times 10^{-12}$	298		
<i>Relative Rate Coefficients</i>			
$(3.7 \pm 0.6) \times 10^{-12}$	292	Campbell et al., 1976	RR (a)
$(5.12 \pm 0.41) \times 10^{-12}$	298 ± 2	Nelson et al., 1990	RR (b)
$(4.42 \pm 0.26) \times 10^{-12}$	298 ± 2	Oh and Andino, 2000	RR (c,d)
$(6.44 \pm 0.43) \times 10^{-12}$	298 ± 2	Oh and Andino, 2000	RR (c,e)
$(5.11 \pm 0.19) \times 10^{-12}$	273	Cheema et al., 2002	RR (f)
$(5.50 \pm 0.17) \times 10^{-12}$	298		
$(5.74 \pm 0.33) \times 10^{-12}$	313		
$(6.20 \pm 0.17) \times 10^{-12}$	343		

6518

Comments

- (a) HO radicals were generated by the dark reaction of H₂O₂-NO₂ mixtures in the presence of CO and an organic compound. From sequential experiments using *n*-butane and 1-propanol, a rate coefficient ratio of $k(\text{HO} + 1\text{-propanol})/k(\text{HO} + n\text{-butane}) = 1.67 \pm 0.27$ (two standard deviations) was derived. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + n\text{-butane}) = 2.22 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 292 K (IUPAC, current recommendation).
- (b) HO radicals were generated by the photolysis of CH₃ONO in air, and the concentrations of 1-propanol and cyclohexane (the reference compound) were measured by GC. The measured rate coefficient ratio $k(\text{HO} + 1\text{-propanol})/k(\text{HO} + \text{cyclohexane})$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{cyclohexane}) = 6.97 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Atkinson, 2003).
- (c) HO radicals were generated by the photolysis of CH₃ONO in air, and the concentrations of 1-propanol and *n*-hexane and *p*-xylene (the reference compounds) were measured by GC. The measured rate coefficient ratios of $k(\text{HO} + 1\text{-propanol})/k(\text{HO} + n\text{-hexane}) = 0.85 \pm 0.05$ and $k(\text{HO} + 1\text{-propanol})/k(\text{HO} + p\text{-xylene}) = 0.45 \pm 0.03$ are placed on an absolute basis by use of rate coefficients at 298 K of $k(\text{HO} + n\text{-hexane}) = 5.20 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson, 2003) and $k(\text{HO} + p\text{-xylene}) = 1.43 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Calvert et al., 2002).
- (d) Relative to HO + *n*-hexane.
- (e) Relative to HO + *p*-xylene.

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- (f) HO radicals were generated by the photolysis of CH₃ONO in air, and the concentrations of 1-propanol and 2,3-dimethylbutane (the reference compound) were measured by GC. The measured rate coefficient ratios of $k(\text{HO} + 1\text{-propanol})/k(\text{HO} + 2,3\text{-dimethylbutane})$ are placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + 2,3\text{-dimethylbutane}) = 1.66 \times 10^{-17} T^2 \exp(407/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson, 2003).

Preferred Values

$k = 5.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 4.6 \times 10^{-12} \exp(70/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 260–380 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.
 $\Delta (E/R) = \pm 100 \text{ K}$.

Comments on Preferred Values

- The preferred values are based on the temperature-dependent absolute rate study of Yujing and Mellouki (2001). At room temperature, the rate coefficients measured by Yujing and Mellouki (2001) are in good agreement with the absolute rate coefficients of Overend and Paraskevopoulos (1976), Wallington and Kurylo (1987) and Nelson et al. (1990), and with the relative rate constant of Nelson et al. (1990). The experimental technique of Campbell et al. (1976) was possibly prone to unrecognized problems, and the relative rate constants of Oh and Andino (2000) measured relative to *n*-hexane and *p*-xylene are respectively 25% higher and 11% lower than the preferred value. The rate coefficients

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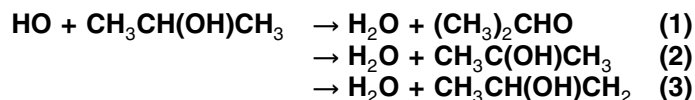
determined by Cheema et al. (2002) relative to that for 2,3-dimethylbutane are in good agreement with the preferred values (to within 15%), although the Cheema et al. (2002) data indicate a positive temperature dependence in contrast to that observed by Yujing and Mellouki (2001) and used as the basis for the preferred values.

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II.A2.28



$$\Delta H^\circ(1) = -58.8 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data ($k = k_1 + k_2 + k_3$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(5.48 \pm 0.55) \times 10^{-12}$	296 ± 2	Overend and Paraskevopoulos, 1978	FP-RA
$5.8 \times 10^{-12} \exp[-(30 \pm 90)/T]$	240–440	Wallington and Kurylo, 1987	FP-RF
$(5.81 \pm 0.34) \times 10^{-12}$	296		
$(5.69 \pm 1.09) \times 10^{-12}$	298 ± 2	Nelson et al., 1990	PR-RA
$1.044 \times 10^{-17} T^{1.86} \exp(736/T)$	293–587	Dunlop and Tully, 1993	PLP-LIF (a)
$(5.10 \pm 0.21) \times 10^{-12}$	293		
$2.80 \times 10^{-12} \exp[(184 \pm 40)/T]$	253–372	Yujing and Mellouki, 2001	PLP-LIF
$(5.17 \pm 0.23) \times 10^{-12}$	298		
<i>Relative Rate Coefficients</i>			
$(5.38 \pm 0.70) \times 10^{-12}$	298 ± 2	Nelson et al., 1990	RR (b)

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Comments

- (a) The reactions of H¹⁶O radicals were studied over the temperature range 293 K to 745 K and the reactions of H¹⁸O radicals were studied at 548 K and 587 K. Non-exponential decays of H¹⁶O radicals were observed over the temperature range 504 K to 600 K and, while exponential H¹⁶O radical decays were observed above 600 K, the rate coefficients were significantly lower than expected from extrapolation of the lower temperature data. These observations are consistent with thermal decomposition of the CH₃CH(OH)CH₂ radical formed in reaction channel (3) [the same radical as formed from HO radical addition to propene] at temperatures >500 K. Hence using H¹⁶O radicals, values of ($k_1+k_2+k_3$) were measured at temperatures ≤500 K and (k_1+k_2) at temperatures >600 K. No regeneration of H¹⁸O radicals from thermal decomposition of the CH₃CH(¹⁶OH)CH₂ radical can occur, and hence the measured H¹⁸O rate coefficients are those for ($k_1+k_2+k_3$).
- (b) HO radicals were generated by the photolysis of CH₃ONO in air. The concentrations of 2-propanol and cyclohexane (the reference organic) were measured by GC. The measured rate coefficient ratio $k(\text{HO} + 2\text{-propanol})/k(\text{HO} + \text{cyclohexane})$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{cyclohexane}) = 6.97 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Atkinson, 2003).

Preferred Values

$k = 5.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 2.6 \times 10^{-12} \exp(200/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range

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250–360 K.

Reliability

$\Delta \log k = \pm 0.08$ at 298 K.

$\Delta (E/R) = \pm 100 \text{ K}$.

Comments on Preferred Values

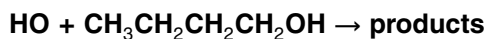
The absolute rate coefficients measured by Dunlop and Tully (1993) and Yujing and Mellouki (2001) are in excellent agreement over the temperature range common to both studies (293–378 K), and the preferred rate coefficients are derived from these two studies (Dunlop and Tully, 1993; Yujing and Mellouki, 2001). The H¹⁸O rate coefficients at 548 K and 587 K and the H¹⁶O rate coefficients at ≤502 K obtained by Dunlop and Tully (1993) and the rate coefficients of Yujing and Mellouki (2001) (253–372 K) were fitted to the three parameter expression $k = CT^2 \exp(-D/T)$, resulting in $k = 4.03 \times 10^{-18} T^2 \exp(792/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 253–587 K. The preferred Arrhenius expression, $k = A \exp(-B/T)$, is centered at 295 K and is derived from the three parameter expression with $A = Ce^{2T^2}$ and $B = D + 2T$. The preferred rate coefficients are within 15% of those measured by Wallington and Kurylo (1987) over the temperature range 250 K to 360 K and are in agreement within the cited error limits with the room temperature absolute and relative rate coefficients of Overend and Paraskevopoulos (1978) and Nelson et al. (1990).

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II.A2.29



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(8.31 \pm 0.63) \times 10^{-12}$	296	Wallington and Kurylo, 1987	FP-RA
$(7.80 \pm 0.20) \times 10^{-12}$	298 \pm 2	Nelson et al., 1990	PR-RA
$5.30 \times 10^{-12} \exp[(146 \pm 92)/T]$	263–372	Yujing and Mellouki, 2001	PLP-LIF
$(8.47 \pm 0.34) \times 10^{-12}$	298		
<i>Relative Rate Coefficients</i>			
$(6.7 \pm 1.3) \times 10^{-12}$	292	Campbell et al., 1976	RR (a)
$(7.97 \pm 0.66) \times 10^{-12}$	298 \pm 2	Nelson et al., 1990	RR (b)
$(1.03 \pm 0.05) \times 10^{-11}$	298 \pm 2	Oh and Andino, 2001	RR (c)

5 Comments

- (a) HO radicals were generated by the dark reaction of $\text{H}_2\text{O}_2\text{-NO}_2$ mixtures in the presence of CO and an organic compound. From sequential experiments using *n*-butane and 1-butanol, a rate coefficient ratio of $k(\text{HO} + 1\text{-butanol})/k(\text{HO} + n\text{-butane}) = 3.00 \pm 0.56$ (two standard deviations) was
10 derived. This rate coefficient ratio is placed on an absolute basis by use of

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a rate coefficient of $k(\text{HO} + n\text{-butane}) = 2.22 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 292 K (IUPAC, current recommendation).

(b) HO radicals were generated by the photolysis of CH_3ONO in air, and the concentrations of 1-butanol and cyclohexane (the reference compound) were measured by GC. The measured rate coefficient ratio $k(\text{HO} + 1\text{-butanol})/k(\text{HO} + \text{cyclohexane})$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{cyclohexane}) = 6.97 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Atkinson, 2003).

(c) HO radicals were generated by the photolysis of CH_3ONO in air, and the concentrations of 1-butanol and *p*-xylene (the reference compound) were measured by GC. The measured rate coefficient ratio $k(\text{HO} + 1\text{-butanol})/k(\text{HO} + p\text{-xylene}) = 0.72 \pm 0.03$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + p\text{-xylene}) = 1.43 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Calvert et al., 2002).

15 Preferred Values

$k = 8.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 5.3 \times 10^{-12} \exp(140/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 260–380 K.

Reliability

20 $\Delta \log k = \pm 0.15$ at 298 K.

$\Delta (E/R) = \pm 200 \text{ K}$.

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Comments on Preferred Values

The absolute rate study of Yujing and Mellouki (2001), the sole temperature-dependence study, is used to derive the preferred values. The 298 K coefficient from the study of Yujing and Mellouki (2001) is in good agreement with the room temperature absolute and relative rate coefficients of Wallington and Kurylo (1987) and Nelson et al. (1990), but is 18% lower than the relative rate coefficient of Oh and Andino (2001). The experimental technique of Campbell et al. (1976) was possibly prone to unrecognized problems.

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Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
$(8.58 \pm 0.49) \times 10^{-12}$	296 ± 2	Chew and Atkinson, 1996	RR (a)
$(8.80 \pm 0.14) \times 10^{-12}$	297 ± 3	Baxley and Wells, 1998	RR (b,c)
$(7.57 \pm 0.44) \times 10^{-12}$	297 ± 3	Baxley and Wells, 1998	RR (b,d)

5 Comments

- (a) HO radicals were generated by the photolysis of CH_3ONO in air, and the concentrations of 2-butanol and cyclohexane (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(\text{HO} + 2\text{-butanol})/k(\text{HO} + \text{cyclohexane}) = 1.24 \pm 0.07$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{cyclohexane}) = 6.92 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (Atkinson, 2003).
- (b) HO radicals were generated by the photolysis of CH_3ONO in air, and the concentrations of 2-butanol and *n*-nonane and dodecane (the reference compounds) were measured by GC. The measured rate coefficient ratios of $k(\text{HO} + 2\text{-butanol})/k(\text{HO} + n\text{-nonane})$ and $k(\text{HO} + 2\text{-butanol})/k(\text{HO} + \text{dodecane})$ are placed on an absolute basis by use of rate coefficients at

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297 K of $k(\text{HO} + n\text{-nonane}) = 9.69 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k(\text{HO} + \text{dodecane}) = 1.32 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson, 2003).

(c) Relative to HO + *n*-nonane.

(d) Relative to HO + dodecane.

5 Preferred Values

$k = 8.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

Comments on Preferred Values

- The preferred value is based on the relative rate coefficient of Chew and Atkinson (1996) and that of Baxley and Wells (1998) relative to HO + *n*-nonane, which are in excellent agreement. The rate coefficient of Baxley and Wells (1998) measured relative to that for HO + dodecane, while in agreement with the other two rate coefficients (Chew and Atkinson, 1996; Baxley and Wells, 1998), is more uncertain because of the small data-base for HO + dodecane, and hence this rate coefficient is not used in the evaluation.

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Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$8.2 \times 10^{-12} \exp[(610 \pm 50)/T]$	231–300	Rudich et al., 1995	PLP-LIF
$(6.4 \pm 0.6) \times 10^{-11}$	298		
<i>Relative Rate Coefficients</i>			
$(3.81 \pm 0.80) \times 10^{-11}$	298 ± 2	Fantechi et al., 1998a	RR (b,c)
$(4.27 \pm 1.80) \times 10^{-11}$	298 ± 2	Fantechi et al., 1998a	RR (b,d)
$(6.43 \pm 0.54) \times 10^{-11}$	295 ± 1	Ferronato et al., 1998	RR (e,f)
$(7.35 \pm 0.78) \times 10^{-11}$	295 ± 1	Ferronato et al., 1998	RR (e,g)
$(5.64 \pm 0.13) \times 10^{-11}$	296 ± 2	Papagni et al., 2001	RR (h)

5 **Comments**

- (a) Rate coefficients for the reactions of HO, H¹⁸O and DO radicals with 2-methyl-3-buten-2-ol were measured, in the presence and absence of O₂ (up to 13.5 Torr (18 mbar) O₂ in the case of the HO radical reaction), over the temperature range 231–410 K. Above ~350 K the rate coefficients decreased with increasing temperature faster than predicted based on extrapolation of the lower temperature data. For the HO radical reaction, the

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rate coefficients in the presence of 2–13.5 Torr of O₂ were up to 15–20% higher than in the absence of O₂, while the measured rate coefficients for the DO radical reaction were invariant to the presence or absence of O₂. HO radicals were observed to be formed in the DO radical reaction, and the rate coefficients of the DO radical and H¹⁸O radical reactions were essentially identical to those for the HO radical reactions in the presence of O₂. These data indicated that the measured rate coefficients from the HO radical reaction in the absence of O₂ are low because of HO radical regeneration, whereas H¹⁸O and DO radical regeneration does not occur from reactions of H¹⁸O and DO radicals with 2-methyl-3-buten-2-ol (HO radicals being formed by elimination of the -OH group in the 2-methyl-3-buten-2-ol in the absence of O₂). The rate coefficient cited is derived (Rudich et al., 1995) from the rate coefficients measured for the HO and DO radical reactions in the presence of O₂ over the temperature range 230–300 K, and is expected to be applicable to atmospheric conditions.

(b) HO radicals were generated by the photolysis of H₂O₂ at 253.7 nm in air at 987±7 mbar pressure. The concentrations of 2-methyl-3-buten-2-ol and isoprene (or propene) [the reference compounds] were measured during the experiments by FTIR spectroscopy. The measured rate coefficient ratios $k(\text{HO} + 2\text{-methyl-3-buten-2-ol})/k(\text{HO} + \text{isoprene})$ and $k(\text{HO} + 2\text{-methyl-3-buten-2-ol})/k(\text{HO} + \text{propene})$ are placed on an absolute basis by use of rate coefficients at 298 K and atmospheric pressure of $k(\text{HO} + \text{isoprene}) = 1.00 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Arey, 2003; IUPAC, current recommendation) and $k(\text{HO} + \text{propene}) = 2.63 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Arey, 2003).

(c) Relative to $k(\text{HO} + \text{isoprene})$.

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(d) Relative to $k(\text{HO} + \text{propene})$.

(e) HO radicals were generated by the photolysis of ¹³CH₃ONO-NO-(CH₃)₂C(OH)CH=CH₂-propene (or ethene) [the reference compounds]-air mixtures at 933 mbar pressure. The concentrations of 2-methyl-3-buten-2-ol and propene (or ethene) were measured by FTIR spectroscopy. The measured rate coefficient ratios of $k(\text{HO} + 2\text{-methyl-3-buten-2-ol})/k(\text{HO} + \text{propene}) = 2.4 \pm 0.2$ and $k(\text{HO} + 2\text{-methyl-3-buten-2-ol})/k(\text{HO} + \text{ethene}) = 8.5 \pm 0.9$ are placed on an absolute basis by use of rate coefficients at 295 K and atmospheric pressure of air of $k(\text{HO} + \text{propene}) = 2.68 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k(\text{HO} + \text{ethene}) = 8.65 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Arey, 2003).

(f) Relative to $k(\text{HO} + \text{propene})$.

(g) Relative to $k(\text{HO} + \text{ethene})$.

(h) HO radicals were generated by the photolysis of CH₃ONO-NO-(CH₃)₂C(OH)CH=CH₂-1,3,5-trimethylbenzene (the reference compound)-air mixtures at 987 mbar pressure. The concentrations of 2-methyl-3-buten-2-ol and 1,3,5-trimethylbenzene were measured by GC. The measured rate coefficient ratio of $k(\text{HO} + 2\text{-methyl-3-buten-2-ol})/k(\text{HO} + 1,3,5\text{-trimethylbenzene}) = 0.995 \pm 0.022$ is placed on an absolute basis by use of a rate coefficient at 296 K of $k(\text{HO} + 1,3,5\text{-trimethylbenzene}) = 5.67 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Arey, 2003).

Preferred Values

$k = 8.2 \times 10^{-12} \exp(610/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 230–300 K.

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$$k = 6.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.15 \text{ at } 298 \text{ K.}$$

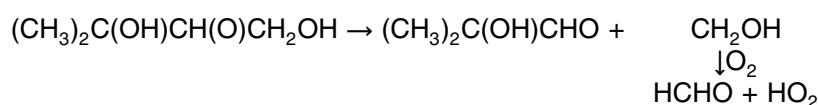
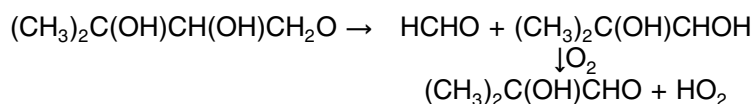
$$5 \quad \Delta (E/R) = \pm 200 \text{ K.}$$

Comments on Preferred Values

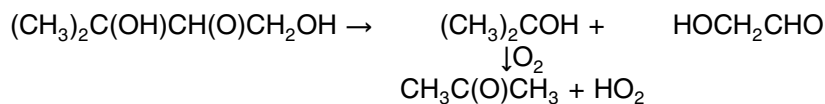
The room temperature rate coefficients of Rudich et al. (1995), Ferronato et al. (1998) and Papagni et al. (2001) are in reasonable agreement, although the rate coefficient of Ferronato et al. (1998) relative to ethene is somewhat higher than those of Rudich et al. (1995) and Papagni et al. (2001) and that of Ferronato et al. (1998) relative to propene. The two relative rate coefficients of Fantechi et al. (1998a) are significantly lower than the values measured by Rudich et al. (1995), Ferronato et al. (1998) and Papagni et al. (2001). The preferred 298 K rate coefficient is the average of the absolute and relative rate coefficients of Rudich et al. (1995), Ferronato et al. (1998) and Papagni et al. (2001), and is identical to the 298 K absolute rate coefficient cited by Rudich et al. (1995). The preferred temperature dependence is that reported by Rudich et al. (1995).

The reaction proceeds almost totally by initial addition of HO to the C=C bond (Fantechi et al., 1998b; Ferronato et al., 1998; Alvarado et al., 1999; Spaulding et al., 2002; Reisen et al., 2003). In the presence of NO at atmospheric pressure of air the observed products are formaldehyde, acetone, glycolaldehyde, 2-hydroxy-2-methylpropanal [(CH₃)₂C(OH)CHO], and dihydroxynitrates [presumed to be (CH₃)₂C(OH)CH(OH)CH₂ONO₂ and (CH₃)₂C(OH)CH(ONO₂)CH₂OH] (Fantechi et al., 1998b; Ferronato et al., 1998; Alvarado et al., 1999; Spaulding et al., 2002; Reisen et al., 2003).

Based on the product studies of Ferronato et al. (1998), Alvarado et al. (1999) and Reisen et al. (2003) carried out in the presence of NO, the product yields are: formaldehyde, 35±4% (Ferronato et al., 1998) and 29±3% (Alvarado et al., 1999); acetone, 52±5% (Ferronato et al., 1998) and 58±4% (Alvarado et al., 1999); glycolaldehyde, 50±5% (Ferronato et al., 1998) and 61±9% (Alvarado et al., 1999); 2-hydroxy-2-methylpropanal, 31±4% (Reisen et al., 2003); and dihydroxynitrates, 5±2% (Alvarado et al., 1999). The reaction mechanism is discussed in detail in Alvarado et al. (1999). Reactions of the (CH₃)₂C(OH)CH(OH)CH₂OO and (CH₃)₂C(OH)CH(OO)CH₂OH peroxy radicals (formed after addition of O₂ to the initially formed (CH₃)₂C(OH)CH(OH)CH₂ and (CH₃)₂C(OH)CHCH₂OH radicals) with NO lead to the formation of the dinitrates (CH₃)₂C(OH)CH(OH)CH₂ONO₂ and (CH₃)₂C(OH)CH(ONO₂)CH₂OH or NO₂ plus the dihydroxyalkoxy radicals (CH₃)₂C(OH)CH(OH)CH₂O and (CH₃)₂C(OH)CH(O)CH₂OH. These dihydroxyalkoxy radicals appear to dominantly decompose at room temperature and atmospheric pressure:



and/or



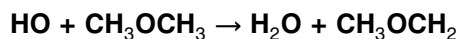
Hence, as observed, the yield of HCHO equals that of (CH₃)₂C(OH)CHO, and the yield of HOCH₂CHO equals that of CH₃C(O)CH₃ (Ferronato et al., 1998; Alvarado et al., 1999; Reisen et al., 2003).

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Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.29 \times 10^{-11} \exp[-(388 \pm 151)/T]$	299–424	Perry et al., 1977	FP-RF
$(3.50 \pm 0.35) \times 10^{-12}$	299		
$1.04 \times 10^{-11} \exp[-(372 \pm 34)/T]$	295–442	Tully and Droege, 1987	PLP-LIF
$(2.95 \pm 0.12) \times 10^{-12}$	295		
$6.7 \times 10^{-12} \exp[-(300 \pm 70)/T]$	240–440	Wallington et al., 1988	FP-RF
$(2.49 \pm 0.22) \times 10^{-12}$	296		
$(2.35 \pm 0.24) \times 10^{-12}$	298 ± 2	Nelson et al., 1990	PR-RA
$6.38 \times 10^{-12} \exp[-(234 \pm 34)/T]$	230–372	Mellouki et al., 1995	PLP-LIF
$(2.82 \pm 0.21) \times 10^{-12}$	295		
$3.39 \times 10^{-24} T^{4.11} \exp[(1221 \pm 252)/T]$	295–650	Arif et al., 1997	PLP-LIF
$(2.95 \pm 0.21) \times 10^{-12}$	295		
$3.02 \times 10^{-20} T^{2.85} \exp[(618 \pm 13)/T]$	295–618	Bonard et al., 2002	PLP-LIF
$(2.67 \pm 0.07) \times 10^{-12}$	298		

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$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
$(2.11 \pm 0.21) \times 10^{-12}$	295 ± 3	Wallington et al., 1989	RR (a)
$(2.97 \pm 0.66) \times 10^{-12}$	298 ± 2	Nelson et al., 1990	RR (b)
2.41×10^{-12}	263	DeMore and Bayes, 1999	RR (c,d)
2.47×10^{-12}	273		
2.70×10^{-12}	293		
2.72×10^{-12}	298		
3.03×10^{-12}	313		
3.23×10^{-12}	333		
3.39×10^{-12}	351		
3.04×10^{-12}	295	DeMore and Bayes, 1999	RR (c,e)
3.25×10^{-12}	305		
3.16×10^{-12}	318		
3.42×10^{-12}	328		
3.81×10^{-12}	336		
3.62×10^{-12}	345		
3.86×10^{-12}	364		
3.18×10^{-12}	306	DeMore and Bayes, 1999	RR (c,f)
3.33×10^{-12}	324		
3.62×10^{-12}	351		
3.82×10^{-12}	361		

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Comments

- 5 (a) HO radicals were generated by the photolysis of CH₃ONO-NO-air mixtures at atmospheric pressure. The concentrations of dimethyl ether and *n*-butane (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(\text{CH}_3\text{OCH}_3)/k(\textit{n}\text{-butane}) = 0.918 \pm 0.090$ is placed on an absolute basis by using a rate coefficient of $k(\textit{n}\text{-butane}) = 2.30 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation).
- 10 (b) HO radicals were generated by the photolysis of CH₃ONO-NO-air mixtures at atmospheric pressure. The concentrations of dimethyl ether and cyclohexane (the reference compound) were measured by GC. The measured rate coefficient ratio $k(\text{CH}_3\text{OCH}_3)/k(\text{cyclohexane})$ is placed on an absolute basis by use of a rate coefficient of $k(\text{cyclohexane}) = 6.97 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Atkinson, 2003).
- 15 (c) HO radicals were generated by the photolysis of O₃ at 254 nm in the presence of water vapor. The concentrations of dimethyl ether and the reference compound were measured by GC.
- 20 (d) Relative to $k(\text{HO} + \textit{n}\text{-butane})$. The measured rate coefficient ratios $k(\text{HO} + \text{dimethyl ether})/k(\text{HO} + \textit{n}\text{-butane})$ are placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \textit{n}\text{-butane}) = 1.81 \times 10^{-17} T^2 \exp(114/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation).
- (e) Relative to $k(\text{HO} + \textit{n}\text{-pentane})$. The measured rate coefficient ratios $k(\text{HO} + \text{dimethyl ether})/k(\text{HO} + \textit{n}\text{-pentane})$ are placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \textit{n}\text{-pentane}) = 2.52 \times 10^{-17} T^2 \exp(158/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson, 2003).

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(f) Relative to $k(\text{HO} + \text{cyclohexane})$. The measured rate coefficient ratios $k(\text{HO} + \text{dimethyl ether})/k(\text{HO} + \text{cyclohexane})$ are placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{cyclohexane}) = 3.26 \times 10^{-17} T^2 \exp(262/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson, 2003).

5 Preferred Values

$k = 2.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 5.7 \times 10^{-12} \exp(-215/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 230–300 K.

Reliability

$\Delta \log k = \pm 0.08$ at 298 K.
 $\Delta (E/R) = \pm 100$ K.

Comments on Preferred Values

The reported room temperature absolute (Perry et al., 1977; Tully and Droege, 1987; Wallington et al., 1988; Nelson et al., 1990; Melloui et al., 1995; Arif et al., 1997; Bonard et al., 2002) and relative (Nelson et al., 1990; Wallington et al., 1989; DeMore and Bayes, 1999) rate coefficients exhibit appreciable scatter, covering a range of a factor of 1.6. The measured temperature dependencies (Perry et al., 1977; Tully and Droege, 1987; Wallington et al., 1988; Melloui et al., 1995; Arif et al., 1997; Bonard et al., 2002; DeMore and Bayes, 1999) are in reasonable agreement. The preferred values are based on the absolute rate coefficient studies of Tully and Droege (1987), Mellouki et al. (1995), Arif et al. (1997) and Bonard et al. (2002), the rate coefficients of

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which are in good agreement and which are between those of the other two absolute temperature-dependent studies of Perry et al. (1977) and Wallington et al. (1988).

Because Arrhenius plots of the data of Mellouki et al. (1995), Arif et al. (1997) and Bonard et al. (2002) show curvature, the rate coefficients of Tully and Droege (1987), Mellouki et al. (1995), Arif et al. (1997) and Bonard et al. (2002) have been fitted to the expression $k = CT^2 \exp(-D/T)$, resulting in $k = 1.14 \times 10^{-17} T^2 \exp(303/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 230–650 K. The preferred Arrhenius expression $k = A \exp(-B/T)$ is centered at 260 K and is derived from the three-parameter expression with $A = C e^2 T^2$ and $B = D + 2T$. The rate coefficients determined by DeMore and Bayes (1999) relative to that for the reaction of HO radicals with *n*-butane are in excellent agreement with the recommendation; however the rate coefficients determined by DeMore and Bayes (1999) relative to those for the reactions of HO radicals with *n*-pentane and cyclohexane are uniformly ~10% higher than the preferred values.

The significant deuterium isotope effect observed by Tully and Droege (1987) indicates that reaction proceeds by initial H-atom abstraction.

References

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- 5 Wallington, T. J., Andino, J. M., Skewes, L. M., Siegl, W. O., and Japar, S. M.: *Int. J. Chem. Kinet.*, 21, 993, 1989.
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6543

II.A2.33

HO + 3-Methylfuran → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
$(9.26 \pm 0.24) \times 10^{-11}$	296 ± 2	Atkinson et al., 1989	RR (a)

5 Comments

- (a) Relative rate method carried out at atmospheric pressure of air. HO radicals were generated by the photolysis of methyl nitrite-NO-air mixtures, and the concentrations of 3-methylfuran and 2,3-dimethyl-2-butene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(\text{HO} + 3\text{-methylfuran})/k(\text{HO} + 2,3\text{-dimethyl-2-butene}) = 0.842 \pm 0.021$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + 2,3\text{-dimethyl-2-butene}) = 1.10 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (Atkinson, 1997).
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Preferred Values

- 15 $k = 9.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

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Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred value is based on the sole study of this reaction by Atkinson et al. (1989). The reaction of HO radicals with 3-methylfuran is expected to proceed almost exclusively by initial HO radical addition to the C=C bonds (Atkinson et al., 1989).

References

- Atkinson, R., Aschmann, S. M., Tuazon, E. C., Arey, J., and Zielinska, B.: Int. J. Chem. Kinet., 21, 593, 1989.
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6545

II.A2.34



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(3.0 \pm 0.3) \times 10^{-12}$	298	Dagaut et al., 1989	FP-RF
<i>Relative Rate Coefficients</i>			
$(2.60 \pm 0.28) \times 10^{-12}$	298	Orlando et al., 1999	RR (a,b)
$(3.52 \pm 0.32) \times 10^{-12}$	298	Orlando et al., 1999	RR (a,c)

Comments

(a) HO radicals were generated by the photolysis of methyl nitrite in synthetic air at 1 bar total pressure. Hydroxyacetone and methanol and ethanol (the reference compounds) were monitored by FTIR spectroscopy. The measured rate coefficient ratios $k(\text{HO} + \text{hydroxyacetone})/k(\text{HO} + \text{methanol}) = 2.8 \pm 0.3$ and $k(\text{HO} + \text{hydroxyacetone})/k(\text{HO} + \text{ethanol}) = 1.1 \pm 0.1$ are placed on an absolute basis using rate coefficients of $k(\text{HO} + \text{methanol}) = 9.3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k(\text{HO} + \text{ethanol}) = 3.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K, respectively (IUPAC, current recommendation).

(b) Relative to OH + methanol.

(c) Relative to OH + ethanol.

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Preferred Values

$k = 3.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

5 Comments on Preferred Values

The preferred value is an average of the absolute and relative rate coefficients of Dagaut et al. (1989) and Orlando et al. (1999), which are in only reasonable agreement.

References

- 10 Dagaut, P., Liu, R., Wallington, T. J., and Kurylo, M. J.: J. Phys. Chem., 93, 7838, 1989.
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6547

II.A2.35

OH + (CH₃)₂C(OH)CHO → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
$(1.51 \pm 0.22) \times 10^{-11}$	296 ± 2	Baker et al., 2004	RR(a)

5 Comments

- (a) HO radicals were generated by the photolysis of CH₃ONO-NO-air mixtures at wavelengths >300 nm. (CH₃)₂C(OH)CHO was generated in situ from the reaction of HO radicals with (CH₃)₂C(OH)CH=CH₂ and its concentration was measured during the reactions using solid phase microextraction fibers pre-coated with *O*-(2,3,4,5,6-pentafluorobenzyl)hydroxylamine for on-fiber derivatization of carbonyl compounds, with subsequent GC analyses. From the time-concentration behavior of (CH₃)₂C(OH)CHO during the reactions, the rate coefficient ratio $k(\text{HO}+(\text{CH}_3)_2\text{C}(\text{OH})\text{CHO})/k\text{HO}+(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}=\text{CH}_2)=0.234\pm 0.033$ was derived. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient at 296 K of $k(\text{HO}+(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}=\text{CH}_2)=6.44 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation).

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Preferred Values

$k = 1.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

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Comments on Preferred Values

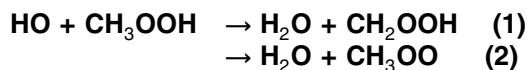
The preferred value is based on the sole study of this reaction. The reaction is expected to proceed mainly by H-atom abstraction from the -CHO group (Baker et al., 2004).

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Baker, J., Arey, J., and Atkinson, R.: J. Phys. Chem. A, 108, 7032, 2004.
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6549

II.A2.36



$$\Delta H^\circ(2) = -139 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data ($k = k_1 + k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$2.93 \times 10^{-12} \exp[(190 \pm 14)/T]$	223–423	Vaghjani and Ravishankara, 1989	(a)
5.54×10^{-12}	298		
$k_2 = 1.78 \times 10^{-12} \exp[(220 \pm 21)/T]$	203–348	Vaghjania and Ravishankara, 1989	(a)
$k_2 = (3.85 \pm 0.23) \times 10^{-12}$	298		
<i>Relative Rate Coefficients</i>			
$(1.02 \pm 0.08) \times 10^{-11}$	~ 298	Niki et al., 1983	RR (b)
$(1.02 \pm 0.11) \times 10^{-11}$	~ 298	Niki et al., 1983	RR (c)

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Comments

(a) H^{16}O , H^{18}O and DO radicals were generated by flash photolysis or pulsed laser photolysis of the following precursors: for H^{16}O , CH_3OOH , H_2^{16}O and $\text{O}_3\text{-H}_2^{16}\text{O}$; for H^{18}O , H_2^{18}O and $\text{O}_3\text{-H}_2^{18}\text{O}$; and for DO, D_2O , $\text{O}_3\text{-D}_2\text{O}$ and $\text{O}_3\text{-D}_2$, and H^{16}O , H^{18}O and DO radicals were monitored by LIF. Rate

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coefficients ($k_1 + k_2$) were obtained from measurements of the decay rates of H^{18}O and DO radicals in the presence of excess CH_3OOH . Rate coefficients k_2 were obtained from the decay rates of H^{16}O radicals in the presence of CH_3OOH . The CH_2OOH radical formed in reaction channel (1) rapidly decomposes to $\text{HO} + \text{HCHO}$, and hence the use of H^{16}O allowed only the rate coefficient k_2 to be measured.

(b) HO radicals were generated by the photolysis of CH_3ONO or $\text{C}_2\text{H}_5\text{ONO}$ in air. The concentrations of CH_3OOH and ethene (the reference compound) were measured by FTIR absorption spectroscopy. The measured rate coefficient ratio of $k(\text{HO} + \text{CH}_3\text{OOH})/k(\text{HO} + \text{ethene}) = 1.20 \pm 0.09$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{ethene}) = 8.52 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and atmospheric pressure of air (Atkinson, 1997).

(c) HO radicals were generated by the photolysis of CH_3ONO in air and the concentrations of CH_3OOH and CH_3CHO (the reference compound) were measured by FTIR absorption spectroscopy. The measured rate coefficient ratio of $k(\text{HO} + \text{CH}_3\text{OOH})/k(\text{HO} + \text{CH}_3\text{CHO}) = 0.68 \pm 0.07$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{CH}_3\text{CHO}) = 1.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (IUPAC, current recommendation).

Preferred Values

$k = 5.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 2.9 \times 10^{-12} \exp(190/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 220–430 K.

$k_1/k = 0.35$ over the temperature range 220–430 K.

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Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

$\Delta (E/R) = \pm 150$ K.

$\Delta (k_1/k) = \pm 0.15$ at 298 K.

Comments on Preferred Values

The preferred values are those of Vaghjiani and Ravishankara (1989). The reasons for the factor of ~ 2 discrepancy with the relative rate data of Niki et al. (1983) are not known (Vaghjiani and Ravishankara, 1989). The preferred branching ratio, also taken from the absolute rate coefficient study of Vaghjiani and Ravishankara (1989), is in reasonable agreement with the earlier measurement of Niki et al. (1983).

References

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6552

II.A2.37

HO + HC(O)OH → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(4.62 \pm 0.78) \times 10^{-13}$	298–430	Wine et al., 1985	FP/PLP-RF (a)
$(4.90 \pm 0.12) \times 10^{-13}$	296	Jolly et al., 1986	PLP-RA (b)
$2.91 \times 10^{-13} \exp[(102 \pm 194)/T]$	297–445	Singleton et al., 1988	PLP-RA
$(4.47 \pm 0.28) \times 10^{-13}$	297		
$(3.7 \pm 0.4) \times 10^{-13}$	298	Dagaut et al., 1988	FP-RF

5 Comments

- (a) H atom formation was also measured by resonance fluorescence, and an H-atom formation yield of 0.75 ± 0.25 measured. At 298 K, the measured rate coefficient for the reaction of the HO radical with DC(O)OH was identical to that for HO radical reaction with HC(O)OH.
- 10 (b) Experiments with added O₂ led to non-exponential and slower HO radical decays, indicating the formation of H atoms from the HO radical reaction with HC(O)OH.

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Preferred Values

$k = 4.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 290–450 K.

5 Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
 $\Delta (E/R) = \pm 250$ K.

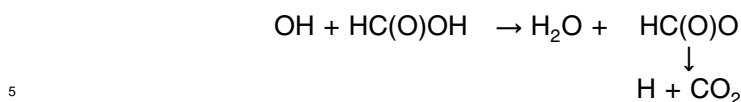
Comments on Preferred Values

A major problem with the determination of the rate coefficient for this reaction concerns the ready dimerization of HC(O)OH. The studies of Wine et al. (1985), Jolly et al. (1986) and Singleton et al. (1988) monitored formic acid in the experimental systems used by UV absorption spectroscopy. The data from these studies (Wine et al., 1985; Jolly et al., 1986; Singleton et al., 1988) agree well, and are in reasonable agreement with the room temperature rate coefficient of Dagaut et al. (1988). The data of Wine et al. (1985) and Singleton et al. (1988) show that the temperature dependence of the rate coefficient is zero within the experimental uncertainties. The average of the rate coefficients of Wine et al. (1985), Jolly et al. (1986) and Singleton et al. (1988) has been used to derive the preferred rate coefficient.

20 The studies of Wine et al. (1985) and Jolly et al. (1986) showed that H atoms are produced in this reaction, with a yield of 0.75 ± 0.25 (Wine et al., 1985). Furthermore, Wine et al. (1985) and Singleton et al. (1988) showed that within the experimental uncertainties the rate coefficient for the reaction of the HO radical with DC(O)OH is identical to that for HC(O)OH at 298 K. Also,

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the room temperature rate coefficients for the reactions of the DO radical with HC(O)OD and DC(O)OD are significantly lower than those for the reactions of the HO radical with HC(O)OH and DC(O)OH (Singleton et al., 1988). The reaction then appears to proceed by,



with overall abstraction of the H (or D) atom from the -OH (or -OD) group being the major pathway at room temperature.

References

- Dagaut, P., Wallington, T. J., Liu, R., and Kurylo, M. J.: *Int. J. Chem. Kinet.*, 20, 331, 1988.
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6555

II.A2.38

HO + CH₃C(O)OH → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.3 \times 10^{-12} \exp[-(170 \pm 20)/T]$	240–440	Dagaut et al., 1988	FP-RF
$(7.4 \pm 0.6) \times 10^{-13}$	298		
$(8.67 \pm 0.65) \times 10^{-13}$	296.8	Singleton et al., 1989	PLP-RA
$(5.63 \pm 0.44) \times 10^{-13}$	326.2		
$(4.88 \pm 0.17) \times 10^{-13}$	356.4		
$(4.09 \pm 0.14) \times 10^{-13}$	396.8		
$(3.95 \pm 0.07) \times 10^{-13}$	446.2		

Preferred Values

$$k = 8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

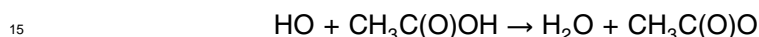
$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

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Comments on Preferred Values

At 298 K, the rate coefficients of Dagaut et al. (1988) and Singleton et al. (1989) are in reasonable agreement. However, at temperatures above 298 K, Dagaut et al. (1988) observed the rate coefficient to increase with increasing temperature, while Singleton et al. (1989) observed the rate coefficient to decrease in a non-Arrhenius manner with increasing temperature. At 400–440 K, the rate coefficients of Dagaut et al. (1988) and Singleton et al. (1989) disagree by a factor of 2.2.

The preferred 298 K rate coefficient is an average of the data of Dagaut et al. (1988) and Singleton et al. (1989). No recommendation is made regarding the temperature dependence. The rate coefficients of Singleton et al. (1989) for the reactions of the HO radical with CH₃C(O)OH, CD₃C(O)OH and CD₃C(O)OD indicate that at room temperature the major reaction channel involves overall H-atom abstraction from the -OH bond:



References

- Dagaut, P., Wallington, T. J., Liu, R., and Kurylo, M. J.: *Int. J. Chem. Kinet.*, 20, 331, 1988.
Singleton, D. L., Paraskevopoulos, G., and Irwin, R. S.: *J. Am. Chem. Soc.*, 111, 5248, 1989.

6557

II.A2.39

HO + C₂H₅C(O)OH → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.8 \times 10^{-12} \exp[-(120 \pm 30)/T]$	298–440	Dagaut et al., 1988	FP-RF
$(1.22 \pm 0.12) \times 10^{-12}$	298		
$(1.07 \pm 0.05) \times 10^{-12}$	298–445	Singleton et al., 1989	PLP-RA
$(1.02 \pm 0.55) \times 10^{-12}$	298		

Preferred Values

$k = 1.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 290–450 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
 $\Delta (E/R) = \pm 300$ K.

Comments on Preferred Values

The rate coefficients measured by Dagaut et al. (1988) and Singleton et al. (1989) are in good agreement and indicate that the rate coefficient for this

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reaction is independent of temperature over the range 298–445 K. The preferred value is an average of all of the rate coefficients of Dagaut et al. (1988) and Singleton et al. (1989), combined with a zero temperature dependence. The reaction is expected to proceed by H-atom abstraction from the C-H bonds of the -CH₃ group and the O-H bond of the -C(O)OH group.

References

- Dagaut, P., Wallington, T. J., Liu, R., and Kurylo, M. J.: *Int. J. Chem. Kinet.*, 20, 331, 1988.
- Singleton, D. L., Paraskevopoulos, G., and Irwin, R. S.: *J. Am. Chem. Soc.*, 111, 5248, 1989.

6559

II.A2.40

HO + CH₃ONO₂ → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(3.4 \pm 0.4) \times 10^{-14}$	298	Gaffney et al., 1986	DF-RF (a)
$8.8 \times 10^{-15} \exp[(1050 \pm 180)/T]$	298–393	Nielsen et al., 1991	PR-RA (b)
$(3.2 \pm 0.5) \times 10^{-13}$	298 ± 2		
$8.2 \times 10^{-13} \exp[-(1020 \pm 60)/T]$	221–414	Talukdar et al., 1997	PLP-LIF (c)
$(2.36 \pm 0.16) \times 10^{-14}$	298		
$4.1 \times 10^{-13} \exp[-(604 \pm 121)/T]$	298–423	Shallcross et al., 1997	DF-RF (d)
$(4.7 \pm 1.0) \times 10^{-14}$	298		
<i>Relative Rate Coefficients</i>			
$(3.8 \pm 1.0) \times 10^{-13}$	303 ± 2	Kerr and Stocker, 1986	RR (e)
$(3.1 \pm 0.7) \times 10^{-13}$	298 ± 2	Nielsen et al., 1991	RR (f)
$(3.0 \pm 0.7) \times 10^{-14}$	307 ± 3	Kakesu et al., 1997	RR (g)

5 Comments

- (a) Conducted at 2.6–4.2 mbar (2.0–3.2 Torr) of He.
- (b) Conducted at 1 bar Ar.

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- (c) In addition to measuring rate coefficients for the reaction of the HO radical with CH_3ONO_2 , rate coefficients were measured for the reactions of the HO radical with CD_3ONO_2 (298–409 K), the DO radical with CH_3ONO_2 (246–353 K) and the H^{18}O radical with CH_3ONO_2 (253–298 K). HO, H^{18}O and DO radicals were generated by the pulsed laser photolysis of HONO at 355 nm and of $\text{O}_3\text{-H}_2\text{O}$ mixtures at 266 nm, photolysis of $\text{O}_3\text{-H}_2^{18}\text{O}$ mixtures at 266 nm, and photolysis of DONO at 355 nm and of $\text{O}_3\text{-D}_2\text{O}$ mixtures at 266 nm, respectively. The diluent gas pressure was varied from 67 mbar (50 Torr) He plus 67 mbar (50 Torr) SF_6 to 133 mbar (100 Torr) He and to 400 mbar (300 Torr) SF_6 , and up to 67 mbar (50 Torr) of O_2 was included in certain experiments. No effect of total pressure, nature of the diluent gas, or presence of O_2 on the measured rate coefficients was observed. The rate coefficients for the reactions of the H^{18}O radical with CH_3ONO_2 were essentially identical to those for the corresponding HO radical reaction, while the measured rate coefficients for the DO radical reaction were ~10–20% higher than the HO radical reaction. No evidence for formation of HO radicals was observed from these H^{18}O and DO radical reactions. The rate coefficients for the reaction of the HO radical with CD_3ONO_2 were a factor of 3 to 4 lower than those for $\text{HO}+\text{CH}_3\text{ONO}_2$ over the temperature range studied (298–409 K).
- (d) The rate coefficient at 298 K was measured over the pressure range 2.7–27 mbar (2–20 Torr) of He, with no effect of pressure being observed. Rate coefficients at 333–423 K were measured over the pressure range 1.3–4.0 mbar (1–3 Torr) of He.
- (e) HO radicals were generated from the photolysis of HONO-air mixtures at atmospheric pressure. The concentrations of methyl nitrate and ethene (the reference compound) were measured by GC. The measured rate co-

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efficient ratio of $k(\text{HO} + \text{methyl nitrate})/k(\text{HO} + \text{ethene}) = 0.046 \pm 0.011$ placed on an absolute basis by use of $k(\text{HO} + \text{ethene}) = 8.32 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 303 K and one atmosphere of air (Atkinson, 1997).

- (f) HO radicals generated by the photolysis of $\text{CH}_3\text{ONO-NO}$ -air mixtures at atmospheric pressure. The decays of CH_3ONO_2 and $(\text{CH}_3)_3\text{CH}$ (the reference compound) were measured by GC. The rate coefficient ratio was placed on an absolute basis by use of $k(\text{HO}+(\text{CH}_3)_3\text{CH})=2.12 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson, 2003).
- (g) HO radicals were generated by photolysis of $\text{O}_3\text{-H}_2\text{O-O}_2$ mixtures at atmospheric pressure at ~290–310 nm. Methyl nitrate and the reference compounds (methane, ethane and HFC-152a) were monitored by GC. The measured rate coefficient ratios are placed on an absolute basis by use of rate coefficients of $k(\text{HO}+\text{CH}_4)=1.85 \times 10^{-12} \exp(-1690/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k(\text{HO}+\text{C}_2\text{H}_6)=6.9 \times 10^{-12} \exp(-1000/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k(\text{HO}+\text{CH}_3\text{CHF}_2)=1.0 \times 10^{-12} \exp(-990/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IPU-PAC, current recommendation). The cited rate coefficient is the unweighted average, with a two standard deviation error limit.

Preferred Values

- $k = 2.3 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 4.0 \times 10^{-13} \exp(-845/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 220–300 K.

Reliability

$$\Delta \log k = \begin{matrix} +0.5 \\ -0.2 \end{matrix} \text{ at 298 K.}$$

$$\Delta (E/R) = \pm 400 \text{ K.}$$

Comments on Preferred Values

5 There are serious discrepancies between the room temperature rate coefficients of Gaffney et al. (1986), Talukdar et al. (1997) and Kakesu et al. (1997) and those of Kerr and Stocker (1986) and Nielsen et al. (1991), of a factor of ~ 10 . Additionally, the temperature dependencies of Nielsen et al. (1991) and Talukdar et al. (1997) differ by ~ 2000 K. The positive temperature-dependence
10 observed by Talukdar et al. (1997) is supported, qualitatively, by the low-pressure absolute rate study of Shallcross et al. (1997), although the rate coefficients of Shallcross et al. (1997) are a factor of ~ 1.3 – 2.0 higher than those of Talukdar et al. (1997) over the temperature range 298–423 K. The reasons for these various discrepancies are not presently known, but we favor the results
15 of the Talukdar et al. (1997) study which are consistent with H- (or D-) atom abstraction to form $\text{H}_2\text{O} + \text{CH}_2\text{ONO}$. The extensive absolute study of Talukdar et al. (1997) shows no effect of the measured rate coefficient on pressure or diluent gas (133 mbar He to 400 mbar SF_6) nor on the presence or absence of up to 67 mbar of O_2 . The experiments of Talukdar et al. (1997) on the reactions
20 $\text{HO} + \text{CH}_3\text{ONO}_2$, $\text{H}^{18}\text{O} + \text{CH}_3\text{ONO}_2$, $\text{DO} + \text{CH}_3\text{ONO}_2$ and $\text{HO} + \text{CH}_3\text{ONO}$ show no formation of HO radicals from the H^{18}O and DO radical reactions with CH_3ONO , and the deuterium isotope effect of $k_H/k_D \sim 4$ at 298 K is totally consistent with H- (or D-) atom abstraction.

The preferred values are obtained from a unit-weighted least-squares analysis of the 221–298 K rate coefficients of Talukdar et al. (1997). Because of
25 the significant discrepancies between the various studies (Gaffney et al., 1986;

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Kakesu et al., 1997; Kerr and Stocker, 1986; Nielsen et al., 1991; Shallcross et al., 1997; Talakdur et al., 1997), large uncertainty limits are assigned to the 298 K rate coefficient and the temperature dependence. Clearly, further absolute rate studies at atmospheric pressure of air are needed.

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II.A2.41



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$4.7 \times 10^{-14} \exp[(716 \pm 138)/T]$	298–373	Nielsen et al., 1991	PR-RA (a)
$(5.3 \pm 0.6) \times 10^{-13}$	298 ± 2		
$3.68 \times 10^{-12} \exp[-(1077/T)]$	223–394	Talukdar et al., 1997	PLP-LIF (b)
$+ 5.32 \times 10^{-14} \exp(126/T)$			
$(1.80 \pm 0.12) \times 10^{-13}$	298		
$3.30 \times 10^{-12} \exp[-(699 \pm 140)/T]$	298–373	Shallcross et al., 1997	DF-RF (c)
$(3.30 \pm 0.68) \times 10^{-13}$	298		
<i>Relative Rate Coefficients</i>			
$(4.9 \pm 2.1) \times 10^{-13}$	303 ± 2	Kerr and Stocker, 1986	RR (d)
$(4.2 \pm 0.3) \times 10^{-13}$	298 ± 2	Nielsen et al., 1991	RR (e)
$(2.2 \pm 0.8) \times 10^{-13}$	304 ± 6	Kakesu et al., 1997	RR (f)

5 Comments

(a) Conducted at 1 bar Ar.

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(b) Extensive study of the reactions of ethyl nitrate with HO radicals (223–394 K), H^{18}O radicals (300 K) and DO radicals (229–378 K). HO, H^{18}O and DO radicals were produced from the pulsed laser photolysis of HONO at 355 nm, of $\text{O}_3\text{-H}_2^{18}\text{O}$ mixtures at 248 nm, and of DONO at 355 nm, respectively. The diluent gas and total pressures were He [67–400 mbar (50–300 Torr)], N_2 [400 mbar (300 Torr)], SF_6 [267 mbar (200 Torr)] or He- SF_6 [133–400 mbar (100–300 Torr)], and O_2 partial pressures of 67 mbar (50 Torr) were used in certain experiments. No effects on the measured rate coefficients were observed on varying the total pressure, the diluent gas, or the partial pressure of O_2 . The measured rate coefficients for the reactions of the H^{18}O and DO radicals with ethyl nitrite were 11–16% higher than that for the HO radical reaction, and no formation of HO radicals was observed in the H^{18}O and DO radical reactions.

(c) The rate coefficient at 298 K was measured over the pressure range 5.7–27 mbar (4.3–19.9 Torr) of He, with no effect of pressure being observed. The rate coefficients at 313 K and 373 K were measured over the pressure range 1.3–4.0 mbar (1–3 Torr) of He.

(d) HO radicals generated by photolysis of HONO-air mixtures at atmospheric pressure. The concentrations of ethyl nitrate and ethene (the reference organic) were measured by GC. The measured rate coefficient ratio of $k(\text{HO} + \text{ethyl nitrate})/k(\text{HO} + \text{ethene}) = 0.059 \pm 0.025$ is placed on an absolute basis by use of a rate coefficient $k(\text{HO} + \text{ethene}) = 8.32 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 303 K and atmospheric pressure of air (Atkinson, 1997).

(e) HO radicals were generated by photolysis of $\text{CH}_3\text{ONO-NO}$ -air mixtures at atmospheric pressure. The concentrations of ethyl nitrate and 2-methylpropane (the reference organic) were measured by GC, and the

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measured rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + 2\text{-methylpropane}) = 2.12 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson, 2003).

5 (f) Relative rate method. HO radicals were generated by the photolysis of $\text{O}_3\text{-H}_2\text{O-O}_2$ mixtures at atmospheric pressure at $\sim 290\text{--}310 \text{ nm}$. The concentrations of ethyl nitrate and the reference compounds ethane and 2-methylpropane were measured by GC. The measured rate coefficient ratios are placed on an absolute basis by use of rate coefficients of $k(\text{HO} + \text{ethane}) = 6.9 \times 10^{-12} \exp(-1000/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k(\text{HO} + 2\text{-methylpropane}) = 1.17 \times 10^{-17} T^2 \exp(213/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson, 2003; IUPAC, current recommendation). The cited rate coefficient is the unweighted average with a two standard deviation error limit.

Preferred Values

$k = 1.8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
15 $k = 6.7 \times 10^{-13} \exp(-395/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 230–300 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
 $\Delta (E/R) = \pm 400 \text{ K}$.

20 Comments on Preferred Values

There are serious discrepancies between the absolute and relative rate studies of Kerr and Stocker (1986) and Nielsen et al. (1991) carried out at $\sim 1 \text{ bar}$
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total pressure and the absolute rate and the relative rate studies of Talukdar et al. (1997) and Kakesu et al. (1997), respectively, in both the room temperature rate coefficient (Nielsen et al., 1991; Talukdar et al., 1997; Kerr and Stocker, 1986; Kakesu et al., 1997) and the temperature dependence (Nielsen et al., 5 1991; Talukdar et al., 1997). The positive temperature-dependence observed by Talukdar et al. (1997) is supported, qualitatively, by the low-pressure absolute rate study of Shallcross et al. (1997), although the rate coefficients of Shallcross et al. (1997) are a factor of ~ 1.8 higher than those of Talukdar et al. (1997). The reasons for these discrepancies are not known, but we favor 10 the results of the extensive Talukdar et al. (1997) study which are consistent with H- (or D-) atom abstraction. The study of Talukdar et al. (1997) showed no effect of total pressure, diluent gas [ranging from 67 mbar (50 Torr) of He to 267 mb (200 Torr) of SF_6 or 400 mbar (300 Torr) N_2] or the presence or absence of O_2 at a partial pressure of 67 mbar (50 Torr) on the measured rate 15 coefficients.

While the study of Talukdar et al. (1997) was not carried out in air at 1 bar pressure, the data obtained strongly suggest that the rate coefficient is consistent with an H-atom abstraction process and that the measured rate coefficients should be appropriate for atmospheric purposes. The Arrhenius plots 20 of the HO and DO radical reactions exhibit significant curvature (Talukdar et al., 1997). The preferred values are based on a unit-weighted least-squares fit of the 233–298 K rate coefficients of Talukdar et al. (1997) to the Arrhenius expression, $k = A \exp(-B/T)$. Large uncertainty limits are assigned because of the discrepancies between the various studies (Kakesu et al., 1997; Kerr and Stocker, 1986; Nielsen et al., 1991; Shallcross et al., 1997; Talukdar et al., 25 1997) noted above. Further absolute rate studies conducted at atmospheric pressure of air are required.

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II.A2.42

HO + 1-C₃H₇ONO₂ → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$5.0 \times 10^{-13} \exp[(140 \pm 144)/T]$	298–368	Nielsen et al., 1991	PR-RA (a)
$(8.2 \pm 0.8) \times 10^{-13}$	298 ± 2		
<i>Relative Rate Coefficients</i>			
$(7.2 \pm 2.3) \times 10^{-13}$	303 ± 2	Kerr and Stocker, 1986	RR (b)
$(5.8 \pm 1.0) \times 10^{-13}$	298 ± 2	Atkinson and Aschmann, 1989	RR (c)
$(7.0 \pm 0.8) \times 10^{-13}$	298 ± 2	Nielsen et al., 1991	RR (d)

5 Comments

- (a) Carried out in 1 bar Ar.
- (b) HO radicals were generated by the photolysis of HONO-air mixtures at atmospheric pressure. The decay rates of 1-propyl nitrate and ethene (the reference organic) were measured by GC and rate coefficient ratio $k(\text{HO} + 1\text{-propyl nitrate})/k(\text{HO} + \text{ethene}) = 0.086 \pm 0.027$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{ethene}) = 8.32 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 303 K and atmospheric pressure of air (Atkinson, 1997).
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- (c) HO radicals were generated by the photolysis of CH₃ONO at ~1 bar air at >300 nm. Experiments were carried out in a 6400 liter Teflon chamber. The concentrations of 1-propyl nitrate and cyclohexane (the reference organic) were measured by GC, and irradiations in the absence of CH₃ONO allowed the photolysis of 1-propyl nitrate to be accurately taken into account in the data analysis. The measured rate coefficient ratio of $k(\text{HO} + 1\text{-propyl nitrate})/k(\text{HO} + \text{cyclohexane}) = 0.083 \pm 0.013$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{cyclohexane}) = 6.97 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Atkinson, 2003).
- (d) HO radicals were generated from the photolysis of CH₃ONO in 1 bar air at >290 nm. The concentrations of 1-propyl nitrate and 2-methylpropane (the reference organic) were measured by GC. The measured rate coefficient ratio $k(\text{HO} + 1\text{-propyl nitrate})/k(\text{HO} + 2\text{-methylpropane})$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + 2\text{-methylpropane}) = 2.12 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Atkinson, 2003).

Preferred Values

$k = 5.8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and 1 bar air.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The absolute and relative rate coefficients of Kerr and Stocker (1986), Atkinson and Aschmann (1989) and Nielsen et al. (1991) are in reasonable agree-

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ment at room temperature. All studies have been carried out at ~1 bar pressure.

The absolute rate coefficient study of Talukdar et al. (1997) for the HO radical reactions with CH₃ONO₂ and C₂H₅ONO₂ is in serious disagreement (by a factor of 13–16 for CH₃ONO₂ and a factor of 2.3–2.9 for C₂H₅ONO₂) with the rate coefficients from the studies of Kerr and Stocker (1986) and Nielsen et al. (1991), while for 2-C₃H₇ONO₂ the 298 K rate coefficients of Talukdar et al. (1997) and Atkinson and Aschmann (1989) disagree by 33% (suggesting for one that the discrepancies decrease as the reactivity of the alkyl nitrate increases). Accordingly, the 298 K rate coefficient of Atkinson and Aschmann (1989) is used for the preferred value and no temperature dependence is recommended (note that by analogy with the reaction of the OH radical with 2-propyl nitrate (IUPAC, this evaluation), the temperature dependence of the rate coefficient is likely to be small). That 1-propyl nitrate is more reactive than 2-propyl nitrate is expected from structure-reactivity relationships (Atkinson and Aschmann, 1989) based on assuming that the reaction proceeds by H-atom abstraction, as concluded by Talukdar et al. (1997) for methyl nitrate, ethyl nitrate and 2-propyl nitrate.

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II.A2.43

HO + 2-C₃H₇ONO₂ → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$4.3 \times 10^{-12} \exp(-1250/T)$ $+ 2.5 \times 10^{-13} \exp(-32/T)$ $(2.88 \pm 0.19) \times 10^{-13}$	233–395 298	Talukdar et al., 1997	PLP-LIF (a)
<i>Relative Rate Coefficients</i>			
$(1.68 \pm 0.42) \times 10^{-13}$	299 ± 2	Atkinson et al., 1982	RR (b)
$(5.3 \pm 2.1) \times 10^{-13}$	295 ± 2	Becker and Wirtz, 1989	RR (c)
$(3.83 \pm 0.49) \times 10^{-13}$	298 ± 2	Atkinson and Aschmann, 1989	RR (d)

Comments

- (a) Experiments were carried out as a function of total pressure and with different diluent gases (133 mbar He to 400 mbar SF₆) and with up to 80 mbar O₂ present. No effect of pressure, diluent gas or presence or absence of O₂ on the measured rate coefficients were observed. Rate coefficients for the reactions of H¹⁸O and DO radicals with 2-propyl nitrate were also measured over the temperature ranges 233–298 K and 230–403 K, respec-

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tively, with 298 K rate coefficients of $(3.15 \pm 0.20) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $(3.6 \pm 0.4) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, respectively.

- (b) HO radicals were generated from the photolysis of CH₃ONO in ~1 bar air at >300 nm. Experiments were carried out in an ~75 liter Teflon chamber and concurrent photolysis of 2-propyl nitrate was indicated from the data analysis. The concentrations of 2-propyl nitrate and cyclohexane (the reference organic) were measured by GC. The measured rate coefficient ratio of $k(\text{HO} + 2\text{-propyl nitrate})/k(\text{HO} + \text{cyclohexane}) = 0.024 \pm 0.006$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{cyclohexane}) = 7.00 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 299 K (Atkinson, 2003).
- (c) HO radicals were generated from the photolysis of CH₃ONO in 1 bar air at 280 nm to 450 nm. Experiments were carried out in a 36.5 liter quartz chamber, and photolysis of 2-propyl nitrate was indicated from the data analysis. The concentrations of 2-propyl nitrate and *n*-butane (the reference organic) were measured by GC-MS and GC, respectively. The measured rate coefficient ratio of $k(\text{HO} + 2\text{-propyl nitrate})/k(\text{HO} + n\text{-butane}) = 0.23 \pm 0.09$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + n\text{-butane}) = 2.30 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 295 K (IUPAC, current recommendation).
- (d) HO radicals were generated by the photolysis of CH₃ONO in ~1 bar air at >300 nm. Experiments were carried out in a 6400 liter Teflon chamber. The concentrations of 2-propyl nitrate and cyclohexane (the reference organic) were measured by GC, and irradiations in the absence of CH₃ONO allowed the photolysis of 2-propyl nitrate to be accurately taken into account in the data analysis. The measured rate coefficient ratio of $k(\text{HO} + 2\text{-propyl nitrate})/k(\text{HO} + \text{cyclohexane}) = 0.055 \pm 0.007$ is placed

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on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{cyclohexane}) = 6.97 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Atkinson, 2003). This study supersedes the earlier study of Atkinson et al. (1982).

Preferred Values

- 5 $k = 2.9 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 6.2 \times 10^{-13} \exp(-230/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 230–300 K.

Reliability

- $\Delta \log k = \pm 0.2$ at 298 K.
10 $\Delta (E/R) = \pm 300 \text{ K}$.

Comments on Preferred Values

- The preferred values are based on the absolute 233–300 K rate coefficients of Talukdar et al. (1997). The extensive study of Talukdar et al. (1997) provided no evidence for the rate coefficient k to depend on total pressure, nature of the diluent gas, or the presence of O_2 at pressures up to 80 mbar (60 Torr).
15 Additionally, the use of DO radicals showed no evidence for the formation of HO radicals as a reaction product. However, as noted in the data sheets for the reactions of the HO radical with CH_3ONO_2 and $\text{C}_2\text{H}_5\text{ONO}_2$, the experiments of Talukdar et al. (1997) were not actually carried out in air at 1 bar total pressure.
20 Arrhenius plots of the rate coefficients for the reactions of HO, H^{18}O and DO radicals with 2-propyl nitrate exhibit significant curvature (especially pronounced for the DO radical reaction for which the measured rate coefficient

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- was independent of temperature over the range 230–269 K). The measured temperature dependencies at around 298 K and below are quite small. The room temperature relative rate coefficient of Atkinson and Aschmann (1989) (which supersedes the earlier data of Atkinson et al., 1982) is 33% higher than
5 the recommended 298 K rate coefficient, which may be considered reasonable agreement because of the low rate coefficient (on the low end of those reported by that research group) and hence small fraction of 2-propyl nitrate reacted during the experiments. The relative rate coefficient of Becker and Wirtz (1989) is almost a factor of 2 higher than the recommendations, but has high cited un-
10 certainties.

We attach rather large uncertainties to the recommended values of the 298 K rate coefficient and E/R until the data of Talukdar et al. (1997) are confirmed by absolute techniques in air at 1 bar pressure.

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20 IUPAC: <http://www.iupac-kinetic.ch.cam.ac.uk/>.
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6576

II.A2.44



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.74 \pm 0.19) \times 10^{-12}$	298 ± 2	Nielsen et al., 1991	PR-RA (a)
<i>Relative Rate Coefficients</i>			
$(1.31 \pm 0.10) \times 10^{-12}$	299 ± 2	Atkinson et al., 1982	RR (b,c)
$(1.65 \pm 0.18) \times 10^{-12}$	298 ± 2	Atkinson and Aschmann, 1989	RR (b,d)
$(1.47 \pm 0.08) \times 10^{-12}$	298 ± 2	Nielsen et al., 1991	RR (b,e)

5 Comments

- (a) Carried out at a total pressure of 1 bar Ar.
- (b) HO radicals were generated by the photolysis of CH_3ONO in air at atmospheric pressure (0.97 bar to 1.0 bar). The concentrations of 1-butyl nitrate and the reference organic were measured by GC.
- 10 (c) The measured rate coefficient ratio of $k(\text{HO} + 1\text{-butyl nitrate})/k(\text{HO} + \text{cyclohexane}) = 0.187 \pm 0.014$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{cyclohexane}) = 7.00 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 299 K (Atkinson, 2003). Experiments were carried out in an ~ 75 liter Teflon

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chamber, and the data were interpreted as involving concurrent photolysis of 1-butyl nitrate.

- (d) Experiments were carried out in a 6400 liter Teflon chamber, and irradiations were also carried out in the absence of CH_3ONO , allowing the photolysis rate to be accurately allowed for in the data analysis. The measured rate coefficient ratio of $k(\text{HO} + 1\text{-butyl nitrate})/k(\text{HO} + \text{cyclohexane}) = 0.237 \pm 0.025$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{cyclohexane}) = 6.97 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Atkinson, 2003). These data supersede those of Atkinson et al. (1982).
- 5
- 10 (e) The measured rate coefficient ratio $k(\text{HO} + 1\text{-butyl nitrate})/k(\text{HO} + 2\text{-methylpropane})$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + 2\text{-methylpropane}) = 2.12 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Atkinson, 2003).

Preferred Values

15 $k = 1.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

Comments on Preferred Values

20 The absolute and relative rate coefficients of Atkinson and Aschmann (1989) (which supersedes the earlier data of Atkinson, 1982) and Nielsen et al. (1991) are in good agreement. The preferred value is an average of the absolute

6578

and relative rate constants of Atkinson and Aschmann (1989) and Nielsen et al. (1991). By analogy with the reaction of the HO radical with 2-propyl nitrate (IUPAC, this evaluation), the temperature dependence of the rate coefficient at temperatures below 300 K is likely to be small.

5 References

- Atkinson, R.: Atmos. Chem. Phys., 3, 2233, 2003.
Atkinson, R. and Aschmann, S. M.: Int. J. Chem. Kinet., 21, 1123, 1989.
Atkinson, R., Aschmann, S. M., Carter, W. P. L., and Winer, A. M.: Int. J. Chem. Kinet., 14, 919, 1982.
10 IUPAC: <http://www.iupac-kinetic.ch.cam.ac.uk/>.
Nielsen, O. J., Sidebottom, H. W., Donlon, M., and Treacy, J.: Chem. Phys. Lett., 178, 163, 1991.

6579

II.A2.45



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
$(6.4 \pm 1.0) \times 10^{-13}$	299 ± 2	Atkinson et al., 1982	RR (a,b)
$(8.6 \pm 1.5) \times 10^{-13}$	298 ± 2	Atkinson and Aschmann, 1989	RR (a,c)

5 Comments

- (a) HO radicals were generated by the photolysis of CH₃ONO in one atmosphere of air. The concentrations of 2-butyl nitrate and the reference organic were measured by GC.
- (b) Experiments were carried out in an ~75 liter Teflon chamber, and the data were interpreted as involving concurrent photolysis of 2-butyl nitrate. The measured rate constant ratio of $k(\text{HO} + 2\text{-butyl nitrate})/k(\text{HO} + \text{cyclohexane}) = 0.091 \pm 0.013$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{cyclohexane}) = 7.00 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 299 K (Atkinson, 2003).
- 10 (c) Experiments were carried out in a 6400 liter Teflon chamber, and irradiations were also carried out in the absence of CH₃ONO allowing the photolysis rate to be accurately allowed for in the data analysis. The measured rate coefficient ratio of $k(\text{HO} + 2\text{-butyl nitrate})/k(\text{HO} + \text{cyclohexane}) =$

6580

0.123±0.021 is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + \text{cyclohexane}) = 6.97 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Atkinson, 2003). These data supersede those of Atkinson et al. (1982).

Preferred Values

5 $k = 8.6 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

10 The preferred value is based on the rate coefficient of Atkinson and Aschmann (1989), which supersedes the earlier study of Atkinson et al. (1982). By analogy with the reaction of the HO radical with 2-propyl nitrate (IUPAC, this evaluation), the temperature dependence of the rate coefficient at temperatures below 300 K is likely to be small.

References

- 15 Atkinson, R.: Atmos. Chem. Phys., 3, 2233, 2003.
 Atkinson, R. and Aschmann, S. M.: Int. J. Chem. Kinet., 21, 1123, 1989.
 Atkinson, R., Aschmann, S. M., Carter, W. P. L., and Winer, A. M.: Int. J. Chem. Kinet., 14, 919, 1982.

6581

II.A2.46

HO + CH₃C(O)OONO₂ → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$\leq 1.7 \times 10^{-13}$	299 ± 1	Winer et al., 1977	FP-RF
$1.23 \times 10^{-12} \exp[-(651 \pm 229)/T]$	273–297	Wallington et al., 1984	FP-RF
$(1.37 \pm 0.05) \times 10^{-13}$	297 ± 2		
$(7.5 \pm 1.4) \times 10^{-14}$	298 ± 2	Tsalkani et al., 1988	DF-EPR
$< 3.0 \times 10^{-14}$	298	Talukdar et al., 1995	FP/PLP-LIF (a)

5 Comments

- (a) Experiments were carried out over the temperature range 253–298 K, using pulsed laser photolysis of HONO at 355 nm, pulsed laser photolysis of O₃-H₂O mixtures at 266 nm, or flash photolysis of H₂O at 165–185 nm to generate HO radicals. The measured HO radical decay rates corresponded to rate coefficients in the range $(0.82\text{--}2.50) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ with no obvious dependence on temperature. The measured HO radical decay rates were attributed to the reaction of HO radicals with HCHO impurity, and a conservative upper limit to the rate coefficient k was cited (see table).
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Preferred Values

$k < 3 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Comments on Preferred Values

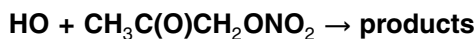
The preferred upper limit to the 298 K rate coefficient is the upper limit reported by Talukdar et al. (1995) from an extensive and careful study. The higher rate coefficients measured by Wallington et al. (1984) and Tsalkani et al. (1988) were almost certainly due to the presence of reactive impurities.

References

- Talukdar, R. K., Burkholder, J. B., Schmoltner, A.-M., Roberts, J. M., Wilson, R. R., and Ravishankara, A. R.: J. Geophys. Res., 100, 14 163, 1995.
- Tsalkani, N., Mellouki, A., Poulet, G., Toupance, G., and Le Bras, G.: J. Atmos. Chem., 7, 409, 1988.
- Wallington, T. J., Atkinson, R., and Winer, A. M.: Geophys. Res. Lett., 11, 861, 1984.
- Winer, A. M., Lloyd, A. C., Darnall, K. R., Atkinson, R., and Pitts Jr., J. N.: Chem. Phys. Lett., 51, 221, 1977.

6583

II.A2.47



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
$< 4.0 \times 10^{-13}$	298 ± 2	Zhu et al., 1991	RR (a)

Comments

(a) HO radicals were generated by the photolysis of $\text{CH}_3\text{ONO-NO-N}_2\text{-O}_2$ mixtures at 1 bar pressure. The concentrations of $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{ONO}_2$ and *n*-butane were measured during the experiments by GC, and the measured rate constant ratio of $k(\text{HO} + \text{CH}_3\text{C}(\text{O})\text{CH}_2\text{ONO}_2)/k(\text{HO} + n\text{-butane}) < 0.17$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + n\text{-butane}) = 2.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation).

Preferred Values

$k < 1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

6584

The preferred value is based on the sole study of Zhu et al. (1991), but with a higher upper limit to reflect additional uncertainties.

References

- 5 IUPAC: <http://www.iupac-kinetic.ch.cam.ac.uk/>.
Zhu, T., Barnes, I., and Becker, K. H.: J. Atmos. Chem., 13, 301, 1991.

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II.A2.48



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
5 $(8.21 \pm 1.38) \times 10^{-13}$	298 ± 2	Zhu et al., 1991	RR (a)

Comments

- 10 (a) HO radicals were generated by the photolysis of $\text{CH}_3\text{ONO-NO-N}_2\text{-O}_2$ mixtures at 1 bar pressure. The concentrations of $\text{CH}_3\text{CH}_2\text{C}(\text{O})\text{CH}_2\text{ONO}_2$ and *n*-butane were measured during the experiments by GC, and the measured rate constant ratio of $k(\text{HO} + \text{CH}_3\text{CH}_2\text{C}(\text{O})\text{CH}_2\text{ONO}_2)/k(\text{HO} + n\text{-butane}) = 0.357 \pm 0.060$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + n\text{-butane}) = 2.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation).

Preferred Values

- 15 $k = 8.2 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

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Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

- 5 The preferred value is based on the sole study of Zhu et al. (1991) but with a higher uncertainty.

References

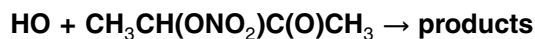
IUPAC: <http://www.iupac-kinetic.ch.cam.ac.uk/>.

Zhu, T., Barnes, I., and Becker, K. H.: J. Atmos. Chem., 13, 301, 1991.

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6587

II.A2.49



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
5 $(1.15 \pm 0.13) \times 10^{-12}$	298 \pm 2	Zhu et al., 1991	RR (a)

Comments

- 10 (a) HO radicals were generated by the photolysis of $\text{CH}_3\text{ONO}-\text{NO}-\text{N}_2-\text{O}_2$ mixtures at 1 bar pressure. The concentrations of $\text{CH}_3\text{CH}(\text{ONO}_2)\text{C}(\text{O})\text{CH}_3$ and *n*-butane were measured during the experiments by GC, and the measured rate constant ratio of $k(\text{HO} + \text{CH}_3\text{CH}(\text{ONO}_2)\text{C}(\text{O})\text{CH}_3)/k(\text{HO} + n\text{-butane}) = 0.499 \pm 0.056$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + n\text{-butane}) = 2.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation).

Preferred Values

- 15 $k = 1.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

6588

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

- 5 The preferred value is based on the sole study of Zhu et al. (1991) but with a higher uncertainty.

References

IUPAC: <http://www.iupac-kinetic.ch.cam.ac.uk/>.

Zhu, T., Barnes, I., and Becker, K. H.: J. Atmos. Chem., 13, 301, 1991.

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6589

II.A2.50



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
$(3.33 \pm 0.40) \times 10^{-12}$	298 ± 2	Grosjean et al., 1993	RR (a)
$(3.76 \pm 0.58) \times 10^{-11}$	275 ± 3	Orlando et al., 2002	RR (b,c)
$(2.88 \pm 0.46) \times 10^{-11}$	275 ± 3	Orlando et al., 2002	RR (b,d)

5 Comments

- 10 (a) Relative rate method carried out at atmospheric pressure of air. HO radicals were generated by the photolysis (using natural sunlight) of ethyl nitrite-air mixtures, and the concentrations of $\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OONO}_2$ (MPAN) and 1-butyl nitrate (the reference compound) were measured by GC with electron capture detection. The measured rate coefficient ratio of $k(\text{HO} + \text{MPAN})/k(\text{HO} + 1\text{-butyl nitrate}) = 2.08 \pm 0.25$ is placed on an absolute basis by use of a rate coefficient of $k(\text{HO} + 1\text{-butyl nitrate}) = 1.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (IUPAC, current recommendation).
- 15 (b) Relative rate method carried out in synthetic air at 0.93–0.97 bar. HO radicals were generated by the photolysis of ethyl nitrite-NO-air mixtures, and the concentrations of $\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OONO}_2$ (MPAN) and ethene and propene (the reference compounds) were measured by in situ FTIR

6590

spectroscopy. Experiments were carried out at 275 ± 3 K to decrease the rate of thermal decomposition of MPAN (IUPAC, current recommendation) in the presence of NO. The measured rate coefficient ratios of $k(\text{HO} + \text{MPAN})/k(\text{HO} + \text{ethene}) = 3.9\pm 0.6$ and $k(\text{HO} + \text{MPAN})/k(\text{HO} + \text{propene}) = 0.95\pm 0.15$ are placed on an absolute basis by use of rate coefficients at 275 K and atmospheric pressure of air of $k(\text{HO} + \text{ethene}) = 9.64 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k(\text{HO} + \text{propene}) = 3.03 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson, 1997).

(c) Relative to HO + ethene.

(d) Relative to HO + propene.

Preferred Values

$k = 2.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \begin{matrix} +0.2 \\ -0.5 \end{matrix}$ at 298 K.

Comments on Preferred Values

The rate coefficients measured in the two studies of Grosjean et al. (1993) and Orlando et al. (2002) disagree by a factor of ~ 10 , for reasons which are not known. The reaction of HO radicals with $\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OONO}_2$ is expected to proceed almost exclusively by initial HO radical addition to the C=C bond (Grosjean et al., 1993; Orlando et al., 2002), and is expected to have a small (and probably negative) temperature dependence at around room temperature. Support for the Orlando et al. (2002) study arises from the structurally

6591

similar compound $\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OCH}_3$ having a rate coefficient for its HO radical reaction of $(2.6\pm 0.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Saunders et al., 1994), which is similar to that measured by Orlando et al. (2002) for HO + MPAN. Accordingly, the preferred value is based on the rate coefficients measured by Orlando et al. (2002) at 275 K, adjusted to 298 K using the temperature dependence observed for HO + propene (Atkinson, 1997), and with appropriately large and asymmetric uncertainties. Formaldehyde and hydroxyacetone have been observed as products of this reaction (Grosjean et al., 1993; Orlando et al., 2002).

References

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Grosjean, D., Williams II, E. L., and Grosjean, E.: Int. J. Chem. Kinet., 25, 921, 1993.
IUPAC: <http://www.iupac-kinetic.ch.cam.ac.uk/>.
Orlando, J. J., Tyndall, G. S., Bertman, S. B., Chen, W., and Burkholder, J. B.: Atmos. Environ., 36, 1895, 2002.
Saunders, S. M., Baulch, D. L., Cooke, K. M., Pilling, M. J., and Smurthwaite, P. I.: Int. J. Chem. Kinet., 26, 113, 1994.

II.A2.51

HO + HCN → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.2 \times 10^{-13} \exp(-400/T)$	296–433	Fritz et al., 1984	FP-RA (a)
$(3.0 \pm 1.0) \times 10^{-14}$	298		

Comments

- (a) The measured rate coefficients were observed to be pressure dependent over the range ~13–600 mbar (~10–450 Torr) of N₂ diluent. The cited rate coefficients are those extrapolated to the high-pressure limit (k_∞) using a simple Lindemann extrapolation.

Preferred Values

$k = 3 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and 1 bar.
 $k = 1.2 \times 10^{-13} \exp(-400/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 290–440 K at 1 bar.

6593

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.
 $\Delta (E/R) = \pm 300$ K.

Comments on Preferred Values

- The preferred values are those of Fritz et al. (1984) with wider error limits. The rate coefficient increases with increasing pressure over this temperature range, and the rate coefficients cited are those extrapolated by Fritz et al. (1984) to the high-pressure limit.
- The reaction proceeds by HO radical addition over this temperature range. At higher temperatures the available rate coefficient data indicate a direct abstraction reaction (1989).

References

Atkinson, R.: J. Phys. Chem. Ref. Data, Monograph, 1, 1, 1989.
Fritz, B., Lorenz, K., Steinert, W., and Zellner, R.: Oxid. Comm., 6, 363, 1984.

6594

II.A2.52

HO + CH₃CN → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
$(2.1 \pm 0.3) \times 10^{-14}$	295 ± 2	Poulet et al., 1984	DF-EPR
$(8.6 \pm 1) \times 10^{-14}$	393		
$6.28 \times 10^{-13} \exp(-1030/T)$	250–363	Kurylo and Knable, 1984	FP-RF
$(1.94 \pm 0.37) \times 10^{-14}$	298		
$1.1 \times 10^{-12} \exp[-(1130 \pm 90)/T]$	256–388	Hynes and Wine, 1991	PLP-LIF (a)
$(2.48 \pm 0.38) \times 10^{-14}$	298		

5 Comments

- (a) No definitive evidence for a pressure dependence of the rate coefficient for the HO+CH₃CN reaction was observed over the pressure range 61–933 mbar (46–700 Torr) of N₂ diluent or 40–840 mbar (30–630 Torr) of He diluent. In the presence of O₂, the HO radical decays were non-exponential indicating regeneration of HO radicals.

6595

Preferred Values

$k = 2.2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (1 bar).

$k = 8.1 \times 10^{-13} \exp(-1080/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250–390 K at 1 bar.

5 Reliability

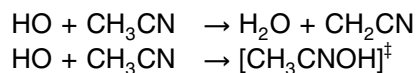
$\Delta \log k = \pm 0.15$ at 298 K.

$\Delta (E/R) = \pm 200$ K.

Comments on Preferred Values

- The preferred 298 K rate coefficient is a unit-weighted average of the rate coefficients of Poulet et al. (1984), Kurylo and Knable (1984) and Hynes and Wine (1991). The temperature dependence is the mean of those determined by Kurylo and Knable (1984) and Hynes and Wine (1991). Hynes and Wine (1991) observed no definitive evidence for a pressure dependence of the rate coefficient for the HO+CH₃CN reaction in N₂ or He diluent over the pressure ranges 61–933 mbar (46–700 Torr) or 40–840 mbar (30–630 Torr), respectively. In the presence of O₂, the HO radical decays were non-exponential (Hynes and Wine, 1991), indicating regeneration of HO radicals. Combined with analogous data for the reactions of HO radicals with CD₃CN (for which the rate coefficient was pressure dependent over the pressure range 53–923 mbar (40–692 Torr) of N₂ diluent) (Hynes and Wine, 1991) and of DO radicals with CH₃CN and CD₃CN (Hynes and Wine, 1991), it appears that the initial HO radical reaction proceeds by H-atom abstraction from the CH₃ group and HO radical addition to the CN group (Hynes and Wine, 1991).

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Subsequent reactions of the addition adduct in the presence of O₂ then lead to the regeneration of HO radicals. In view of the possibility of a pressure dependence of the 298 K rate coefficient at low total pressures (Hynes and Wine, 1991) (≤ 0.1 bar), the preferred values are applicable to atmospheric conditions.

Tyndall et al. (2001) have observed the formation of formyl cyanide, HC(O)CN, from reaction of HO radicals with CH₃CN at atmospheric pressure of synthetic air using FTIR spectroscopy, and a formation yield of HC(O)CN of 40±20% was obtained. The details of the reaction mechanism, including that for formation of HC(O)CN, are presently not known.

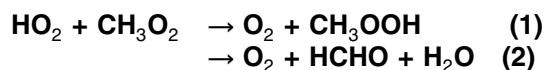
References

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 Kurylo, M. J. and Knable, G. L.: J. Phys. Chem., 88, 3305, 1984.
 15 Poulet, G., Laverdet, G., Jourdain, J. L., and Le Bras, G.: J. Phys. Chem., 88, 6259, 1984.
 Tyndall, G. S., Orlando, J. J., Wallington, T. J., and Hurley, M. D.: J. Phys. Chem. A, 105, 5380, 2001.

6597

Appendix 2a: HOx + VOC continued reactions

II.A2a.53



$$\Delta H^\circ(1) = -155 \text{kJ} \cdot \text{mol}^{-1}$$

5 $\Delta H^\circ(2) = -374 \text{kJ} \cdot \text{mol}^{-1}$

6598

Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$7.7 \times 10^{-14} \exp[(1296 \pm 364)/T]$	274–338	Cox and Tyndall, 1980	MM-AS (a)
$(6.5 \pm 1.0) \times 10^{-12}$	298		
$(5.4 \pm 1.1) \times 10^{-12}$	300	Jenkin et al., 1988	MM-IR-AS (b)
$3.0 \times 10^{-13} \exp[(720 \pm 100)/T]$	228–380	Dagaut et al., 1988	FP-AS (c)
$(2.9 \pm 0.4) \times 10^{-12}$	298		
$(4.8 \pm 0.2) \times 10^{-12}$	300	Moortgat et al., 1989	MM-IR-AS (d)
$4.4 \times 10^{-13} \exp[(780 \pm 55)/T]$	248–573	Lightfoot et al., 1990	FP-AS (e)
$(6.2 \pm 1.0) \times 10^{-12}$	298		
$2.9 \times 10^{-13} \exp(862 \pm 44)/T]$	248–700	Lightfoot et al., 1991	FP-AS (f)
$(5.13 \pm 0.55) \times 10^{-12}$	298	Boyd et al., 2003	PLP-AS (g)
<i>Branching Ratios</i>			
$k_1/k = 0.92 \pm 0.05$	295	Wallington and Japar, 1990; Wallington, 1991	P-FTIR (h)
$k_2/k = 1/[1 + 498 \exp(-1160/T)]$	218–298	Elrod et al., 2001	DF-CIMS (i)
$k_2/k = 0.11 \pm 0.02$	298		

Comments

- 5 (a) MM study of photolysis of Cl_2 in the presence of $\text{CH}_4\text{-H}_2\text{-O}_2$ mixtures at 1013 mbar (760 Torr) pressure. CH_3O_2 and HO_2 radicals were monitored by absorption at 250 nm and 210 nm, respectively.
- (b) MM study of photolysis of Cl_2 in the presence of $\text{CH}_4\text{-H}_2\text{O}_2\text{-O}_2$ mixtures. HO_2 radicals were monitored by IR absorption with a tunable diode
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- laser and CH_3O_2 monitored by UV absorption at 260 nm. $\sigma(\text{CH}_3\text{O}_2) = 3.53 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ was determined at 260 nm. k determined from observed perturbation of the second-order kinetics of the HO_2 radical self-reaction by the presence of CH_3O_2 in large excess. Experiments were
5 carried out at a total pressure of 13 mbar (10 Torr). Similar experiments on mixtures of $\text{Cl}_2\text{-H}_2\text{-CH}_4\text{-O}_2$ were performed at 1013 mbar (760 Torr) total pressure and 303 K and yielded $k = (6.8 \pm 0.9) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, which was taken as confirmation of the value obtained at 13 mbar (10 Torr).
- 10 (c) FP-UV absorption study involving $\text{Cl}_2\text{-CH}_3\text{OH-CH}_4\text{-O}_2\text{-N}_2$ mixtures at total pressures of 133 mbar (100 Torr); $\sigma(\text{HO}_2)$ and $\sigma(\text{CH}_3\text{O}_2)$ were determined over the wavelength range 215 nm to 280 nm. At 250 nm $\sigma(\text{CH}_3\text{O}_2) = 3.3 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ was determined. First- or second-order kinetics conditions were not obtainable for either HO_2 or CH_3O_2 and k was determined from computer modeling of the absorption decay curves.
- 15 (d) Study of the photooxidation of CH_3CHO at 933 mbar (700 Torr), with double multipath spectrometer, combining both IR and UV absorption spectrometry for monitoring reactants and products, together with modulated photolysis for transient detection. Transient absorptions were assigned to peroxy radicals and the rate coefficient was obtained from kinetic analysis
20 by computer simulation.
- (e) FP-UV absorption study of $\text{Cl}_2\text{-CH}_3\text{OH-CH}_4\text{-O}_2\text{-N}_2$ mixtures at pressures of 160 mbar or 1013 mbar (120 Torr or 760 Torr). Revised cross-section data were used, $\sigma(\text{HO}_2) = 5.3 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ at 210 nm and $\sigma(\text{CH}_3\text{O}_2) = 3.6 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ at 260 nm.
- 25 (f) FP-UV absorption study of $\text{Cl}_2\text{-CH}_3\text{OH-CH}_4\text{-O}_2\text{-N}_2$ mixtures at 1013 mbar (760 Torr) and over the temperature range 600 K to 719 K. The
6600

temperature-dependent rate coefficient listed above was derived by the authors from a re-analysis of all of their data, including previous studies from flash photolysis experiments.

- 5 (g) PLP-UV absorption study of $\text{H}_2\text{O}_2\text{-CH}_4\text{-O}_2\text{-N}_2$ mixtures at 1013 mbar (760 Torr) and 298 K. Conditions were chosen such that HO_2 was in excess, with initial concentration ratios $[\text{HO}_2]/[\text{CH}_3\text{O}_2]$ in the range 4–10. k was determined from simulation of transient decay traces recorded at 270 nm and either 210 nm or 220 nm. The signal at 270 nm was dominated by CH_3O_2 absorption, with its decay being almost entirely due to the reaction with HO_2 . The signal at 210 nm or 220 nm was mainly due to HO_2 absorption, with its self-reaction making the major contribution to its removal.
- 10 (h) Photolysis of F_2 in the presence of CH_4 and H_2 in synthetic air or O_2 at total pressures in the range 20 mbar (15 Torr) to 933 mbar (700 Torr). CH_3OOH , CH_4 , and a number of minor products were monitored by FTIR.
- 15 (i) Turbulent fast-flow system operating at total pressures of 133 mbar (100 Torr). CH_3O_2 was produced by reaction of CH_4 with F atoms and subsequent addition of O_2 . The CH_3O_2 was mixed with HO_2 produced by the $\text{H}+\text{O}_2+\text{M}$ reaction. Concentrations of CH_3O_2 , CH_3OOH , CH_2O , and HO_2 were monitored by time-resolved CIMS. Values of k_2 were derived by detailed modelling of the $[\text{CH}_2\text{O}]$ profile. Values of the branching ratio are based on the NASA expression for k (NASA Evaluation, 1997).
- 20

Preferred Values

25 $k = 5.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 3.8 \times 10^{-13} \exp(780/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 225–6601

580 K.

$k_2/k = 0.1$ at 298 K.

$k_2/k = 1/[1 + 498 \exp(-1160/T)]$ over the temperature range 220–298 K.

Reliability

5 $\Delta \log k = \pm 0.3$ at 298 K.

$\Delta(E/R) = \pm 500$ K.

$\Delta(k_2/k) = \pm 0.1$ at 298 K.

$\Delta(E_2/R - E/R) = \pm 500$ K.

Comments on Preferred Values

10 The discrepancies in the data for this reaction, due in part to the different values of the UV absorption cross sections used in various studies, remain unresolved.

The preferred rate coefficient at 298 K is the mean of the values of Cox and Tyndall (1980), Jenkin et al. (1988), Dagaut et al. (1988), Moortgat et al. (1989),
15 Lightfoot et al. (1990) and Boyd et al. (2003). The recommended temperature coefficient is that reported by Lightfoot et al. (1991), selected on the basis of their wider range of temperatures than previous studies (Cox and Tyndall, 1980; Dagaut et al., 1988). The A-factor was then adjusted to fit the preferred value of k at 298 K.

20 The studies of Kurylo et al. (1987), Jenkin et al. (1988) and Lightfoot et al. (1990) show that the room temperature rate coefficient is independent of pressure over the range 13 mbar to 1013 mbar (10 Torr to 760 Torr).

The most direct studies of the branching ratio are those of Wallington and Japar (1990), Wallington (1991) and Elrod et al. (2001). These studies confirm
25 that the contribution of channel (2) is small at 298 K ($k_2/k \approx 0.1$), supporting

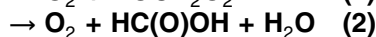
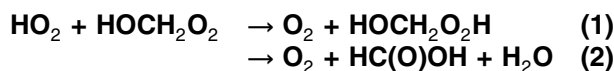
the earlier findings of Jenkin et al. (1988), Moortgat et al. (1989) and Lightfoot et al. (1991). The only information on the temperature dependence of the branching ratio comes from the study of Elrod et al. (2001) and suggests that it increases significantly in going to lower temperatures, reaching a value of $k_2/k \approx 0.31$ at 218 K. Provisionally the expression for k_2/k derived by Elrod et al. (2001) is accepted with substantial error limits until confirmatory studies on both the temperature and pressure dependence are available.

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$$\Delta H^\circ(2) = -473.1 \text{ kJ} \cdot \text{mol}^{-1}$$

5 Rate coefficient data ($k = k_1 + k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$5.6 \times 10^{-15} \exp[(2300 \pm 1100)/T]$	275–333	Veyret et al., 1989	FP-AS (a)
$(1.2 \pm 0.4) \times 10^{-11}$	295		
$(1.2 \pm 0.3) \times 10^{-11}$	298	Burrows et al., 1989	MM-IR (b)
<i>Branching Ratios</i>			
$k_2/k = 0.40 \pm 0.15$	298	Burrows et al., 1989	MM-IR (c)

Comments

- (a) Flash photolysis of Cl_2 in the presence of HCHO or CH_3OH and O_2 at total pressures of 110 mbar to 230 mbar (85 Torr to 170 Torr), with time-resolved absorption spectroscopy detection of HO_2 and HOCH_2O_2 radicals. The rate coefficient k was obtained from a computer simulation of the absorption profiles based on a mechanism of nine elementary reactions.

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- (b) MM study of Cl₂-HCHO-O₂ mixtures at total pressures of 930 mbar (700 Torr), with diode laser IR spectroscopy detection of HO₂ and HOCH₂O₂ radicals. The rate coefficient k was obtained from a computer simulation of [HO₂] absorption profiles based on a mechanism of eight elementary reactions.
- (c) Same experimental system as for comment (b). The branching ratio was determined from a computer simulation of the quantum yields of HC(O)OH formation.

Preferred Values

- $k = 1.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 5.6 \times 10^{-15} \exp(2300/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 275–335 K.
 $k_2/k = 0.4$ at 298 K.

Reliability

- $\Delta \log k = \pm 0.3$ at 298 K.
 $\Delta (E/R) = \pm 1500$ K.
 $\Delta(k_2/k) = 0.4$ at 298 K.

Comments on Preferred Values

- The two studies (Veyret et al., 1989; Burrows et al., 1989) of the rate coefficient at 298 K are in good agreement and confirm that this reaction is fast compared with the HO₂ radical reactions with CH₃O₂ and C₂H₅O₂ radicals. The

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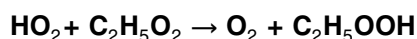
- reaction is presumed to proceed via a six-membered cyclic intermediate, analogous to that proposed for the formation of HCHO, CH₃OH and O₂ from the interaction of CH₃O₂ radicals (Jenkin et al., 1988). Both the temperature dependence and the branching ratio require independent confirmation. In addition, there is the possibility that the rate coefficient could be both pressure and bath-gas dependent.

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$$\Delta H^\circ = -159 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(6.3 \pm 0.9) \times 10^{-12}$	295	Cattell et al., 1986	MM-IR-AS (a)
$5.6 \times 10^{-13} \exp[(650 \pm 125)/T]$	248–380	Dagaut et al., 1988	FP-AS (b)
$(5.3 \pm 1.0) \times 10^{-12}$	298		FP-AS (c)
$1.6 \times 10^{-13} \exp[(1260 \pm 130)/T]$	248–480	Fenter et al., 1993	
$(1.10 \pm 0.21) \times 10^{-11}$	298		
$6.9 \times 10^{-13} \exp[(702 \pm 69)/T]$	210–363	Maricq and Szente, 1994	FP-AS (d)
$(8.3 \pm 1.5) \times 10^{-12}$	295		
$(8.14 \pm 0.38) \times 10^{-12}$	298	Boyd et al., 2003	PLP-AS (e)

Comments

(a) MM spectrometry system with HO_2 and $\text{C}_2\text{H}_5\text{O}_2$ radicals generated simultaneously by photolysis of Cl_2 in the presence of $\text{C}_2\text{H}_6\text{-CH}_3\text{OH-O}_2\text{-N}_2$ mixtures at pressures of 3.2 mbar (2.4 Torr). HO_2 radicals were monitored by IR absorption with a tunable diode laser and $\text{C}_2\text{H}_5\text{O}_2$ radicals were monitored by UV absorption at 260 nm. The rate coefficient, k , was determined

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from the observed perturbation of the second-order kinetics of the HO_2 self-reaction when $\text{C}_2\text{H}_5\text{O}_2$ was present in large excess, and shown to be essentially independent of pressure over the range 3.2 mbar to 1013 mbar (2.4 Torr to 760 Torr).

(b) Flash photolysis of Cl_2 in the presence of $\text{C}_2\text{H}_6\text{-CH}_3\text{OH-O}_2\text{-N}_2$ mixtures at total pressures of 33 mbar to 533 mbar (25 Torr to 400 Torr). Composite transient absorption decay curves for HO_2 and $\text{C}_2\text{H}_5\text{O}_2$ radicals were measured at 230 nm, 250 nm and 280 nm. Kinetic analysis derived from computer modeling of experimental data.

(c) FP-UV absorption study of $\text{Cl}_2\text{-C}_2\text{H}_6\text{-O}_2\text{-N}_2$ mixtures at 1013 mbar (760 Torr) total pressure. Rate coefficients were derived from simultaneous computer analyses of several decay curves collected at different wavelengths.

(d) FP-UV absorption study of $\text{F}_2\text{-H}_2\text{-C}_2\text{H}_6\text{-O}_2\text{-N}_2$ mixtures at a total pressure of ~ 270 mbar (~ 200 Torr). Rate coefficients were derived from computer simulation of time-resolved decay curves.

(e) PLP-UV absorption study of $\text{H}_2\text{O}_2\text{-C}_2\text{H}_6\text{-O}_2\text{-N}_2$ mixtures at 1013 mbar (760 Torr) and 298 K. Conditions were chosen such that HO_2 was in excess, with initial concentration ratios $[\text{HO}_2]/[\text{C}_2\text{H}_5\text{O}_2]$ in the range 4–10. k was determined from simulation of transient decay traces recorded at 270 nm and either 210 nm or 220 nm. The signal at 270 nm was dominated by $\text{C}_2\text{H}_5\text{O}_2$ absorption, with its decay being almost entirely due to the reaction with HO_2 . The signal at 210 nm or 220 nm was mainly due to HO_2 absorption, with its self-reaction making the major contribution to its removal.

Preferred Values

$k = 7.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 3.8 \times 10^{-13} \exp(900/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–500 K.

5 Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

$\Delta (E/R) = \pm 400$ K.

Comments on Preferred Values

The room temperature rate coefficients of Fenter et al. (1993), Maricq and Szente (1994) and Boyd et al. (2003) are in reasonable agreement with the previous direct studies of Cattell et al. (1986) and Dagaut et al. (1988). We have based our recommendations on the average value of k_{298} from these five studies. However, the temperature coefficient of Fenter et al. (1993) is almost a factor of two higher than those of Dagaut et al. (1988) and Maricq and Szente (1994), indicating a systematic error in one or more of the studies. The rate coefficients determined in all of these studies depend upon the values of σ (HO_2) and σ ($\text{C}_2\text{H}_5\text{O}_2$), the latter of which is not well established. Clearly more work is needed on this reaction and in the meantime we recommend an E/R value corresponding to the rounded-off mean of the three determinations (Dagaut et al., 1988; Fenter et al., 1993; Maricq and Szente, 1994), with relatively large error limits.

The FTIR spectroscopic product study of Wallington and Japar (1990) has shown that this reaction is dominated by a single channel at 298 K, to yield $\text{C}_2\text{H}_5\text{OOH} + \text{O}_2$. The results of Spittler et al. (2000) and Hasson et al. (2004)

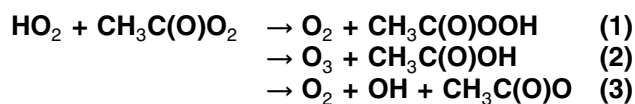
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have confirmed this, with the former study demonstrating that this continues to be the case over the temperature range 284 K to 312 K.

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$$\Delta H^\circ(1) = -180 \text{kJ} \cdot \text{mol}^{-1}$$

$$\Delta H^\circ(2) = -132 \text{kJ} \cdot \text{mol}^{-1}$$

$$5 \quad \Delta H^\circ(3) = -13 \text{kJ} \cdot \text{mol}^{-1}$$

6611

Rate coefficient data ($k = k_1 + k_2 + k_3$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$4.3 \times 10^{-13} \exp[(1040 \pm 100)/T]$	253–368	Moortgat et al., 1989	FP-AS (a)
$(1.3 \pm 0.3) \times 10^{-11}$	298		
$3.9 \times 10^{-13} \exp[(1350 \pm 250)/T]$	269–363	Crawford et al., 1999	PLP-IR-AS (b)
$(4.4 \pm 1.6) \times 10^{-11}$	297		
$6.4 \times 10^{-13} \exp[(925 \pm 120)/T]$	273–403	Tomas et al., 2001	FP-AS (c)
$(1.51 \pm 0.07) \times 10^{-11}$	293		
<i>Branching Ratios</i>			
$k_1/k \approx 0.75$	298	Niki et al., 1985	FTIR (d)
$k_2/k \approx 0.25$			
$k_2/k = 0.33 \pm 0.07$	253–368	Moortgat et al., 1989	FP-AS (e)
$k_1/k_2 = 3.3 \times 10^2 \exp[(-1430 \pm 480)/T]$	263–333	Horie and Moortgat, 1992	FTIR (f)
$k_1/k_2 = 2.7$	298		
$k_2/k = 0.12 \pm 0.04$	295	Crawford et al., 1999	PLP-FTIR (g)
$k_2/k = 0.20 \pm 0.02$	298–373	Tomas et al., 2001	FP-AS (h)
$k_1/k = 0.40 \pm 0.16$	298	Hasson et al., 2004	UVP-FTIR/HPLC (i)
$k_2/k = 0.20 \pm 0.08$			
$k_3/k = 0.40 \pm 0.16$			

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Comments

- 5 (a) Flash photolysis of Cl_2 in the presence of $\text{CH}_3\text{CHO}-\text{CH}_3\text{OH}-\text{N}_2$ mixtures at total pressures of 800 mbar to 866 mbar (600 Torr to 650 Torr). $[\text{CH}_3\text{CO}_3]$ was monitored by UV absorption over the wavelength range 195 nm to 280 nm and the absorption cross-section measured relative to $\Delta(\text{HO}_2)=5.3 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ at 210 nm. Rate coefficients were derived from a computer simulation of absorption traces at a range of wavelengths, based on a mechanism including secondary removal of $\text{CH}_3\text{C}(\text{O})\text{O}_2$. The mechanism assumed that the $\text{CH}_3\text{C}(\text{O})\text{O}_2+\text{HO}_2$ reaction proceeds by channels (1) and (2).
10
- (b) Pulsed laser photolysis of $\text{Cl}_2-\text{CH}_3\text{OH}-\text{CH}_3\text{CHO}-\text{O}_2-\text{N}_2$ mixtures at a total pressure of about 67 mbar (50 Torr). The progress of the reaction was followed by time-resolved UV absorption measurements over the range 200 nm to 300 nm and by monitoring $[\text{HO}_2]$ by infrared laser diode absorption at 1117.5 cm^{-1} . Because of the difficulty of deconvoluting the UV spectra, values of k were determined from the infrared measurements by fitting the $[\text{HO}_2]$ profiles using a detailed mechanism. The mechanism assumed that the $\text{CH}_3\text{C}(\text{O})\text{O}_2+\text{HO}_2$ reaction proceeds by channels (1) and (2).
15
- (c) Flash photolysis of $\text{Cl}_2-\text{CH}_3\text{CHO}-\text{CH}_3\text{OH}-\text{O}_2-\text{N}_2$ mixtures. The progress of the reaction was followed by time-resolved UV absorption measurements at 207 nm and 250 nm. Values of k were derived by simulation of the absorption measurements at 207 nm, using a detailed chemical mechanism. The mechanism assumed that the $\text{CH}_3\text{C}(\text{O})\text{O}_2+\text{HO}_2$ reaction proceeds by channels (1) and (2).
20
- (d) FTIR study of irradiated $\text{Cl}_2-\text{HCHO}-\text{CH}_3\text{CHO}-\text{O}_2$ mixtures. The branching ratio was based on the analysis of the products $\text{CH}_3\text{C}(\text{O})\text{OOH}$,
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$\text{CH}_3\text{C}(\text{O})\text{OH}$ and O_3 , with the assumption that the reaction proceeds via channels (1) and (2).

- (e) Derived from the same experiments as in Comment (a) by making allowance for absorption by O_3 product.
- 5 (f) FTIR study of irradiated $\text{CH}_3\text{C}(\text{O})\text{C}(\text{O})\text{CH}_3$ in the presence of $\text{Ar}-\text{O}_2$ mixtures at total pressures of 973 mbar to 1026 mbar (730 Torr to 770 Torr). The reaction products CO_2 , CO , HCHO , $\text{HC}(\text{O})\text{OH}$, $\text{CH}_3\text{C}(\text{O})\text{OH}$, $\text{CH}_3\text{C}(\text{O})\text{OOH}$, CH_3OH , H_2O_2 and O_3 were analyzed by matrix-isolation FTIR spectroscopy combined with a molecular-beam sampling technique. The branching ratio k_1/k_2 was derived from the yields of $\text{CH}_3\text{C}(\text{O})\text{OH}$ and O_3 .
10
- (g) UV irradiation of $\text{Cl}_2-\text{CH}_3\text{CHO}-\text{CH}_3\text{OH}-\text{air}$ mixtures in a smog chamber fitted with an FTIR detection system. Branching ratios were derived from the yields of $\text{CH}_3\text{C}(\text{O})\text{OOH}$ and $\text{CH}_3\text{C}(\text{O})\text{OH}$ which gave $k_2/k=0.10\pm0.02$ at 295 K. Branching ratios were also derived from the O_3 yields determined from the kinetics traces at long reaction times in experiments performed to obtain the rate coefficient [see Comment (b)]. These experiments gave $k_2/k=0.16\pm0.04$ at 295 K. The value cited in the Table is a weighted mean of values from all the experiments. The O_3 yield measurements suggest only a small increase in k_2/k as temperature is lowered from 359 K to 265 K. The interpretation of the results assumed that the $\text{CH}_3\text{C}(\text{O})\text{O}_2+\text{HO}_2$ reaction proceeds by channels (1) and (2).
15
20
- (h) Branching ratios were derived from the O_3 yields at long reaction times in experiments described in Comment (c). There was no detectable change in k_2/k with change in temperature from 298 K to 373 K.
25

(i) Continuous photolysis of Cl_3 in the presence of $\text{CH}_3\text{CHO}-\text{CH}_3\text{OH}-\text{O}_2-\text{N}_2$ mixtures at a total pressure of 1066 mbar (800 Torr). Yields of CH_3OOH and $\text{CH}_3\text{C}(\text{O})\text{OOH}$ (by HPLC) and CH_3OOH , $\text{CH}_3\text{C}(\text{O})\text{OOH}$, $\text{CH}_3\text{C}(\text{O})\text{OH}$ and CO_2 (by FTIR) were measured as a function of the initial concentration ratio $[\text{CH}_3\text{OH}]_0/[\text{CH}_3\text{CHO}]_0$ over the range 0 to 5, corresponding to conditions over which dominant removal of $\text{CH}_3\text{C}(\text{O})\text{O}_2$ changes from its self reaction to the reaction with HO_2 . The results were analysed by simulation using a detailed chemical mechanism taking account of the sequential formation of CH_3O_2 in the system.

Preferred Values

$k = 1.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 5.2 \times 10^{-13} \exp(983/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250–400 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
 $\Delta (E/R) = \pm 500 \text{ K}$.

Comments on Preferred Values

Several studies have obtained evidence for the existence of reaction channels (1) and (2) (Niki et al., 1985; Moortgat et al., 1989; Horie and Moortgat, 1992; Crawford et al., 1999; Tomas et al., 2001), with reasonably consistent branching ratios being reported. However, the product yields measured in the

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recent study of Hasson et al. (2004), and their dependence on reagent conditions (see comment (i)), cannot be interpreted in terms of the reaction of $\text{CH}_3\text{C}(\text{O})\text{O}_2$ with HO_2 proceeding via channels (1) and (2) alone. Hasson et al. (2004) interpreted their observations in terms of a major contribution to the reaction being made by the OH radical-forming channel (3), which also leads to subsequent formation of CH_3O_2 . The results of the original product study of Niki et al. (1985) at high $[\text{HO}_2]/[\text{CH}_3\text{C}(\text{O})\text{O}_2]$ (i.e. when $\text{CH}_3\text{C}(\text{O})\text{O}_2$ is mainly removed via reaction with HO_2) also provide some support for this interpretation, through the reported observation of significant formation of CH_3OOH , and because the products of channels (1) and (2), $\text{CH}_3\text{C}(\text{O})\text{OH}$ and $\text{CH}_3\text{C}(\text{O})\text{OOH}$, only account for $\approx 50\%$ of the loss of the $\text{CH}_3\text{C}(\text{O})\text{O}_2$ precursor, CH_3CHO . The participation of channel (3) leads to potential errors in both the absolute and relative branching ratios in the majority of the earlier studies, through possible secondary formation of $\text{CH}_3\text{C}(\text{O})\text{OH}$ from the reaction of CH_3O_2 with $\text{CH}_3\text{C}(\text{O})\text{O}_2$, and the regeneration of both $\text{CH}_3\text{C}(\text{O})\text{O}_2$ and HO_2 from reactions of OH. However, the relative branching ratio determination of Horie and Moortgat (1992) relied on the observed formation of $\text{CH}_3\text{C}(\text{O})\text{OOH}$ and O_3 , which are almost certainly specific products of reaction channels (1) and (2), respectively. The 298 K value of $k_1/k_2=2.7$ of Horie and Moortgat (1992) is in reasonable agreement with the value of 2 reported by Hasson et al. (2004). Independent verification of the participation of channel (3) is required.

There are substantial differences among the available kinetics measurements of k , which are also subject to further potential uncertainty because channel (3) was generally not taken into account in the analyses. Prior to recognition of this, Tyndall et al. (2001) have made a comparison of the studies of Moortgat et al. (1989) and Crawford et al. (1999) using updated absorption cross-sections and taking into account present understanding of the effects of the $\text{HO}_2+\text{CH}_3\text{CHO}$ reaction. Their reanalysis of the $[\text{HO}_2]$ decay traces published

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in these studies favours the values of k obtained by Moortgat et al. (1989). Tyndall et al. (2001) also point out that the values of k reported by Crawford et al. (1999) are high compared with those from analogous $\text{RO}_2 + \text{HO}_2$ reactions. Their conclusions are supported by the more recent study of Tomas et al. (2001) who used sufficiently low concentrations to avoid effects due to the $\text{HO}_2 + \text{CH}_3\text{CHO}$ reaction. Their results are in excellent agreement with those of Moortgat et al. (1989). Our preferred expression for k is therefore provisionally based on the mean of the values of E/R obtained by Moortgat et al. (1989) and Tomas et al. (2001), combined with an A -factor to give a value of k at 298 K which is the mean of the values obtained in the same two studies. It is recognised, however, that the likely regeneration of both $\text{CH}_3\text{C}(\text{O})\text{O}_2$ and HO_2 from channel (3) under the experimental conditions employed in all the reported kinetics studies, but not accounted for in the analyses, leads to the possibility that the observed removal kinetics may underestimate the overall rate coefficient: although the extent of any underestimate could only be obtained from reanalysis of the original data. This is reflected in the uncertainty assigned to the preferred values.

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II.A2a.57



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate coefficients</i>			
$(4.8 \pm 1.5) \times 10^{-12}$	298	Jenkin and Cox, 1991	MM-AS (a)
$\sim 2.0 \times 10^{-11}$	298	Anastasi et al., 1991	PR-AS (b)
$(1.2 \pm 0.3) \times 10^{-11}$	296	Murrells et al., 1991	PLP-AS (c)
$(1.17 \pm 0.22) \times 10^{-11}$	298	Boyd et al., 2003	PLP-AS (d)

5 Comments

(a) MM study with $\text{HOCH}_2\text{CH}_2\text{O}_2$ radicals being generated from the photolysis of $\text{HOCH}_2\text{CH}_2\text{OI}$ in the presence of O_2 and N_2 at total pressures of 13 mbar, 133 mbar and 1013 mbar (10 Torr, 100 Torr, and 760 Torr) in a slow flow system. The modulated absorption spectrum in the range 205 nm to 310 nm showed that additional transient species were absorbing, and these were ascribed to $\text{HOCH}_2\text{CH}_2\text{OOI}$ and HO_2 . The rate coefficient was obtained from computer simulations of the time-resolved absorption waveforms at 220 nm to 310 nm for experiments at 13 mbar (10 Torr) pressure.

(b) Pulse radiolysis study, with $\text{HOCH}_2\text{CH}_2\text{O}_2$ radicals being generated from $\text{CH}_4\text{-O}_2\text{-H}_2\text{O-SF}_6$ and $\text{CH}_3\text{CH}_2\text{OH-O}_2\text{-SF}_6$ mixtures at total pressures of 6619

1013 mbar (760 Torr). $[\text{HOCH}_2\text{CH}_2\text{O}_2]$ was monitored by absorption at 230 nm and k derived from kinetic modelling of absorption profiles.

(c) Pulsed laser photolysis study, with $\text{HOCH}_2\text{CH}_2\text{O}_2$ radicals being generated from photolysis of $\text{HOCH}_2\text{CH}_2\text{Cl}$ in the presence of O_2 and N_2 at total pressures of 973 mbar (730 Torr). The rate coefficient was obtained by modelling the observed absorption profiles on the basis of a simplified mechanism of four reactions.

(d) PLP-UV absorption study of $\text{H}_2\text{O}_2\text{-C}_2\text{H}_4\text{-O}_2\text{-N}_2$ mixtures at 1013 mbar (760 Torr) and 298 K. Conditions were chosen such that HO_2 was in excess, with initial concentration ratios $[\text{HO}_2]/[\text{HOCH}_2\text{CH}_2\text{O}_2]$ in the range 4–10. k was determined from simulation of transient decay traces recorded at 270 nm and either 210 nm or 220 nm. The signal at 270 nm was dominated by $\text{HOCH}_2\text{CH}_2\text{O}_2$ absorption, with its decay being almost entirely due to the reaction with HO_2 . The signal at 210 nm or 220 nm was mainly due to HO_2 absorption, with its self-reaction making the major contribution to its removal.

Preferred Values

$$k = 1.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

20 $\Delta \log k = \pm 0.2$ at 298 K.

The preferred value of k is based on the results of the pulsed laser photolysis studies of Murrells et al. (1991) and Boyd et al. (2003), which are in excellent agreement.

5 The earlier determinations of Jenkin and Cox (1991) and Anastasi et al. (1991) were subject to errors in the magnitude and shape of the HOCH₂CH₂O₂ absorption spectrum, respectively, which influenced the derived values of k . Murrells et al. (2001) demonstrated that cross-sections reported by Jenkin and Cox (1991), from molecular modulation studies of the photolysis of HOCH₂CH₂I, are low by a factor of approximately two. Jenkin and Cox (1991) made the assumption that the photolysis of HOCH₂CH₂I in their system yielded entirely HOCH₂CH₂O₂ radicals, which was apparently not the case. Increasing $\sigma_{230}(\text{HOCH}_2\text{CH}_2\text{O}_2)$ by a factor of two in a re-interpretation (Murrells et al., 1991) of the data of Jenkin and Cox (1991) yielded a revised value of $k = (8.4 \pm 3.0) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 13 mbar pressure, in fair agreement with the current recommendation. The approximate value of k derived by Anastasi et al. (1991) from pulsed radiolysis experiments is almost a factor of two higher than our recommended value. We have not taken this value of Anastasi et al. (1991) into account, because of the differences in the absorption spectrum of the radical observed compared with the consistent spectra shapes reported by Jenkin and Cox (1991) and Murrells et al. (1991) (see the data sheet for the Reaction 2 HOCH₂CH₂O₂ (products)).

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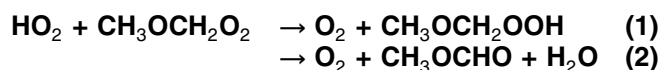
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II.A2a.58



Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Branching Ratios</i>			
$k_1/k = 0.53 \pm 0.08$	295	Wallington et al., 1993	P-FTIR (a)
$k_2/k = 0.40 \pm 0.04$			

5 Comments

- (a) HO_2 and $\text{CH}_3\text{OCH}_2\text{O}_2$ radicals were generated from the steady-state photolysis of Cl_2 in the presence of $\text{CH}_3\text{OH}-\text{CH}_3\text{OCH}_3-\text{O}_2$ mixtures at a total pressure of 930 mbar (700 Torr). Branching ratios were derived from FTIR analyses of CH_3OCHO and $\text{CH}_3\text{OCH}_2\text{OOH}$ products, which accounted for (93±12)% of the CH_3OCH_3 loss.

Preferred Values

$$k_1/k = 0.60 \text{ at } 298 \text{ K.}$$

$$k_2/k = 0.40 \text{ at } 298 \text{ K.}$$

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Reliability

$$\Delta(k_1/k) = \pm 0.10 \text{ at } 298 \text{ K.}$$

$$\Delta(k_2/k) = \pm 0.10 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

- 5 The reaction between HO_2 radicals and $\text{CH}_3\text{OCH}_2\text{O}_2$ radicals is analogous to that between HO_2 radicals and HOCH_2O_2 radicals in that there are two channels of nearly equal importance at room temperature producing (i) the hydroperoxide plus O_2 and (ii) a carbonyl product, H_2O and O_2 . In contrast, the HO_2 reactions with unsubstituted alkyl peroxy radicals, RO_2 , appear to have only a single channel, producing the alkyl hydroperoxide.

10 It has been proposed (Wallington et al., 1993) that the reaction between HO_2 and substituted RO_2 radicals yielding the carbonyl compounds proceeds through a six-member transition state similar to that suggested by Russell (1957) to explain the molecular products from the interactions of RO_2 radicals.

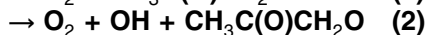
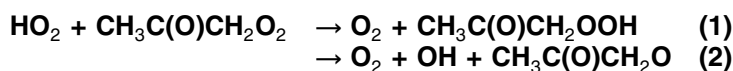
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II.A2a.59



$$\Delta H^\circ = -161 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(9.0 \pm 1.0) \times 10^{-12}$	298	Bridier et al., 1993	FP-AS (a)
<i>Branching Ratios</i>			
$k_1/k = 0.33 \pm 0.10$	298	Hasson et al., 2004	UVP-FTIR/HPLC (b)
$k_2/k = 0.67 \pm 0.20$	298		

Comments

(a) Flash photolysis of Cl_2 in the presence of $\text{CH}_3\text{C(O)CH}_3\text{-CH}_3\text{OH-O}_2\text{-N}_2$ mixtures at a total pressure of 1013 mbar (760 Torr). The rate coefficient k was derived from a kinetic analysis of absorption-time profiles measured at 210 nm and 230 nm.

(b) Continuous photolysis of Cl_2 in the presence of $\text{CH}_3\text{C(O)CH}_3\text{-CH}_3\text{OH-O}_2\text{-N}_2$ mixtures at a total pressure of 1066 mbar (800 Torr). Yields of CH_3OOH , $\text{CH}_3\text{C(O)OOH}$ and $\text{CH}_3\text{C(O)CH}_2\text{OOH}$ (by HPLC) and $\text{CH}_3\text{C(O)OOH}$, HCHO, CO and CO_2 (by FTIR) were measured as a function of the initial

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concentration ratio $[\text{CH}_3\text{OH}]_0/[\text{CH}_3\text{C(O)CH}_3]_0$ over the range 0 to 0.5, corresponding to conditions over which dominant removal of $\text{CH}_3\text{C(O)CH}_2\text{O}_2$ changes from its self reaction to the reaction with HO_2 . The results were analysed by simulation using a detailed chemical mechanism taking account of the sequential formation of $\text{CH}_3\text{C(O)O}_2$ and CH_3O_2 in the system.

Preferred Values

$$k = 9.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The preferred value of k is provisionally based on the sole determination, reported by Bridier et al. (1993). Although this value seems reasonable in comparison with other $\text{RO}_2 + \text{HO}_2$ reactions, it has been obtained from the kinetic analysis of a complex chemical system, with only product channel (1) represented in the mechanism. The yields of $\text{CH}_3\text{C(O)CH}_2\text{OOH}$ measured in the recent product study of Hasson et al. (2004) suggest that other channels occur, with the best interpretation of the results obtained from inclusion of the OH radical-forming channel (2) as the main product channel. Under these circumstances, the likely regeneration of both $\text{CH}_3\text{C(O)CH}_2\text{O}_2$ and HO_2 under the experimental conditions employed by Bridier et al. (1993) leads to the possibility that the observed removal kinetics may underestimate the overall rate coefficient: although the extent of any underestimate could only be obtained

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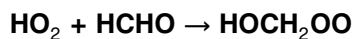
from reanalysis of the original data. Independent verification of the participation of channel (2) is therefore required, in addition to further kinetics studies to reduce the uncertainty in the preferred value.

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II.A2a.60



$$\Delta H^\circ = -68.1 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.1 \pm 0.4) \times 10^{-13}$	273	Barnes et al., 1985	S-FTIR (a)
$7.7 \times 10^{-15} \exp[(625 \pm 550)/T]$	275–333	Veyret et al., 1989	FP-AS (b)
5 $(6.0 \pm 0.7) \times 10^{-14}$	295		

Comments

(a) FTIR spectroscopic study in a 420 L reaction chamber. HO₂ radicals were generated from the thermal decomposition of HO₂NO₂ in the presence of HCHO, NO₂ and synthetic air at a total pressure of 530 mbar (400 Torr). The rate coefficient, *k*, was obtained from a computer simulation of the rates of decay of HCHO and rates of formation of HC(O)OH and HOCH₂O₂NO₂, based on a reaction scheme consisting of nine elementary reactions.

15 (b) Flash photolysis of Cl₂ in the presence of HCHO or CH₃OH and O₂ with long-path absorption measurements of HO₂ and HOCH₂O₂ radicals at total pressures of 110 mbar to 230 mbar (85 Torr to 170 Torr). The rate co-

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efficient, k , was obtained from a computer simulation of the absorption profiles based on a mechanism of five elementary reactions.

Preferred Values

$k = 7.9 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

5 $k = 9.7 \times 10^{-15} \exp(625/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 275–333 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

$\Delta (E/R) = \pm 600$ K.

10 *Comments on Preferred Values*

The studies of Barnes et al. (1985) and of Veyret et al. (1989) are in excellent agreement regarding this rate coefficient, and both are in good agreement with the earlier data of Veyret et al. (1982). The preferred expression for the rate coefficient is derived by taking an average value of the rate coefficients
15 of Barnes et al. (1985) [$k(273 \text{ K}) = 1.1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$] and Veyret et al. (1989) [$k(275 \text{ K}) = 8.0 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$] together with the value of E/R determined by Veyret et al. (1989).

This reaction is believed to proceed via the initial formation of the adduct radical, $\text{HO}_2\text{CH}_2\text{O}$, which rapidly isomerizes to the product radical, HOCH_2OO
20 via H-atom transfer.

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References

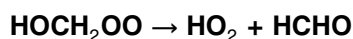
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$$\Delta H^\circ = 68.1 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

k/s^{-1}	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
20_{-10}^{+20}	273	Barnes et al., 1985	S-FTIR (a)
$2.0 \times 10^{12} \exp[-(7000 \pm 2000)/T]$	275–333	Veyret et al., 1989	FP-AS (b)
100 ± 50	295		

Comments

- (a) FTIR spectroscopic study in a 420 L reaction chamber. HO_2 radicals were generated from thermal decomposition of HO_2NO_2 in the presence of HCHO, NO_2 and synthetic air at a total pressure of 533 mbar (400 Torr). The rate coefficient, k , was derived from a computer simulation of the rates of decay of HCHO and rates of formation of HCOOH and $\text{HOCH}_2\text{O}_2\text{NO}_2$ based on a reaction scheme consisting of nine elementary reactions.
- (b) Flash photolysis of Cl_2 in the presence of HCHO or CH_3OH and O_2 with long-path absorption measurements of $[\text{HO}_2]$ and $[\text{HOCH}_2\text{O}_2]$ at total pressures of 113 mbar to 227 mbar (85 Torr to 170 Torr). The rate coefficient, k ,

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was obtained from a computer simulation of the absorption profiles based on a mechanism of five elementary reactions.

Preferred Values

$$k = 1.5 \times 10^2 \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k = 2.4 \times 10^{12} \exp(-7000/T) \text{ s}^{-1} \text{ over the temperature range } 275\text{--}330 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

$$\Delta (E/R) = \pm 2000 \text{ K.}$$

Comments on Preferred Values

- The studies of Barnes et al. (1985) and of Veyret et al. (1989) are in good agreement regarding the rate coefficient of this reaction. The preferred rate equation has been obtained by taking the average of the rate coefficients at 273 K to 275 K from these studies together with the E/R determined by Veyret et al. (1989). It should be pointed out that the value of the equilibrium constant, K_1 , for the reaction $\text{HO}_2 + \text{HCHO} \rightleftharpoons \text{HOCH}_2\text{O}_2$ (1,-1), $K_1 = 5.0 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1}$ at 298 K, derived from the kinetic study of Veyret et al. (1989) (which is identical to the value obtained from our recommended data for k_1 and k_{-1}), is in excellent agreement with the value of $K_1 = 4.0 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1}$ at 298 K obtained independently by Burrows et al. (1989) from molecular modulation studies. The above value of K_1 is, however, considerably smaller than the value of $K_1 = 3.4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1}$ at 298 K reported by Zabel et al. (1987)

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from EPR spectroscopic measurements of the ratio of concentrations of HO₂ and HOCH₂O₂ radicals in the photolysis of HCHO-O₂ mixtures.

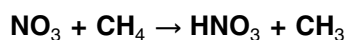
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Appendix 3: NO₃ + VOC

II.A3.62



$$\Delta H^\circ = 12.4 \text{ kJ}\cdot\text{mol}^{-1}$$

5 Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$< 4 \times 10^{-16}$	298	Burrows et. al., 1985	(a)
$\leq 2 \times 10^{-17}$	298 ± 2	Wallington et. al., 1986	FP-A (b)
$\leq 8 \times 10^{-19}$	302	Boyd et. al., 1991	(c)
<i>Relative Rate Coefficients</i>			
$< 5 \times 10^{-21}$	~ 298	Cantrell et. al., 1987	(d)

Comments

- (a) NO₃ radicals were generated by the modulated photolysis of Cl₂-ClONO₂-N₂ or F₂-HNO₃-N₂ mixtures and monitored by optical absorption at 662 nm.
- 10 (b) NO₃ radicals were generated by the flash photolysis of ClONO₂-He mixtures and detected by optical absorption at 662 nm.

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- (c) Stopped-flow system with optical absorption detection of NO₃ radicals at 662 nm. The occurrence of secondary reactions was expected to lead to a stoichiometry factor of ≥ 2 , resulting in the upper limit to the rate coefficient cited in the table.
- 5 (d) Relative rate method. Upper limit to the rate coefficient was derived from the absence of observed CO and CO₂ formation after addition of CH₄ to N₂O₅-NO₃-NO₂-N₂ mixtures. An equilibrium constant for the NO₂+NO₃ ↔ N₂O₅ reactions of 2.90×10^{-11} cm³ molecule⁻¹ at 298 K (IUPAC, current recommendation) has been used to derive the rate coefficient
- 10 cited.

Preferred Values

$k < 1 \times 10^{-18}$ cm³ molecule⁻¹ s⁻¹ at 298 K.

Comments on Preferred Values

15 The preferred value is based on the upper limits to the rate coefficients obtained by Cantrell et al. (1987) and Boyd et al. (1991), and is consistent with the higher upper limits reported by Burrows et al. (1985) and Wallington et al. (1986).

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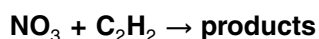
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II.A3.63



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$4.9 \times 10^{-13} \exp[-(2742 \pm 542)/T]$ $(5.1 \pm 3.5) \times 10^{-17}$	295–523 295 ± 2	Canosa-Mas et al., 1988a, b	DF-A
<i>Relative Rate Coefficients</i>			
$\leq 3.0 \times 10^{-17}$	298 ± 2	Atkinson et al., 1987	RR (a)

5 Comments

- (a) NO_3 radicals were generated by the thermal decomposition of N_2O_5 . The concentrations of acetylene and ethene (the reference organic) were measured by GC. The measured rate coefficient ratio of $k(\text{NO}_3 + \text{C}_2\text{H}_5)/k(\text{NO}_3 + \text{C}_2\text{H}_4) \leq 0.14$ at $298 \pm 2 \text{ K}$ is placed on an absolute basis by use of a rate coefficient of $k(\text{NO}_3 + \text{C}_2\text{H}_4) = 2.1 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation).

Preferred Values

$k < 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
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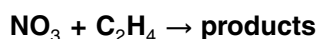
Comments on Preferred Values

- The measurement of rate coefficients for low reactivity organics is complicated by the possibility of secondary reactions, leading to erroneously high measured rate coefficients. The relative rate measurements of Atkinson et al. (1987) show C_2H_2 to be significantly less reactive than C_2H_4 . The preferred value of the upper limit to the rate coefficient is sufficiently high to be consistent with the data of Canosa-Mas et al. (1988a). Until there are confirmatory data for the reported temperature dependence of this rate coefficient (Canosa-Mas et al. (1988b)), no temperature dependence is recommended.

10 References

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 IUPAC: <http://www.iupac-kinetic.ch.cam.ac.uk/>.

II.A3.64



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$6.29 \times 10^{-12} \exp[-(3103 \pm 145)/T]$	295–523	Canosa-Mas et al., 1988a, b	DF-A
$(1.85 \pm 0.24) \times 10^{-16}$	295 ± 2		
$(1.7 \pm 0.5) \times 10^{-16}$	300	Biggs et al., 1991; Boyd et al., 1991	(a)
<i>Relative Rate Coefficients</i>			
$(2.16 \pm 0.20) \times 10^{-16}$	296 ± 2	Atkinson et al., 1988	RR (b)

5 Comments

- (a) Stopped-flow technique with optical absorption of the NO_3 radical at 662 nm. The influence of the reaction $\text{NO}_2 + \text{NO}_3 + \text{He} \rightarrow \text{N}_2\text{O}_5 + \text{He}$ was taken into account by numerical modeling, leading to a stoichiometry factor for NO_3 radical decays of ~ 1.9 and the cited rate coefficient for the elementary $\text{NO}_3 + \text{ethene}$ reaction.
- (b) NO_3 radicals were generated by the thermal decomposition of N_2O_5 . A series of rate coefficient ratios were measured, with the concentrations of the organic compounds involved being measured by GC. Based on

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rate coefficient ratios for the sets of organic compounds ethene vs. 2,3-dimethylbutane, 2,3-dimethylbutane vs. tetrahydrofuran, tetrahydrofuran vs. propene, propene vs. thiophene, thiophene vs. bicyclo[2.2.2]-2-octene, and bicyclo[2.2.2]-2-octene vs. *trans*-2-butene, a rate coefficient ratio of $k(\text{NO}_3 + \text{ethene})/k(\text{NO}_3 + \text{trans-2-butene}) = 0.000554 \pm 0.000050$ was obtained. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(\text{NO}_3 + \text{trans-2-butene}) = 3.89 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (Atkinson, 1997).

Preferred Values

$k = 2.1 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 3.3 \times 10^{-12} \exp(-2880/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 270–340 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
 $\Delta (E/R) = \pm 500 \text{ K}$.

Comments on Preferred Values

The preferred rate coefficient is derived using the absolute rate coefficient data of Canosa-Mas et al. (1988a, b) and the relative rate coefficient of Atkinson et al. (1988). These data were fitted to the three parameter expression $k = CT^2 \exp(-D/T)$, resulting in $k = 4.88 \times 10^{-18} T^2 \exp(-2282/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 295–523 K. The preferred Arrhenius expression, $k = A$

6640

$\exp(-B/T)$, is centered at 300 K and is derived from the three parameter expression with $A=C e^2 T^2$ and $B=D + 2T$.

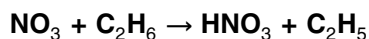
The preferred rate coefficient is in agreement with the 300 K rate coefficient of Biggs et al. (1991) and Boyd et al. (1991).

5 References

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II.A3.65



$$\Delta H^\circ = -3.9 \text{ kJ} \cdot \text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$\leq 4 \times 10^{-18}$	298 ± 2	Wallington et al., 1986	FP-A (a)
$5.7 \times 10^{-12} \exp[-(4426 \pm 337)/T]$	453–553	Bagley et al., 1990	DF-A
2.0×10^{-18}	298*		
5 $\leq (2.7 \pm 0.2) \times 10^{-17}$	302	Boyd et al., 1991	(b)

Comments

- (a) NO_3 radicals were generated by the flash photolysis of ClONO_2 -He mixtures and detected by optical absorption at 662 nm.
- (b) Stopped-flow system with optical absorption detection of the NO_3 radical
 10 at 662 nm. Secondary reactions were expected to lead to a stoichiometry factor of ≥ 2 , leading to the upper limit to the rate coefficient cited in the table.

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Preferred Values

$k < 1 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Comments on Preferred Values

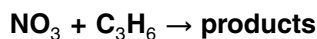
5 Extrapolation of the absolute rate coefficients obtained by Bagley et al. (1990) over the temperature range 453–553 K to 298 K leads to a 298 K rate coefficient of $2 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, probably uncertain to at least a factor of 2 due to the long extrapolation and possible non-Arrhenius behavior of the rate coefficient for this reaction. The preferred upper limit is based on the upper limit of Wallington et al. (1986) and extrapolation to 298 K of the elevated
10 temperature rate coefficients of Bagley et al. (1990).

References

- Bagley, J. A., Canosa-Mas, C., Little, M. R., Parr, A. D., Smith, S. J., Waygood, S. J., and Wayne, R. P.: J. Chem. Soc. Faraday Trans., 86, 2109, 1990.
Boyd, A. A., Canosa-Mas, C. E., King, A. D., Wayne, R. P., and Wilson, M. R.:
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Wallington, T. J., Atkinson, R., Winer, A. M., and Pitts Jr., J. N.: J. Phys. Chem., 90, 4640, 1986.

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II.A3.66



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$4.74 \times 10^{-13} \exp[-(1171 \pm 66)/T]$	298–423	Canosa-Mas et al., 1991	DF-A
$(9.3 \pm 1.2) \times 10^{-15}$	298		
<i>Relative Rate Coefficients</i>			
$(5.4 \pm 1.4) \times 10^{-15}$	300	Morris and Niki, 1974	RR (a)
$(9.2 \pm 0.6) \times 10^{-15}$	300	Japar and Niki, 1975	RR (a)
$(6.4 \pm 1.3) \times 10^{-15}$	298 ± 1	Atkinson et al., 1984	RR (a)
$(7.4 \pm 2.0) \times 10^{-15}$	298 ± 1	Atkinson et al., 1984	RR (b)
$(9.45 \pm 0.47) \times 10^{-15}$	296 ± 2	Atkinson et al., 1988	RR (c)

5 Comments

- (a) NO_3 radicals were generated from the thermal decomposition of N_2O_5 . The experimental data were relative to the equilibrium coefficient K for the $\text{NO}_3 + \text{NO}_2 \leftrightarrow \text{N}_2\text{O}_5$ reactions, and are placed on an absolute basis by use of $K = 2.90 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}$ at 298 K and $2.26 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}$
10 at 300 K (IUPAC, current recommendation).

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- (b) NO_3 radicals were generated from the thermal decomposition of N_2O_5 . The concentrations of propene and *trans*-2-butene were measured by GC, and a rate coefficient ratio of $k(\text{NO}_3 + \text{propene})/k(\text{NO}_3 + \textit{trans}\text{-2-butene}) = 0.019 \pm 0.005$ obtained. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(\text{NO}_3 + \textit{trans}\text{-2-butene}) = 3.90 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Atkinson, 1997).
- (c) NO_3 radicals were generated by the thermal decomposition of N_2O_5 . A series of rate coefficient ratios were measured, with the concentrations of the organic compounds involved being measured by GC. Based on rate coefficient ratios for the sets of organic compounds, propene vs. thiophene, thiophene vs. bicyclo[2.2.2]-2-octene, and bicyclo[2.2.2]-2-octene vs. *trans*-2-butene, a rate coefficient ratio of $k(\text{NO}_3 + \text{propene})/k(\text{NO}_3 + \textit{trans}\text{-2-butene}) = 0.0243 \pm 0.0012$ at $296 \pm 2 \text{ K}$ was obtained. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(\text{NO}_3 + \textit{trans}\text{-2-butene}) = 3.89 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (Atkinson, 1997).

Preferred Values

$k = 9.5 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 4.6 \times 10^{-13} \exp(-1155/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 290–430 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
 $\Delta (E/R) = \pm 300 \text{ K}$.

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Comments on Preferred Values

The preferred values are derived using the room temperature relative rate coefficient of Atkinson et al. (1988) and the 298–423 K absolute rate coefficients of Canosa-Mas et al. (1991). The preferred 298 K rate coefficient is in reasonable agreement with the relative rate measurements of Morris and Niki (1974), Japar and Niki (1975) and Atkinson et al. (1984) when the differing values of the equilibrium constant used for the $\text{N}_2\text{O}_5 \leftrightarrow \text{NO}_3 + \text{NO}_2$ reactions are taken into account, and considering the uncertainties in this equilibrium constant.

The NO_3 radical reaction with propene proceeds by initial addition, leading to the formation under simulated tropospheric conditions of HCHO, CH_3CHO and $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{ONO}_2$ (Bandow et al., 1980; Shepson et al., 1985; Barnes et al., 1990; Hjorth et al., 1990; Atkinson, 1997).

References

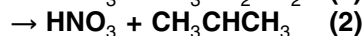
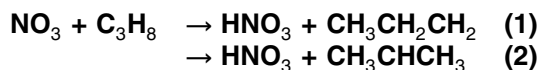
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 Morris Jr., E. D. and Niki, H.: J. Phys. Chem., 78, 1337, 1974.
 Shepson, P. B., Edney, E. O., Kleindienst, T. E., Pittman, J. H., Namie, G. R.,
 5 and Cupitt, L. T.: Environ. Sci. Technol., 19, 849, 1985.

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II.A3.67



$$\Delta H^0 (1) = -3.5 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^0 (2) = -17.7 \text{ kJ}\cdot\text{mol}^{-1}$$

5 Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$\leq (4.8 \pm 1.7) \times 10^{-17}$	298	Boyd et al., 1991	(a)

Comments

- (a) Stopped-flow system with optical absorption detection of the NO_3 radical at 662 nm. The occurrence of secondary reactions is expected to lead to a stoichiometry factor of ≥ 2 , resulting in the upper limit to the rate coefficient cited in the table.
 10

Preferred Values

$$k \leq 7 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

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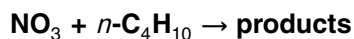
The preferred value is based on the upper limit derived by Boyd et al. (1991).

References

- Boyd, A., Canosa-Mas, C. E., King, A. D., Wayne, R. P., and Wilson, M. R.: J. Chem. Soc. Faraday Trans., 87, 2913, 1991.

6649

II.A3.68



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$\leq 2 \times 10^{-17}$	298 ± 2	Wallington et al., 1986	FP-A (a)
$(4.5 \pm 0.6) \times 10^{-17}$	298	Bagley et al., 1990	DF-A
$(1.44 \pm 0.12) \times 10^{-16}$	333		
$(4.6 \pm 1.2) \times 10^{-16}$	373		
$(1.12 \pm 0.12) \times 10^{-15}$	423		
$(3.2 \pm 0.3) \times 10^{-15}$	473		
$(9.0 \pm 0.4) \times 10^{-15}$	523		
<i>Absolute Rate Coefficients</i>			
$(6.6 \pm 1.7) \times 10^{-17}$	296 ± 2	Atkinson et al., 1984	RR (b)

5 Comments

- (a) NO_3 radicals were generated by the flash photolysis of ClONO_2 at wavelengths >180 nm and monitored by optical absorption at 662 nm.
- (b) NO_3 radicals were produced by the thermal decomposition of N_2O_5 , and the concentrations of *n*-butane and *n*-heptane (the reference organic) were

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measured by GC. A rate coefficient ratio of $k(\text{NO}_3 + n\text{-butane})/k(\text{NO}_3 + n\text{-heptane}) = 0.48 \pm 0.12$ was obtained and is placed on an absolute basis by use of a rate coefficient of $k(\text{NO}_3 + n\text{-heptane}) = 1.37 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (Atkinson, 1991).

5 Preferred Values

$k = 4.6 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 2.8 \times 10^{-12} \exp(-3280/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 290–430 K.

Reliability

10 $\Delta \log k = \pm 0.2$ at 298 K.
 $\Delta (E/R) = \pm 400 \text{ K}$.

Comments on Preferred Values

The preferred values are based on the absolute rate coefficients measured by Bagley et al. (1990) over the temperature range 298–423 K (at temperatures
15 above 423 K the Arrhenius plot exhibits upward curvature, especially above 473 K). A least-squares analysis of the 298–423 K rate coefficients of Bagley et al. (1990) results in the preferred Arrhenius expression. The preferred rate coefficient at 298 K is at least a factor of 2 higher than the upper limit reported by Wallington et al. (1986), but is in agreement within the measurement un-
20 certainties with the relative rate coefficient of Atkinson et al. (1984). At room temperature and below the reaction proceeds mainly by H-atom abstraction from the CH_2 groups (Bagley et al., 1990; Atkinson, 1991).

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References

- Atkinson, R.: J. Phys. Chem. Ref. Data, 20, 459, 1991.
Atkinson, R., Plum, C. N., Carter, W. P. L., Winer, A. M., and Pitts Jr., J. N.: J. Phys. Chem., 88, 2361, 1984.
5 Bagley, J. A., Canosa-Mas, C., Little, M. R., Parr, A. D., Smith, S. J., Waygood, S. J., and Wayne, R. P.: J. Chem. Soc. Faraday Trans., 86, 2109, 1990.
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6652

II.A3.69

NO₃ + CH₂=C(CH₃)CH=CH₂ (isoprene) → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.3 \pm 0.14) \times 10^{-12}$	298	Benter and Schindler, 1988	DF-MS
$3.03 \times 10^{-12} \exp[-(450 \pm 70)/T]$	251–381	Dlugokencky and Howard, 1989	F-LIF (a)
$(6.52 \pm 0.78) \times 10^{-13}$	297		
$(7.30 \pm 0.44) \times 10^{-13}$	298	Wille et al., 1991	DF-MS
$(8.26 \pm 0.60) \times 10^{-13}$	298	Wille et al., 1991; Lancar et al., 1991	DF-MS
$(1.07 \pm 0.20) \times 10^{-12}$	295 ± 2	Ellermann et al., 1992	PR-A (b)
$(7.3 \pm 0.2) \times 10^{-13}$	298 ± 2	Suh et al., 2001	F-CIMS (c)
<i>Relative Rate Coefficients</i>			
$(5.94 \pm 0.16) \times 10^{-13}$	295 ± 1	Atkinson et al., 1984	RR (d)
$(1.21 \pm 0.20) \times 10^{-12}$	298 ± 2	Barnes et al., 1990	RR (e)
$(6.86 \pm 0.55) \times 10^{-13}$	298	Berndt and Böge, 1997	RR (f)

5 Comments

(a) NO₂ radicals were generated by thermal decomposition of N₂O₅ in a flow system at total pressures of 1.0–1.1 Torr (1.3–1.5 mbar), and monitored by LIF.

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(b) NO₃ radicals were generated by pulse radiolysis of SF₆-HNO₃-isoprene mixtures at 1 bar total pressure, and monitored by optical absorption at 662 nm.

5 (c) NO₃ radicals were generated by thermal decomposition of N₂O₅ in a flow system at total pressures of 5.1–6.0 Torr (6.8–8.0 mbar), and monitored by CIMS using the reaction NO₃+SF₆⁻ → NO₃⁻+SF₆.

10 (d) Relative rate method carried out at atmospheric pressure of air. NO₃ radicals were generated by thermal decomposition of N₂O₅. The concentrations of isoprene and *trans*-2-butene (the reference compound) were measured by GC. Small corrections (2–4%) to the measured isoprene concentrations were made to take into account the gas-phase reaction of isoprene with NO₂ (Atkinson et al., 1984; Atkinson, 1997). The resulting rate coefficient ratio of $k(\text{NO}_3 + \text{isoprene})/k(\text{NO}_3 + \text{trans-2-butene}) = 1.53 \pm 0.04$ is placed on an absolute basis by use of a rate coefficient of $k(\text{NO}_3 + \text{trans-2-butene}) = 3.88 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 295 K (Atkinson, 1997).

20 (e) Relative rate method carried out at atmospheric pressure of synthetic air. NO₃ radicals were generated by thermal decomposition of N₂O₅. The concentrations of isoprene and *trans*-2-butene (the reference compound) were measured by GC. No corrections for the reaction of isoprene with NO₂ were found to be necessary. The measured rate coefficient ratio of $k(\text{NO}_3 + \text{isoprene})/k(\text{NO}_3 + \text{trans-2-butene}) = 3.1 \pm 0.5$ is placed on an absolute basis by use of a rate coefficient of $k(\text{NO}_3 + \text{trans-2-butene}) = 3.90 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Atkinson, 1997).

25 (f) Relative rate method carried out in a flow system at a total pressure of 6.8 mbar (5.1 Torr) of N₂. NO₃ radicals were generated by thermal decomposition of N₂O₅. The concentrations of isoprene and *trans*-2-butene (the

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reference compound) were measured by GC. The measured rate coefficient ratio of $k(\text{NO}_3 + \text{isoprene})/k(\text{NO}_3 + \text{trans-2-butene}) = 1.76 \pm 0.14$ is placed on an absolute basis by use of a rate coefficient of $k(\text{NO}_3 + \text{trans-2-butene}) = 3.90 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Atkinson, 1997).

5 Preferred Values

$k = 7.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 3.15 \times 10^{-12} \exp(-450/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250–390 K.

Reliability

10 $\Delta \log k = \pm 0.2$ at 298 K.
 $\Delta (E/R) = \pm 200 \text{ K}$.

Comments on Preferred Values

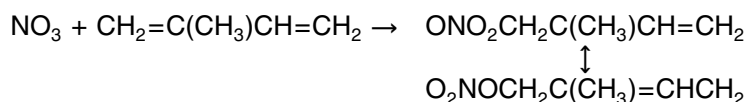
The measured room temperature rate coefficients range over a factor of 2.2, irrespective of whether absolute or relative rate methods were used. The study of Wille et al. (1991) is stated to supersede the earlier study of Benter and Schindler (1988) carried out over a more restricted range of conditions (and in which heterogeneous reactions between isoprene and F_2 could have occurred; Wille et al., 1991). The only temperature dependent measurements of the kinetics of this reaction are from Dlugokencky and Howard (1989). The preferred 298 K rate coefficient is an average of the room temperature absolute and relative rate coefficients of Dlugokencky and Howard (1989), Wille et al. (1991), Lancar et al. (1991), Suh et al. (2001), Atkinson et al. (1984) and

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Berndt and Böge (1997), which are in reasonably good agreement. The temperature dependence of Dlugokencky and Howard (1989) is accepted, and the pre-exponential factor is calculated from the 298 K preferred rate coefficient and the temperature dependence.

5 The reaction proceeds by initial addition of the NO_3 radical to the carbon-carbon double bonds (Atkinson, 1997). At low pressures the products are NO_2 plus an oxirane (Atkinson, 1997). The formation yield of the oxirane decreases with increasing total pressure and with increasing O_2 concentration (Atkinson, 1997), with oxirane formation at atmospheric pressure of air being of no importance (Atkinson, 1997; Skov et al., 1994). Using in situ FTIR spectroscopy, Skov et al. (1992) reported that the products formed at atmospheric pressure of air are $\text{O}_2\text{NOCH}_2\text{C}(\text{CH}_3)=\text{CHCHO}$ as the major product, and with $\text{O}_2\text{NOCH}_2\text{CH}=\text{C}(\text{CH}_3)\text{CHO}$, $\text{O}_2\text{NOCH}_2\text{C}(\text{O})\text{C}(\text{CH}_3)=\text{CH}_2$, $\text{O}_2\text{NOCH}_2\text{CH}(\text{OH})\text{C}(\text{CH}_3)=\text{CH}_2$ and $\text{O}_2\text{NOCH}_2\text{C}(\text{CH}_3)=\text{CHCH}_2\text{OH}$ as minor products. Using atmospheric pressure ionization tandem mass spectrometry Kwok et al. (1996) observed $\text{O}_2\text{NOCH}_2\text{C}(\text{CH}_3)=\text{CHCHO}$ (and isomers), $\text{O}_2\text{NOCH}_2\text{C}(\text{CH}_3)=\text{CHCH}_2\text{OH}$ (and isomers), $\text{O}_2\text{NOCH}_2\text{C}(\text{CH}_3)=\text{CHCH}_2\text{OOH}$ (and isomers), and $\text{HOCH}_2\text{C}(\text{CH}_3)=\text{CHCHO}$ (and isomers) as products of the reaction (again at atmospheric pressure of air). Kwok et al. (1996) also observed the formation of methacrolein and methyl vinyl ketone, with measured formation yields of each of these α,β -unsaturated carbonyls being $3.5 \pm 1.4\%$.

20 The FTIR study of Skov et al. (1992) indicates that the NO_3 radical adds dominantly to the 1- and 4-positions, in a 3.5:1 ratio. At atmospheric pressure of air, the reaction then proceeds mainly by,



25 followed by addition of O_2 to form the corresponding peroxy radicals

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ONO₂CH₂C(OO)(CH₃)CH=CH₂ and O₂NOCH₂C(CH₃)=CHCH₂OO. These peroxy radicals then react with NO, NO₂, HO₂ and organic peroxy radicals (Atkinson, 1997), depending on the concentrations of these species.

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II.A3.70

NO₃ + α-Pinene → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.19 \times 10^{-12} \exp[(490 \pm 70)/T]$	261–384	Dlugokencky and Howard, 1989	F-LIF(a)
$(6.18 \pm 0.74) \times 10^{-12}$	298		
$3.5 \times 10^{-13} \exp[(841 \pm 144)/T]$	298–423	Martínez et al., 1998	DF-LIF(b)
$(5.9 \pm 0.8) \times 10^{-12}$	298		
<i>Relative Rate Coefficients</i>			
$(5.82 \pm 0.16) \times 10^{-12}$	295 ± 1	Atkinson et al., 1984	RR(c)
$(6.56 \pm 0.94) \times 10^{-12}$	298 ± 2	Barnes et al., 1990	RR(d)

5 Comments

- (a) NO₃ radicals were generated by the thermal decomposition of N₂O₂ at ~400 K. Experiments were carried out in a low-pressure flow tube at ~1.3–1.4 mbar of He diluent. The NO₂ yield at 1.3 mbar He and 298 K was 67%.
- 10 (b) Carried out under conditions such that a second-order kinetic analysis was necessary.

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- (c) NO_3 radicals were generated by the thermal decomposition of N_2O_5 . The concentrations of α -pinene and 2-methyl-2-butene (the reference compound) were monitored by GC in reacting N_2O_5 - NO_2 - α -pinene-2-methyl-2-butene-air mixtures at 980 mbar pressure in a ~ 6400 L Teflon chamber. The measured rate coefficient ratio $k(\text{NO}_3 + \alpha\text{-pinene})/k(\text{NO}_3 + 2\text{-methyl-2-butene}) = 0.621 \pm 0.017$ is placed on an absolute basis by use of a rate coefficient at 295 K of $k(\text{NO}_3 + 2\text{-methyl-2-butene}) = 9.37 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Arey, 2003a).
- (d) NO_3 radicals were generated by the thermal decomposition of N_2O_5 . The concentrations of α -pinene and 2-methyl-2-butene (the reference compound) were monitored by GC in reacting N_2O_5 - α -pinene-2-methyl-2-butene-air mixtures at 1 bar pressure in a 420 L glass reaction vessel. The measured rate coefficient ratio $k(\text{NO}_3 + \alpha\text{-pinene})/k(\text{NO}_3 + 2\text{-methyl-2-butene}) = 0.70 \pm 0.10$ is placed on an absolute basis by use of a rate coefficient at 298 K of $k(\text{NO}_3 + 2\text{-methyl-2-butene}) = 9.37 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Arey, 2003a).

Preferred Values

$k = 6.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 1.2 \times 10^{-12} \exp(490/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 260–390 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.
 $\Delta (E/R) = \pm 300$ K.

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Comments on Preferred Values

The room temperature relative rate coefficients of Atkinson et al. (1984) and Barnes et al. (1990) and the absolute rate coefficients of Dlugokencky and Howard (1989) and Martínez et al. (1998) are in excellent agreement. However, the temperature dependencies obtained by Dlugokencky and Howard (1989) and Martínez et al. (1998) differ significantly. Because the study of Dlugokencky and Howard (1989) extends to lower temperatures representative of the troposphere, the data from the studies of Atkinson et al. (1984), Dlugokencky and Howard (1989) and Barnes et al. (1990) are used in the evaluation of the rate coefficient for this reaction. The preferred values are obtained from a least-squares fit of the rate coefficients of Atkinson et al. (1984), Dlugokencky and Howard (1989) and Barnes et al. (1990). There is no evidence for a pressure dependence of the rate coefficient over the range ~ 1 –1000 mbar, at least at room temperature.

The reaction proceeds by initial addition of NO_3 to the C=C bond. At low pressures or in the absence of O_2 , the initially formed nitrooxyalkyl radicals eliminate NO_2 and form α -pinene oxide (Dlugokencky and Howard, 1989; Atkinson, 1991; Berndt and Böge, 1997). At atmospheric pressure of air, O_2 addition to the nitrooxyalkyl radicals forms two nitrooxyalkyl peroxy radicals, although some α -pinene oxide ($3 \pm 0.5\%$) is still observed at 1 bar of air (Wängberg et al., 1997). The nitrooxyalkyl peroxy radicals then react with HO_2 radicals, organic peroxy radicals, NO , NO_2 , and NO_3 radicals, leading to the observed products (Atkinson and Arey, 2003a, b). Under laboratory conditions, the observed products and their yields at atmospheric pressure of air are: pinonaldehyde, $62 \pm 4\%$ (Wängberg et al., 1997) and 69% (Hallquist et al., 1999); 2-hydroxypinan-3-nitrate, $5 \pm 0.4\%$ (Wängberg et al., 1997); 3-oxopinane-2-nitrate, $3 \pm 0.2\%$ (Wängberg et al., 1997); and α -pinene oxide, $3 \pm 0.5\%$ (Wängberg et al., 1997).

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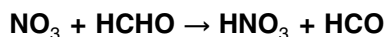
al., 1997), with a total organic nitrate yield of 14–19% (Wängberg et al., 1997; Hallquist et al., 1999). Note that the products formed in the atmosphere, and their yields, may be different from those observed in laboratory studies, because of the differing concentrations (both absolute and relative) of HO₂, RO₂ and NO₃ radicals and NO and NO₂.

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II.A3.71



$$\Delta H^\circ = -57.1 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
5.6×10^{-16}	298 ± 2	Cantrell et al., 1985	(a)
<i>Relative Rate Coefficients</i>			
$(5.01 \pm 0.41) \times 10^{-16}$	298 ± 1	Atkinson et al., 1984	(b,c)
$(8.4 \pm 1.5) \times 10^{-16}$	298 ± 2	Cantrell et al., 1985	(c,d)
5 $(1.21 \pm 0.25) \times 10^{-15}$	295 ± 2	Hjorth et al., 1988	(b,c,d,e)

Comments

- (a) NO₃ radicals were generated in situ from the reaction NO₂+O₃ →NO₃+O₂. NO₃ radical concentrations were measured by differential optical absorption spectroscopy (DOAS), and the rate coefficient derived from the concentrations of reactants and products measured by FTIR absorption spectroscopy and by DOAS (for the NO₃ radical and NO₂).
- 10 (b) NO₃ radicals were generated by the thermal decomposition of N₂O₅.

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- (c) Relative to the equilibrium coefficient K for the reactions $\text{NO}_2 + \text{NO}_3 \leftrightarrow \text{N}_2\text{O}_5$. The experimental data are placed on an absolute basis by use of an equilibrium coefficient of $K = 2.90 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}$ at 298 K and $4.22 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}$ at 295 K (IUPAC, current recommendation).
- (d) NO_3 radicals were generated in situ from the reaction $\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3 + \text{O}_2$.
- (e) Note that while the equilibrium coefficient used in the data analysis of Hjorth et al. (1988) was stated to be from Graham and Johnston (1978) ($3.43 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}$ at 295 K), the value used (Hjorth et al., 1988) was $1.88 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}$.

Preferred Values

$k = 5.6 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

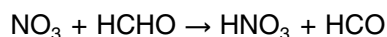
Comments on Preferred Values

The relative rate coefficients measured by Atkinson et al. (1984), Cantrell et al. (1985) and Hjorth et al. (1988) disagree by a factor of ~ 2.5 when a consistent temperature-dependent equilibrium coefficient for the $\text{NO}_2 + \text{NO}_3 \leftrightarrow \text{N}_2\text{O}_5$ reactions is used to place the rate coefficients on an absolute basis. The rate coefficient obtained by Cantrell et al. (1985) from experiments in which NO_3

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radicals were measured directly by DOAS (and hence derivation of the rate coefficient does not involve the equilibrium coefficient for the $\text{NO}_2 + \text{NO}_3 \leftrightarrow \text{N}_2\text{O}_5$ reactions) falls within the range of these relative rate coefficients (Atkinson et al., 1984; Cantrell et al., 1985; Hjorth et al., 1988).

Accordingly, the preferred value of $k = 5.6 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K is based on the absolute rate measurements of Cantrell et al. (1985), with the uncertainty limits reflecting the single absolute study. While no temperature dependence of the rate coefficient has been measured to date, by analogy with the NO_3 radical reaction with CH_3CHO a pre-exponential factor of $\sim 2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is expected, and hence $k(\text{NO}_3 + \text{HCHO}) \sim 2 \times 10^{-12} \exp(-2440/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. This reaction proceeds by H-atom abstraction.

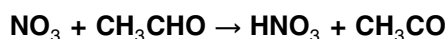


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II.A3.72



$$\Delta H^\circ = -53.0 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.44 \times 10^{-12} \exp[-(1860 \pm 300)/T]$	264–374	Dlugokencky and Howard, 1989	F-LIF (a)
$(2.74 \pm 0.33) \times 10^{-15}$	298		
$6.2 \times 10^{-11} \exp[-(2826 \pm 866)/T]$	298–433	Cabañas et al., 2001	DF-LIF (b)
$(3.2 \pm 0.8) \times 10^{-15}$	298 ± 2		
<i>Relative Rate Coefficients</i>			
$(2.17 \pm 0.55) \times 10^{-15}$	300	Morris and Niki, 1974	RR (c)
$(2.08 \pm 0.52) \times 10^{-15}$	298 ± 1	Atkinson et al., 1984	RR (c)
$(2.69 \pm 0.52) \times 10^{-15}$	299 ± 1	Cantrell et al., 1986	RR (c)
$(2.62 \pm 0.29) \times 10^{-15}$	298 ± 2	D'Anna et al., 2001a, b	RR (d)

Comments

(a) NO_3 radicals were generated by the thermal dissociation of N_2O_5 in a flow system. Initial NO_3 radical concentrations were $(0.6\text{--}3.0) \times 10^{10} \text{ molecule cm}^{-3}$.

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(b) Initial NO_3 radical concentrations were $(0.6\text{--}3.0) \times 10^{12} \text{ molecule cm}^{-3}$.

(c) The cited rate coefficients are relative to the equilibrium coefficient K for the reactions $\text{NO}_2 + \text{NO}_2 \leftrightarrow \text{N}_2\text{O}_5$, with values of $K = 2.90 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}$ at 298 K, $2.56 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}$ at 299 K and $2.26 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1}$ at 300 K being used (IUPAC, current recommendation) to place the measured rate coefficient ratios on an absolute basis.

(d) Relative rate method, with NO_3 radicals being generated by the thermal dissociation of N_2O_5 . Experiments were carried out in 1 atmosphere of air with measurements of acetaldehyde and 1-butene (the reference compound) by FTIR spectroscopy. The measured rate coefficient ratio $k(\text{NO}_3 + \text{acetaldehyde})/k(\text{NO}_3 + 1\text{-butene}) = 0.194 \pm 0.021$ is placed on an absolute basis by use of a rate coefficient of $k(\text{NO}_3 + 1\text{-butene}) = 1.35 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Atkinson, 1997). Experiments with acetaldehyde- d_1 (CH_3CDO) yielded a rate coefficient ratio $k(\text{NO}_3 + \text{CH}_3\text{CHO})/k(\text{NO}_3 + \text{CH}_3\text{CDO}) = 2.37 \pm 0.08$ at $298 \pm 2 \text{ K}$ (D'Anna et al., 2001b).

Preferred Values

$k = 2.7 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 1.4 \times 10^{-12} \exp(-1860/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 260–380 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
 $\Delta (E/R) = \pm 500 \text{ K}$.

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The rate coefficients measured relative to the equilibrium coefficient for the reactions $\text{NO}_2 + \text{NO}_3 \leftrightarrow \text{N}_2\text{O}_5$ are subject to significant uncertainties arising from uncertainties in the equilibrium coefficient for these reactions, and the relative rate coefficients of Morris and Niki (1974), Atkinson et al. (1984) and Cantrell et al. (1986) are therefore not used in the evaluation of the rate coefficient for this reaction (although they are in agreement with the absolute room temperature rate coefficient of Dlugokencky and Howard (1989)). The room temperature rate coefficient of D'Anna et al. (2001a, b), determined relative to that for the reaction of NO_3 radicals with 1-butene, is in excellent agreement with the absolute rate coefficient measured by Dlugokencky and Howard (1989). The absolute study of Cabañas et al. (2001) employed much higher initial NO_3 radical concentrations than did Dlugokencky and Howard (1989) (by a factor of ~ 100) and the measured rate coefficients (Cabañas et al., 2001) are significantly less precise and show a significantly higher temperature dependence.

The preferred values are based upon the absolute rate coefficient study of Dlugokencky and Howard (1989). The significant deuterium isotope effect observed by D'Anna et al. (2001b) indicates that, as expected, the reaction proceeds by H- (or D-) atom abstraction from the -CHO (or -CDO) group.

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II.A3.73



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.7 \times 10^{-11} \exp[-(2250 \pm 192)/T]$ $(6.0 \pm 0.6) \times 10^{-15}$	298–433 298 ± 2	Cabañas et al., 2001	DF-LIF
<i>Relative Rate Coefficients</i>			
$(5.80 \pm 0.48) \times 10^{-15}$	298 ± 2	D'Anna and Nielsen, 1997	RR (a)
$(7.28 \pm 0.41) \times 10^{-15}$	296 ± 2	Papagni et al., 2001	RR (b)
$(6.18 \pm 0.57) \times 10^{-15}$	298 ± 2	D'Anna et al., 2001	RR (a)

5 Comments

(a) Relative rate method, with NO_3 radicals being generated by the thermal dissociation of N_2O_5 . Experiments were carried out in 1 atmosphere of air with measurements of propanal and propene (the reference compound) by FTIR spectroscopy. The measured rate coefficient ratios $k(\text{NO}_3 + \text{propanal})/k(\text{NO}_3 + \text{propene}) = 0.61 \pm 0.05$ (D'Anna and Nielsen, 1997) and 0.65 ± 0.06 (D'Anna et al., 2001) are placed on an absolute basis by use of a rate coefficient of $k(\text{NO}_3 + \text{propene}) = 9.5 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (IUPAC, current recommendation).

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(b) Relative rate method, with NO_3 radicals being generated by the thermal dissociation of N_2O_5 . Experiments were carried out in 1 atmosphere of air with measurements of propanal and methacrolein (the reference compound) by GC. The measured rate coefficient ratio $k(\text{NO}_3 + \text{propanal})/k(\text{NO}_3 + \text{methacrolein}) = 2.14 \pm 0.12$ is placed on an absolute basis by use of a rate coefficient of $k(\text{NO}_3 + \text{methacrolein}) = 3.4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (IUPAC, current recommendation).

Preferred Values

$k = 6.4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

10 Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of the room temperature relative rate coefficients of D'Anna et al. (1997, 2001) and Papagni et al. (2001), which are in reasonable agreement and which also agree with the absolute room temperature rate coefficient of Cabañas et al. (2001). Because of the higher temperature dependence obtained by Cabañas et al. (2001) for the reactions of NO_3 radicals with acetaldehyde and butanal than by other investigators (IUPAC, this evaluation) and because the rate coefficient at 298 K calculated from the Arrhenius expression of Cabañas et al. (2001) is 50% higher than their measured value, the Cabañas et al. (2001) data are not used in the evaluation of the rate coefficient for this reaction, and no recommendation is made

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concerning the temperature dependence for this reaction.

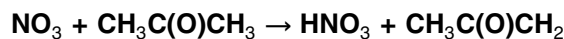
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6671

II.A3.74



$$\Delta H^\circ = -15.5 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
5 $\leq (8.5 \pm 2.5) \times 10^{-18}$	302	Boyd et al., 1991	(a)

Comments

- (a) Stopped flow system with detection of the NO_3 radical by optical absorption at 662 nm. Secondary reactions were believed to be important and a stoichiometry factor of ≥ 2 has been used to obtain the cited upper limit to the rate coefficient.
- 10

Preferred Values

$$k < 3 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The upper limit to the preferred value is derived from the overall rate coefficient of $(1.7 \pm 0.5) \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ measured by Boyd et al. (1991),

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with no account taken of the expected greater than unity stoichiometry.

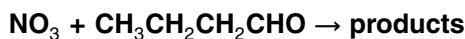
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6673

II.A3.75



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.26 \times 10^{-12} \exp(-1478/T)$	267–332	Ullerstam et al., 2000	DF-RA (a)
$(1.1 \pm 0.1) \times 10^{-14}$	296		
$7.6 \times 10^{-11} \exp[-(2466 \pm 505)/T]$	298–433	Cabañas et al., 2001	DF-LIF
$(1.46 \pm 0.16) \times 10^{-14}$	298 ± 2		
<i>Relative Rate Coefficients</i>			
$(1.09 \pm 0.09) \times 10^{-14}$	298 ± 2	D'Anna and Nielsen, 1997	RR (b)
$(1.04 \pm 0.11) \times 10^{-14}$	297 ± 2	Ullerstam et al., 2000	RR (c)
$(1.15 \pm 0.06) \times 10^{-14}$	296 ± 2	Papagni et al., 2001	RR (d)
$(1.23 \pm 0.11) \times 10^{-14}$	298 ± 2	D'Anna et al., 2001	RR (b)

5 Comments

- (a) Carried out in the presence of 20% O₂ in the diluent gas to minimize secondary reactions (experiments in the absence of O₂ yielded rate coefficients a factor of ~3 higher (Ullerstam et al., 2000)). The Arrhenius expression cited in the table is obtained from a least-squares analysis of the measured rate coefficients at 267 K, 296 K and 332 K.

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- (b) Relative rate method, with NO_3 radicals being generated by the thermal dissociation of N_2O_5 . Experiments were carried out in 1 atmosphere of air with measurements of butanal and 1-butene (the reference compound) by FTIR spectroscopy. The measured rate coefficient ratios $k(\text{NO}_3 + \text{butanal})/k(\text{NO}_3 + \text{1-butene}) = 0.81 \pm 0.06$ (D'Anna and Nielsen, 1997) and 0.91 ± 0.08 (D'Anna et al., 2001) are placed on an absolute basis by use of a rate coefficient of $k(\text{NO}_3 + \text{1-butene}) = 1.35 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Atkinson, 1997).
- (c) Relative rate method, with NO_3 radicals being generated by the thermal dissociation of N_2O_5 . Experiments were carried out in 1 atmosphere of synthetic air or N_2 with measurements of butanal and propene (the reference compound) by FTIR spectroscopy. The measured rate coefficient ratios $k(\text{NO}_3 + \text{butanal})/k(\text{NO}_3 + \text{propene}) = 1.1 \pm 0.1$ is placed on an absolute basis by use of a rate coefficient of $k(\text{NO}_3 + \text{propene}) = 9.42 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 297 K (IUPAC, current recommendation). The rate coefficient ratio was independent of the presence or absence of O_2 .
- (d) Relative rate method, with NO_3 radicals being generated by the thermal dissociation of N_2O_5 . Experiments were carried out in 1 atmosphere of air with measurements of butanal and methacrolein (the reference compound) by GC. The measured rate coefficient ratio $k(\text{NO}_3 + \text{butanal})/k(\text{NO}_3 + \text{methacrolein}) = 3.38 \pm 0.15$ is placed on an absolute basis by use of a rate coefficient of $k(\text{NO}_3 + \text{methacrolein}) = 3.4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (IUPAC, current recommendation).

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Preferred Values

$k = 1.1 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 1.7 \times 10^{-12} \exp(-1500/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 260–340 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

$\Delta (E/R) = \pm 500 \text{ K}$.

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of the room temperature relative rate coefficients of D'Anna and Nielsen (1977), D'Anna et al. (2001), Ullerstam et al. (2000) and Papagni et al. (2001) and the absolute rate coefficient of Ullerstam et al. (2000) (measured in the presence of O_2). The absolute rate coefficient measured at 298 K by Cabañas et al. (2001) is 20–40% higher than the other absolute and relative rate coefficients (D'Anna and Nielsen, 1997; D'Anna et al., 2001; Papagni et al., 2001; Ullerstam et al., 2000), possibly indicating the occurrence of secondary reactions. The two measurements of the temperature dependence (Cabañas et al., 2001; Ullerstam et al., 2000) disagree significantly, with the pre-exponential factor derived from the study of Cabañas et al. (2001) being within a factor of ~ 5 of gas kinetic. The preferred temperature dependence is that obtained from the study of Ullerstam et al. (2000), with a high uncertainty.

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II.A3.76



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$2.9 \times 10^{-12} \exp(-1724 \pm 142)/T$	264–364	Ullerstam et al., 2000	DF-LPA (a)
$(0.9 \pm 0.1) \times 10^{-14}$	298		
$1.0 \times 10^{-10} \exp[-(2598 \pm 384)/T]$	298–433	Cabañas et al., 2003	DF-LIF (b)
$(1.61 \pm 0.13) \times 10^{-14}$	298		
<i>Relative Rate Coefficients</i>			
$(1.26 \pm 0.14) \times 10^{-14}$	298	D'Anna et al., 2001	RR-FTIR (c)
$(1.20 \pm 0.20) \times 10^{-14}$	298	Ullerstam et al., 2000	RR-FTIR (d)

5 Comments

- (a) NO_3 radicals were generated by $\text{F} + \text{HNO}_3$ reaction at 2.5 mbar total pressure and monitored by long path absorption at 661.8 nm; pseudo first-order conditions. Experiments conducted with and without 20% O_2 added to the He carrier gas to inhibit potential secondary reactions. With added O_2 the rate coefficients were approximately a factor of 3 lower, but showed a similar E_a .
- 10 The cited 298 K value was obtained in the presence of O_2 ; the

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Arrhenius expression was obtained by correction of all data for contribution of secondary reactions.

- (b) NO_3 radicals were generated by $\text{F} + \text{HNO}_3$ reaction at 1.5 mbar total pressure, and monitored by LIF excited at 662 nm. Secondary reactions were considered to be unimportant but no supporting tests were reported.
- (c) Relative rate method carried out at 1013 mbar pressure of air. NO_3 radicals were generated by thermal decomposition of N_2O_5 . The concentrations of 2-methylpropanal and 1-butene (the reference compound) were measured by GC. The resulting rate coefficient ratio of $k(\text{NO}_3 + 2\text{-methylpropanal})/k(\text{NO}_3 + 1\text{-butene}) = 0.93 \pm 0.10$ is placed on an absolute basis by use of a rate coefficient of $k(\text{NO}_3 + 1\text{-butene}) = 1.35 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Atkinson, 1997).
- (d) Relative rate method carried out at 1013 mbar pressure of air. NO_3 radicals were generated by thermal decomposition of N_2O_5 . The concentrations of 2-methylpropane and propenal (the reference compound) were measured by GC. The resulting rate coefficient ratio of $k(\text{NO}_3 + 2\text{-methylpropanal})/k(\text{NO}_3 + \text{propene}) = 1.3 \pm 0.10$ is placed on an absolute basis by use of a rate coefficient of $k(\text{NO}_3 + \text{propene}) = 9.5 \pm 1.2 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (IUPAC, 2004).

Preferred Values

$k = 1.25 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 4.0 \times 10^{-12} \exp(-1720/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 260–420 K.

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Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
 $\Delta (E/R) = \pm 300$ K.

Comments on Preferred Values

The room temperature rate coefficients from relative rate measurements are in excellent agreement. The results of the absolute determinations at 298 K are in less good agreement and are higher; the measurements are complicated by secondary reactions leading to excessive NO_3 loss. Ullerstam et al. (2000) show that the observed rate coefficient is reduced in the presence of O_2 due to suppression the secondary reactions. Their value of k at 298 K with O_2 present is within experimental uncertainty of the relative rate values. The preferred value at 298 K is a mean of the values from the relative rate studies.

The temperature dependence of the rate coefficient was only investigated in the absolute studies. The data are presented in Fig. 5. Ullerstam et al. (2000) observed a similar activation energy both with and without O_2 present, suggesting that the temperature dependence is not influenced significantly by secondary reactions. The data of Cabañas et al. above 298 K actually agree well with those of Ullerstam et al. (2000) (without O_2); their apparently larger temperature dependence and unreasonably high A-factor, results from inclusion of the lower 298 K value, which must be considered suspect without proper correction for secondary reactions. The preferred temperature dependence adopts the E/R value of Ullerstam et al. (2000) with an A factor adjusted to give the preferred value of k at 298 K.

The reaction products are likely to be $\text{HNO}_3 + (\text{CH}_3)_2\text{CHC(O)}$.

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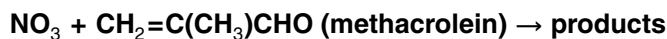
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Ullerstam, M., Langer, S., and Ljungström, E.: Int. J. Chem. Kinet., 32, 294, 2000.

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II.A3.77



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$\leq 8 \times 10^{-15}$	298	Rudich et al., 1996	F-A (a)
<i>Relative Rate Coefficients</i>			
$(4.46 \pm 0.58) \times 10^{-15}$	296 ± 2	Kwok et al., 1996	RR (b)
$(3.08 \pm 0.18) \times 10^{-15}$	298 ± 2	Chew et al., 1997	RR (c)
$(3.50 \pm 0.15) \times 10^{-15}$	298 ± 2	Chew et al., 1997	RR (d)
$(3.72 \pm 0.47) \times 10^{-15}$	296 ± 2	Canosa-Mas et al., 1999	RR (e)

5 Comments

- (a) NO_3 radicals were generated by thermal decomposition of N_2O_5 in a flow system at total pressures of 1.5–3 Torr (2–4 mbar), and monitored by absorption at 661.9 nm.
- (b) Relative rate method carried out at atmospheric pressure of air. NO_3 radicals were generated by thermal decomposition of N_2O_5 . The concentrations of methacrolein and propene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(\text{NO}_3 + \text{methacrolein})/k(\text{NO}_3 + \text{propene}) = 0.48 \pm 0.06$ is placed on an absolute

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basis by use of a rate coefficient of $k(\text{NO}_3 + \text{propene}) = 9.29 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (IUPAC, current recommendation).

- (c) Relative rate method carried out at atmospheric pressure of air. NO_3 radicals were generated by thermal decomposition of N_2O_5 . The concentrations of methacrolein and propene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(\text{NO}_3 + \text{methacrolein})/k(\text{NO}_3 + \text{propene}) = 0.324 \pm 0.017$ is placed on an absolute basis by use of a rate coefficient of $k(\text{NO}_3 + \text{propene}) = 9.5 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (IUPAC, current recommendation).
- (d) Relative rate method carried out at atmospheric pressure of air. NO_3 radicals were generated by thermal decomposition of N_2O_5 . The concentrations of methacrolein and 1-butene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(\text{NO}_3 + \text{methacrolein})/k(\text{NO}_3 + 1\text{-butene}) = 0.259 \pm 0.011$ is placed on an absolute basis by use of a rate coefficient of $k(\text{NO}_3 + 1\text{-butene}) = 1.35 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (Atkinson, 1997).
- (e) Relative rate method carried out at atmospheric pressure of N_2 . NO_3 radicals were generated by thermal decomposition of N_2O_5 . The concentrations of methacrolein and propene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(\text{NO}_3 + \text{methacrolein})/k(\text{NO}_3 + \text{propene}) = 0.40 \pm 0.05$ is placed on an absolute basis by use of a rate coefficient of $k(\text{NO}_3 + \text{propene}) = 9.29 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (IUPAC, current recommendation). An absolute rate coefficient of $(9.6 \pm 2.0) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was also measured at $300 \pm 7 \text{ K}$ using a discharge flow system with LIF detection of NO_3 radicals.

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Preferred Values

$k = 3.4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

5 *Comments on Preferred Values*

The 298 K preferred value is the average of the relative rate coefficients of Chew et al. (1998) (which supersedes the earlier and less extensive study of Kwok et al., 1996) and Canosa-Mas et al. (1999), which are in good agreement and are consistent with the upper limit reported by Rudich et al. (1996).

- 10 The room temperature rate coefficient is similar to that for reaction of NO_3 radicals with acetaldehyde (IUPAC, this evaluation), and the reaction is expected to proceed mainly by H-atom abstraction from the CHO group.

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II.A3.78**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$\leq 1.2 \times 10^{-16}$	298	Rudich et al., 1996	F-A (a)
<i>Relative Rate Coefficients</i>			
$< 6 \times 10^{-16}$	296 ± 2	Kwok et al., 1996	RR (b)
$(5.0 \pm 1.2) \times 10^{-16}$	296 ± 2	Canosa-Mas et al., 1999	RR (c)

5 Comments

- (a) NO_3 radicals were generated by thermal decomposition of N_2O_5 in a flow system at total pressures of 1.5–3 Torr (2–4 mbar), and monitored by absorption at 661.9 nm. A rate coefficient of $(1.0 \pm 0.2) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was measured but an upper limit cited because of the difficulty in measuring such low reaction rate coefficients (Rudich et al., 1996).
- (b) Relative rate method carried out at atmospheric pressure of air. NO_3 radicals were generated by thermal decomposition of N_2O_5 . The concentrations of methyl vinyl ketone and propene (the reference compound) were measured by GC. The measured upper limit to the rate coefficient ratio of $k(\text{NO}_3 + \text{methyl vinyl ketone})/k(\text{NO}_3 + \text{propene}) < 0.06$ is placed

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on an absolute basis by use of a rate coefficient of $k(\text{NO}_3 + \text{propene}) = 9.29 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (IUPAC, current recommendation).

5 (c) Relative rate method carried out at atmospheric pressure of N_2 . NO_3 radicals were generated by thermal decomposition of N_2O_5 . The concentrations of methyl vinyl ketone and ethene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(\text{NO}_3 + \text{methyl vinyl ketone})/k(\text{NO}_3 + \text{ethene}) = 2.53 \pm 0.59$ is placed on an absolute basis by use of a rate coefficient of $k(\text{NO}_3 + \text{ethene}) = 1.96 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (IUPAC, current recommendation). An absolute rate coefficient of $(3.2 \pm 0.6) \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was also measured at $296 \pm 1 \text{ K}$ using a discharge flow system with LIF detection of NO_3 radicals.

Preferred Values

$k < 6 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

15 *Comments on Preferred Values*

The rate coefficient measured in the relative rate study of Canosa-Mas et al. (1999) is consistent with the upper limit obtained by Kwok et al. (1996) but not with the rate coefficient (or cited upper limit) determined in the absolute rate study of Rudich et al. (1996). Although Canosa-Mas et al. (1999) also 20 obtained an absolute rate coefficient in reasonable agreement with their relative rate coefficient, the absolute rate coefficient must be viewed as an upper limit because of the potential for secondary reactions (as observed by Canosa-Mas et al. (1999) in the same study for the reactions of NO_3 radicals with acrolein

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and methacrolein).

The preferred upper limit to the rate coefficient is that measured by Kwok et al. (1996) and is sufficiently high to encompass the rate coefficients obtained by Canosa-Mas et al. (1999).

5 **References**

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10 Rudich, Y., Talukdar, R. K., Fox, R. W., and Ravishankara, A. R.: J. Phys. Chem., 100, 5374, 1996.

NO₃ + Pinonaldehyde → products**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
$(2.40 \pm 0.38) \times 10^{-14}$	299 ± 2	Hallquist et al., 1997	RR (a)
$(6.0 \pm 2.0) \times 10^{-14}$	300 ± 5	Gladius et al., 1997	RR (b)
$(1.99 \pm 0.52) \times 10^{-14}$	296 ± 2	Alvarado et al., 1998	RR (c,d)
$(2.16 \pm 0.53) \times 10^{-14}$	296 ± 2	Alvarado et al., 1998	RR (c,e)
$(1.93 \pm 0.44) \times 10^{-14}$	296 ± 2	Alvarado et al., 1998	RR (c,f)

5 **Comments**

10 (a) NO₃ radicals were generated by the thermal decomposition of N₂O₅ in N₂O₅-pinonaldehyde-propene (the reference compound)-air mixtures at 1013±5 mbar pressure. The concentrations of pinonaldehyde and propene were measured by FTIR spectroscopy. Dark decays of pinonaldehyde in the 153 L chamber used were observed, and taken into account in the data analysis. The measured rate coefficient ratio $k(\text{NO}_3 + \text{pinonaldehyde})/k(\text{NO}_3 + \text{propene})$ is placed on an absolute basis by use of a rate coefficient of $k(\text{NO}_3 + \text{propene}) = 9.5 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (IUPAC, current recommendation).

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5 (b) NO₃ radicals were generated by the thermal decomposition of N₂O₅ in N₂O₅-pinonaldehyde-1-butene (the reference compound)-air mixtures at 987±7 mbar pressure. The concentrations of pinonaldehyde and 1-butene were measured by FTIR spectroscopy. Dark decays of pinonaldehyde in the 480 L chamber used were observed, and taken into account in the data analysis. The measured rate coefficient ratio $k(\text{NO}_3 + \text{pinonaldehyde})/k(\text{NO}_3 + 1\text{-butene})$ is placed on an absolute basis by use of a rate coefficient of $k(\text{NO}_3 + 1\text{-butene}) = 1.38 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 300 K (Atkinson and Arey, 2003).

10 (c) NO₃ radicals were generated by the thermal decomposition of N₂O₅ in N₂O₅-pinonaldehyde-reference compound (propene, 1-butene or thiophene)-air mixtures at 987 mbar pressure. The concentrations of pinonaldehyde, propene, 1-butene and thiophene were measured by GC. No dark decays of pinonaldehyde (<5%) were observed in the
15 7000 L Teflon chamber used. The measured rate coefficient ratios $k(\text{NO}_3 + \text{pinonaldehyde})/k(\text{NO}_3 + \text{propene}) = 2.09 \pm 0.54$, $k(\text{NO}_3 + \text{pinonaldehyde})/k(\text{NO}_3 + 1\text{-butene}) = 1.64 \pm 0.40$ and $k(\text{NO}_3 + \text{pinonaldehyde})/k(\text{NO}_3 + \text{thiophene}) = 0.49 \pm 0.11$ are placed on an absolute basis by use of rate coefficients at 296 K of $k(\text{NO}_3 + \text{propene}) = 9.5 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation), $k(\text{NO}_3 + 1\text{-butene}) = 1.32 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson and Arey, 2003) and $k(\text{NO}_3 + \text{thiophene}) = 3.93 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson, 1991).

(d) Relative to $k(\text{NO}_3 + \text{propene})$.

(e) Relative to $k(\text{NO}_3 + 1\text{-butene})$.

25 (f) Relative to $k(\text{NO}_3 + \text{thiophene})$.

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Preferred Values

$k = 2.0 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.25$ at 298 K.

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Comments on Preferred Values

Pinonaldehyde is a low volatility product of the atmospheric reactions of α -pinene which is prone to wall losses, making measurement of its reaction rate coefficients difficult. The available rate coefficients are all from relative rate studies carried out at room temperature, and range over a factor of ~ 3 (Hallquist et al., 1997; Glasius et al., 1997; Alvarado et al., 1998). The rate coefficient measured by Glasius et al. (1997) is a factor of ~ 2.5 – 3 higher than those of Hallquist et al. (1997) and Alvarado et al. (1998), possibly because of unresolved wall adsorption problems. The preferred values are based on the study of Alvarado et al. (1998) carried out in a large volume Teflon chamber in which no wall losses of pinonaldehyde were observed.

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II.A3.80

NO₃ + 3-methylfuran → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
$(1.31 \pm 0.02) \times 10^{-11}$	296 ± 2	Alvarado et al., 1996	RR (a)
$(2.86 \pm 0.06) \times 10^{-11}$	295 ± 2	Kind et al., 1996	RR (b)

5 Comments

(a) Relative rate method carried out at one atmosphere of air. NO₃ radicals were generated by thermal decomposition of N₂O₅. The concentrations of 3-methylfuran and 2-methyl-2-butene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(\text{NO}_3 + 3\text{-methylfuran})/k(\text{NO}_3 + 2\text{-methyl-2-butene}) = 1.40 \pm 0.02$ is placed on an absolute basis by use of a rate coefficient of $k(\text{NO}_3 + 2\text{-methyl-2-butene}) = 9.37 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson, 1997).

(b) Relative rate method carried out in a flow system at a total pressure of 6.8 mbar of N₂. NO₃ radicals were generated by thermal decomposition of N₂O₅. The concentrations of 3-methylfuran and 2,3-dimethyl-2-butene (the reference compound) were measured by GC. The measured rate coefficient ratio of $k(\text{NO}_3 + 3\text{-methylfuran})/k(\text{NO}_3 + 2,3\text{-dimethyl-2-butene}) = 0.50 \pm 0.01$ is placed on an absolute basis by use of a rate coefficient of

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$k(\text{NO}_3 + 2,3\text{-dimethyl-2-butene}) = 5.72 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Atkinson, 1997). In the same study, the measured rate coefficient for the reaction of NO₃ radicals with furan was shown to be independent of total pressure (of N₂ diluent) over the range 6.8–200 mbar.

5 Preferred Values

$k = 1.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

Comments on Preferred Values

10 The rate coefficients measured in the relative rate studies of Alvarado et al. (1996) and Kind et al. (1996) disagree by a factor of 2.2, for unknown reasons. The preferred value is a simple average of the rate coefficients from these two studies (Alvarado et al., 1996; Kind et al., 1996), with a large uncertainty limit. The reaction of NO₃ radicals with 3-methylfuran proceeds by initial addition of the NO₃ radical to the C=C bonds (Kind et al., 1996).

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6694

II.A3.81



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
$(1.6 \pm 0.6) \times 10^{-16}$	296 ± 2	Canosa-Mas et al., 1999	RR (a)

5 Comments

(a) Relative rate method carried out at one atmosphere of air. $\text{CH}_2=\text{CH}(\text{CH}_3)\text{C}(\text{O})\text{OONO}_2$ (MPAN) was prepared in situ from the reaction of NO_3 radicals (generated from the thermal decomposition of N_2O_5) with methacrolein. After complete consumption of N_2O_5 and methacrolein, ethene (the reference compound) was added and several additions of N_2O_5 were made to the collapsible 56 L chamber. The concentrations of MPAN and ethene were measured during the experiments by FTIR spectroscopy. The measured rate coefficient ratio of $k(\text{NO}_3 + \text{MPAN})/k(\text{NO}_3 + \text{ethene}) = 0.79 \pm 0.28$ (two standard deviations) is placed on an absolute basis by use of a rate coefficient of $k(\text{NO}_3 + \text{ethene}) = 2.0 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K (IUPAC, current recommendation). Dark decays of MPAN and dilution due to successive additions of N_2O_5 to the chamber were taken into account in the data analysis.

6695

Preferred Values

$k = 1.6 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.7$ at 298 K.

5 Comments on Preferred Values

The preferred value is based on the sole study of this reaction by Canosa-Mas et al. (1999), with large uncertainty limits because of the difficult nature of the experiments and the need for large dilution corrections (cited as being up to 40%). The reaction of NO_3 radicals with MPAN proceeds by initial addition of the NO_3 radical to the C=C bond (Canosa-Mas et al., 1999). On the basis of the recommended rate coefficients for the reactions of MPAN with HO radicals and O_3 and those for the reactions of ethene, propene and 2-methylpropene with HO and NO_3 radicals and O_3 (Atkinson, 1997; IUPAC, current recommendation), the rate coefficient for the reaction of NO_3 radicals with MPAN may be expected to be significantly higher than the measured value (i.e., $\sim 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K).

References

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Canosa-Mas, C. E., King, M. D., Shallcross, D. E., and Wayne, R. P.: Phys. Chem. Chem. Phys., 1, 2411, 1999.
IUPAC: <http://www.iupac-kinetic.ch.cam.ac.uk/>.

6696

II.A3.82

NO₃ + CH₃OH → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$\leq 6 \times 10^{-16}$	298 ± 2	Wallington et al., 1987	FP-A
$1.25 \times 10^{-12} \exp[-(2562 \pm 241)/T]$	294–473	Canosa-Mas et al., 1989	DF-A
$(2.1 \pm 1.1) \times 10^{-16}$	294		
$1.06 \times 10^{-12} \exp[-(2093 \pm 803)/T]$	258–367	Langer and Ljungström, 1995	DF-A (a)
$(1.32 \pm 0.24) \times 10^{-16}$	295		

Comments

- (a) The cited Arrhenius expression leads to a rate coefficient at 295 K of $8.8 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, clearly in disagreement with the measured value. A unit-weighted least-squares analysis of the rate coefficients measured by Langer and Ljungström (1995) (Table 3 of Langer and Ljungström, 1995) leads to $k = 9.36 \times 10^{-13} \exp[-(2652 \pm 312)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, where the indicated error is one standard deviation.

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Preferred Values

$k = 1.3 \times 10^{-16} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 9.4 \times 10^{-13} \exp(-2650/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250–370 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.
 $\Delta (E/R) = \pm 700 \text{ K}$.

Comments on Preferred Values

The reported rate coefficients of Canosa-Mas et al. (1989) are higher by factors of 1.6–2.1 than those of Langer and Ljungström (1995) over the temperature range common to both studies (294–373 K). Clearly there are systematic errors in one or both of these studies. Based on the observation that for the NO₃ radical reaction with 2-propanol the data of Langer and Ljungström (1995) may still be an upper limit to the rate coefficient, the preferred values were derived from the data of Langer and Ljungström (1995) using the Arrhenius parameters given in Comment (a). The preferred 298 K rate coefficient is calculated from the resulting Arrhenius expression. It is possible that the preferred values are still high because of the potential for secondary reactions in slowly reacting systems using absolute rate methods.

References

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II.A3.83



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$\leq 9 \times 10^{-16}$	298 ± 2	Wallington et. al., 1987	FP-A
$6.99 \times 10^{-13} \exp [-(1815 \pm 419)/T]$	273–367	Langer and Ljungström, 1995	DF-A
$(1.81 \pm 0.26) \times 10^{-15}$	297		

5 Preferred Values

$k < 2 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Comments on Preferred Values

By analogy with the data for the reaction of the NO_3 radical with 2-propanol,
10 it is likely that the rate coefficients of Langer and Ljungström (1995) are high because of the occurrence of secondary reactions. The preferred value is based on the upper limit to the rate coefficient determined by Wallington et al. (1987), and is consistent with the 298 K rate coefficient of Langer and Ljungström (1995) calculated from their Arrhenius expression. No recommen-
15 dation is made concerning the temperature dependence.

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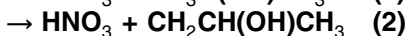
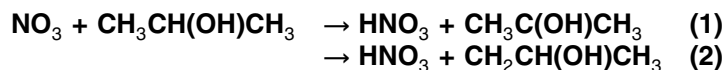
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Langer, S. and Ljungström, E.: J. Chem. Soc. Faraday Trans., 91, 405, 1995.
Wallington, T. J., Atkinson, R., Winer, A. M., and Pitts Jr., J. N.: Int. J. Chem. Kinet., 19, 243, 1987.

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II.A3.84



Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$\leq 2.3 \times 10^{-15}$	298 ± 2	Wallington et al., 1987	FP-A
$1.54 \times 10^{-12} \exp[-(1743 \pm 1009)/T]$	273–364	Langer and Ljungström, 1995	DF-A
$(3.13 \pm 0.64) \times 10^{-15}$	295		
<i>Relative Rate Coefficients</i>			
$\leq (1.8 \pm 0.2) \times 10^{-15}$	298 ± 2	Chew et al., 1998	RR (a)
$k_1 = (1.4 \pm 0.3) \times 10^{-15}$	298 ± 2	Chew et al., 1998	RR (a)

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Comments

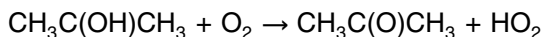
(a) NO_3 radicals were generated by the thermal decomposition of N_2O_5 in air at atmospheric pressure. Experiments were carried out in a ~7000 liter Teflon chamber, and the concentrations of 2-propanol and methacrolein (the reference organic) were measured by GC. Rate coefficient ratios $k(\text{NO}_3 + 2\text{-propanol})/k(\text{NO}_3 + \text{methacrolein})$ were measured as a function of initially added NO_2 over the range $(0\text{--}2.4) \times 10^{14} \text{ molecule cm}^{-3}$ ($\sim 2 \times 10^{16} \text{ molecule cm}^{-3}$ of ethane were added when no NO_2 was initially

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added). The rate coefficient ratios were independent of initial NO₂ concentration in the range (0–4.8) × 10¹³ molecule cm⁻³, but increased for initial NO₂ concentrations ≥ 9.6 × 10¹³ molecule cm⁻³. Acetone was observed as a reaction product, presumably from channel (1) followed by,

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with a yield of ~0.76 ± 0.09 at initial NO₂ concentrations of (0–4.8) × 10¹³ molecule cm⁻³, decreasing at higher initial NO₂ concentrations. The values of $k(\text{NO}_3 + 2\text{-propanol})$ (yield of acetone)/ $k(\text{NO}_3 + \text{methacrolein})$ were independent of initial NO₂ concentration over the entire range studied ((0–2.4) × 10¹⁴ molecule cm⁻³), with an average value of 0.40 ± 0.06 for experiments with initial NO₂ concentrations of (0–4.8) × 10¹³ molecule cm⁻³. The observed behavior is interpreted as involving a gas-phase reaction of 2-propanol with the NO₃ radical and a reaction (gas-phase or heterogeneous) of N₂O₅ with 2-propanol to form nitrates (Langer and Ljungström, 1995). The rate coefficient k is obtained from the rate coefficient ratio $k(\text{NO}_3 + 2\text{-propanol})/k(\text{NO}_3 + \text{methacrolein}) = 0.519 \pm 0.053$ at low added NO₂ concentrations, combined with a rate coefficient ratio of $k(\text{NO}_3 + \text{methacrolein}) = 3.4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 ± 2 K (IUPAC, current recommendation). This overall rate coefficient could still be an upper limit, and the true rate coefficient may be the value obtained for k_1 obtained from the ratio $k(\text{NO}_3 + 2\text{-propanol})$ (yield of 2-acetone)/ $k_2(\text{NO}_3 + \text{methacrolein}) = 0.40 \pm 0.06$ and the rate coefficient of $k(\text{NO}_3 + \text{methacrolein})$ (IUPAC, current recommendation).

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Preferred Values

$k = 1.4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k_1/k = 1.0$ at 298 K.

Reliability

5 $\Delta \log k = \pm 0.3$ at 298 K.
 $\Delta (k_1/k) = \pm 0.3$ at 298 K.

Comments on Preferred Values

The room temperature values for the overall reaction rate coefficient k and for k_1 obtained by Chew et al. (1998) are consistent with the upper limit to the rate coefficient of Wallington et al. (1987), but are a factor of ~2 lower than the absolute rate coefficient of Langer and Ljungström (1995). It is expected that the reaction of the NO₃ radical occurs almost entirely by H-atom abstraction from the tertiary C-H bond (and hence that $k_1/k \sim 1.0$) (Atkinson, 1991). This expectation is consistent with the data of Chew et al. (1998). The 298 K preferred value is based on the value of k_1 obtained by Chew et al. (1998) with the expectation that $k_1/k = 1.0$ (Atkinson, 1991). No temperature dependence is recommended.

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References

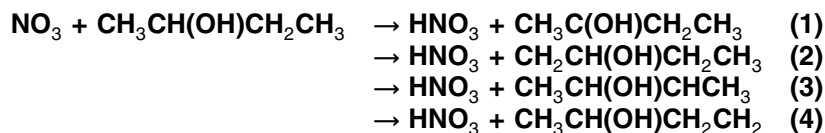
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IUPAC: <http://www.iupac-kinetic.ch.cam.ac.uk/>.

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 Wallington, T. J., Atkinson, R., Winer, A. M., and Pitts, Jr., J. N.: Int. J. Chem. Kinet., 19, 243, 1987.

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II.A3.85



Rate coefficient data ($k=k_1+k_2+k_3+k_4$)

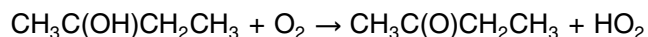
$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
$\leq (2.6 \pm 0.3) \times 10^{-15}$	298 ± 2	Chew et al., 1998	RR (a)
$k_1 = (2.0 \pm 0.3) \times 10^{-15}$	298 ± 2	Chew et al., 1998	RR (a)

5 Comments

(a) NO_3 radicals were generated by the thermal decomposition of N_2O_5 in air at atmospheric pressure. Experiments were carried out in a ~ 7000 liter Teflon chamber, and the concentrations of 2-butanol and methacrolein (the reference organic) were measured by GC. Rate coefficient ratios $k(\text{NO}_3 + 2\text{-butanol})/k(\text{NO}_3 + \text{methacrolein})$ were measured as a function of initially added NO_2 over the range $(0-2.4) \times 10^{-14} \text{ molecule cm}^3$ ($\sim 2 \times 10^{16} \text{ molecule cm}^{-3}$ of ethane were added when no NO_2 was initially added). The rate coefficient ratios were independent of initial NO_2 concentration in the range $(0-4.8) \times 10^{13} \text{ molecule cm}^{-3}$, but increased for initial NO_2 concentrations $\geq 9.6 \times 10^{13} \text{ molecule cm}^{-3}$. 2-Butanone was observed as a

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reaction product, presumably from channel (1) followed by,



5 with a yield of $\sim 0.79 \pm 0.09$ at initial NO_2 concentrations of $(0-4.8) \times 10^{13}$ molecule cm^{-3} , and decreasing at higher initial NO_2 concentrations. The values of $k(\text{NO}_3 + 2\text{-butanol})$ (yield of 2-butanone)/ $k(\text{NO}_3 + \text{methacrolein})$ were independent of initial NO_2 concentration over the entire range studied ($(0-2.4) \times 10^{14}$ molecule cm^{-3}), with an average value of 0.60 ± 0.07 for experiments with initial NO_2 concentrations of $(0-4.8) \times 10^{13}$ molecule cm^{-3} .
10 The observed behavior is interpreted as involving a gas-phase reaction of 2-butanol with the NO_3 radical and a reaction (gas-phase or heterogeneous) of N_2O_5 with 2-butanol to form nitrates (Langer and Ljungström, 1995). The rate coefficient k is obtained from the rate coefficient ratio $k(\text{NO}_3 + 2\text{-butanol})/k(\text{NO}_3 + \text{methacrolein}) = 0.754 \pm 0.065$ at low added NO_2 concentrations, combined with a rate coefficient ratio of $k(\text{NO}_3 + \text{methacrolein}) = 3.4 \times 10^{-15}$ cm^3 molecule $^{-1}$ s $^{-1}$ at 298 ± 2 K (IUPAC, current recommendation). This overall rate coefficient could still be an upper limit, and the true-rate coefficient may be the value obtained for k_1 obtained from the ratio $k(\text{NO}_3 + 2\text{-butanol})$ (yield of 2-butanone)/ $k_2(\text{NO}_3 + \text{methacrolein}) = 0.60 \pm 0.07$ and the rate coefficient $k(\text{NO}_3 + \text{methacrolein})$ (IUPAC, current recommendation).
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Preferred Values

$k = 2.0 \times 10^{-15}$ cm^3 molecule $^{-1}$ s $^{-1}$ at 298 K.
 $k_1/k = 1.0$ at 298 K.

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Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
 $\Delta (k_1/k) = \pm 0.3$ at 298 K.

Comments on Preferred Values

5 The preferred values are based on the sole study of Chew et al. (1998). In view of the magnitude of the rate coefficient compared to that for the reaction of the NO_3 radical with *n*-butane (IUPAC, 2002), the reaction is expected to occur almost totally at the tertiary C-H bond (i.e., $k_1/k=1.0$). The preferred value therefore uses the measured rate coefficient k_1 combined with the expectation
10 that $k_1/k=1.0$.

References

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IUPAC: <http://www.iupac-kinetic.ch.cam.ac.uk/>.
15 Langer, S. and Ljungström, E.: J. Chem. Soc. Faraday Trans., 91, 405, 1995.

II.A3.86



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$4.6 \times 10^{-14} \exp[-(400 \pm 35)/T]$	267–400	Rudich et al., 1996	F-A (a)
$(1.21 \pm 0.09) \times 10^{-14}$	298		
$(2.1 \pm 0.3) \times 10^{-14}$	294	Hallquist et al., 1996	DF-A
<i>Relative Rate Coefficients</i>			
$(1.55 \pm 0.55) \times 10^{-14}$	294	Hallquist et al., 1996	RR (b)
$(8.7 \pm 3.0) \times 10^{-15}$	298 ± 2	Fantechi et al., 1998a	RR (c)
$(1.0 \pm 0.2) \times 10^{-14}$	297 ± 2	Noda et al., 2002	RR (d)
$(1.1 \pm 0.1) \times 10^{-14}$	297 ± 2	Noda et al., 2002	RR (e)

5 Comments

- (a) NO_3 radicals were generated by the thermal decomposition of N_2O_5 at 400 K in a flow system, and NO_3 radical concentrations were measured by visible tunable diode laser absorption at 661.9 nm.
- (b) NO_3 radicals were generated by the thermal decomposition of N_2O_5 in N_2O_5 - $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}=\text{CH}_2$ -propene (the reference compound)-diluent

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(not specified) mixtures at 1013 mbar pressure. The concentrations of 2-methyl-3-buten-2-ol and propene were measured by FTIR spectroscopy, and the measured rate coefficient ratio $k(\text{NO}_3 + 2\text{-methyl-3-buten-2-ol})/k(\text{NO}_3 + \text{propene})$ is placed on an absolute basis by use of a rate coefficient of $k(\text{NO}_3 + \text{propene}) = 9.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 294 K (IUPAC, current recommendation).

(c) NO_3 radicals were generated by the thermal decomposition of N_2O_5 in N_2O_5 - $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}=\text{CH}_2$ -propene (the reference compound)-air mixtures at 987 ± 7 mbar pressure. The concentrations of 2-methyl-3-buten-2-ol and propene were measured by FTIR spectroscopy, and the measured rate coefficient ratio $k(\text{NO}_3 + 2\text{-methyl-3-buten-2-ol})/k(\text{NO}_3 + \text{propene})$ is placed on an absolute basis by use of a rate coefficient of $k(\text{NO}_3 + \text{propene}) = 9.5 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (IUPAC, current recommendation).

(d) NO_3 radicals were generated by the thermal decomposition of N_2O_5 in N_2O_5 - $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}=\text{CH}_2$ -propene (the reference compound)-air (or N_2) mixtures at ~ 1.02 bar pressure. The concentrations of 2-methyl-3-buten-2-ol and propene were measured by FTIR spectroscopy, and the measured rate coefficient ratio $k(\text{NO}_3 + 2\text{-methyl-3-buten-2-ol})/k(\text{NO}_3 + \text{propene})$ is placed on an absolute basis by use of a rate coefficient of $k(\text{NO}_3 + \text{propene}) = 9.4 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 297 K (IUPAC, current recommendation).

(e) NO_3 radicals were generated by the thermal decomposition of N_2O_5 in N_2O_5 - $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}=\text{CH}_2$ -butanal (the reference compound)-air (or N_2) mixtures at 1.01 ± 0.01 bar pressure. The concentrations of 2-methyl-3-buten-2-ol and butanal were measured by collection onto solid phase microextraction fibers with GC analyses. The measured rate coefficient ratio

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$k(\text{NO}_3 + 2\text{-methyl-3-buten-2-ol})/k(\text{NO}_3 + \text{butanal})$ is placed on an absolute basis by use of a rate coefficient of $k(\text{NO}_3 + \text{butanal}) = 1.1 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 297 K (IUPAC, current recommendation).

Preferred Values

- 5 $k = 1.2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 4.6 \times 10^{-14} \exp(-400/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 260–400 K.

Reliability

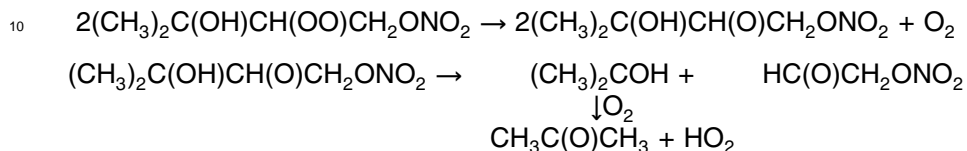
- 10 $\Delta \log k = \pm 0.2$ at 298 K.
 $\Delta (E/R) = \pm 200 \text{ K}$.

Comments on Preferred Values

At room temperature, the relative rate coefficients of Hallquist et al. (1996), Fantechi et al. (1998a) and Noda et al. (2002) are in agreement, within
15 the combined error limits, with the absolute rate coefficient of Rudich et al. (1996). However, the absolute rate coefficient of Hallquist et al. (1996) is a factor of 1.7 higher than that of Rudich et al. (1996). The absolute data of Rudich et al. (1996) are the basis for the preferred values. The reaction proceeds by initial addition of NO_3 to the C=C bond (Fantechi et al.,
20 1998b; Noda et al., 2000), forming (after addition of O_2) the peroxy radicals $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}(\text{ONO}_2)\text{CH}_2\text{OO}$ and $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}(\text{OO})\text{CH}_2\text{ONO}_2$ (and mainly the $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}(\text{OO})\text{CH}_2\text{ONO}_2$ radical (see below)). Reactions of

6711

these peroxy radicals with HO_2 radicals, organic peroxy radicals, NO, NO_2 , and NO_3 radicals will lead to the products observed in the atmosphere (Atkinson and Arey, 2003). Under laboratory conditions, the observed products at atmospheric pressure of air are acetone and $\text{O}_2\text{NOCH}_2\text{CHO}$, with measured molar yields of $68.7 \pm 7.1\%$ (Fantechi et al., 1998b) and $63 \pm 6\%$ (Noda et al., 2000) for acetone and $67 \pm 8\%$ for 2-nitrooxyacetaldehyde (Noda et al., 2000). These observed products presumably arise from self-reaction of the $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}(\text{OO})\text{CH}_2\text{ONO}_2$ peroxy radical, followed by decomposition of the resulting $(\text{CH}_3)_2\text{C}(\text{OH})\text{CH}(\text{O})\text{CH}_2\text{ONO}_2$ radical:



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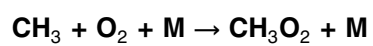
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Appendix 4: Carbon radical Reactions

II.A4.87



$$\Delta H^\circ = -136.0 \text{ kJ}\cdot\text{mol}^{-1}$$

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Low-pressure rate coefficients

Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$2.6 \times 10^{-31} [\text{N}_2]$	298	Basco et al., 1972	FP-AS (a)
$3.1 \times 10^{-31} [\text{N}_2]$	298	Parkes, 1977	MM-AS (b)
$4.5 \times 10^{-31} [\text{N}_2]$	296	Selzer and Bayes, 1983	PLP-MS (c)
$(7.0 \pm 1.0) \times 10^{-31} [\text{Ar}]$	298	Cobos et al., 1985	PLP-AS (d)
$(8.0 \pm 1.0) \times 10^{-31} [\text{N}_2]$	298		
$(4.8 \pm 0.6) \times 10^{-31} [\text{Ar}]$	298	Pilling and Smith, 1985	PLP-AS (e)
$(1.0 \pm 0.3) \times 10^{-30} (T/300)^{-3.3} [\text{Ar}]$	334–582	Keiffer et al., 1987	PLP-AS (f)
<i>Relative Rate Coefficients</i>			
$6.1 \times 10^{-33} \exp(1000/T) [\text{N}_2]$	259–339	Washida and Bayes, 1976	DF-MS (g)
$1.8 \times 10^{-31} [\text{N}_2]$	298		
$8.0 \times 10^{-32} \exp(243/T) [\text{Ar}]$	230–568	Pratt and Wood, 1984	(h)
$1.8 \times 10^{-31} [\text{Ar}]$	298		
$(7.56 \pm 1.1) \times 10^{-31} (T/300)^{-3.64} [\text{N}_2]$	264–370	Kaiser, 1993	(i)

Comments

- 5 (a) Pressure range 40 mbar to 500 mbar. Lindemann-Hinshelwood plot was used for extrapolation to k_0 and k_∞

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- (b) Molecular modulation spectroscopy. Pressure range 25 mbar to 1000 mbar. Lindemann-Hinshelwood extrapolation to k_0 and k_∞ .
- (c) Pressure varied between 0.6 mbar and 8 mbar.
- 5 (d) Pressure of the bath gases N_2 , Ar and O_2 varied between 0.2 mbar and 150 bar. Falloff curves were constructed with $F_c=0.27$, $N=1.47$ and $k_\infty=2.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The low value of the theoretically modeled F_c leads to a high limiting value of k_0 extracted from the measurements.
- 10 (e) Pressures of bath gas Ar varied between 4.2 mbar and 645 mbar. Falloff curves constructed using $F_c=0.57$ (including strong and weak collision contributions).
- (f) Measurements in the pressure range 25 mbar to 790 mbar. Falloff curves constructed with $F_c=0.6$. Various fitting procedures were applied and discussed.
- 15 (g) The rate coefficients $k(\text{CH}_3+\text{O}_2+\text{M} \rightarrow \text{CH}_3\text{O}_2+\text{M})$ plus $k(\text{CH}_3+\text{O}_2 \rightarrow \text{HCHO}+\text{HO})$ were measured relative to $k(\text{O} + \text{CH}_3 \rightarrow \text{products})$. Evaluation with $k(\text{O}+\text{CH}_3)=1.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. Extrapolation to k_0 .
- 20 (h) Discharge-flow system at pressures of 2.6 mbar to 13 mbar. CH_3 radicals were produced from the $\text{H}+\text{C}_2\text{H}_4$ reaction. Reaction rates were determined from the effect of added O_2 on the radical combination products. Falloff curves were constructed assuming that k_∞ and F_c are independent of temperature.
- 25 (i) Mixtures of Cl_2 , CH_4 , diluent (N_2 , Ar , He , or SF_6) were irradiated with a fluorescent lamp. The CH_4 loss and CH_3Cl formation were measured by

6716

GC. Data were obtained (for N₂ or O₂) between 3 mbar and 13 bar at 297 K, 25 mbar and 2 bar at 370 K and 50 mbar and 15 bar at 264 K. The data were fitted using $F_c=0.48$ at 264 K, 0.46 at 297 K and 0.42 at 370 K.

Preferred Values

5 $k_0 = 1.0 \times 10^{-30} (T/300)^{-3.3} [\text{N}_2] \text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$ over the temperature range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.2$ at 298 K.

$\Delta n = \pm 1$.

10 Comments on Preferred Values

The evaluation uses the results of Keiffer et al. (1987) and Kaiser (1993), although different values of F_c were employed. The temperature dependence of F_c applied in Keiffer et al. (1987) does not extend to temperatures below 300 K. The calculated values of F_c from Cobos et al. (1985) are preferred, i.e.,

15 $F_c=0.27$ at 300 K.

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High-pressure rate coefficients

Rate coefficient data

$k_\infty/\text{cm}^3 \text{molecule}^{-1} \text{s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
1.8×10^{-12}	298	Van den Bergh and Callear, 1971	FP-AS (a)
5×10^{-13}	298	Basco et al., 1972	FP-AS (b)
1.2×10^{-12}	298	Parkes, 1977	FP-AS (c)
2.2×10^{-12}	295	Hochanadel et al., 1977	FP-AS (d)
$(2.2 \pm 0.3) \times 10^{-12} (T/300)^{0.94}$	200–400	Cobos et al., 1985	PLP-AS (e)
$(1.05 \pm 0.12) \times 10^{-12}$	298	Pilling and Smith, 1985	PLP-AS (f)
$(1.2 \pm 0.2) \times 10^{-12} (T/300)^{1.2}$	334–582	Keiffer et al., 1987	PLF-AS (g)
<i>Relative Rate Coefficients</i>			
1.7×10^{-12}	298	Laufer and Bass, 1975	FP-GC (i)
$(1.31 \pm 0.1) \times 10^{-12} (T/300)^{1.2}$	264–370	Kaiser, 1993	(j)

Comments

- 5 (a) Pressure range 40 mbar to 400 mbar of C₃H₈. RRKM extrapolation to k_∞ .
 (b) See comment (a) for k_0 .
 (c) See comment (b) for k_0 .
 (d) 12 percent falloff correction applied using the results of Basco et al. (1972).

6718

- (e) See comment (d) for k_0 .
- (f) See comment (e) for k_0 .
- (g) See comment (f) for k_0 .
- (h) See comment (g) for k_0 .
- 5 (i) Pressure range 66 mbar to 920 mbar, RRKM extrapolation to k_∞ . Rate measured relative to $\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6$ and evaluated with $k(\text{CH}_3 + \text{CH}_3 \rightarrow \text{C}_2\text{H}_6) = 9.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ from the same work.
- (j) See comment (i) for k_0 .

Preferred Values

- 10 $k = 9.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and 1 bar of air.
 $k_\infty = 1.8 \times 10^{-12} \exp(T/300)^{1.1} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–300 K.

Reliability

- $\Delta \log k_\infty = \pm 0.3$ at 298 K.
- 15 $\Delta n = \pm 1$.

Comments on Preferred Values

The preferred value is an average of earlier results from Cobos et al. (1985) and Keiffer et al. (1987) and the more recent determination by Kaiser (1993).

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II.A4.88

CH₃ + O₃ → products

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$5.1 \times 10^{-12} \exp[-(210 \pm 84)/T]$	243–384	Ogryzlo et al., 1981;	FP-MS (a)
$(2.53 \pm 0.54) \times 10^{-12}$	298	Paltenghi et al., 1984	
$(2.2 \pm 0.3) \times 10^{-12}$	298	Albaladejo et al., 2002	PLP-LIF (b)

Comments

- 5 (a) Flash photolysis of CH₃NO₂ at 193 nm in a flow system with He carrier gas at pressures of ~2.7 mbar (~2 Torr). [CH₃] was monitored by photoionization MS under pseudo-first-order conditions; no product analyses. The original data of Ogryzlo et al. (1981) were revised by Peltenghi et al. (1984) on the basis of a correction for the pressure drop along the flow tube between the reaction vessel and the manometer.
- 10 (b) Pulsed laser photolysis of CH₃Br at 193 nm and 133 mbar (100 Torr) He coupled with laser-excited fluorescence detection of CH₃O at 292.4 nm in a slow-flow cell. The rate coefficient for total removal of CH₃ was determined by numerical analysis of the temporal profiles of the CH₃O signal.
- 15 The calibration of the CH₃O concentration was performed by comparing LIF signals with those for the reaction CH₃+NO₂ obtained under identical conditions. The CH₃O absolute yield from the CH₃O+O₃ reaction was measured to be 0.044±0.013 and leads to $k=(9.68\pm 1.10)\times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the reaction channel CH₃+O₃ → CH₃O+O₂.

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Preferred Values

$k = 2.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 4.7 \times 10^{-12} \exp(-210/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 240–400 K.

5 Reliability

$\Delta \log k = \pm 0.3$ at 298 K.
 $\Delta (E/R) = \pm 200$ K.

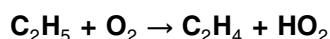
Comments on Preferred Values

- 10 The preferred values are based on the mean of the revised calculations by Paltenghi et al. (1984) of the earlier data of Ogryzlo et al. (1981) and of the data of Albaladejo et al. (2002).

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II.A4.89



$$\Delta H^\circ = -54.1 \text{ kJ}\cdot\text{mol}^{-1}$$

5 Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.1 \pm 0.5) \times 10^{-13}$	295	Plumb and Ryan, 1981	(a)
$<10^{-13}$	1000	Wagner et al., 1990	PLP-MS (b)
<i>Relative Rate Coefficients</i>			
1.9×10^{-14} (133 mbar, air)	298	Kaiser et al., 1990	(c)
3.8×10^{-15} (1 bar, air)	298		
9.8×10^{-16} (8 bar, air)	298		

Comments

10 (a) Discharge flow system. C_2H_5 radicals were generated from the reaction $\text{Cl} + \text{C}_2\text{H}_6 \rightarrow \text{HCl} + \text{C}_2\text{H}_5$. C_2H_5 and C_2H_4 were measured directly by MS. The rate coefficient k was determined from the measured yields of C_2H_4 . k found to be independent of pressure (0.8 mbar to 13 mbar).

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(b) Experimental and theoretical study of the $\text{C}_2\text{H}_5 + \text{O}_2$ reaction. Experiments were carried out in tubular flame reactor. C_2H_5 radicals were formed by laser photolysis of $\text{C}_2\text{H}_5\text{Br}$ or $\text{CCl}_4\text{-C}_2\text{H}_6$ mixtures. Concentrations of C_2H_5 and C_2H_4 were monitored by photoionization MS.

5 (c) Study of the yields of C_2H_4 produced relative to the C_2H_6 consumed (GC analysis) in a system in which C_2H_5 radicals were generated from UV irradiation of $\text{Cl}_2\text{-C}_2\text{H}_6\text{-O}_2\text{-N}_2$ (or air) mixtures. Up to 8 bar the percentage of C_2H_4 produced, relative to the C_2H_6 consumed, decreased from 12% to 0.02%, following a $P^{(-0.8 \pm 0.1)}$ pressure dependence in air. The listed pressure-dependent k values are relative to values of $k(\text{C}_2\text{H}_5 + \text{O}_2 + \text{M} \rightarrow \text{C}_2\text{H}_5\text{O}_2 + \text{M})$ calculated from the recommended values of Baldwin et al. (1980).

10

Preferred Values

$k = 3.8 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and 1 bar of air.

15 $k = 1.9 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and 0.133 bar of air.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

Comments on Preferred Values

20 The recommended pressure-dependent values of k_{298} are from the product study of Kaiser et al. (1990). Increasing the pressure, therefore, decreases the apparent rate coefficient of this reaction. At a given pressure, increasing the temperature leads to an increasing yield of C_2H_4 .

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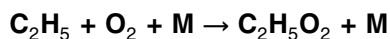
For a full discussion of the mechanism of the $C_2H_5+O_2$ reaction see Wagner et al. (1990), Miller et al. (2000) and Miller and Klippenstein (2001). It is clear that for atmospheric conditions the interaction of C_2H_5 with O_2 to form $C_2H_5O_2$ radicals is by far the dominant pathway. The work of Kaiser (1995) provides information on the mechanism of C_2H_4 formation. According to this, the reaction proceeds via a rearrangement of the excited $C_2H_5O_2$ adduct with an energy barrier of (4.6 ± 1.0) $\text{kJ}\cdot\text{mol}^{-1}$.

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II.A4.90



$$\Delta H^\circ = -149.6 \text{ kJ}\cdot\text{mol}^{-1}$$

Low-pressure rate coefficients

Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(7.5 \pm 2) \times 10^{-29}$ [He]	295	Plumb and Ryan, 1981	DF-MS (a)
7.5×10^{-29} [He]	298	Slagle et al., 1984	DF-MS (b)
$1.96 \times 10^{-5} T^{-8.24} \exp(-2150/T)$ [He]	296–850	Wagner et al., 1990	PLP-MS (c)
5.9×10^{-29} [He]	298		
<i>Relative Rate Coefficients</i>			
$(6.5 \times 2.0) \times 10^{-29}$ [He]	298	Kaiser et al., 1990	(d)

Comments

- (a) Measurements at 2×10^{16} molecule cm^{-3} to 3.4×10^{17} molecule cm^{-3} of He, extrapolated to k_0 and k_∞ with $F_c=0.85$.

6726

- (b) Bath gas concentration varied between 1.6×10^{16} molecule cm^{-3} and 2.4×10^{17} molecule cm^{-3} . Data in agreement with values measured by Plumb and Ryan (1981).
- (c) Experiments carried out in a heatable tubular reactor. He pressures from 0.7 mbar to 20 mbar were used.
- (d) C_2H_5 radicals were produced by UV irradiation of mixtures of Cl_2 - C_2H_6 - O_2 . The consumed C_2H_6 was determined by either FTIR or GC with flame ionization detection (which also allowed the amount of $\text{C}_2\text{H}_5\text{Cl}$ formed to be measured). Rate coefficients were measured as a function of pressure (4 mbar to 2000 mbar) relative to that of the reaction $\text{C}_2\text{H}_5 + \text{Cl}_2 \rightarrow \text{C}_2\text{H}_2\text{Cl} + \text{Cl}$, and placed on an absolute basis by use of a rate coefficient of $k(\text{C}_2\text{H}_5 + \text{Cl}_2) = 2.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 7 mbar.

Preferred Values

$k_0 = 5.9 \times 10^{-29} (T/300)^{-3.8} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–300 K.

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.
 $\Delta n = \pm 1$.

Comments on Preferred Values

We prefer the extensive results from Wagner et al. (1990) because the falloff extrapolation k_0 was done with a careful theoretical analysis. Falloff

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extrapolations were made with theoretically derived (Wagner et al., 1990) values of $F_c = 0.64$ at 200 K and 0.54 at 300 K.

High-pressure rate coefficients

Rate coefficient data

$k_\infty / \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(4.4 \pm 0.5) \times 10^{-12}$	295	Plumb and Ryan, 1981	DF-MS (a)
4.4×10^{-12}	300	Slagle et al., 1984	DF-MS (b)
$1.3 \times 10^{-12} \exp(420/T)$	298–400	Munk et al., 1986	(c)
5.3×10^{-12}	298		
$3.67 \times 10^{-14} T^{0.772} \exp(287/T)$	296–850	Wagner et al., 1990	PLP-MS (d)
7.8×10^{-12}	298		
<i>Relative Rate Coefficients</i>			
$(9.2 \pm 0.9) \times 10^{-12}$	298	Kaiser et al., 1990	(e)
$(8.1 \pm 0.3) \times 10^{-12}$	260–380	Kaiser, 1995	(f)
$2.9 \times 10^{-12} \exp(289/T)$	243–475	Dilger et al., 1996	(g)
7.6×10^{-12}	298		

Comments

- (a) See comment (a) for k_0 .
- (b) See comment (b) for k_0 .
- 5 (c) Pulse radiolysis in H_2 at 1 bar. C_2H_4 radicals were generated from the reaction of $H+C_2H_4$. $C_2H_5O_2$ radicals were monitored by absorption at 240 nm.
- (d) See comment (c) for k_0 .
- (e) See comment (d) for k_0 .
- 10 (f) Photolysis of Cl_2 in the presence of C_2H_6 , O_2 and $M=He$ or N_2 at a pressure of 773 mbar. k_∞ was measured relative to the reaction $C_2H_5 + Cl_2 \rightarrow C_2H_5Cl_2 + Cl$ for which a rate coefficient of $1.04 \times 10^{-11} \exp(300/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was employed (Kaiser, 1990; Timonen and Gutman, 1986).
- 15 (g) Muon relaxation method in longitudinal magnetic fields. $MuCH_2CH_2$ radicals were generated by addition of muonium ($Mu=\mu^+ e^-$) to C_2H_4 . Total pressures of N_2 varied between 1.5 bar and 60 bar.

Preferred Values

$k = 7.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and 1 bar of air.

$k_\infty = 7.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 200–300 K.

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Reliability

$\Delta \log k_\infty = \pm 0.2$ over the temperature range 200–300 K.

Comments on Preferred Values

As for k_0 , we prefer the extensive data from Wagner et al. (1990) because of
5 the combination with a careful theoretical analysis. We assume a temperature independent rate coefficient k_∞ below 300 K. Falloff curves were fitted (Wagner et al., 1990) with an expression $F_c = [0.58 \exp(-T/1250) + 0.42 \exp(-T/183)]$ which leads to $F_c = 0.64$ at 200 K and 0.54 at 300 K. Within the stated error limits, the available data all agree with the preferred values based on Wagner et al. (1990). QRRK calculations (Bozzelli and Dean, 1990) of the reaction are
10 less realistic than the RRKM calculations of Wagner et al. (1990). The analysis of the reaction system is complicated because there is a coupling of the addition reaction with the reaction forming C_2H_4 , i.e., $C_2H_5 + O_2 \rightarrow C_2H_4 + HO_2$ (see the analysis in Wagner et al., 1990; Miller et al., 2000; Miller and Klippenstein,
15 2001).

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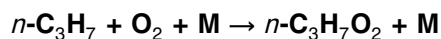
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II.A4.91



High-pressure rate coefficients

$k_\infty/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(5.5 \pm 0.9) \times 10^{-12}$	298	Ruiz and Bayes, 1984	FP-MS (a)
6×10^{-12}	297	Slagle et al., 1985	PLP-MS (b)

5 Comments

- (a) No pressure dependence detected between 1.3 mbar and 5 mbar of He or N₂.
- (b) *n*-C₃H₇ radicals were produced by CO₂ laser photolysis of C₆F₇C₄H₉. Only weak pressure dependences were observed over the range of He or N₂ pressures from 0.5 mbar to 9 mbar. The rate coefficient decreased from $6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ to $2.8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 297 K to 635 K.

Preferred Values

- $k = 6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and 1 mbar to 10 mbar of air.
 15 $k \approx k_\infty$ at 298 K and 1 bar of air.

6732

$k_{\infty} = 8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 200–300 K.

Reliability

$\Delta \log k_{\infty} = \pm 0.2$ over the range 200–300 K.

5 *Comments on Preferred Values*

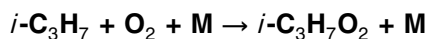
The available experimental data are consistent with each other (Ruiz and Bayes, 1984; Slagle et al., 1985). Because they were obtained at total pressures below 130 mbar, we estimate that some falloff corrections have to be applied and these are taken into account in the preferred values. These values are
10 consistent with experiments for the reactions $\text{C}_2\text{H}_5 + \text{O}_2 + \text{M} \rightarrow \text{C}_2\text{H}_5\text{O}_2 + \text{M}$ and $i\text{-C}_3\text{H}_7 + \text{O}_2 + \text{M} \rightarrow i\text{-C}_3\text{H}_7\text{O}_2 + \text{M}$ (see this evaluation).

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II.A4.92



$\Delta H^\circ = -158.9 \text{ kJ}\cdot\text{mol}^{-1}$

5 **High-pressure rate coefficients**

Rate coefficient data

$k_{\infty}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.41 \pm 0.24) \times 10^{-11}$	298	Ruiz and Bayes, 1984	FP-MS (a)
8.3×10^{-12}	300	Munk et al., 1986	(b)

Comments

(a) No pressure dependence detected for He or N₂ pressures from 1.3 mbar
10 to 5 mbar.

(b) Pulse radiolysis in H₂ at 1 bar. *i*-C₃H₇ radicals were generated by the addition of H atoms to C₃H₆ and *i*-C₃H₇O₂ detected by UV absorption at 253 nm. Absorption spectrum of *i*-C₃H₇ was also detected.

6734

Preferred Values

$k \approx k_{\infty}$ at 298 K and 1 bar of air.

$k_{\infty} = 1.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 200–300 K.

5 Reliability

$\Delta \log k_{\infty} = \pm 0.3$ over the range 200–300 K.

Comments on Preferred Values

The preferred values are the average of the results from Ruiz and Bayes (1984) and Munk et al. (1986). Falloff corrections are probably within the
10 uncertainties of the average. The rate coefficient k_{∞} for this reaction appears consistent with those for the reactions $\text{C}_2\text{H}_5 + \text{O}_2 + \text{M} \rightarrow \text{C}_2\text{H}_5\text{O}_2 + \text{M}$ and $n\text{-C}_3\text{H}_7 + \text{O}_2 + \text{M} \rightarrow n\text{-C}_3\text{H}_7\text{O}_2 + \text{M}$ (see this evaluation).

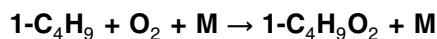
References

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15 132, 417, 1986.

Ruiz, R. P. and Bayes, K. D.: J. Phys. Chem., 88, 2592, 1984.

6735

II.A4.93



High-pressure rate coefficients

Rate coefficient data

$k_{\infty}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
5 $(7.5 \pm 1.4) \times 10^{-12}$	300	Lenhardt et al., 1980	FP-MS (a)

Comments

(a) 1-Butyl radicals were generated by the flash photolysis of 1-butyl iodide and detected by MS. No pressure dependence of the rate coefficients was observed over the range 1.3 mbar to 5.3 mbar of He.

10 Preferred Values

$k_{\infty} = 7.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k_{\infty} = \pm 0.5$ at 298 K.

6736

Comments on Preferred Values

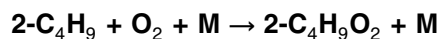
The preferred value is based on the study of Lenhardt et al. (1980). Because this is the only study of this reaction, we assign large error limits. This reaction should be close to the high pressure limit at atmospheric pressure.

5 References

Lenhardt, T. M., McDade, C. E., and Bayes, K. D.: J. Chem. Phys., 72, 304, 1980.

6737

II.A4.94



High-pressure rate coefficients

Rate coefficient data

$k_\infty/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.66 \pm 0.22) \times 10^{-11}$	300	Lenhardt et al., 1980	FP-MS (a)

Comments

(a) 2-Butyl radicals were generated by the flash photolysis of 2-butyl iodide and detected by MS. No pressure dependence of the rate coefficients was observed over the range 1.3 mbar to 5.3 mbar of He.

10 Preferred Values

$k_\infty = 1.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k_\infty = \pm 0.5$ at 298 K.

6738

The preferred value is based on the study of Lenhardt et al. (1980).

References

- 5 Lenhardt, T. M., McDade, C. E., and Bayes, K. D.: J. Chem. Phys., 72, 304, 1980.

6739

II.A4.95



High-pressure rate coefficients

Rate coefficient data

$k_\infty/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
5 1.45×10^{-12}	298	Cox et al., 1990	(a)

Comments

- 10 (a) Pulse radiolysis of $\text{CH}_3\text{C(O)CH}_3\text{-O}_2\text{-SF}_6$ mixtures at 1 bar of SF_6 . $\text{CH}_3\text{C(O)CH}_2$ radicals were formed from the reaction of F atoms with $\text{CH}_3\text{C(O)CH}_3$. At the monitoring wavelength of 310 nm both $\text{CH}_3\text{C(O)CH}_2$ and $\text{CH}_3\text{C(O)CH}_2\text{O}_2$ absorb, with the absorption cross-section of the peroxy radical being a factor of 1.7 greater than that of the $\text{CH}_3\text{C(O)CH}_2$ radical. The rate coefficient was evaluated by simulations of the above reaction together with the reaction $\text{CH}_3\text{C(O)CH}_2 + \text{CH}_3\text{C(O)CH}_2\text{O}_2 \rightarrow 2 \text{CH}_3\text{C(O)CH}_2\text{O}$.

15 Preferred Values

$k \approx k_\infty$ at 298 K and 1 bar of air.
 $k_\infty = 1.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

6740

Reliability

$\Delta \log k_{\infty} = \pm 0.5$ at 298 K.

Comments on Preferred Values

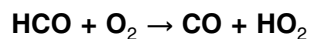
- 5 The preferred values are based on the study of Cox et al. (1990). Because this is the only study of this reaction, we assign large error limits. Near atmospheric pressure this reaction should be close to the high pressure limit.

References

- 10 Cox, R. A., Munk, J., Nielsen, O. J., Pagsberg, P., and Ratajczak, E.: Chem. Phys. Lett., 173, 206, 1990.

6741

II.A4.96



$$\Delta H^\circ = -139.0 \text{ kJ}\cdot\text{mol}^{-1}$$

5 Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(5.6 \pm 0.9) \times 10^{-12}$	300	Shibuya et al., 1977	FP-AS (a)
$5.5 \times 10^{-11} T^{-(0.4 \pm 0.3)}$	298–503	Veyret and Lesclaux, 1981	FP-AS (b)
$(5.6 \pm 0.6) \times 10^{-12}$	298		
$(4.65 \pm 0.6) \times 10^{-12}$	295	Langford and Moore, 1984	PLP-AS (c)
$1.3 \times 10^{-11} \exp[-(204 \pm 180)/T]$	295–713	Timonen et al., 1988	PLP-MS (d)
6.2×10^{-12}	295		
$3.2 \times 10^{-12} \exp(87/T)$	200–398	Stief et al., 1990	DF-MS (e)
4.3×10^{-12}	298		
4.3×10^{-12}	298	Dóbé et al., 1995	DF-LMR (f)
$(2.2) \times 10^{-12} \exp[(170 \pm 22)/T]$	200–298	Nesbitt et al., 1999	DF-MS (g)
$(4.0 \pm 0.6) \times 10^{-12}$	298		
$(5.9 \pm 0.5) \times 10^{-12}$	295	Ninomiya et al., 2000	PLP-AS (h)
$(5.0 \pm 0.7) \times 10^{-12}$	294 ± 2	Hanoune et al., 2001	PLP-AS (i)
<i>Relative Rate Coefficients</i>			
$(5.7 \pm 1.2) \times 10^{-12}$	297	Washida et al., 1974	RR (j)
$(6.3 \pm 1.5) \times 10^{-12}$	295	Ninomiya et al., 2000	RR (k)

6742

Comments

- (a) Flash photolysis of CH₃CHO-O₂ mixtures; HCO monitored by time-resolved absorption at 613.8 nm. There was no pressure effect on *k* for pressures of up to 690 mbar (520 Torr) of He.
- 5 (b) Flash photolysis of HCHO and CH₃CHO; HCO was monitored by laser absorption at 614.5 nm at total pressures of 17 mbar to 660 mbar (13 Torr to 500 Torr).
- (c) Pulsed laser photolysis of HCHO or (CHO)₂ with monitoring of HCO by absorption at total pressures of up to 1330 mbar (1000 Torr).
- 10 (d) Pulsed laser photolysis of CH₃CHO; HCO was monitored by photoionization MS at pressures of 0.69 mbar to 1.22 mbar (0.52 Torr to 0.92 Torr).
- (e) Discharge-flow system. HCO radicals were generated from Cl+HCHO and monitored by photoionization MS.
- (f) HCO radicals were generated by the reaction of F atoms with HCHO. The total pressure was 1.7 mbar of He. The yield of HO₂ radicals was measured relative to the formation yield of HO₂ radicals from the reaction of F atoms with H₂O₂, and determined to be 1.00±0.05.
- 15 (g) Same experimental technique as in comment (e). The rate constant measured at 398 K seems to indicate a slight positive temperature dependence for *T*>300 K in qualitative agreement with Timonen et al. (1988).
- 20 (h) Pulsed laser photolysis of CH₃CHO at 266 nm; HCO was monitored by cavity ring-down spectroscopy at 613.5 nm at total pressures of 5.32–13.3 mbar (4–10 Torr) of N₂.

6743

- (i) Pulsed laser photolysis of a mixture of H₂CO and Cl₂ at 355 nm with monitoring of the R5 or R6 transition in CO by tunable diode laser absorption in the range 6.4–62.0 mbar (4.8–46.5 Torr). Only data with [O₂]>5×10¹⁵ molecule cm⁻³ have been used in the analysis.
- 5 (j) Discharge flow system with HCO being monitored by photoionization MS. *k* measured relative to *k*(O + HCO → products) = 2.1×10⁻¹⁰ cm³ molecule⁻¹ s⁻¹ (measured in the same apparatus) by observing the effect of O₂ on [HCO] in a flowing mixture of O₂-C₂H₄; *k*/*k*(O+HCO)=(2.74±0.21)×10⁻².
- 10 (k) Based on the ratio of the rate constants *k*(HCO+O₂)/*k*(HCO+Cl₂)=0.85±0.02 measured in a smog chamber coupled to FTIR detection. The absolute value of *k* (HCO+Cl₂) used to place the relative rate on an absolute basis was (7.4±1.7)×10⁻¹² cm³ molecule s⁻¹.

15 Preferred Values

$k = 5.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 200–300 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

20 $\Delta (E/R) = \pm 150 \text{ K}$.

6744

The preferred value of the rate coefficient at 298 K is the average of the room-temperature rate coefficients of Shibuya et al. (1977), Veyret and Lesclaux (1981), Langford and Moore (1984), Timonen et al. (1988), Stief et al. (1990),
5 Dóbé et al. (1995), Nesbitt et al. (1999), Ninomiya et al. (2000) and Hanoune et al. (2001). Taken together, the temperature-dependent studies of Veyret and Lesclaux (1981), Timonen et al. (1988), Stief et al. (1990) and Nesbitt et al. (1999) suggest that the rate coefficient of this reaction has a slight negative temperature dependence over the range 200 to 298 K and possibly a small
10 positive temperature dependence above 300 K. However, within the measurement uncertainties the rate coefficient can be considered to be independent of temperature over the range 200–400 K.

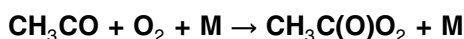
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6745

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Washida, N., Martinez, R. I., and Bayes, K. D.: *Z. Naturforsch.*, 29a, 251, 1974.
5

II.A4.97



$$\Delta H^\circ = -162.0 \text{ kJ}\cdot\text{mol}^{-1}$$

5 High-pressure rate coefficients

Rate coefficient data

$k_\infty/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.0 \pm 0.4) \times 10^{-12}$	298	McDade et al., 1982	(a)
$(5.4 \pm 1.9) \times 10^{-12}$	296	Kaiser and Wallington, 1995	RR (b)
$(5.7 \pm 1.9) \times 10^{-12}$	295 ± 2	Tyndall et al., 1997	RR (c)
$(5.9 \pm 1.9) \times 10^{-12}$	228		
$(4.4 \pm 0.7) \times 10^{-12}$	295	Sehested et al., 1998	PR-AS (d)

Comments

10 (a) Flow system with CH_3CO generated from pulsed photolysis of $\text{CH}_3\text{C(O)CH}_3$ or $\text{CH}_3\text{C(O)CH}_2\text{COCH}_3$. $[\text{CH}_3\text{CO}]$ was monitored by photoionization mass spectrometry and kinetics evaluated from pseudo-first-order decays of CH_3CO . The pressure range was 1.3 mbar to 5 mbar.

6747

5 (b) Measurement of the rate coefficient ratio for $k(\text{CH}_3\text{CO}+\text{Cl}_2)/k(\text{CH}_3\text{CO}+\text{O}_2)=7.9\pm 0.5$ at 930 mbar total pressure. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(\text{CH}_3\text{CO}+\text{Cl}_2)=(4.3\pm 1.5)\times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Tyndall et al., 1999).

10 (c) Measurement of the rate coefficient ratios $k(\text{CH}_3\text{CO}+\text{Cl}_2)/k(\text{CH}_3\text{CO}+\text{O}_2)$ at 228 K and 298 K over the pressure range 0.13 mbar to 1460 mbar. The rate constant k was observed to increase with increasing pressure, with the rate coefficient k approaching the high-pressure limit above ~ 400 mbar. The rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(\text{CH}_3\text{CO}+\text{Cl}_2)=(4.3\pm 1.5)\times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Tyndall et al., 1999).

15 (d) Pulse radiolysis of a mixture of CH_3CHO and O_2 in 1 bar of SF_6 coupled with transient UV absorption spectroscopy of $\text{CH}_3\text{C(O)O}_2$ at 260 nm. Numerical modeling was used with a complex reaction mechanism.

Preferred Values

$k_\infty = 5.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 220–300 K.

Reliability

20 $\Delta \log k_\infty = \pm 0.2$ over the temperature range 220–300 K.

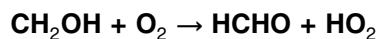
The preferred values are based on the data of Sehested et al. (1998) and Tyndall et al. (1997) using the temperature-independent reference rate constant for $\text{CH}_3\text{CO} + \text{Cl}_2$ of Tyndall et al. (1999).

5 **References**

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 Tyndall, G. S., Orlando, J. J., Kegley-Owen, C. S., Wallington, T. J., and Hurley, M. D.: Int. J. Chem. Kinet., 31, 776, 1999.

6749

II.A4.98



$$\Delta H^\circ = -76.2 \text{ kJ}\cdot\text{mol}^{-1}$$

5 **Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(9.5 \pm 2.5) \times 10^{-12}$	298	Grotheer et al., 1985	DF-MS (a)
$(1.06 \pm 0.25) \times 10^{-11}$	296	Dóbe et al., 1985	DF-LMR (b)
$(1.05 \pm 0.47) \times 10^{-11}$	296		
$(8.6 \pm 2.0) \times 10^{-12}$	298	Payne et al., 1988	DF-MS (c)
$2.5 \times 10^{-9} T^{-1.0} +$	370–684	Grotheer et al., 1988	DF-MS (d)
$4.0 \times 10^{-10} \exp(-2525/T)$			
$5.6 \times 10^{-9} \exp(-1700/T)$	215–250	Nesbitt et al., 1988	DF-MS (e)
$(8.61 \pm 1.14) \times 10^{-12}$	300		
$(8.8 \pm 0.2) \times 10^{-12}$	298	Pagsberg et al., 1989	PR-AS (f)
$(1.17 \pm 0.12) \times 10^{-11}$	296	Miyoshi et al., 1990	PLP-MS (g)
$(1.00 \pm 0.14) \times 10^{-11}$	294	Hanoune et al., 2001	PLP-AS (h)

6750

Comments

- (a) CH₂OH was generated from Cl+CH₃OH at total pressures of 0.4 mbar to 1.2 mbar (0.3 Torr to 0.9 Torr). *k* was derived from the rate of disappearance of CH₂OH in excess O₂ by MS.
- 5 (b) CH₂OH was generated from F+CH₃OH at total pressures of 0.69 mbar to 6.5 mbar (0.52 Torr to 4.9 Torr). Two values of *k* were derived from the rate of disappearance of CH₂OH and of the appearance of HO₂, both monitored by LMR spectroscopy.
- (c) CH₂OH was generated from Cl + CH₃OH at total pressures of ~1.3 mbar (~1 Torr). *k* was derived from the rate of disappearance of CH₂OH in excess O₂ by MS.
- 10 (d) As for comment (a) at pressures of ~1.1 mbar (~ 0.8 Torr).
- (e) As for comment (c) at pressures of ~1.3 mbar (~ 1 Torr).
- (f) CH₂OH was generated from F+CH₃OH at total pressures of 1 bar (760 Torr). *k* was derived from the rate of disappearance of CH₂OH in excess of O₂ by absorption at 285.5 nm.
- 15 (g) Pulsed laser photolysis of CH₃C(O)CH₂OH, with the decay of CH₂OH being monitored by photoionization MS, at total pressures of 1.7 mbar to 7.3 mbar (1.3 Torr to 5.5 Torr).
- 20 (h) Pulsed laser photolysis of a mixture of CH₃OH and Cl₂ at 355 nm with monitoring of HCHO at 1707.9 cm⁻¹ by tunable diode laser absorption in the range 7.71–20.22 mbar (5.8–15.2 Torr). Only data with [O₂] > 2 × 10¹⁵ molecule cm⁻³ have been used in the analysis.

6751

Preferred Values

$k = 9.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

5 $\Delta \log k = \pm 0.12$ at 298 K.

Comments on Preferred Values

The rate coefficient at 298 K is now well established for this reaction, and our recommendation is the average of the results of Grotheer et al. (1985), Dóbé et al. (1985), Payne et al. (1988), Nesbitt et al. (1988), Pagsberg et al. (1989), Miyoshi et al. (1990) and Hanoune et al. (2001). The earlier data of Wang et al. (1984) and Radford (1980) are rejected on the basis that they involved high concentrations of radicals, leading to mechanistic complications (Radford, 1980). The two studies of the temperature dependence of this reaction (Grotheer et al., 1989, Nesbitt et al., 1988) indicate that the rate coefficient follows a complicated non-Arrhenius behavior over the range 200 K to 700 K. The existing data on the temperature dependence are difficult to explain and more work is needed to confirm the observed temperature dependence of this reaction before a recommendation can be made.

15

20 Grotheer et al. (1988) have carried out experiments replacing CH₃OH by CH₃OD and have observed no kinetic effect for the CH₂OH/CH₂OD+O₂ reactions.

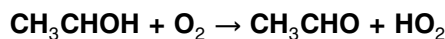
6752

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6753

II.A4.99



$$\Delta H^\circ = -87.6 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.4 \times 10^{-8} T^{-1.2} + 8.0 \times 10^{-10} \exp(-2525/T)$	300–682	Grotheer et al., 1988	DF-MS (a)
1.56×10^{-11}	300		
$(1.3 \pm 0.2) \times 10^{-11}$	300	Anastasi et al., 1989	PR-AS (b)
$(2.8 \pm 0.2) \times 10^{-11}$	293	Miyoshi et al., 1989	PLP-MS (c)

Comments

- (a) CH_3CHOH was generated from $\text{Cl} + \text{C}_2\text{H}_5\text{OH}$ in the presence of a large excess of O_2 at total pressures of ~ 1 mbar (~ 0.8 Torr). The rate coefficient k was derived from the disappearance of CH_3CHOH , as monitored by low electron energy MS.
- (b) Pulsed radiolysis of $\text{Ar-SF}_6\text{-HCl-C}_2\text{H}_5\text{OH-O}_2$ mixtures at total pressures of 1 bar (760 Torr) and with $[\text{SF}_6] \gg [\text{HCl}] \gg [\text{C}_2\text{H}_5\text{OH}] \gg [\text{O}_2]$. CH_3CHOH was

6754

generated from $\text{Cl} + \text{C}_2\text{H}_5\text{OH}$ and monitored by UV absorption at 260 nm.

(c) Pulsed laser photolysis of $\text{CH}_3\text{C}(\text{O})\text{CH}(\text{OH})\text{CH}_3$ in a large excess of He at total pressures of 2.7 mbar to 9.3 mbar (2 Torr to 7 Torr). CH_3CHOH was monitored by photoionization MS in the presence of excess O_2 .

5 Preferred Values

$k = 1.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

10 The preferred value of k_{298} is the mean of the results of Grotheer et al. (1989), Anastasi et al. (1989) and Miyoshi et al. (1989). The rather large discrepancy between the data of Miyoshi et al. (1989) and the other two studies (Grotheer et al., 1989; Anastasi et al., 1989) could be due to the different sources of generation of the CH_3CHOH radical. CH_3CHOH radical generation
15 involving Cl attack on $\text{C}_2\text{H}_5\text{OH}$ (Grotheer et al., 1989; Anastasi et al., 1989) may not be as clean a source as is the photolysis of $\text{CH}_3\text{COCHOHCH}_3$ (Miyoshi et al., 1989).

The temperature dependence of the rate coefficient determined by Grotheer et al. (1989) shows a marked non-Arrhenius behavior, but this needs
20 to be confirmed before a recommendation can be made. Evidence for the reaction between CH_3CHOH and O_2 yielding CH_3CHO as a major product comes from the product study of the photooxidation of ethanol by Carter et al. (1979).

6755

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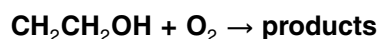
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II.A4.100



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(3.0 \pm 0.4) \times 10^{-12}$	293	Miyoshi et al., 1989	PLP-MS (a)

5 Comments

(a) Pulsed laser photolysis of $\text{ClCH}_2\text{CH}_2\text{OH}$ and $\text{BrCH}_2\text{CH}_2\text{OH}$ in a large excess of He at total pressures of 2.7 mbar to 9.3 mbar (2 Torr to 7 Torr). $\text{CH}_2\text{CH}_2\text{OH}$ radicals were monitored by photoionization MS in the presence of excess O_2 .

10 Preferred Values

$k = 3.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

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Comments on Preferred Values

The direct measurements of this rate coefficient (Miyoshi et al., 1989), from the pulsed laser photolysis of either $\text{ClCH}_2\text{CH}_2\text{OH}$ or $\text{BrCH}_2\text{CH}_2\text{OH}$ as the radical source, showed a good level of consistency. By analogy with the reactions

5 $\text{C}_2\text{H}_5 + \text{O}_2 + \text{M} \rightarrow \text{C}_2\text{H}_5\text{O}_2 + \text{M}$ and $\text{CH}_3\text{CO} + \text{O}_2 + \text{M} \rightarrow \text{CH}_3\text{CO}_3 + \text{M}$ (this evaluation), the rate coefficient for this reaction is expected to be close to the high-pressure limit under the experimental conditions employed. The UV absorption spectrum of the $\text{HOCH}_2\text{CH}_2\text{O}_2$ radical has been observed by pulse radiolysis of $\text{SF}_6\text{-H}_2\text{O}$ mixtures (Anastasi et al., 1991) and pulsed laser photolysis of H_2O_2 in the

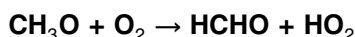
10 presence of C_2H_4 and O_2 (Murrells et al., 1991). These observations indicate that the reaction between $\text{CH}_2\text{CH}_2\text{OH}$ radicals and O_2 leads predominantly to the adduct peroxy radical.

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6758

II.A5.101



$$\Delta H^\circ = -111.2 \text{ kJ}\cdot\text{mol}^{-1}$$

5 **Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.05 \times 10^{-13} \exp(-1310/T)$	413–628	Gutman et al., 1982	PLP-LIF (a)
1.3×10^{-15}	298		
$5.5 \times 10^{-14} \exp(-1000/T)$	298–450	Lorenz et al., 1985	PLP-LIF (b)
1.9×10^{-15}	298		
$2.3 \times 10^{-14} (1000/T)^{-9.5}$ $\times \exp(2768/T)$	298–973	Wantuck et al., 1987	PLP-LIF (c)
2.1×10^{-15}	298		

Comments

- (a) CH₃O generated from pulsed laser photolysis of CH₃ONO at 266 nm. [CH₃O] was monitored by LIF at a total pressure of 53 mbar (40 Torr).
- 10 (b) Pulsed laser photolysis of CH₃ONO with monitoring of CH₃O by LIF, at pressures of 100 mbar (75 Torr) of He. At 298 K the rate coefficient was

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shown to be independent of pressure over the range 10 mbar to 200 mbar (7.5 Torr to 150 Torr) of He.

- 5 (c) Pulsed laser photolysis of CH₃OH or CH₃ONO at 193 nm in the presence of O₂ plus 33 mbar (25 Torr) of Ar. CH₃O radicals were monitored by LIF. Non-Arrhenius behavior was observed over entire temperature range and fitted by the cited empirical equation. Rate coefficients combined with the data of Gutman et al. (1982) and Lorenz et al. (1985) were found to obey a double exponential expression, with $k = (1.5 \times 10^{-10} \exp(-6028/T) + 3.6 \times 10^{-14} \exp(-880/T)) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

10 **Preferred Values**

$k = 1.9 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 7.2 \times 10^{-14} \exp(-1080/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 290–610 K.

Reliability

- 15 $\Delta \log k = \pm 0.2$ at 298 K.
 $\Delta (E/R) = \pm 300$ K.

Comments on Preferred Values

- 20 The direct measurements of the rate coefficients by Lorenz et al. (1985) (298 K to 450 K) and Wantuck et al. (1987) (298 K to 973 K) are in good agreement with the similar measurements of Gutman et al. (1982) (413 K to 608 K), where the temperature ranges overlap. The preferred values are derived from a least-squares analysis of these three sets of data (Gutman et al., 1982; Lorenz

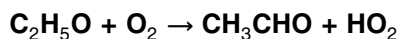
et al., 1985; Wantuck et al., 1987) over the temperature range 298 K to 608 K. The higher temperature measurements of Wantuck et al. (1987) give a clear indication of non-Arrhenius behavior over the extended temperature range. The anomalously low A-factor for a simple H-atom transfer reaction and the possibility of a more complicated mechanism have both been noted (NASA, 1997).

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 NASA Evaluation No. 12, 1997 (see references in Introduction).
 Wantuck, P. J., Oldenborg, R. C., Baughcum, J. L., and Winn, K. R.: J. Phys. Chem., 91, 4653, 1987.

6761

II.A5.102



$$\Delta H^\circ = -135.7 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
8.0×10^{-15}	296	Gutman et al., 1982	PLP-LIF (a)
9.8×10^{-15}	353		
$7.1 \times 10^{-14} \exp[-(552 \pm 64)/T]$	295–411	Hartmann et al., 1990	PLP-LIF (b)
$(1.08 \pm 0.20) \times 10^{-14}$	295		
$2.4 \times 10^{-14} \exp[-(325 \pm 120)/T]$	295–354	Fittschen et al., 1999	PLP-LIF (c)
8.1×10^{-15}	298		

Comments

- (a) Pulsed laser photolysis of $\text{C}_2\text{H}_3\text{ONO}$ at 266 nm, with $\text{C}_2\text{H}_5\text{O}$ radicals being monitored by LIF at a total pressure of 53 mbar (40 Torr).
 (b) Pulsed laser photolysis of $\text{C}_2\text{H}_5\text{ONO}$ at 266 nm in $\text{C}_2\text{H}_5\text{ONO-O}_2\text{-He}$ mixtures, with LIF monitoring of $\text{C}_2\text{H}_5\text{O}$ radicals in the wavelength range 310 nm to 330 nm. Studies were carried out at a total pressure of 35 mbar (26 Torr).

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- 5 (c) Pulsed laser photolysis of C₂H₅ONO at 248 nm in C₂H₅ONO-O₂-He mixtures at 133 mbar (100 Torr) with LIF detection of C₂H₅O radicals excited at 323 nm and fluorescence detection to the red of 375 nm. The upper temperature limit was set by the unimolecular decomposition rate of ethoxy radical.

Preferred Values

$k = 8.1 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 2.4 \times 10^{-14} \exp(-325/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 295–354 K.

10 Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

$\Delta (E/R) = \pm 300$ K.

Comments on Preferred Values

15 The preferred rate constant at 298 K is that of Gutman et al. (1982) and Fittschen et al. (1999). Their temperature dependence over the common range 296–353 K is in excellent agreement and is therefore recommended here. The relative rate measurements of Zabarnick and Hecklen (1985) yield a value of k_{298} which is consistent with the preferred value within the recommended error limits.

20 It should be noted that the A-factor for the above reaction is very low, but in keeping with that for the analogous reaction $\text{CH}_3\text{O} + \text{O}_2 \rightarrow \text{HCHO} + \text{HO}_2$.

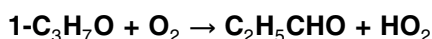
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6764

II.A5.103



$$\Delta H^\circ = -131.4 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.4 \times 10^{-14} \exp[-(108 \pm 61)/T]$	223–303	Mund et al., 1998	PLP-LIF (a)
9.8×10^{-15}	298		
$(2.5 \times 10^{-14} \exp[-(240 \pm 60)/T])$	289–381	Fittschen et al., 1999	PLP-LIF (b)
1.1×10^{-14}	298		
<i>Relative Rate Coefficients</i>			
$2.8 \times 10^{-13} \exp[-(879 \pm 117)/T]$	247–393	Zabarnick and Heicklen, 1985	RR (c)
1.5×10^{-14}	298		

Comments

- (a) Pulsed laser photolysis of propyl-nitrite at 351 nm with laser-induced fluorescence detection of *n*-propoxy radical in the range 6–110 mbar He.
- (b) Pulsed laser photolysis of 1-C₃H₇ONO at 351 nm in 1-C₃H₇ONO-O₂-He mixtures in the range 40–133 mbar (30–100 Torr) with LIF detection of 1-C₃H₇O excited at 349 nm and fluorescence detection to the red of 375 nm.

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The upper temperature limit is set by the unimolecular decomposition rate of *n*-propoxy radical.

- (c) Photolysis at 366 nm of *n*-C₃H₇ONO in a static system in the presence of NO, O₂, and N₂ at total pressures of >200 mbar (>150 Torr). Rate data were based on the measured quantum yields of C₂H₅CHO product. The rate coefficient *k* was measured relative to *n*-C₃H₇O+NO → products with $k(n\text{-C}_3\text{H}_7\text{O}+\text{O}_2)/k(n\text{-C}_3\text{H}_7\text{O}+\text{NO})=6.8 \times 10^{-3} \exp(-879/T)$, and is placed on an absolute basis by use of $k(n\text{-C}_3\text{H}_7\text{O}+\text{NO})=4.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature.

Preferred Values

$k = 2.6 \times 10^{-14} \exp(-253/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 220–380 K.

$k = 1.0 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

$\Delta (E/R) = \pm 500 \text{ K}$.

Comments on Preferred Values

The preferred values are based on the absolute rate study of Fittschen et al. (1999), which is in excellent agreement with Mund et al. (1998) in the overlapping temperature range. The temperature dependence is that of both data

sets taking into account the A factor that differs by a factor of two. The rate coefficients derived from the relative rate study of Zabarnick and Heicklen (1985) are in significant disagreement with the absolute rate data (Mund et al., 1998; Fittschen et al., 1999).

5 References

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6767

II.A5.104



$$\Delta H^\circ = -150.3 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.51 \times 10^{-14} \exp[-(200 \pm 140)/T]$	294–384	Balla et al., 1985	PLP-LIF (a)
7.72×10^{-15}	298		
$1.4 \times 10^{-14} \exp[-(217 \pm 49)/T]$	288–313	Mund et al., 1998, 1999	PLP-LIF (b)
6.8×10^{-15}	298		
$1.6 \times 10^{-14} \exp[-(265 \pm 24)/T]$	218–364	Fittschen et al., 1999	PLP-LIF (c)
6.6×10^{-15}	298		
5 $(8.7 \pm 2.5) \times 10^{-15}$	296	Deng et al., 2000	PLP-LIF (d)

Comments

- (a) Pulsed laser photolysis of 2-propyl nitrite at 355 nm, with LIF detection of 2-C₃H₇O radicals. The pressure range was 1.3 mbar to 67 mbar (1 Torr to 50 Torr).
- 10 (b) Pulsed laser photolysis of propyl nitrite at 351 nm with laser-induced fluorescence detection of *i*-propoxy radical in the range 6–110 mbar He.

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- (c) Pulsed laser photolysis of 2-C₃H₇ONO at 351 nm in 2-C₃H₇ONO-O₂-He mixtures in the range 67–267 mbar (50–200 Torr) with LIF detection of 2-C₃H₇O excited at 347 nm and fluorescence detection to the red of 375 nm. The upper temperature limit is set by the unimolecular decomposition rate of *i*-propoxy radical.
- (d) Pulsed laser photolysis of 2-propyl nitrite at 355 nm with laser-induced fluorescence detection of *i*-propoxy radical.

Preferred Values

$$k = 7.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$
$$k = 1.5 \times 10^{-14} \exp(-230/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 210\text{--}390 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.2 \text{ at } 298 \text{ K.}$$

$$\Delta (E/R) = \pm 200 \text{ K.}$$

Comments on Preferred Values

The results of Balla et al. (1985), Mund et al. (1998, 1999) and Fittschen et al. (1999) are in excellent agreement. The preferred values are based on the temperature-dependent data of Balla et al. (1985), Mund et al. (1998, 1999) and Fittschen et al. (1999).

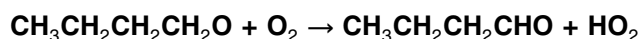
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6770

II.A5.105



$$\Delta H^\circ = -127.4 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
7.7×10^{-15}	298	Hoffmann et al., 1992	PLP-LIF (a)
$(1.4 \pm 0.7) \times 10^{-14}$	293 ± 3	Hein et al., 1999	PLP-AS/LIF (b)
<i>Relative Rate Coefficients</i>			
$6.8 \times 10^{-13} \exp[-(1178 \pm 176)/T]$	265–393	Morabito and Hecklen, 1987	RR (c)
1.3×10^{-14}	298		

Comments

(a) Pulsed laser photolysis of Cl_2 in the presence of $n\text{-C}_4\text{H}_{10}\text{-O}_2\text{-NO}$ mixtures in a flow system at total pressures of 10 mbar to 50 mbar (7.5 Torr to 37.5 Torr). Time-resolved monitoring of OH radicals was carried out by CW-laser absorption, and of NO_2 by LIF. The rate coefficient was derived from a computer simulation of OH radical and NO_2 temporal profiles.

(b) Pulsed laser photolysis at 248 nm of a mixture of 1-bromobutane, O_2 and NO in N_2 at 50 mbar total pressure in a slow-flow system. OH

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and NO_2 were monitored in real-time using laser long-path absorption at 308.417 nm and cw laser-excited fluorescence after excitation at 488 nm, respectively. The rate coefficient was derived from a computer simulation of the OH and NO_2 temporal concentration profiles.

(c) Photolysis of 1-butyl nitrite at 366 nm in the presence of NO and O_2 . Rate data were derived from the quantum yields of product formation, and a rate coefficient ratio of $k(1\text{-C}_4\text{H}_9\text{O}+\text{O}_2)/k(1\text{-C}_4\text{H}_9\text{O}+\text{NO})=1.67 \times 10^{-2} \exp[-(1178 \pm 176)/T]$ was obtained. This rate coefficient ratio is placed on an absolute basis using a rate coefficient of $k(1\text{-C}_4\text{H}_9\text{O}+\text{NO})=4.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature.

Preferred Values

$$k = 1.4 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

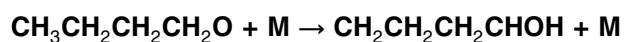
Based on the indirect study of Hein et al. (1999) which is in good agreement with the relative rate technique by Morabito and Hecklen (1987) at 298 K.

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6773

II.A5.106



$$\Delta H^\circ = -14.7 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

k/s^{-1}	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(3.5 \pm 2) \times 10^4$	293 ± 3	Hein et al., 1999	PLP-AS/LIF (a)
<i>Relative Rate Coefficients</i>			
2.2×10^5	303	Carter et al., 1979	S-GC (b)
$(2.1 \pm 0.5) \times 10^5$	296	Cox et al., 1981	S-GC (c)
$(2.7 \pm 0.2) \times 10^5$	298	Niki et al., 1981	S-FTIR (d)

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Comments

- 5 (a) Pulsed laser photolysis at 248 nm of a mixture of 1-bromobutane, O₂ and NO in N₂ at 50 mbar total pressure in a slow-flow system. HO and NO₂ were monitored in real-time using laser long-path absorption at 308.417 nm and cw laser-excited fluorescence after excitation at 488 nm, respectively. The rate coefficient was derived from a computer simulation of the HO and NO₂ temporal concentration profiles and is believed to be in the fall-off range.
- 10 (b) Smog chamber photolysis of *n*-C₄H₁₀-NO_x-air mixtures at 1 bar pressure. End-product analysis of C₃H₇CHO by GC. $k/k(1\text{-C}_4\text{H}_9\text{O}+\text{O}_2)=1.6\times 10^{19}$ molecule cm⁻³ obtained from yields of C₃H₇CHO and the rate of disappearance of *n*-C₄H₁₀. The above value of k is calculated by using a rate coefficient of $k=1.4\times 10^{-14}$ cm³ molecule⁻¹ s⁻¹ for the reference reaction 1-C₄H₉O + O₂ → C₃H₇CHO + HO₂ at 298 K (see this evaluation).
- 15 (c) Smog chamber photolysis of *n*-C₄H₁₀-HONO-air mixtures at 1 bar (760 Torr) pressure. End product analysis of C₃H₇CHO by GC. $k/k(1\text{-C}_4\text{H}_9\text{O}+\text{O}_2)=(1.5\pm 0.5)\times 10^{19}$ molecule cm⁻³ was derived from the yields of C₃H₇CHO and the rate of disappearance of *n*-C₄H₁₀ as a function of [O₂]. Above value of k was calculated by using a rate coefficient of $k=1.4\times 10^{-14}$ cm³ molecule⁻¹ s⁻¹ for the reference reaction, 1-C₄H₉O + O₂ → C₃H₇CHO + HO₂ at 298 K (see this evaluation).
- 20 (d) Photolysis of 1-C₄H₉ONO-air mixtures at 930 mbar (700 Torr) pressure in an FTIR cell. $k/k(1\text{-C}_4\text{H}_9\text{O}+\text{O}_2)=(1.9\pm 0.2)\times 10^{19}$ molecule cm⁻³ was derived from yields of C₃H₇CHO and the rate of disappearance of 1-C₄H₉ONO. Above value of k calculated using a rate coefficient

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cient of $k=1.4\times 10^{-14}$ cm³ molecule⁻¹ s⁻¹ for the reference reaction, 1-C₄H₉O+O₂ → C₃H₇CHO+HO₂ at 298 K (this evaluation).

Preferred Values

- 5 $k = 2.4 \times 10^{11} \exp(-4130/T) \text{ s}^{-1}$ at 298 K over the temperature range 295–400 K and 1 bar pressure.
- $k = 2.3 \times 10^5 \text{ s}^{-1}$ at 298 K and 1 bar pressure.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.
 $\Delta (E/R) = \pm 1000$ K.

10 Comments on Preferred Values

The preferred rate coefficient at room temperature is the mean from the studies of Carter et al. (1979), Cox et al. (1981) and Niki et al. (1981). The preferred A factor is an estimate of Baldwin et al. (1977) from transition-state theory on the basis of a mechanism involving a 1,5-H-atom shift.

- 15 The preferred value of $E/R=4130$ K follows from the preferred values of k_{298} and the A-factor. Large uncertainties have been assigned to these preferred values and direct measurements of the rate coefficient and its temperature coefficient are needed.

20 This procedure for obtaining the preferred rate parameters follows the pattern of Atkinson (1997).

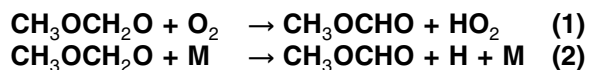
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II.A5.107



Rate coefficient data

$k_1.k_2^{-1}/\text{cm}^3 \text{ molecule}^{-1}$	Temp./K	Reference	Technique/Comments
$k_1[\text{O}_2] \sim k_2(1 \text{ bar, air})$	295	Jenkin et al., 1993	RR (a)

5 Comments

- (a) Steady-state photolysis of $\text{Cl}_2\text{-CH}_3\text{OCH}_3\text{-O}_2\text{-N}_2$ mixtures at pressures of 13.3 mbar to 1013 mbar (10 Torr to 760 Torr) with long-path FTIR analyses, and molecular modulation studies of similar reactant mixtures with UV absorption monitoring of $\text{CH}_3\text{OCH}_2\text{O}_2$ radicals. In both systems,
10 kinetic treatments indicate that Reactions (1) and (2) were competing under the conditions of the experiments.

Preferred Values

No quantitative recommendations.

Comments on Preferred Values

- 15 Although the results listed above for the reactions of the $\text{CH}_3\text{OCH}_2\text{O}$ radical are not quantitative, for the purposes of atmospheric modelling studies it is rec-

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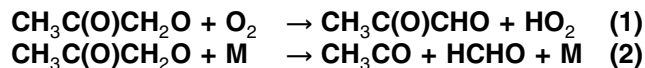
ommended that the above qualitative information on the ratios k_1/k_2 be used to decide if one or the other of the alkoxy radical reaction pathways predominates, or if both pathways should be considered.

References

- 5 Jenkin, M. D., Hayman, G. D., Wallington, T. J., Hurley, M. D., Ball, J. C., Nielsen, O. J., and Ellermann, T.: J. Phys. Chem., 97, 11 712, 1993.

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II.A5.108



Rate coefficient data

$k_1.k_2^{-1}/\text{cm}^3 \text{ molecule}^{-1}$	Temp./K	Reference	Technique/Comments
$k_1[\text{O}_2] \ll k_2$ (1 bar, air)	298	Jenkin et al., 1993	RR (a)
$k_1[\text{O}_2] \ll k_2$ (1 bar, air)	298	Bridier et al., 1993	RR (b)
$k_1[\text{O}_2] \ll k_2$ (1 bar, O ₂ /N ₂)	225–298	Orlando et al., 2000	S-FTIR (c)

5 Comments

- (a) Steady-state photolysis of Cl₂-CH₃C(O)CH₃-O₂-N₂ mixtures at 930 mbar (700 Torr) with long-path FTIR and long-path UV visible diode array spectroscopy analyses of products. Data indicate that Reaction (2) predominated over Reaction (1) under the conditions of the experiments.
- 10 (b) Flash photolysis of Cl₂-CH₃C(O)CH₃-air mixtures at 1 bar pressure with UV absorption monitoring of CH₃C(O)CH₂O₂ radicals. Data indicate that Reaction (2) predominated over Reaction (1) under the conditions of the experiments.
- 15 (c) Mixtures of Cl₂/acetone/O₂ pressurised to 1 atm with N₂ with and without NO_x were irradiated in a static chamber using a filtered Xe-arc lamp. The diagnostic products HCHO and methylglyoxal (CH₃C(O)CHO) and others

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were monitored using in situ long pathlength FTIR absorption. The independence of HCHO and CH₃C(O)CHO yields on the O₂ partial pressure varied from 66 to 865 mbar was taken as an indication of the predominance of (2) over (1) across the entire temperature range 225–298 K, even at 1 atm of O₂: $k_2/k_1=1.5\times 10^{20}$ and 1.0×10^{20} molecule cm⁻³ at 298 and 225 K, respectively.

Preferred Values

No quantitative recommendations.

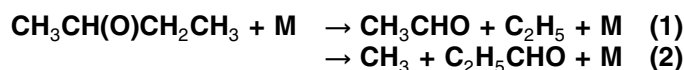
Comments on Preferred Values

Although the results listed above for the reactions of the CH₃C(O)CH₂O radical are not quantitative, for the purposes of atmospheric modelling studies it is recommended that the above qualitative information on the ratios k_1/k_2 be used to decide if one or the other of the alkoxy radical reaction pathways predominates, or if both pathways should be considered. All three studies listed above point towards the predominance of the decomposition pathway under atmospheric conditions down to 225 K.

References

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II.A5.109



$$\Delta H^\circ(1) = 24.6 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = 28.5 \text{ kJ}\cdot\text{mol}^{-1}$$

5 Rate coefficient data

k/s^{-1}	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$k_1 = (3.5 \pm 2) \times 10^3$	293	Hein et al., 1998	PLP-AS/LIF (a)
<i>Relative Rate Coefficients</i>			
$k_1 = 6.3 \times 10^{14} \exp(-7700/T)$	440–471	Batt and McCulloch, 1976	S-GC (b)
$k_1 = 3.8 \times 10^3$	298		
$k_1 = 2.2 \times 10^4$	303	Carter et al., 1979	S-GC (c)
$k_1 = 1.8 \times 10^4$	296	Cox et al., 1981	S-GC (d)
$k_1 = 6.3 \times 10^{13} \exp(-7600/T)$	363–503	Heiss et al., 1991	F-TLC/
$k_1 = 5.3 \times 10^2$	298		HPLC (e)
<i>Branching Ratios</i>			
$k_1/k_2 = 0.59 \exp(1350/T)$	399–493	Drew et al., 1985	S-GC (f)
$k_1/k_2 = 55$	298		

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Comments

- (a) Pulsed laser photolysis at 193 or 248 nm of a mixture of 2-bromobutane, O_2 and NO in N_2 at 50 mbar total pressure in a slow-flow system. HO and NO_2 were monitored in real-time using laser long-path absorption at 308.417 nm and cw laser-excited fluorescence after excitation at 488 nm, respectively. The rate coefficient was derived from a computer simulation of the HO and NO_2 temporal concentration profiles and is in the fall-off region at the total pressure used.
- (b) Pyrolysis of 2-butyl nitrite in the presence of NO at pressures of ~ 1 bar (~ 760 Torr) in a static system. End-product analysis of CH_3CHO by GC. Results were derived relative to the reaction $2\text{-C}_4\text{H}_9\text{O} + \text{NO} \rightarrow 2\text{-C}_4\text{H}_9\text{ONO}$ for which a value of $k = 4.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was taken, independent of temperature.
- (c) Smog chamber photolysis of $n\text{-C}_4\text{H}_{10}\text{-NO}_x$ -air mixtures at 1 bar pressure. End-product analysis of CH_3CHO and $\text{CH}_3\text{COC}_2\text{H}_5$ by GC yielded k_1/k_2 ($2\text{-C}_4\text{H}_9\text{O} + \text{O}_2$) = $3.15 \times 10^{18} \text{ molecule cm}^{-3}$. The above value of k_1 was obtained taking $k = 7 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the reference reaction $2\text{-C}_4\text{H}_9\text{O} + \text{O}_2 \rightarrow \text{CH}_3\text{C}(\text{O})\text{C}_2\text{H}_5 + \text{HO}_2$.
- (d) Similar experiments as in comment (b) with $n\text{-C}_4\text{H}_{10}\text{-HONO}$ -air mixtures yielding k_1/k_2 ($2\text{-C}_4\text{H}_9\text{O} + \text{O}_2$) = $(2.60 \pm 0.35) \times 10^{18} \text{ molecule cm}^{-3}$. The above value of k_1 was obtained taking $k = 7 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the reference reaction $2\text{-C}_4\text{H}_9\text{O} + \text{O}_2 \rightarrow \text{CH}_3\text{C}(\text{O})\text{C}_2\text{H}_5 + \text{HO}_2$.
- (e) Pyrolysis of $(2\text{-C}_4\text{H}_7\text{O})_2$ in a stream of $\text{O}_2\text{-N}_2$ with end-product analyses. Rate data derived from a computer simulation of yields of CH_3CHO and $\text{CH}_3\text{C}(\text{O})\text{C}_2\text{H}_5$ and assuming that $k = 2.6 \times 10^{-14}$

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$\exp(-100/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the competing reaction $2\text{-C}_4\text{H}_9\text{O} + \text{O}_2 \rightarrow \text{CH}_3\text{C}(\text{O})\text{C}_2\text{H}_5 + \text{HO}_2$.

(f) Static thermal generation of radicals from $\text{F} + 2\text{-C}_4\text{H}_9\text{OH}$ with end-product analysis of CH_3CHO and $\text{C}_2\text{H}_5\text{CHO}$ by GC.

5 Preferred Values

$k_1 = 2 \times 10^{14} \exp(-6860/T) \text{ s}^{-1}$ over the temperature range 300–500 K and 1 bar pressure.

$k_1 = 2 \times 10^4 \text{ s}^{-1}$ at 298 K and 1 bar pressure.

10 Reliability

$\Delta \log k_1 = \pm 0.3$ at 298 K.

$\Delta (E_1/R) = \pm 500 \text{ K}$.

Comments on Preferred Values

The preferred 298 K value is based on the measured ratios of $k/k(2\text{-butoxy} + \text{O}_2)$ of Carter et al. (1979) and Cox et al. (1981), using a rate coefficient of $k(2\text{-butoxy} + \text{O}_2) = 7 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ to place the rate coefficient ratio on an absolute basis. The temperature-dependence is derived assuming a pre-exponential factor of $A = 2 \times 10^{14} \text{ s}^{-1}$ with E/R calculated to fit the 298 K value of K. The effect of pressure on the value of k_1 has not been reported, but it is to be expected that at 1 bar pressure the value of k_1 is close to the high-pressure limit (Hein et al., 1998).

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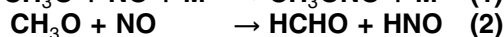
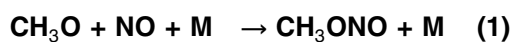
Although the branching ratio (k_1/k_2) reported by Drew et al. (1985) seems reasonable, it requires further confirmation before a recommendation can be made. None of the other studies (Batt and McCulloch, 1976; Carter et al., 1979; Cox et al., 1981) of the decomposition of the 2- $\text{C}_4\text{H}_9\text{O}$ radicals has reported $\text{C}_2\text{H}_5\text{CHO}$ as a product of the decomposition reaction, and it is possible that the radical generation system of Drew et al. (1985) is more complicated than they suggested.

References

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II.A5.110



$$\Delta H^\circ(1) = -172.7 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -103.1 \text{ kJ}\cdot\text{mol}^{-1}$$

5 Low-pressure rate coefficients

Rate coefficient data

$k_{01}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.35 \times 10^{-29} (T/298)^{-3.8} [\text{Ar}]$	296–573	Frost and Smith, 1990	PLF-LIF (a)
$1.8 \times 10^{-29} (T/300)^{-3.2} [\text{Ar}]$	220–473	McCaulley et al., 1990	DF-LIF (b)
$k_2 = (4.8 \pm 0.4) \times 10^{-12}$	298	Daële et al., 1995	DF-LIF (c)
$2.65 \times 10^{-29} (T/298)^{-2.8} [\text{He, Ar}]$	248–473	Caralp et al., 1998	DF/PLP-LIF (d)
$k_2 = 1.25 \times 10^{-11} \exp(-1015/T)$ $+ 1.92 \times 10^{-12} (T/298)^{-2.56}$			

Comments

- 10 (a) Rate coefficients were measured up to 165 mbar of Ar or CF_4 diluent. Evaluation of the chemical activation system $\text{CH}_3\text{O} + \text{NO} \rightarrow \text{CH}_3\text{ONO}^*$, $\text{CH}_3\text{ONO}^* + \text{M} \rightarrow \text{CH}_3\text{ONO} + \text{M}$, and $\text{CH}_3\text{ONO}^* \rightarrow \text{HCHO} + \text{HNO}$ were carried out using an extended Lindemann-Hinshelwood mechanism. At low
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pressures the disproportionation reaction $\text{CH}_3\text{O} + \text{NO} \rightarrow \text{HCHO} + \text{HNO}$ dominates ($k_2 = 5.0 \times 10^{-12} (T/298)^{-0.6} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). Assuming that Reactions (1) and (2) involve the same intermediate complex, k_2 is expected to decrease with increasing pressure following the relationship
5 $k_2 = k_{02} k_1 / k_{01}$.

(b) Measurements were made over the pressure range 1 mbar to 6.6 mbar in He or Ar. The disproportionation reaction $\text{CH}_3\text{O} + \text{NO} \rightarrow \text{HCHO} + \text{HNO}$ was measured by molecular beam MS ($k_2 = 1.3 \times 10^{-12} \exp(250/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$).

10 (c) Analysis by LIF and mass spectrometry. Experiments at 298 K and 1.3 mbar of He.

(d) Two sets of experiments, using DF over the range 0.6–7 mbar and 248–473 K, or PLP over the range 39–658 mbar and 284–364 K. Results with the bath gases He (mostly used) and Ar (some experiments) essentially agreed. Extensive RRKM modelling allowed to separate k_1 and k_2 . Falloff curves for k_1 evaluated with $F_c = \exp(-T/900)$. The overall rate constant is assumed to be of the form $k = k_1 ([\text{M}]) + k_2$.
15

Preferred Values

$k_{01} = 2.6 \times 10^{-29} (T/300)^{-2.8} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–400 K.
20

$k_2 = 2.3 \times 10^{-12} (T/300)^{-0.7} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–300 K.

Reliability

$\Delta \log k_{01} = \pm 0.1$ at 298 K.

$\Delta n = \pm 0.5$

$\Delta \log k_2 = \pm 0.2$ at 298 K.

5 Comments on Preferred Values

The preferred values are based on the extensive work by Caralp et al. (1998) which includes and supersedes the earlier results from Frost and Smith (1990), McCaully et al. (1990) and Daële et al. (1995) as well as by Ohmori et al. (1993) in the middle of the falloff curve. The results are represented in the form of $k = k_1$
10 $([M]) + k_2$, where $k_1(M)$ is based on k_{01} such as preferred here, $k_{\infty 1}$ such as given below and $F_c = \exp(-T/900)$ for $M = \text{He, Ar and N}_2$. It remains to be investigated whether k_2 decreases with increasing pressure (common intermediate of Reactions (1) and (2)) or is pressure independent (direct Reaction (2)).

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High-pressure rate coefficients

Rate coefficient data

$k_{\infty 1}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
2.1×10^{-11}	440–473	Batt et al., 1977	(a)
$(2.08 \pm 0.12) \times 10^{-11}$	298	Sanders et al., 1980	(b)
1.4×10^{-11}	298	Zellner, 1987	PLP-AS (c)
$3.6 \times 10^{-11} (T/298)^{-0.6}$	296–573	Frost and Smith, 1990	PLF-LIF (d)
$(2.45 \pm 0.31) \times 10^{-11}$	300	Dóbé et al., 1994	DF-LIF (e)
$3.26 \times 10^{-11} (T/298)^{-0.6}$	248–473	Caralp et al., 1998	PLP-LIF (f)

Comments

- 5 (a) Thermal decomposition of methyl nitrite in the presence of NO and $(\text{CH}_3)_3\text{CH}$. Combination of these data with the equilibrium constant gives the value indicated. For the second channel, $k(\text{CH}_3\text{O} + \text{NO} \rightarrow \text{CH}_2\text{O} + \text{HNO})/k_{\infty}(\text{CH}_3\text{O} + \text{NO} \rightarrow \text{CH}_3\text{ONO}) = 0.17$ was estimated.
- 10 (b) Photolysis of methyl nitrite at 266 nm with CH_3O detection by LIF at He pressure of 13 mbar to 66 mbar. HNO as a reaction product was also detected by LIF; however, no absolute estimate of its yield could be made.
- (c) Falloff curve was measured over the range 5 mbar to 500 mbar. Extrapolations carried out using $F_c = 0.6$.

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- (d) See comment (a) for k_0 .
- (e) CH_3O radicals and HCHO from Reaction (2) detected by LIF. The branching ratio for HCHO formation varied between 0.84 and 0.26 over the pressure range 1 mbar to 11 mbar.
- 5 (f) See comment (d) for k_0 .

Preferred Values

$k_{\infty 1} = 3.3 \times 10^{-11} (T/300)^{-0.6} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–400 K.

Reliability

- 10 $\Delta \log k_{\infty 1} = \pm 0.5$ at 298 K.
 $\Delta n = \pm 0.5$

Comments on Preferred Values

- The recommended value is from the most extensive study by Caralp et al. (1998) which supersedes and includes earlier work. The results are in accord with an RRKM modelling of the chemical activation system. Batt (1987) cites a rate coefficient ratio of $k_2/k < 0.05$ from a study at 433–473 K, consistent with our preferred values.
- 15

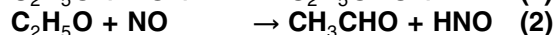
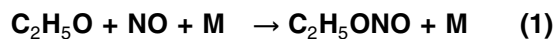
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6792

II.A5.111



$$\Delta H^\circ(1) = -178.5 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -127.6 \text{ kJ}\cdot\text{mol}^{-1}$$

5 Low-pressure rate coefficients

Rate coefficient data

$k_{01}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.2 \pm 1.2) \times 10^{-28} [\text{He}]$	298	Daële et al., 1995	DF-LIF/MS (a)

Comments

- 10 (a) $\text{C}_2\text{H}_5\text{O}$ radicals were generated by the reaction of F atoms with $\text{C}_2\text{H}_5\text{OH}$. Measurements were carried out at 0.7 mbar, 1.3 mbar and 2.6 mbar. The rate coefficient k_{01} was obtained from a Lindemann-Hinshelwood analysis, assuming identical intermediates in Reactions (1) and (2); $k_2 = (1.1 \pm 0.5) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was derived.

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Preferred Values

$$k_{01} = 2.2 \times 10^{-28} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_2 = 1.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

- 5 $\Delta \log k_{01} = \pm 0.3$ at 298 K.
 $\Delta \log k_2 = \pm 0.5$ at 298 K.

Comments on Preferred Values

- 10 The preferred values are from Daële et al. (1995) assuming that Reactions (1) and (2) can be separated by Lindemann-Hinshelwood extrapolation and $k = k_1([\text{M}]) + k_2$. We assume equal values of k_{01} for He and N_2 as third bodies. In contrast to the simple Lindemann-Hinshelwood evaluation of Daële et al. (1995) corresponding to $F_c = 1$, we recommend to use $F_c = 0.6$ for a construction of the falloff curve for $k_1([\text{M}])$.

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High-pressure rate coefficients

Rate coefficient data

$k_{\infty 1}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(4.4 \pm 0.4) \times 10^{-11}$	298	Frost and Smith, 1990	PLP-LIF (a)
$(3.1 \pm 0.8) \times 10^{-11}$	298	Daële et al., 1995	DF-LIF/MS (b)
$(3.7 \pm 0.7) \times 10^{-11} (T/300)^{0.2}$	286–388	Fittschen et al., 1999	PLP-LIF (c)

Comments

- 5 (a) The rate coefficient k_1 is found not to depend on the pressure between 20 mbar and 130 mbar of Ar.
- (b) See comment (a) for k_0 .
- (c) Measurements over the range 39–658 mbar of He. Results assumed to be in the high pressure range. Values taken from table of results, not abstract.

10 Preferred Values

$k_{\infty 1} = 4.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–400 K.

Reliability

$\Delta \log k_{\infty 1} = \pm 0.3$ at 298 K.

$\Delta n = \pm 0.5$

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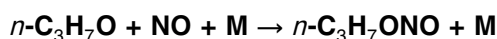
Comments on Preferred Values

- The preferred value of $k_{\infty 1}$ is from Frost and Smith (1990), in close agreement with Fittschen et al. (1999). For the falloff curve of Reaction (1), $F_c=0.6$ is chosen. The value of k_2 derived in Daële et al. (1995) with the preferred $k_{\infty 1}$ is in good agreement with the ratio $k_2/k_{\infty 1} = 0.3$ observed in Baker and Shaw (1965).

References

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II.A5.112



High-pressure rate coefficients

Rate coefficient data

$k_\infty/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(3.8 \pm 0.1) \times 10^{-11} (T/300)^{-1.2}$	289–380	Fittschen et al., 1999	PLP-LIF (a)

Comments

(a) Measurements over the range 40–133 mbar of He. Results assumed to be in the high pressure range. The observed temperature dependence may be the result of falloff effects.

10 Preferred Values

$$k_\infty = 3.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k_\infty = \pm 0.3 \text{ at } 298 \text{ K.}$$

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Comments on Preferred Values

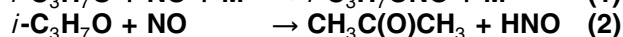
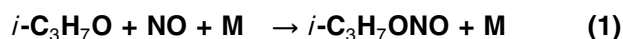
The only available measurement from Fittschen et al. (1999) gives similar results as for $i\text{-C}_3\text{H}_7\text{O} + \text{NO} + \text{M} \rightarrow i\text{-C}_3\text{H}_7\text{ONO} + \text{M}$. The apparent temperature coefficient may be due to falloff effects (its origin needs to be clarified).

5 References

Fittschen, C., Frenzel, A., Imrik, K., and Devolder, P.: *Int. J. Chem. Kinet.*, 31, 800, 1999.

6798

II.A5.113



$$\Delta H^\circ(2) = -142.2 \text{ kJ}\cdot\text{mol}^{-1}$$

High-pressure rate coefficients

5 Rate coefficient data

$k_{\infty 1}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
3.4×10^{-11}	298	Balla et al., 1985	PLP-LIF (a)
$(3.3 \pm 0.1) \times 10^{-11} (T/300)^{-1.3}$	286–389	Fittschen et al., 1999	PLP-LIF (b)

Comments

(a) No pressure dependence of the rate coefficient was observed over the range 1.3–6 mbar. The small negative temperature dependence [$k = 1.2 \times 10^{-11} \exp(310/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$] observed over the range 298–383 K may be attributed to falloff effects.

(b) Measurements over the range 40–667 mbar of He. Results assumed to be in the high pressure range. The observed temperature dependence corresponding to $k_{\infty 1} = 8.9 \times 10^{-12} \exp(397/T)$ may be attributed to falloff effects.

6799

Preferred Values

$k_{\infty 1} = 3.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k_2 = 6.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and 27–270 mbar pressure.

Reliability

5 $\Delta \log k_{\infty 1} = \pm 0.3$ at 298 K.

$\Delta \log k_2 = \pm 0.5$ at 298 K.

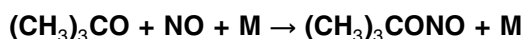
Comments on Preferred Values

The preferred value of $k_{\infty 1}$ is based on the studies of Balla et al. (1985) and Fittschen et al. (1999). The apparent temperature coefficient of $k_{\infty 1}$ differs from that of $k_{\infty 1}$ for $\text{C}_2\text{H}_5\text{O} + \text{NO} + \text{M}$. It remains to be clarified whether falloff effects are responsible for the different behavior. The value of k_2 is obtained from the preferred $k_{\infty 1}$ and the rate coefficient ratio $k_2/k_1 = 0.19 \pm 0.03$ (independent of temperature) cited in Batt and Milne (1977).

References

- 15 Balla, R. J., Nelson, H. H., and McDonald, J. R.: Chem Phys., 99, 323, 1985.
Batt, L. and Milne, R. T.: Int. J. Chem. Kinet., 9, 141, 1977.
Fittschen, C., Frenzel, A., Imrik, K., and Devolder, P.: Int. J. Chem. Kinet., 31, 800, 1999.

II.A5.114



High-pressure rate coefficients

Rate coefficient data

$k_\infty/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(4.17 \pm 0.12) \times 10^{-11} (T/200)^{-1.27}$	200–390	Blitz et al., 1999	LP-LIF (a)
$(2.74 \pm 0.5) \times 10^{-11} (T/300)^{-1.52}$	223–304	Lotz and Zellner, 2000	LP-LIF (b)

Comments

- (a) Pulsed excimer laser photolysis of *tert*-butyl nitrite at 351 nm with and without added NO, using LIF detection of *tert*-butoxy and NO. Experiments in 92–658 mbar of He showed no pressure dependence of the rate coefficient.
- (b) Pulsed excimer laser photolysis of di-*tert*-butyl peroxide with added NO using LIF of *tert*-butoxy. No pressure dependence detected over the range 6.6–105 mbar of N₂.

6801

Preferred Values

$k_\infty = 2.6 \times 10^{-11} (T/300)^{-1.4} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–400 K.

Reliability

- $\Delta \log k_\infty = \pm 0.3$ at 298 K.
 $\Delta n = \pm 0.5$.

Comments on Preferred Values

The studies of Blitz et al. (1999) and Lotz and Zellner (2000) using different sources of *tert*-butoxy radicals are in good agreement. The preferred values present the average of the two results.

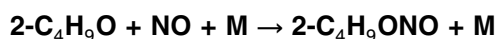
References

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 Lotz, Ch. and Zellner, R.: Phys. Chem. Chem. Phys., 2, 2353, 2000.

15

6802

II.A5.115



High-pressure rate coefficients

Rate coefficient data

$k_\infty/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.48 \pm 0.5) \times 10^{-11} (T/300)^{-1.2}$	223–311	Deng et al., 2000	PLP-LIF (a)

Comments

(a) Measurements over the range 66–230 mbar of N_2 . Results assumed to be in the high pressure range. The observed temperature dependence may be the result of falloff effects.

10 Preferred Values

$$k_\infty = 2.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k_\infty = \pm 0.5 \text{ at } 298 \text{ K.}$$

6803

Comments on Preferred Values

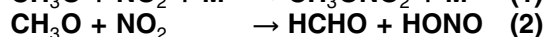
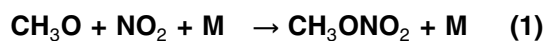
The only available measurement from Deng et al. (2000) gives similar results as for smaller alkoxy radicals reacting with NO. The apparent temperature coefficient may be due to falloff effects (its origin needs to be clarified).

5 References

Deng, W., Wang, C., Katz, D. R., Gawinski, G. G., Davis, A. J., and Dibble, T. S.: Chem. Phys. Lett., 330, 541, 2000.

6804

II.A5.116



$$\Delta H^\circ(1) = -171.5 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -238.5 \text{ kJ}\cdot\text{mol}^{-1}$$

5 Low-pressure rate coefficients

Rate coefficient data

$k_{01}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$2.6 \times 10^{-29} (T/300)^{-4.5} [\text{He}]$	220–473	McCaulley et al., 1985	DF-LIF (a)
$(5.2 \pm 1.9) \times 10^{-29} [\text{He}]$	298	Frost and Smith, 1990	PLP-LIF (b)
$(9.0 \pm 1.9) \times 10^{-29} [\text{Ar}]$	298		
$(11 \pm 3) \times 10^{-29} [\text{CF}_4]$	298		
$(4.9 \pm 1.2) \times 10^{-29} [\text{Ar}]$	390		
$(5.3 \pm 0.2) \times 10^{-29} [\text{He}]$	298	Biggs et al., 1993	DF-LIF (c)
$(5.3 \pm 0.3) \times 10^{-29} (T/297)^{-4.4} [\text{Ar}]$	233–356	Wollenhaupt and Rowley, 2000	PLP-LIF (d)
$(3.93 \pm 0.05) \times 10^{-29} (T/300)^{-1.74} [\text{He}]$	250–390	Martínez et al., 2000	PLP-LIF (e)

6805

Comments

- (a) CH_3O radicals were produced by IR laser dissociation of $\text{C}_6\text{F}_5\text{OCH}_3$ to yield CH_3 , followed by $\text{CH}_3 + \text{NO}_2 \rightarrow \text{CH}_3\text{O} + \text{NO}$. Pressure range 0.8 mbar to 5 mbar. Direct measurements of the branching ratio k_1/k_2 were not possible. A separation was performed by assuming that Reaction (1) was in the low pressure limit. A value of $k_2 = 9.6 \times 10^{-12} \exp(-1150/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (with relatively large error limits) was estimated.
- (b) Pulsed laser photolysis of $\text{CH}_3\text{ONO-NO}$ mixtures at 266 nm. Rate coefficients were measured over the pressure ranges 40 mbar to 130 mbar of He, 8 mbar to 130 mbar of Ar, and 40 mbar to 100 mbar of CF_4 . Falloff curves were fitted to the experimental data using F_c values of 0.41, 0.44, and 0.48 for He, Ar, and CF_4 , respectively. The recombination Reaction (1) appears to dominate over Reaction (2).
- (c) Pressures of He varied from 1.3 mbar to 13 mbar. Extrapolations were performed using $F_c = 0.6$, an RRKM analysis was also done. A value $k_{01} = 5.9 \times 10^{-29} [\text{He}] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was obtained.
- (d) Pulsed laser photolysis of CH_3ONO . Rate coefficients were measured over the range 13–263 mbar of Ar. Falloff curves represented with temperature-independent $F_c = 0.6$, alternatively temperature-dependent F_c between 0.66 at 223 K and 0.55 at 356 K was used. $k_2/k_1 \approx 0.1$ at 13 mbar and 356 K, whereas $k_2/k_1 < 0.01$ was derived at 13 mbar and 233 K.
- (e) Measurements over the pressure range 66–789 mbar. Falloff extrapolation with $F_c = 0.6$.

6806

Preferred Values

$k_{01} = 8.1 \times 10^{-29} (T/300)^{-4.5} [\text{N}_2] \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–400 K.

$k_2 = 9.6 \times 10^{-12} \exp(-1150/T) \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

5 Reliability

$\Delta \log k_{01} = \pm 0.3$ at 298 K.

$\Delta n = \pm 1$.

$\Delta \log k_2 = \pm 0.5$

Comments on Preferred Values

10 The agreement between the studies of Frost and Smith (1990, 1993), Biggs et al. (1993), Wollenhaupt and Crowley (2000) and Martínez et al. (2000) appears satisfactory, in particular if the different ways of treating the falloff curve are taken into account. We assume similar values of k_{01} for M=Ar and N₂. Falloff curves are constructed with $F_c=0.44$ at 300 K such as chosen in Frost and Smith (1990, 1993).
15 The preferred value is average of the results from Frost and Smith (1990, 1993) and Wollenhaupt and Crowley (2000) after reevaluation of the data from Wollenhaupt and Crowley (2000) with $F_c=0.44$. Reaction (2) appears to play only a minor role at pressures above 10 mbar. The value of k_2 remains relatively uncertain.

6807

High-pressure rate coefficients

Rate coefficient data

$k_{\infty 1}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.0 \pm 0.4) \times 10^{-11}$	295	Frost and Smith, 1990	PLP-LIF (a)
$(1.86 \pm 0.05) \times 10^{-11} (T/297)^{-1.87}$	233–356	Wollenhaupt and Rowley, 20004	PLP-LIF (b)
$(2.40 \pm 0.02) \times 10^{-11} (T/300)^{-0.88}$	250–390	Martínez et al., 2000	PLP-LIF (c)
$(1.3 \pm 0.1) \times 10^{-11}$	300	Kukui et al., 2000	PLP-LIF (d)
<i>Relative Rate Coefficients</i>			
1.5×10^{-11}	298	Wiebe et al., 1973	(e)
$(1.0 \pm 0.5) \times 10^{-11}$	392–420	Batt and Rattray, 1979	(f)
$(1.4 \pm 0.1) \times 10^{-11}$	298	Biggs et al., 1993	DF-LIF (g)
<i>Branching Ratios</i>			
$k_1/k = 0.92 \pm 0.08$	298	Wiebe et al., 1973	(e)
$k_2/k_1 = \leq 0.05$	384–424	Batt and Rattray, 1979	(f)

Comments

5 (a) See comment (b) for k_0 .

(b) See comment (d) for k_0 .

(c) See comment (e) for k_0 .

6808

- (d) Photolysis of $\text{CH}_3\text{SSCH}_3\text{-NO}_2$ mixtures with LIF detection of CH_3O . Measurements over the range 16–805 mbar of He. The given value is for about 750 mbar. No falloff extrapolation.
- (e) Steady-state photolysis of CH_3ONO in the presence of NO-O_2 and $\text{NO-NO}_2\text{-N}_2$ mixtures at 10 mbar to 500 mbar. Relative rate coefficients were derived from $\Phi(\text{CH}_3\text{ONO}_2)$, with $k(\text{CH}_3\text{O}+\text{NO})/k=1.3$ at 298 K. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(\text{CH}_3\text{O}+\text{NO}\rightarrow\text{CH}_3\text{ONO})=2\times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ over the range 200 K to 400 K.
- (f) Static reaction vessel, CH_3O formed from pyrolysis of CH_3OOCH_3 in the presence of $\text{NO-NO}_2\text{-CF}_4$ at a total pressure of 675 mbar. Relative rate coefficients were determined from end-product analysis of CH_3ONO and CH_3ONO_2 by GC $k(\text{CH}_3\text{O}+\text{NO}\rightarrow\text{CH}_3\text{ONO})/k=2.03\pm 0.47$ was obtained over the range 392 K to 420 K. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(\text{CH}_3\text{O}+\text{NO}\rightarrow\text{CH}_3\text{ONO})=2\times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ over the range 200 K to 400 K. k_1/k_2 was determined from pyrolysis of CH_3OOCH_3 in the presence of NO_2 and N_2 and shown to be pressure dependent.
- (g) See comment (c) for k_0 . An RRKM extrapolation leads to the value $k_{\infty}=2.1\times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$.

Preferred Values

$k_1 = 1.5 \times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ at 298 K and 1 bar of air.

$k_{\infty 1} = 2.1 \times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$, independent of temperature over the range 200–400 K.

6809

Reliability

$\Delta \log k_{\infty} = \pm 0.3$ at 298 K.

$\Delta n = \pm 0.5$

Comments on Preferred Values

- The preferred $k_{\infty 1}$ value is based on Frost and Smith (1990, 1993), Wollenhaupt and Crowley (2000), Martínez et al. (2000) and Kukui et al. (2000). Falloff curves are constructed with $F_c=0.44$ from Frost and Smith (1990, 1993). Reaction (2) appears to be only of minor importance. Differences in the apparent temperature dependences of $k_{\infty 1}$ in part are due to different F_c -values used in the falloff extrapolations.

References

- Batt, L. and Rattray, G. N.: *Int. J. Chem. Kinet.*, 11, 1183, 1979.
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- Martínez, E., Albaladejo, J., Jiménez, E., Notario, A., and Díaz de Mera, Y.: *Chem. Phys. Lett.*, 329, 191, 2000.
- McCaulley, J. A., Anderson, S. M., Jeffries, J. B., and Kaufman, F.: *Chem. Phys. Lett.*, 115, 180, 1985.
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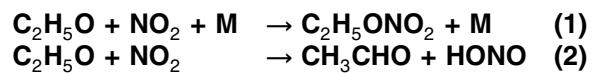
6810

95, 7, 1973.

Wollenhaupt, M. and Crowley, J. N.: J. Phys. Chem. A, 104, 6429, 2000.

6811

II.A5.117



$$\Delta H^\circ(1) = -171.7 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -263.2 \text{ kJ}\cdot\text{mol}^{-1}$$

5 High-pressure rate coefficients

Rate coefficient data

$k_{\infty 1}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.8 \pm 0.3) \times 10^{-11}$	295	Frost and Smith, 1990	PLP-LIF (a)

Comments

10 (a) The same rate coefficients were measured in the presence of 2 mbar or 130 mbar of He.

Preferred Values

$k_{\infty 1} = 2.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 200–300 K.

6812

Reliability

$\Delta \log k_{\infty 1} = \pm 0.3$ at 298 K.

$\Delta n = \pm 0.5$

Comments on Preferred Values

- 5 The value of $k_{\infty 1}$ is based on the data of Frost and Smith (1990), being consistent with values for related reactions such as $\text{RO} + \text{NO} + \text{M} \rightarrow \text{RONO} + \text{M}$ (with $\text{M} = \text{CH}_3, \text{C}_2\text{H}_5,$ and $i\text{-C}_3\text{H}_7$) or $\text{CH}_3\text{O} + \text{NO}_2 + \text{M} \rightarrow \text{CH}_3\text{ONO}_2 + \text{M}$. Reaction (2) appears to be of minor importance, with a rate coefficient ratio of $k_2/k_1 = 0.1 \pm 0.01$ at ~ 450 K being cited by Batt (1987).

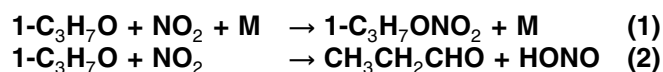
10 References

Batt, L.: *Int. Rev. Phys. Chem.*, 6, 53, 1987.

Frost, M. J. and Smith, I. W. M.: *J. Chem. Soc. Faraday Trans.*, 86, 1751, 1990.

6813

II.A5.118



$\Delta H^\circ(1) = -165.9 \text{ kJ}\cdot\text{mol}^{-1}$

$\Delta H^\circ(2) = -258.7 \text{ kJ}\cdot\text{mol}^{-1}$

5 High-pressure rate coefficients

Rate coefficient data

$k_{\infty 1}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(3.6 \pm 0.4) \times 10^{-11}$	296	Mund et al., 1998	PLP-LIF (a)

Comments

- 10 (a) The rate coefficient was observed to be independent of total pressure over the range 6.7 mbar to 53 mbar of He.

Preferred Values

$k_{\infty 1} = 3.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K .

6814

Reliability

$\Delta \log k_{\infty 1} = \pm 0.3$ at 298 K.

Comments on Preferred Values

5 The preferred value is based on the sole study of Mund et al. (1998) with expanded uncertainty limits. The rate coefficient is of a similar magnitude to other RO+NO₂ reactions (see data sheets in this evaluation for CH₃O+NO₂, C₂H₅O+NO₂ and 2-C₃H₇O+NO₂).

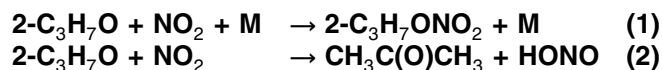
10 Although no statement on the branching ratio k_1/k_2 may be made on the basis of this work, it is expected that $k_1/k_2 < 0.2$.

References

Mund, C., Fockenberg, Ch., and Zellner, R.: Ber. Bunsenges. Phys. Chem., 102, 709, 1998.

6815

II.A5.119



$$\Delta H^\circ(1) = -171.7 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -277.6 \text{ kJ}\cdot\text{mol}^{-1}$$

5 High-pressure rate coefficients

Rate coefficient data

$k_{\infty 1}/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
3.5×10^{-11}	298	Balla et al., 1985	PLP-LIF (a)
$(3.3 \pm 0.3) \times 10^{-11}$	296	Mund et al., 1998	PLP-LIF (b)

Comments

10 (a) By extrapolation to zero laser power, a rate coefficient of $k_{\infty 1} = 1.5 \times 10^{-11} \exp[(250 \pm 200)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was derived from measurements over the temperature range 295 K to 384 K. No pressure dependence was observed between 1.3 mbar and 13 mbar.

(b) The measured rate coefficient was observed to be independent of total pressure over the range 6.7 mbar to 106 mbar of He.

6816

Preferred Values

$k_{\infty 1} = 3.4 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 200–300 K.

Reliability

- 5 $\Delta \log k_{\infty 1} = \pm 0.2$ at 298 K.

Comments on Preferred Values

The recommendation is based on the data of Balla et al. (1985) and Mund et al. (1998). The value of $k_{\infty 1}$ is consistent with other related reactions such as $\text{RO} + \text{NO} + \text{M} \rightarrow \text{RONO} + \text{M}$ and $\text{RO} + \text{NO}_2 + \text{M} \rightarrow \text{RONO}_2 + \text{M}$ (with $\text{R} = \text{CH}_3, \text{C}_2\text{H}_5, i\text{-C}_3\text{H}_7$, see this evaluation). It is estimated that $k_2/k_{\infty 1} < 0.2$, Batt (1987) cites a rate coefficient ratio of $k_2/k_1 = 0.027 \pm 0.006$ at ~ 450 K, indicating that Reaction (2) is of negligible importance under atmospheric conditions.

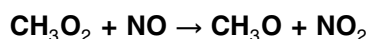
References

- 15 Balla, R. J., Nelson, H. H., and McDonald, J. R.: Chem. Phys., 99, 323, 1985.
Mund, Ch., Fockenberg, Ch., and Zellner, R.: Ber. Bunsenges. Phys. Chem., 102, 709, 1998.
Batt, L.: Int. Rev. Phys. Chem., 6, 53, 1987.

6817

Appendix 6: RO_2 reactions

II.A6.120



$$\Delta H^\circ = -48.8 \text{ kJ}\cdot\text{mol}^{-1}$$

5 Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(8.0 \pm 2.0) \times 10^{-12}$	295	Plumb et al., 1979	DF-MS (a)
$(3.0 \pm 1.7) \times 10^{-12}$	298	Adachi and Basco, 1979	FP-AS
$(7.1 \pm 1.4) \times 10^{-12}$	298	Sander and Watson, 1980	FP-AS (b)
$(6.5 \pm 2.0) \times 10^{-12}$	298	Cox and Tyndall, 1979, 1980	MMS-AS (c)
$(8.1 \pm 1.6) \times 10^{-12}$	240–339	Ravishankara et al., 1981	PLP-LIF (d)
$2.1 \times 10^{-12} \exp[(380 \pm 250)/T]$	218–365	Simonaitis and Heicklen, 1981	FP-AS (e)
$(7.7 \pm 0.9) \times 10^{-12}$	298		
$(8.6 \pm 2.0) \times 10^{-12}$	295	Plumb et al., 1981	DF-MS (f)
$(7 \pm 2) \times 10^{-12}$	298	Zellner et al., 1986	PLP-AS (g)
$(8.8 \pm 1.4) \times 10^{-12}$	295	Sehested et al., 1993	PR-UV (h)
$(11.2 \pm 1.4) \times 10^{-12}$	298	Masaki et al., 1994	PLP-MS (i)
$2.8 \times 10^{-12} \exp[(285 \pm 60)/T]$	199–429	Villalta et al., 1995	F-CIMS (j)
$(7.5 \pm 1.3) \times 10^{-12}$	298		
$(7.5 \pm 1.0) \times 10^{-12}$	298	Helleis et al., 1996	DF-MS (k)
$9.2 \times 10^{-13} \exp[(600 \pm 140)/T]$	203–295	Scholtens et al., 1999	F-CIMS (l)
$(7.8 \pm 2.2) \times 10^{-12}$	298		

6818

Comments

- (a) Flow tube at 8 ± 2 Torr (11 ± 2.6 mbar) He. Direct detection of CH_3O_2 (generated in $\text{O} + \text{C}_2\text{H}_4 + \text{O}_2$) via electron impact mass spectrometry.
- (b) Data obtained at 75, 350 and 700 Torr (100, 467 and 933 mbar) He, and 700 Torr (933 mbar) N_2 . CH_3O_2 formed by $\text{Cl} + \text{CH}_4 + \text{O}_2$.
- (c) Data obtained at 540 Torr (720 mbar) $\text{N}_2 + \text{O}_2$. CH_3O_2 formed by $\text{Cl} + \text{CH}_4 + \text{O}_2$.
- (d) CH_3O_2 generated by photolysis of $\text{CH}_3\text{N}_2\text{CH}_3$ in presence of O_2 . Rate data obtained via LIF detection of NO_2 .
- (e) Pressures of 70 to 600 Torr (93 to 800 mbar) CH_4 . CH_3O_2 formed by $\text{Cl} + \text{CH}_4 + \text{O}_2$.
- (f) Flow tube at 5.8 Torr (7.7 mbar) He, direct detection of CH_3O_2 (generated in $\text{Cl} + \text{CH}_4 + \text{O}_2$) via electron impact mass spectrometry.
- (g) Experiments conducted at 10 Torr (13.3 mbar) He or N_2 . CH_3O_2 generated by photolysis of $\text{CH}_3\text{N}_2\text{CH}_3$ in presence of O_2 . Rate data obtained by measuring CH_3O_2 by absorption spectroscopy, LIF used to observe formation of CH_3O .
- (h) Experiments conducted in 760 Torr (1013 mbar) SF_6 and O_2 . CH_3O_2 generated in $\text{F} + \text{CH}_4 (+\text{O}_2)$ and NO_2 formation monitored to derive kinetic information.
- (i) Experiments conducted in 3–6 Torr (4–8 mbar) $\text{N}_2 + \text{O}_2$. Mass spectrometry using photo-ionisation detection of CH_3O_2 , which was formed in the 193 nm photo-dissociation of acetone in the presence of O_2 .

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- (j) Experiments conducted in 2–5.5 Torr (2.7–7.3 mbar) He. CH_3O_2 generated by thermal decomposition of $\text{CH}_3\text{CH}_2\text{ONO}$ in the presence of O_2 . Mass spectrometry using chemi-ionisation detection of CH_3^+ generated in $\text{O}_2^+ + \text{CH}_3\text{O}_2$.
- (k) Experiments conducted in 1.7 Torr (2.3 mbar) He, CH_3O_2 generated in $\text{F} + \text{CH}_4 (+\text{O}_2)$. Electron impact detection of CH_3O_2 in excess NO. Measurements using deuterated methyl peroxy gave $k(\text{CD}_3\text{O}_2 + \text{NO}) = (8.6 \pm 1.0) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
- (l) Turbulent flow reactor at 100 Torr (133 mbar) N_2 total pressure. CH_3O_2 generated in $\text{F} + \text{CH}_4 (+\text{O}_2)$ and detected as $\text{CH}_3\text{OOH}^+(\text{H}_2\text{O})_n$ following proton transfer from H_3O^+ .

Preferred Values

- $k = 7.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 2.95 \times 10^{-12} \exp(285/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–430 K.

Reliability

- $\Delta \log k = \pm 0.05$ at 298 K.
 $\Delta (E/R) = \pm 100$ K.

Comments on Preferred Values

- This reaction has been subject of intensive investigation using several different experimental techniques. With the exception of the data of Adachi and

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Basco (1979), the data at room temperature are in very good agreement. The recommended value of the rate coefficient at 298 K is the average of the results from Scholtens et al. (1999), Helleis et al. (1996), Villalta et al. (1995), Plumb et al. (1981), Ravishankara et al. (1981) and Simonaitis and Heicklen (1981).
5 The temperature dependence of the rate coefficient is described by three sets of data (Simonaitis and Heicklen, 1981; Villalta et al., 1995; Scholtens et al., 1999) which are in good agreement at temperatures above 230 K. At lower temperatures there is some deviation, with the datasets of Scholtens et al. (1999) and Simonaitis and Heicklen (1981) deviating from Arrhenius behaviour. These
10 data sets were obtained at higher pressures than that of Villalta et al. (1995) and the possibility of a pressure dependence in the rate coefficient at low temperatures has been discussed (Scholtens et al., 1999). The data from the studies at higher pressures are however not of sufficient quality to confirm this, and the data of Villalta et al. (1995) which covers the largest temperature range, and
15 is of superior precision, provides the basis of the recommended temperature dependence, which has been adjusted for the average 298 K rate coefficient.

The formation of CH_3O and NO_2 products has been confirmed (Ravishankara et al., 1981; Zellner et al., 1986) whereas the alternative reaction channel of the peroxy + NO reaction leading to the formation of alkyl nitrate
20 has never been observed for CH_3O_2 and accounts for <1% of the overall reaction at room temperature and below. This is consistent with an upper limit of 0.3% for formation of CH_3ONO at 295 K and 100 Torr N_2 (Scholtens et al., 1999).

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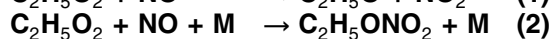
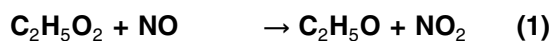
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6822

II.A6.121



$$\Delta H^\circ(1) = -45.2 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -217.0 \text{ kJ}\cdot\text{mol}^{-1}$$

5 Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.7 \pm 0.2) \times 10^{-12}$	298	Adachi and Basco, 1979	FP-AS
$(8.9 \pm 3.0) \times 10^{-12}$	295	Plumb et al., 1982	DF-MS
$(8.5 \pm 1.2) \times 10^{-12}$	298	Sehested et al., 1993	PR-AS
$(8.2 \pm 1.6) \times 10^{-12}$	295	Däele et al., 1995	DF-MS (a)
$2.6 \times 10^{-12} \exp[(380 \pm 70)/T]$	207–403	Eberhard and Howard, 1996	F-CIMS (b)
$(9.3 \pm 1.6) \times 10^{-12}$	298		
$3.1 \times 10^{-12} \exp[(330 \pm 110)/T]$	220–355	Maricq and Szente, 1996	PLP-AS (c)
$(10.0 \pm 1.5) \times 10^{-12}$	295		
$3.8 \times 10^{-12} \exp[(290 \pm 110)/T]$	213–299	Ranschaert et al., 2000	F-CIMS (d)
$(10.1 \pm 0.9) \times 10^{-12}$	299		
<i>Branching Ratio</i>			
$k_2/k \leq 0.014$ (1 bar)	299	Atkinson et al., 1982	(e)
$k_2/k = 1.2 \times 10^{-3} \exp(610/T)$	213–298	Ranschaert et al., 2000	(f)
$k_2/k = 0.006$ (100 Torr N_2)	298		
$k_2/k = 0.02$ (100 Torr N_2)	213		

6823

Comments

- (a) Conventional discharge flow system with LIF detection of $\text{C}_2\text{H}_5\text{O}$ product. k determined by simulation of experimental $\text{C}_2\text{H}_5\text{O}$ profiles.
- (b) Ethylperoxy radicals formed by the thermal decomposition of *n*-propyl nitrate in the presence of O_2 , or by RF discharge through $\text{C}_2\text{H}_5\text{I}$ (also in the presence of O_2). Pseudo first order kinetics with excess NO and CIMS detection of $\text{C}_2\text{H}_5\text{O}_2$ as the ethyl peroxy negative ion.
- (c) Excimer laser photolysis of Cl_2 - C_2H_6 -NO- O_2 - N_2 mixtures. Time-resolved measurements of $\text{C}_2\text{H}_5\text{O}_2$ decay and $\text{C}_2\text{H}_5\text{ONO}$ formation using diode array UV absorption spectroscopy, and of NO loss and NO_2 formation using diode laser absorption spectroscopy.
- (d) Turbulent flow reactor at 100 Torr (133 mbar) N_2 total pressure. $\text{C}_2\text{H}_5\text{O}_2$ detected as $\text{C}_2\text{H}_5\text{OOH}^+(\text{H}_2\text{O})_n$ and $\text{C}_2\text{H}_5\text{ONO}_2$ detected as $\text{C}_2\text{H}_5\text{ONO}_2\text{H}^+(\text{H}_2\text{O})_n$ following proton transfer from H_3O^+ .
- (e) GC analysis of $\text{C}_2\text{H}_5\text{ONO}_2$ product from photo-oxidation of C_2H_6 in Cl_2 - C_2H_6 -NO-air mixtures.
- (f) Ranschaert, Schneider and Elrod (2000) also present temperature dependent values of the rate coefficient $k_2 = 1.6 \times 10^{-15} \exp(1160/T)$ for the temperature range 213 to 299 K and 100 Torr (133 mbar) N_2 pressure. The authors state that the branching ratios are associated with large errors as the measurements were conducted near the detection limit for $\text{C}_2\text{H}_5\text{ONO}_2$ and were complicated by secondary chemistry.

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Preferred Values

$k = 9.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 2.6 \times 10^{-12} \exp(380/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–410 K.

5 $k_2/k \leq 0.014$ at 298 K and 1 bar pressure.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta (E/R) = \pm 50 \text{ K}$.

Comments on Preferred Values

10 With the exception of the measurement of Adachi and Basco (1979), all measurements at room temperature are in excellent agreement. The preferred value of the rate coefficient at room temperature is an average of the data from Plumb et al. (1982), Sehested et al. (1993), Däele et al. (1995), Eberhard and Howard (1996), Maricq and Szente (1996) and Ranschaert et al. (2000). The temperature coefficients (E/R) from the three temperature dependent studies
15 (Eberhard and Howard, 1996; Maricq and Szente, 1996; Ranschaert et al., 2000) also show good agreement. The preferred value was obtained from a weighted fit (using the authors estimated errors) to the data of all three studies, and reflects the higher precision of the Eberhard and Howard (1996) dataset.
20 The two sets of data (Ranschaert et al., 2000; Atkinson et al., 1982) for the branching ratio for $\text{C}_2\text{H}_5\text{ONO}_2$ formation are self consistent at the common temperature of 298 K, and show that this channel is minor under atmospheric conditions.

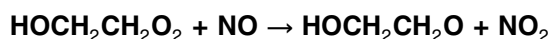
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6826

II.A6.122



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(9 \pm 4) \times 10^{-12}$	298	Becker et al., 1991	PLP-LIF (a)

5 Comments

(a) Pulsed laser photolysis of H_2O_2 in the presence of $\text{C}_2\text{H}_4\text{-O}_2\text{-NO}$ mixtures at a total pressure of 1 bar [760±5 Torr]. Relative HO radical concentrations were determined as a function of time using LIF, and simulated by a mechanism consisting of 11 reactions, of which k of above reaction was the most sensitive.

Preferred Values

$k = 9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

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Comments on Preferred Values

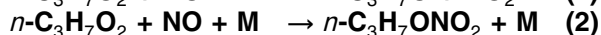
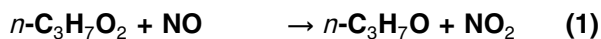
The rate coefficient reported by Becker et al. (1991), which is recommended, is consistent with the rate coefficients of the reactions of other peroxy radicals with NO. Independent confirmation is needed to reduce the error limits. The hydroxy-alkoxy product has been shown to be formed with sufficient internal energy that prompt dissociation can take place as well as thermal decomposition and reaction with O_2 of the collisionally stabilised radical (Orlando et al., 1998; Vereecken et al., 1999).

References

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II.A6.123



Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$2.9 \times 10^{-12} \exp[(350 \pm 60)/T]$ $(9.4 \pm 1.6) \times 10^{-12}$	201–402 298	Eberhard and Howard, 1996	F-CIMS(a)
<i>Branching Ratio</i>			
$k_2/k = 0.020 \pm 0.009$ (1 bar)	299	Atkinson et al., 1982; Carter and Atkinson, 1989	(b)

5 Comments

- (a) $n\text{-C}_3\text{H}_7\text{O}_2$ radicals were produced by pyrolysis of $n\text{-C}_3\text{H}_7\text{ONO}_2$ in the presence of O_2 and detected by CIMS. Pseudo-first order kinetics with excess NO.
- 10 (b) Based on yield of $n\text{-C}_3\text{H}_7\text{ONO}_2$ product from photo-oxidation of C_3H_8 in NO_x -air mixtures. Carter and Atkinson (1989) revised the analysis of original data to provide the value quoted.

6829

Preferred Values

- $k = 9.4 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 2.9 \times 10^{-12} \exp(350/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–410 K.
- 5 $k_2/k = 0.020$ at 298 K and 1 bar pressure.

Reliability

- $\Delta \log k = \pm 0.2$ at 298 K.
 $\Delta (E/R) = \pm 100$ K.
 $\Delta \log k_2/k = \pm 0.02$ at 298 K and 1 bar pressure.

10 Comments on Preferred Values

The measurements of Eberhard and Howard (1996) provide the only experimental data on this rate coefficient. The value of k_{298} is in line with the most recent measurements for reactions of ethyl peroxy and 2-propyl peroxy radicals with NO. The negative temperature coefficient is also consistent with that observed for the rate coefficient for other $\text{RO}_2 + \text{NO}$ reactions. The recommendation accepts the Arrhenius expression of Eberhard and Howard (1996).

The preferred branching ratio for n -propyl nitrate formation is that measured by Atkinson et al. (1982), as revised by Carter and Atkinson (1989).

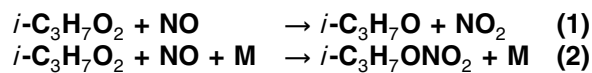
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6831

II.A6.124



$$\Delta H^\circ(1) = -40.5 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -212.2 \text{ kJ}\cdot\text{mol}^{-1}$$

5 Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(5.0 \pm 1.2) \times 10^{-12}$	290	Peeters et al., 1992	DF-MS (a)
$2.7 \pm 10^{-12} \exp[(360 \pm 60)/T]$	201–401	Eberhard et al., 1996	F-CIMS (b)
$(9.0 \pm 1.5) \times 10^{-12}$	298		
$(9.1 \pm 1.5) \times 10^{-12}$	298	Eberhard and Howard, 1996	F-CIMS (c)
<i>Branching Ratio</i>			
$k_2/k = 0.042 \pm 0.003$ (1 bar air)	299	Atkinson et al., 1982; Carter and Atkinson, 1989	(d)

Comments

(a) Low pressure flow tube at 2 Torr (2.7 mbar) He. Rate constant derived from analysis of NO_2 growth profiles.

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- (b) $i\text{-C}_3\text{H}_7\text{O}_2$ radicals produced by reaction of O_2 with $i\text{-C}_3\text{H}_7$ radicals produced by thermal decomposition of isobutyl nitrate. $i\text{-C}_3\text{H}_7\text{O}_2$ was detected as its parent negative ion formed by reaction with O_2 . k determined by pseudo-first order loss of $i\text{-C}_3\text{H}_7\text{O}_2$ in the presence of NO.
- 5 (c) $i\text{-C}_3\text{H}_7\text{O}_2$ produced by reaction of O_2 with $i\text{-C}_3\text{H}_7$ produced in a low frequency RF discharge through i -propyl iodide.
- (d) Photolysis of $\text{CH}_3\text{ONO-NO-C}_3\text{H}_8$ -air mixtures at a total pressure of 1 bar. The branching ratio was determined from the measured yields of $i\text{-C}_3\text{H}_7\text{ONO}_2$ and the consumption of C_3H_8 . Carter and Atkinson (1989) have re-evaluated the branching ratio, cited above, from the original data (Atkinson et al., 1982) on the basis of revised data for the rate coefficients of the HO radical reactions with alkanes.
- 10

Preferred Values

- $k = 9.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
- 15 $k = 2.7 \times 10^{-12} \exp(360/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–410 K.
- $k_2/k = 0.042$ at 298 K and 1 bar pressure.

Reliability

- $\Delta \log k = \pm 0.1$ at 298 K.
- 20 $\Delta (E/R) = \pm 100 \text{ K}$.
- $\Delta \log(k_2/k) = \pm 0.3$ at 298 K and 1 bar pressure.

6833

Comments on Preferred Values

The data from Eberhard et al. (1996) and Eberhard and Howard (1996) using improved techniques for radical generation and detection give a rate coefficient at 298 K which is almost a factor of 2 higher than the value obtained by Peeters et al. (1992), and is close to the value obtained for a range of alkyl peroxy radicals at 298 K. The preferred value for k_{298} and the temperature dependence is that reported by Eberhard et al. (1996).

5

The recommended branching ratio is that recalculated by Carter and Atkinson (1989) based on the original data of Atkinson et al. (1982), and using updated data for the HO radical reactions with alkanes.

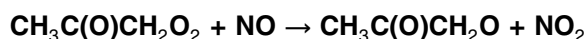
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- 20

6834

II.A6.125



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(8.0 \pm 2.0) \times 10^{-12}$	295	Sehested et al., 1998	PR-AS (a)

5 **Comments**

(a) $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}_2$ was formed in the pulsed radiolysis of $\text{CH}_3\text{C}(\text{O})\text{CH}_3\text{-SF}_6\text{-O}_2$ mixtures, and the kinetics of the title reaction followed by monitoring formation of NO_2 in real time by absorption spectroscopy. The influence of secondary chemistry on formation of NO_2 was estimated by numerical simulation of an assumed reaction scheme.

Preferred Values

$k = 8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

6835

Comments on Preferred Values

The recommendation is based on the sole study of the reaction of Sehested et al. (1998), with appropriately expanded error limits. The value of the rate coefficient at room temperature is consistent with reactions of other unsubstituted peroxy radicals with NO. The temperature dependence of the rate coefficient is also expected to be consistent with other $\text{RO}_2\text{+NO}$ reactions, and the expression: $k = 2.8 \times 10^{-12} \exp(300/T)$ has been recommended (Tyndall et al., 2001).

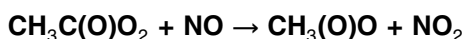
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6836

II.A6.126



$$\Delta H^\circ = -93 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$2.1 \times 10^{-12} \exp[(570 \pm 140)/T]$	228–354	Maricq and Szente, 1996	PLP-AS (a)
$(1.4 \pm 0.2) \times 10^{-11}$	298		
$8.1 \times 10^{-12} \exp[(270 \pm 60)/T]$	200–402	Villalta and Howard, 1996	F-CIMS (b)
$(2.0 \pm 0.3) \times 10^{-11}$	298		
$(2.0 \pm 0.3) \times 10^{-11}$	295	Sehested et al., 1998	PR-A (c)
$6.0 \times 10^{-12} \exp[(320 \pm 40)/T]$	218–370	Moise et al., 1999	F-CIMS (d)
$(2.0 \pm 0.3) \times 10^{-11}$	296		
<i>Relative Rate Coefficients</i>			
$8.9 \times 10^{-12} \exp[(312 \pm 46)/T](1 \text{ bar air})$	247–298	Seefeld et al., 1997	(e)
$(2.5 \pm 0.4) \times 10^{-11} (1 \text{ bar air})$	298		
$(2.17 \pm 0.23) \times 10^{-11} (0.93 \text{ bar})$	295	Sehested et al., 1998	(f)

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Comments

- (a) Pulsed laser photolysis of $\text{Cl}_2\text{-CH}_3\text{CHO-O}_2\text{-NO}$ mixtures at 351 nm. Time-resolved absorption spectroscopy using a gated diode array for $\text{CH}_3\text{C(O)O}_2$ in the UV and using a diode laser for NO and NO_2 in the IR. Correction to k required for competing reactions of $\text{CH}_3\text{C(O)O}_2$.
- (b) $\text{CH}_3\text{C(O)O}_2$ produced by thermal decomposition of peroxyacetyl nitrate and detected by CIMS through its reaction with SF_6^- . NO_2 , CH_3 and CO_2 were positively identified as products implying rapid decomposition of $\text{CH}_3\text{C(O)O}$ to CH_3 and CO_2 . Experiments conducted at pressures of 1.2–6 Torr (1.6–8 mbar) He.
- (c) Pulse radiolysis of $\text{CH}_3\text{CHO-O}_2\text{-CO}_2\text{-NO}$ and $\text{CH}_3\text{CHO-O}_2\text{-SF}_6\text{-NO}$ mixtures at 1 bar pressure. The rate coefficient was obtained from the formation of NO_2 , measured by absorption at 400.5 nm.
- (d) $\text{CH}_3\text{C(O)O}_2$ produced by thermal decomposition of peroxyacetyl nitrate and detected by CIMS through its reaction with SF_6^- . Experiments conducted at 2–5 Torr (2.7–6.7 mbar) He.
- (e) $\text{CH}_3\text{C(O)O}_2$ produced by steady state photolysis of biacetyl in the presence of O_2 . Yields of peroxyacetyl nitrate were measured as a function of the $[\text{NO}]/[\text{NO}_2]$ ratio. Data gave $k/k(\text{CH}_3\text{C(O)O}_2+\text{NO}_2)=2.44\pm 0.18$ at 1 bar, independent of temperature over the range 247 K to 298 K. The expression in the table is calculated using the recommended value for $k(\text{CH}_3\text{C(O)O}_2+\text{NO}_2)$ at 1 bar pressure (IUPAC, this evaluation).
- (f) $\text{CH}_3\text{C(O)O}_2$ radicals were produced by photolysis of $\text{Cl}_2\text{-CH}_3\text{CHO-O}_2$ mixtures, and reactants and products monitored by FTIR spectroscopy. The measured rate coefficient ratio

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$k(\text{CH}_3\text{C}(\text{O})\text{O}_2+\text{NO})/k(\text{CH}_3\text{C}(\text{O})\text{O}_2+\text{NO}_2)=2.07\pm 0.21$ at 932 mbar N_2 is placed on an absolute basis using the recommended value of $k(\text{CH}_3\text{C}(\text{O})\text{O}_2+\text{NO}_2)$ (IUPAC, this evaluation).

Preferred Values

- 5 $k = 2.0 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 7.5 \times 10^{-12} \exp(290/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–350 K.

Reliability

- $\Delta \log k = \pm 0.15$ at 298 K.
10 $\Delta (E/R) = \pm 250 \text{ K}$.

Comments on Preferred Values

- The direct measurements at 298 K of Villalta and Howard (1996), Moise et al. (1999) and Sehested et al. (1998) are in excellent agreement, all obtaining values of $2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, and provide the basis of the 298 K recommendation. Those of Maricq and Szenté (1996) give a value of $k(298)$ approximately 30% lower. Of the three temperature dependent data sets, those of Villalta and Howard (1996) and Moise et al. (1999) agree within the error limits and present a significantly weaker dependence than the more highly scattered data of Maricq and Szenté (1996). The recommended temperature dependence was obtained by weighted least squares fitting to the data of Villalta and Howard (1996) and Moise et al. (1999).

The earlier data for k , obtained relative to $k(\text{CH}_3\text{C}(\text{O})\text{O}_2+\text{NO}_2)$ (Cox et al.,

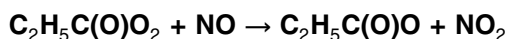
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1976; Cox and Roffey, 1977; Hendry and Kenley, 1977; Kirchner et al., 1990; Tuazon et al., 1991), are generally consistent with this recommendation.

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II.A6.127



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(6.7 \pm 1.7) \times 10^{-12} \exp[(340 \pm 80)/T]$	226–406	Froyd and Lovejoy, 1999	F-CIMS(a)
$(2.1 \pm 0.2) \times 10^{-11}$	298		
<i>Relative Rate Coefficients</i>			
$1.25 \times 10^{-11} \exp(240/T)$	249–302	Seefeld and Kerr, 1997	RR(b)
$(2.8 \pm 0.4) \times 10^{-11}$	298		
$(2.3 \pm 0.2) \times 10^{-11}$	302	Kerr and Stocker, 1985	RR(c)

5 Comments

(a) Low pressure flow tube at 1.5 to 15 Torr (2–20 mbar) He or N₂. C₂H₅C(O)O₂ was formed by thermal decomposition of C₂H₅C(O)ONO₂ and detected as C₂H₅C(O)O₂⁻ or C₂H₅C(O)O⁻ following reaction with SF₆⁻ or I⁻. Results at 15 Torr N₂ analysed to set an upper limit to the association reaction of $k_0(298 \text{ K}) < 1.9 \times 10^{-30} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$.

(b) Ratio $k/k(\text{C}_2\text{H}_5\text{C}(\text{O})\text{O}_2 + \text{NO}_2) = 2.33 \pm 0.38$, independent of temperature over the range 249–302 K. C₂H₅C(O)O₂ produced by photolysis of C₂H₅C(O)Cl in a flow system at 1 atm pressure with analysis of
6841

C₂H₅C(O)O₂NO₂ by GC, as a function of the [NO]/[NO₂] ratio. k calculated with $k(\text{C}_2\text{H}_5\text{C}(\text{O})\text{O}_2 + \text{NO}_2) = k(\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{NO}_2)$ from the present evaluation [in Arrhenius form, $k_\infty(\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{NO}_2) = 5.4 \times 10^{-12} \exp(240/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the range 250 K to 300 K (IUPAC, this evaluation)]. Also showed that the above rate constant ratio was 11% lower than the corresponding ratio for CH₃C(O)O₂, which is consistent with a higher rate coefficient for the RO₂+NO₂ (+M) reaction for the C₃ acylperoxy radical.

(c) Ratio $k/k(\text{C}_2\text{H}_5\text{C}(\text{O})\text{O}_2 + \text{NO}_2) = 1.89 \pm 0.21$. k calculated with $k(\text{C}_2\text{H}_5\text{C}(\text{O})\text{O}_2 + \text{NO}_2) = k_\infty(\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{NO}_2)$ from the present evaluation (in Arrhenius form, $k_\infty(\text{CH}_3\text{C}(\text{O})\text{O}_2 + \text{NO}_2) = 5.4 \times 10^{-12} \exp(240/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the range 250 K to 300 K (IUPAC, this evaluation)].

Preferred Values

$k = 2.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 6.7 \times 10^{-12} \exp(340/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range
15 220–410 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

$\Delta (E/R) = \pm 200 \text{ K}$.

Comments on Preferred Values

20 The preferred values are based on the absolute determination of Froyd and Lovejoy (1999). The relative rate measurements (Seefeld and Kerr, 1997; Kerr and Stocker, 1985) are in agreement with this number, but suffer from the lack

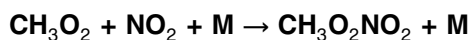
of an absolute measurement for $k(\text{C}_2\text{H}_5\text{C}(\text{O})\text{O}_2 + \text{NO}_2)$, the reference reaction rate coefficient (see comments above).

References

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5 Kerr, J. A. and Stocker, D. W.: J. Photochem., 28, 475, 1985.
Seefeld, S. and Kerr, J. A.: Environ. Sci. Technol., 31, 2949, 1997.

6843

II.A6.128



$$\Delta H^\circ = -92.7 \text{ kJ}\cdot\text{mol}^{-1}$$

Low-pressure rate coefficients

5 Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.33 \pm 0.08) \times 10^{-30}[\text{N}_2]$	298	Sander and Watson, 1980	FP-AS (a)
$2.2 \times 10^{-30} (T/300)^{-2.5}[\text{N}_2]$	253–353	Ravishankara et al., 1980	FP-AS (b)
$(1.46 \pm 0.50) \times 10^{-30}[\text{SF}_6]$	295	Wallington et al., 1999	PR-AS (c)

Comments

- (a) Pressure range 70 mbar to 900 mbar for the bath gases He, N_2 , and SF_6 . Analysis of the falloff curve was carried out with a theoretical F_c value of 0.39, in good agreement with the fitted value of $F_c=0.4\pm 0.10$.
10
- (b) Pressure range 100 mbar to 950 mbar. Analyses of the falloff curves at 253 K, 298 K and 353 K were carried out with $F_c=0.4$ independent of temperature.
- (c) Pulse radiolysis study in 0.5–14 bar of SF_6 . Evaluating the falloff curve with
15 $F_c=0.40$.

6844

Preferred Values

$k_0 = 2.5 \times 10^{-30} (T/300)^{-5.5} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250–350 K.

Reliability

- 5 $\Delta \log k_0 = \pm 0.3$ at 298 K.
 $\Delta n = \pm 1$.

Comments on Preferred Values

10 The preferred values are based on the results from Sander and Watson (1980) and the theoretical analysis from Destriau and Troe (1990). These values are based on a theoretically determined value of $F_c=0.36$ at 300 K.

High-pressure rate coefficients

Rate coefficient data

$k_\infty/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(8.0 \pm 1.0) \times 10^{-12}$	298	Sander and Watson, 1980	FP-AS (a)
$7 \times 10^{-12} (T/298)^{-3.5}$	253–353	Ravishankara et al., 1980	FP-AS (b)
$(1.8 \pm 0.25) \times 10^{-11}$	295	Wallington et al., 1999	PR-AS (c)

6845

Comments

- (a) See comment (a) for k_0 .
- 5 (b) See comment (b) for k_0 . The large negative temperature coefficient is probably an artifact of the interpretation. If a larger negative temperature exponent for k_0 and a smaller F_c value at higher temperature are used, the large negative temperature exponent of k_∞ will decrease.
- (c) See comment (c) for k_0 .

Preferred Values

10 $k = 4.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and 1 bar of air.
 $k_\infty = 1.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 250–350 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ at 298 K.
 $\Delta n = \pm 0.5$

15 *Comments on Preferred Values*

20 The preferred values are based on the high pressure study from Wallington et al. (1999). An experimental value of $F_c=0.36$ at 298 K appears well established. Less complete information on the falloff range is obtained from the experiments by Cox and Tyndall (1980), who measured $k=1.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 700 mbar of N_2 and $1.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 66 mbar

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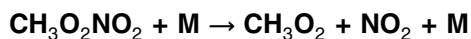
of Ar at 275 K, and Bridier et al. (1992) who measured $k=(4.4\pm 0.4)\times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ at 298 K in 1 bar of air. The apparent observation of a pressure independent rate coefficient k over the range 66 mbar to 760 mbar of Ar reported by Adachi and Basco (1980) is not confirmed by Sander and Watson (1980) and Ravishankara et al. (1980). ΔH is taken from the equilibrium measurements of Bridier et al. (1992).

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6847

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$$\Delta H^\circ = 92.7 \text{ kJ}\cdot\text{mol}^{-1}$$

Low-pressure rate coefficients

5 Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$9.0 \times 10^{-5} \exp(-9694/T)[\text{N}_2]$	248–273	Zabel et al., 1989	(a)
$6.7 \times 10^{-19} [\text{N}_2]$	298*		

Comments

- (a) Rate of decomposition of CH₃O₂NO₂ followed by FTIR spectroscopy after generation in a reaction chamber, with subsequent addition of NO to scavenge CH₃O₂ radicals. Falloff curves were fitted with $F_c=0.4$.

Preferred Values

$$k_0 = 6.8 \times 10^{-19} [\text{N}_2] \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_0 = 9 \times 10^{-5} \exp(-9690/T) [\text{N}_2] \text{ s}^{-1} \text{ over the temperature range } 250\text{--}300 \text{ K.}$$

6848

Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.

$\Delta (E/R) = \pm 500$ K.

Comments on Preferred Values

- 5 The preferred values correspond to the data and analysis from Zabel et al. (1989). A theoretical analysis of these data and those of the reverse reaction from Sander and Watson (1980) and Ravishankara et al. (1980) in Destriau and Troe (1990) gave an internally consistent picture (with $\Delta H^\circ = 88.5$ kJ mol⁻¹). Slightly lower limiting rate coefficients were obtained in Bridier et al. (1992) where a value of $F_c=0.6$ was used. Direct measurements of the equilibrium constant $K_c=k/k_1=2.73 \times 10^{-28} \exp(10910/T)$ cm³ molecule⁻¹ from Bridier et al. (1992) lead to $\Delta H=92.7$ kJ mol⁻¹ and provide an indication for the internal consistency of the rate data.

High-pressure rate coefficients

15 Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$2.1 \times 10^{16} \exp(-10920/T)$	256–268	Bahta et al., 1982	(a)
2.6	298*		
$1.1 \times 10^{16} \exp(-10560/T)$	248–273	Zabel et al., 1989	(b)
4.5	298*		

6849

Comments

- (a) CH₃O₂NO₂ generated by photolysis of Cl₂ in the presence of NO₂, CH₄ and O₂. Kinetics were monitored in the presence of NO by UV absorption at 250 nm. At 460 mbar, $k=6 \times 10^{15} \exp(-10620/T)$ s⁻¹. The given value of k_∞ is derived with $F_c=0.6$. The data depend to some extent on the rate coefficient for the reaction CH₃O₂+NO→CH₃O+NO₂.
- 5
- (b) See comment (a) for k_0 .

Preferred Values

$k = 1.8$ s⁻¹ at 298 K and 1 bar of air.

10 $k_\infty = 4.5$ s⁻¹ at 298 K.

$k_\infty = 1.1 \times 10^{16} \exp(-10560/T)$ s⁻¹ over the temperature range 250–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ at 298 K.

$\Delta (E/R) = \pm 500$ K.

15 Comments on Preferred Values

See comments on preferred values of k_0 .

References

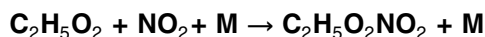
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6851

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$$\Delta H^\circ = -67.7 \text{ kJ}\cdot\text{mol}^{-1}$$

Low-pressure rate coefficients

5 Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$4.8 \times 10^{-29}[\text{N}_2]$	254	Elfers et al., 1990	(a)

Comments

- (a) Thermal decomposition of $\text{C}_2\text{H}_5\text{O}_2\text{NO}_2$ in a glass reaction chamber in the presence of differing initial $[\text{NO}_2]/[\text{NO}]$ ratios at total pressures of 10 mbar to 1000 mbar. $\text{C}_2\text{H}_5\text{O}_2\text{NO}_2$ was prepared in situ by the photolysis of $\text{Cl}_2\text{-C}_2\text{H}_6\text{-O}_2\text{-NO}_2\text{-N}_2$ mixtures. $\text{C}_2\text{H}_5\text{O}_2\text{NO}_2$, NO_2 and NO concentrations were monitored by longpath FTIR absorption and rate coefficient ratios for the reaction of $\text{C}_2\text{H}_5\text{O}_2$ with NO and NO_2 were obtained. The reported rate coefficient for $\text{C}_2\text{H}_5\text{O}_2 + \text{NO}_2$ was derived using a rate coefficient of $8.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the reaction $\text{C}_2\text{H}_5\text{O}_2 + \text{NO} \rightarrow \text{C}_2\text{H}_5\text{O} + \text{NO}_2$. Falloff curves were constructed based on the theoretical analysis from Destriau and Troe (1990) with $F_c = 0.31$ and $k_\infty = 7.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

6852

Preferred Values

$k_0 = 1.3 \times 10^{-29} (T/300)^{-6.2} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–300 K.

Reliability

- 5 $\Delta \log k_0 = \pm 0.3$ at 298 K.
 $\Delta n = \pm 1$.

Comments on Preferred Values

10 The preferred values are based on the data from Elfers et al. (1990) and the analysis from Destriau and Troe (1990). The temperature dependence is from the theoretical analysis of Destriau and Troe (1990). Falloff extrapolations were made with $F_c=0.31$ at 250 K to 300 K such as given from the theoretical analysis of Destriau and Troe (1990).

High-pressure rate coefficients

Rate coefficient data

$k_\infty/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
15 1.0×10^{-11}	254	Elfers et al., 1990	(a)

6853

Comments

(a) See comment (a) for k_0 .

Preferred Values

- $k = 6.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and 1 bar of air.
5 $k_\infty = 8.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 200–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ over the temperature range 200–300 K.

Comments on Preferred Values

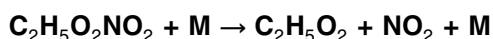
10 See comments on k_0 . The theoretical analysis in Destriau and Troe (1990) also includes information from studies of the reverse reaction measured in Zabel et al. (1989).

References

- Destriau, M. and Troe, J.: Int. J. Chem. Kinet., 22, 915, 1990.
15 Elfers, F., Zabel, F., and Becker, K. H.: Chem. Phys. Lett., 168, 14, 1990.
Zabel, F., Reimer, A., Becker, K. H., and Fink, E. H.: J. Phys. Chem., 93, 5500, 1989.

6854

II.A6.131



$$\Delta H^\circ = 67.7 \text{ kJ}\cdot\text{mol}^{-1}$$

Low-pressure rate coefficients

5 Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$4.8 \times 10^{-4} \exp(-9285/T) [\text{N}_2]$	245–273	Zabel et al., 1989	FTIR (a)

Comments

(a) Unimolecular decay of $\text{C}_2\text{H}_5\text{O}_2\text{NO}_2$ followed at total pressures ranging from 10 mbar to 800 mbar. Falloff extrapolation with $F_c=0.3$.

10 Preferred Values

$$k_0 = 1.4 \times 10^{-17} [\text{N}_2] \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_0 = 4.8 \times 10^{-4} \exp(-9285/T) [\text{N}_2] \text{ s}^{-1} \text{ over the temperature range } 250\text{--}300 \text{ K.}$$

6855

Reliability

$$\Delta \log k_0 = \pm 0.5 \text{ at } 298 \text{ K.}$$

$$\Delta (E/R) = \pm 1000 \text{ K.}$$

Comments on Preferred Values

5 The dissociation data are consistent with experimental recombination data from Elfers et al. (1989) and the theoretical analysis from Zabel et al. (1989) and Destriau and Troe (1990). Falloff curves are constructed with $F_c=0.31$ (over the range 250 K to 300 K).

High-pressure rate coefficients

10 Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$8.8 \times 10^{15} \exp(-10440/T)$	245–273	Zabel et al., 1989	FTIR(a)

Comments

(a) See comment (a) for k_0 .

6856

Preferred Values

$k = 4.0 \text{ s}^{-1}$ at 298 K and 1 bar of air.

$k_{\infty} = 5.4 \text{ s}^{-1}$ at 298 K.

$k_{\infty} = 8.8 \times 10^{15} \exp(-10440/T) \text{ s}^{-1}$ over the temperature range 250–300 K.

5 Reliability

$\Delta \log k_{\infty} = \pm 0.5$ at 300 K.

$\Delta (E/R) = \pm 1000 \text{ K}$.

Comments on Preferred Values

See comments on k_0 .

10 References

Destriau, M. and Troe, J.: *Int. J. Chem. Kinet.*, 22, 915, 1990.

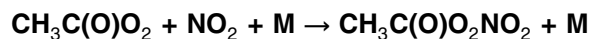
Elfers, G., Zabel, F., and Becker, K. H.: *Chem. Phys. Lett.*, 168, 14, 1990.

Zabel, F., Reimer, A., Becker, K. H., and Fink, E. H.: *J. Phys. Chem.*, 93, 5500, 1989.

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$\Delta H^\circ = -119 \text{ kJ}\cdot\text{mol}^{-1}$

Low-pressure rate coefficients

5 Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$5.1 \times 10^{-29} [\text{N}_2]$	298	Basco and Parmar, 1987	FP-AS (a)
$(2.7 \pm 1.5) \times 10^{-28} (T/298)^{-7.1} [\text{air}]$	248–393	Bridier et al., 1991	FP-AS (b)

Comments

(a) Photolysis of $\text{Cl}_2\text{-CH}_3\text{CHO-O}_2\text{-N}_2$ and NO_2 at total pressures of 100 mbar to 800 mbar. Extrapolation of falloff curve with theoretically modeled value of $F_c=0.19$.

(b) The falloff curves were fitted using $F_c=0.30$. The discrepancy with the data of Basco and Parmar (1987) is attributed to an oversimplified kinetic scheme used in Basco and Parmar (1987).

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Preferred Values

$k_0 = 2.7 \times 10^{-28} (T/300)^{-7.1} [\text{N}_2] \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250–300 K.

5 Reliability

$\Delta \log k_0 = \pm 0.4$ at 298 K.

$\Delta n = \pm 2$.

Comments on Preferred Values

10 The data from Basco and Parmar (1987) and Addison et al. (1980) are a factor of 2–3 lower than those from Bridier et al. (1991). The more extensive and internally consistent study of $\text{CH}_3\text{C}(\text{O})\text{OONO}_2$ (PAN) formation and dissociation in Bridier et al. (1991) is preferred. Falloff extrapolations were performed with a modeled value of $F_c=0.3$.

High-pressure rate coefficients

15 Rate coefficient data

$k_\infty/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
6.1×10^{-12}	298	Basco and Parmar, 1987	FP-AS (a)
$(1.21 \pm 0.05) \times 10^{-11} (T/298)^{-0.9}$	248–393	Bridier et al., 1991	FP-AS (b)
$(1.0 \pm 0.2) \times 10^{-11}$ (0.93 bar)	295	Sehested et al., 1998	PR-A (c)

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Comments

(b) See comment (a) for k_0 .

(c) See comment (b) for k_0 .

5 (d) $\text{CH}_3\text{C}(\text{O})\text{O}_2$ radicals were generated from the pulsed radiolysis of $\text{CH}_3\text{CHO}-\text{O}_2-\text{CO}_2-\text{NO}_2$ and $\text{CH}_3\text{CHO}-\text{SF}_6-\text{O}_2-\text{NO}_2$ mixtures and the disappearance rate of NO_2 monitored by absorption at 400.5 and 452 nm.

Preferred Values

$k = 1.0 \times 10^{-11} \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and 1 bar of air.

10 $k_\infty = 1.2 \times 10^{-11} (T/300)^{-0.9} \text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250–300 K.

Reliability

$\Delta \log k_\infty = \pm 0.2$ at 298 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

15 See comments on k_0 . The measurement of Sehested et al. (1998) is in very good agreement with the results from Bridier et al. (1991) which form the basis of the preferred value.

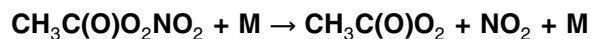
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II.A6.133



$$\Delta H^\circ = 119 \text{ kJ}\cdot\text{mol}^{-1}$$

Low-pressure rate coefficients

5 Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(4.9 \pm 0.3) \times 10^{-3} \exp(-12100/T) [\text{N}_2]$	300–330	Bridier et al., 1991	FTIR (a)
$1.1 \times 10^{-20} [\text{N}_2]$	298*		

Comments

- (a) Rate of the thermal decomposition of $\text{CH}_3\text{C(O)OONO}_2$ (PAN) measured by FTIR absorption spectroscopy in the presence of an excess of NO to scavenge CH_3CO_3 radicals. Pressure range 10 mbar to 790 mbar of N_2 .
10 Falloff curves were analyzed with $F_c=0.30$.

Preferred Values

$$k_0 = 1.1 \times 10^{-20} [\text{N}_2] \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_0 = 4.9 \times 10^{-3} \exp(-12100/T) [\text{N}_2] \text{ s}^{-1} \text{ over the temperature range } 300\text{--}330 \text{ K.}$$

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Reliability

$\Delta \log k_0 = \pm 0.5$ at 298 K.

$\Delta (E/R) = \pm 1000$ K.

Comments on Preferred Values

- 5 The data base of Bridier et al. (1991) is large enough to allow for a falloff extrapolation to k_0 , in part because falloff curves for PAN dissociation and recombination were measured independently. Falloff extrapolations were made with a modeled value of $F_c=0.3$; see the evaluation of the data from Bridier et al. (1991) in Zabel (1995).

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High-pressure rate coefficients

Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(3.3 \pm 0.2) \times 10^{-4}$	297	Niki et al., 1985	FTIR (a)
2.2×10^{-4}	298	Senum et al., 1986	FTIR (b)
$2.52 \times 10^{16} \exp(-13573/T)$	283–313	Tuazon et al., 1991	FTIR (c)
4.2×10^{-4}	298		
$(4.0 \pm 0.8) \times 10^{16} \exp(-13600/T)$	300–330	Bridier et al., 1991	(d)
6.1×10^{-4}	298*		
$2.5 \times 10^{17} \exp[-(14340 \pm 250)/T]$	302–323	Roberts and Bertman, 1992	GC (e)
3.2×10^{-4}	298*		
3.1×10^{-4}	298	Roumelis and Glavas, 1992	GC (f)
$1.6 \times 10^{16} \exp[-(13539 \pm 1060)/T]$	288–298	Grosjean et al., 1994	GC (g)
3.0×10^{-4}	298		

Comments

- 5 (a) Decay of $\text{CH}_3\text{C}(\text{O})\text{O}_2^{15}\text{NO}_2$ in the presence of $^{14}\text{NO}_2$ at a total pressure of 900 mbar of N_2 .
- (b) Decay of $\text{CH}_3\text{C}(\text{O})\text{O}_2\text{NO}_2$ (PAN) in the presence of NO at a total pressure of 16 mbar.

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- (c) Thermal decomposition of PAN in an environmental chamber in the presence of 970 mbar of synthetic air or N₂.
- (d) See comment (a) for k_0 .
- (e) Thermal decomposition of PAN at 1 bar total pressure. PAN concentrations were measured by GC with electron capture detection.
- (f) Thermal decomposition of PAN in N₂ as well as in the presence of O₂, NO₂ and NO at 1 bar total pressure. The products methyl nitrate and NO₂ in PAN-N₂ mixtures were measured by GC. In the presence of large amounts of O₂, no methyl nitrate was formed at 333 K, indicating that the decomposition of PAN to methyl nitrate and CO₂ does not occur. The data obtained were simulated with 23 reactions.
- (g) Thermal decomposition of PAN in 1 bar of air. PAN was measured by GC with electron capture detection.

Preferred Values

- $k = 3.3 \times 10^{-4} \text{ s}^{-1}$ at 298 K and 1 bar of air.
 $k_\infty = 3.8 \times 10^{-4} \text{ s}^{-1}$ at 298 K.
 $k_\infty = 5.4 \times 10^{16} \exp(-13830/T) \text{ s}^{-1}$ over the temperature range 300–330 K.

Reliability

- $\Delta \log k_\infty = \pm 0.3$ at 298 K.
 $\Delta (E/R) = \pm 300 \text{ K}$.

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Comments on Preferred Values

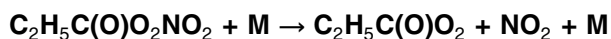
- The reported values from Bridier et al. (1991), Tuazon et al. (1991), Roberts and Bertman, (1992) and Roumelis and Glavas (1992) as well as the selected more recent measurements from Sehested et al. (1998) are all in very good agreement at 298 K and are preferred here. The direct PAN decompositions to methyl nitrate and CO₂ (Roumelis and Glavas, 1992; Orlando et al., 1992) or to CH₃C(O)O and NO₃ (Orlando et al., 1992) are very slow compared to the decomposition to CH₃C(O)O₂+NO₂.

References

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II.A6.134



Low-pressure rate coefficients

5 Rate coefficient data

k_0/s^{-1}	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.7 \times 10^{-3} \exp(-11280/T) [\text{N}_2]$	291–320	Kirchner et al., 1999	(a)

Comments

- 10 (a) Experiments in a 420 L reaction chamber with photolytic generation of radicals forming peroxy nitrates. Decomposition of propionyl peroxy nitrate followed in the dark by FTIR spectrometry. Experiments between 11.5 and 1013 mbar of N_2 . Falloff extrapolations with $F_c=0.36$.

Preferred Values

$$k_0 = 6.2 \times 10^{-20} [\text{N}_2] \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_0 = 1.7 \times 10^{-3} \exp(-11280/T) [\text{N}_2] \text{ s}^{-1} \text{ over the temperature range } 290\text{--}320 \text{ K.}$$

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Reliability

$$\Delta \log k_0 = \pm 0.5 \text{ at } 298 \text{ K.}$$

$$\Delta (E/R) = \pm 2000 \text{ K.}$$

Comments on Preferred Values

- 5 The only available low pressure data from Kircher et al. (1999) appear consistent with the more extensive data base for the high-pressure range. The falloff curve is constructed with $F_c=0.36$.

High-pressure rate coefficients

Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$2 \times 10^{15} \exp(-12800/T)$	300–315	Mineshos and Glavas, 1991	(a)
4.4×10^{-4}	298*		
$8.3 \times 10^{16} \exp(-13940/T)$	291–320	Kirchner et al., 1999	(b)
10 4.0×10^{-4}	298		

Comments

- (a) Thermal decomposition of propionyl peroxy nitrate (PPN) in a 4.5 liter glass flask in the presence of 1 bar of N_2 . PPN and the products ethyl nitrate,

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NO₂, and methyl nitrate were analyzed by GC at 323 K. In the presence of NO, ethyl nitrate was the major product observed.

(b) See comment (a) for k_0 . Limited data from earlier work are also considered.

5 Preferred Values

$k = 3.6 \times 10^{-4} \text{ s}^{-1}$ at 298 K and 1 bar of air.

$k_\infty = 4.0 \times 10^{-4} \text{ s}^{-1}$ at 298 K.

$k_\infty = 8.3 \times 10^{16} \exp(-13940/T) \text{ s}^{-1}$ over the temperature range 290–320 K.

Reliability

10 $\Delta \log k_\infty = \pm 0.2$ at 298 K.

$\Delta (E/R) = \pm 1000 \text{ K}$.

Comments on Preferred Values

The values from Kirchner et al. (1999) and Minoshos and Glavas (1991) are in good agreement.

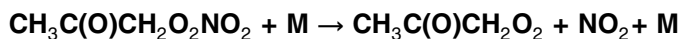
15 References

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II.A6.135



High-pressure rate coefficients

Rate coefficient data

k_∞/s^{-1}	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
1.0 $\times 10^{16} \exp(-10630/T)$	246–262	Kirchner et al., 1999	(a)

Comments

(a) Experiments in a 420 L reaction chamber with photolytic generation of radicals forming peroxy nitrates. Decomposition of acetyl peroxy nitrate in the dark followed by FTIR spectrometry. Measurements in 10, 100, and 800 mbar of N₂. Rate coefficients at 10 mbar are about a factor of 2 smaller than at 800 mbar.

Preferred Values

$k_\infty = 1.0 \times 10^{16} \exp(-10630/T) \text{ s}^{-1}$ over the temperature range 240–260 K and at a pressure of 1 bar.

6870

Reliability

$\Delta \log k_{\infty} = \pm 0.5$ at 250 K.

$\Delta (E/R) = \pm 2000$ K.

Comments on Preferred Values

- 5 The only available rate data from Kirchner et al. (1999) appear consistent with data for related reactions.

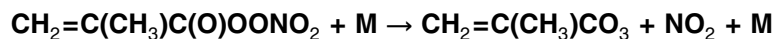
References

Kirchner, F., Mayer-Figge, A., Zabel, F., and Becker, K. H : Int. J. Chem. Kinet., 31, 127, 1999.

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Rate coefficient data

k/s^{-1}	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.58 \times 10^{16} \exp[-(13488 \pm 504)/T]$	302.25–323.55	Roberts and Bertman, 1992	(a)
3.5×10^{-4}	298*		

5 Comments

- (a) The thermal decomposition of $\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OONO}_2$ (MPAN) was studied in one atmosphere of air, with added NO to ensure that $\text{CH}_2=\text{C}(\text{CH}_3)\text{C}(\text{O})\text{OO}$ radicals reacted with NO (to form $\text{NO}_2 + \text{CO}_2 + \text{CH}_2=\text{C}(\text{CH}_3)$) rather than reacting with NO_2 to reform MPAN. MPAN concentrations were measured by GC with electron capture detection.
- 10

Preferred Values

$k = 3.5 \times 10^{-4} \text{ s}^{-1}$ at 298 K and 1 bar.

- $k = 1.6 \times 10^{16} \exp(-13500/T) \text{ s}^{-1}$ over the temperature range 290–330 K at 1 bar.
- 15

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Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

$\Delta (E/R) = \pm 1000$ K.

Comments on Preferred Values

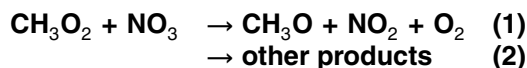
- 5 The preferred values are based on the sole study of this reaction by Roberts and Bertman (1992). The preferred values for the decomposition of MPAN are very similar to those for the thermal decomposition of $\text{CH}_3\text{C}(\text{O})\text{OONO}_2$ (PAN) (Roberts and Bertman, 1992; IUPAC, see also this evaluation). The rate coefficients measured by Roberts and Bertman (1992) are expected, by analogy with the corresponding PAN decomposition (IUPAC, this evaluation), to be very close to the high pressure limit at 1 bar of air.

References

Roberts, J. M. and Bertman, S. B.: *Int. J. Chem. Kinet.*, 24, 297, 1992.

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II.A6.137



$$\Delta H^\circ(1) = -32.3 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.3 \pm 0.7) \times 10^{-12}$	298	Crowley et al., 1990	MMS-AS (a)
$(1.0 \pm 0.6) \times 10^{-12}$	298	Biggs et al., 1994a, b	DF-LIF/AS (b)
$(1.2 \pm 0.6) \times 10^{-12}$	298	Daële et al., 1995	DF-LIF/MS (c)
$(1.3 \pm 0.2) \times 10^{-12}$	298	Helleis et al., 1996	DF-MS (d)
<i>Branching Ratios</i>			
$k_2/k > 0.9$	298	Kukui et al., 1995	DF-LIF/MS (e)

Comments

- (a) Computer simulation of NO_3 absorption profiles formed in the modulated photolysis of HNO_3 in the presence of CH_4 and O_2 .
- (b) CH_3O product of Reaction (1) measured by LIF; NO_3 by visible absorption spectroscopy. Pressure = 3.5 mbar. Modelling of CH_3O time-dependence gave $k/k(\text{CH}_3\text{O} + \text{NO}_3) = 0.43 \pm 0.09$. k calculated with

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$k(\text{CH}_3\text{O}+\text{NO}_3)=(2.3\pm 0.7)\times 10^{-12}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ obtained in a similar study in the same apparatus.

(c) CH_3O measured by LIF; NO_3 by titration with 2,3-dimethylbutene. The rate coefficient was extracted by numerical simulation from the $\text{CH}_3\text{O}+\text{NO}_3$ reactant system.

(d) CD_3O_2 decay measured directly in excess NO_3 . Numerical simulation to take into account the re-formation of CD_3O_2 from $\text{CD}_3\text{O}+\text{NO}_3$.

(e) Based on observations of DCDO formation from the $\text{CD}_3\text{O}+\text{NO}_3$ reaction and the relative rates of reactions of CD_3O and CD_3O_2 with NO_3 .

10 Preferred Values

$k = 1.3 \times 10^{-12}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ at 298 K.
 $k_2/k = 0$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

15 Comments on Preferred Values

None of the experimental studies for this reaction can be described as definitive or direct. In the flow tube measurements, a quasi-equilibrium between CH_3O_2 and CH_3O radicals is established and concentrations and decay kinetics are influenced by reactions of both radicals. The ratio $k_1/k(\text{CH}_3\text{O}+\text{NO}_3)$ should be well determined but values of 0.43 (Biggs et al., 1994b), 0.66 (Biggs et al., 1994a) and 0.30 (Daële et al., 1995) were obtained. The quasi-equilibrium is

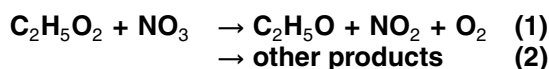
avoided by using O_2 to scavenge CH_3O in the work of Crowley et al. (1990) but the need to simulate a complex reaction system, and the possible influence of a dark reaction (Crowley et al., 1993) that generated NO_3 reduce the reliability of these experiments.

5 The method used by Helleis et al. (1996) to determine k_1 is the most direct. Their analysis considers all of the available information on the secondary chemistry and their value is recommended with wide error limits. The value reported by Kukui et al. (1995) differs substantially from those of Biggs et al. (1994a, b), Daële et al. (1995) and Helleis et al. (1996) and was not included in the evaluation of the rate coefficient. Their work (Kukui et al., 1995) suggests channel (1) 10 is the predominant pathway, with $k_2/k < 0.10$.

References

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II.A6.138



$$\Delta H^\circ(1) = -28.7 \text{ kJ}\cdot\text{mol}^{-1}$$

5 Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.5 \pm 1.5) \times 10^{-12}$	298	Biggs et al., 1995	DF-LIF/AS (a)
$(2.3 \pm 0.5) \times 10^{-12}$	298	Ray et al., 1996	DF-LIF/MS (b)

Comments

10 (a) LIF detection of $\text{C}_2\text{H}_5\text{O}$. Detection of NO_3 by absorption spectroscopy at 662 nm. k was derived by modelling the kinetics of $\text{C}_2\text{H}_5\text{O}_2 + \text{NO}_3$ in systems using $\text{C}_2\text{H}_5 + \text{O}_2$ and $\text{C}_2\text{H}_5\text{O} + \text{NO}_3$ to generate $\text{C}_2\text{H}_5\text{O}_2$. Pressure = 2.9 mbar of He.

(b) LIF detection of $\text{C}_2\text{H}_5\text{O}$. MS detection of NO_3 . k was derived from a model simulation of system using $\text{C}_2\text{H}_5\text{O}_2$ as initial reactant, with NO_3 in excess.

Preferred Values

15 $k_1 = 2.3 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
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Reliability

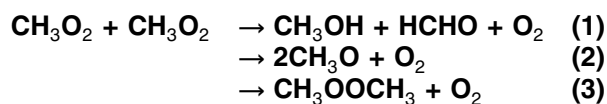
$\Delta \log k = \pm 0.2$ at 298 K.

Comments on Preferred Values

5 Both studies of this reaction used basically the same technique and gave similar results (Biggs et al., 1995; Ray et al., 1996). Extraction of values for k relies on modelling of the reaction system because radical concentrations are controlled by coupling between the $\text{C}_2\text{H}_5\text{O}_2 + \text{NO}_3$ reaction and the reaction of the product $\text{C}_2\text{H}_5\text{O}$ with NO_3 , which regenerates $\text{C}_2\text{H}_5\text{O}_2$. The study of Ray et al. (1996) gave better defined k values and is the basis of the recommendation.
10 Channel (1) is most important, and Biggs et al. (1995) suggest that $k_1/k \approx 0.8$.

References

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II.A6.139


$$\Delta H^\circ(1) = -331.0 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = 13.6 \text{ kJ}\cdot\text{mol}^{-1}$$

$$5 \quad \Delta H^\circ(3) = -146.5 \text{ kJ}\cdot\text{mol}^{-1}$$

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Rate coefficient data ($k=k_1+k_2+k_3$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(5.2 \pm 0.9) \times 10^{-13}$	298	Cox and Tyndall, 1980	MM-UVAS (a,b)
$(3.7 \pm 0.7) \times 10^{-13}$	298	Sander and Watson, 1980	FP-UVAS (a,c)
$1.40 \times 10^{-13} \exp[(223 \pm 41)/T]$	250–420	Sander and Watson, 1981	FP-UVAS (a,d)
$(3.0 \pm 0.5) \times 10^{-13}$	298		
$(4.4 \pm 1.0) \times 10^{-13}$	298	McAdam et al., 1987	FP-UVAS (a,e)
$1.3 \times 10^{-13} \exp[(220 \pm 70)/T]$	228–380	Kurylo and Wallington, 1987	FP-UVAS (a,f)
$(2.7 \pm 0.45) \times 10^{-13}$	298		
$(3.5 \pm 0.5) \times 10^{-13}$	298	Jenkin et al., 1988	MM-UVAS (a,g)
$(3.6 \pm 0.55) \times 10^{-13}$	300	Simon et al., 1990	MM-UVAS (a,h)
$1.3 \times 10^{-13} \exp(365/T)$	248–573	Lightfoot et al., 1990	FP-UVAS (a,i)
$(4.1 \pm 0.9) \times 10^{-13}$	300		
<i>Branching Ratios</i>			
$k_2/k = 1/\{1 + \exp[(1131 \pm 30)/T]/(17 \pm 5)\}$	223–333	Horie et al., 1990	P-FTIR (j)
$k_2/k = 0.30$	298		
$k_2/k = 0.41 \pm 0.04$	296	Tyndall et al., 1998	P-FTIR (j)
$k_3/k < 0.06$	296		

Comments

- (a) k is defined by $-d[\text{CH}_3\text{O}_2]/dt = 2k[\text{CH}_3\text{O}_2]^2$ and was derived from the measured overall second-order decay of CH_3O_2 radicals k_{obs} by correcting for

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secondary removal of the CH_3O_2 radicals.

- (b) $[\text{CH}_3\text{O}_2]$ determined by absorption at 250 nm in modulated photolysis of Cl_2 - CH_4 - O_2 mixtures. $k/\sigma(250\text{ nm})=1.33\times 10^5\text{ cm s}^{-1}$, $\sigma=3.9\times 10^{-18}\text{ cm}^2\text{ molecule}^{-1}\text{ s}^{-1}$ at 250 nm.
- 5 (c) Flash-photolysis of $(\text{CH}_3)_2\text{N}_2$ - O_2 and Cl_2 - CH_4 - O_2 mixtures. $[\text{CH}_3\text{O}_2]$ monitored by long path UV absorption giving $k/\sigma=(1.06\pm 0.07)\times 10^5\text{ cm s}^{-1}$ at 245 nm and $(2.84\pm 0.36)\times 10^5\text{ cm s}^{-1}$ at 270 nm. Value quoted is a mean value using σ values obtained by Hochanadel et al. (1977). Small effects of varying O_2 and adding CO are reported.
- 10 (d) Flash-photolysis of Cl_2 - CH_4 - O_2 mixtures. σ determined from absorption at $t=0$ extrapolated from decay curves and estimate of $[\text{CH}_3\text{O}_2]_0$ from change in Cl_2 concentration in flash. $\sigma(250\text{ nm})=(2.5\pm 0.4)\times 10^{-18}\text{ cm}^2\text{ molecule}^{-1}$ at 298 K, and $k/\sigma(250\text{ nm})=(5.6\pm 0.8)\times 10^4\text{ exp}[(223\pm 41)/T]\text{ cm s}^{-1}$ (250 K to 420 K) were obtained.
- 15 (e) Flash-photolysis of Cl_2 in the presence of CH_4 and O_2 over the pressure range 169 mbar to 530 mbar (120 Torr to 400 Torr). $[\text{CH}_3\text{O}_2]$ monitored by UV absorption. $k_{\text{obs}}/\sigma(250\text{ nm})=1.34\times 10^5\text{ cm s}^{-1}$ and $\sigma(250\text{ nm})=4.4\times 10^{-18}\text{ cm}^2\text{ molecule}^{-1}$ were obtained. k_{obs}/k taken to be 1.35.
- 20 (f) Flash-photolysis of Cl_2 in the presence of CH_4 - O_2 - N_2 mixtures at pressures between 67 mbar and 530 mbar (50 Torr and 400 Torr). $k_{\text{obs}}=(1.7\pm 0.4)\times 10^{-13}\text{ exp}[(220\pm 70)/T]\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ determined from measured values of $k_{\text{obs}}/\sigma(250)$ by taking $\sigma(250)=3.30\times 10^{-18}\text{ cm}^2\text{ molecule}^{-1}$ as previously determined by same authors. Here we have

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taken $k_{\text{obs}}/k=1.35$ to calculate k . k_{obs} shown to be independent of pressure over the range 67 mbar to 530 mbar (50 Torr to 400 Torr) at 298 K.

- (g) Modulated photolysis of Cl_2 in the presence of CH_4 - O_2 mixtures at a total pressure of 1 bar (760 Torr). $k_{\text{obs}}/\sigma(250\text{ nm})=1.11\times 10^5\text{ cm s}^{-1}$ and $\sigma(250\text{ nm})=(4.25\pm 0.5)\times 10^{-18}\text{ cm}^2\text{ molecule}^{-1}$ were obtained leading to $k_{\text{obs}}=(4.7\pm 0.5)\times 10^{-13}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$. Cited value of k obtained by taking $k_{\text{obs}}/k=1.35$ to allow for secondary removal of CH_3O_2 .
- 5
- (h) Modulated photolysis of Cl_2 in the presence of CH_4 - O_2 mixtures at pressures of 320 mbar (240 Torr). $k_{\text{obs}}/\sigma(250\text{ nm})=1.16\times 10^5\text{ cm s}^{-1}$ and $\sigma(250\text{ nm})=4.14\times 10^{-18}\text{ cm}^2\text{ molecule}^{-1}$ were obtained, leading to $k_{\text{obs}}=(4.8\pm 0.5)\times 10^{-13}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$. The cited value of k was obtained by taking $k_{\text{obs}}/k=1.35$ to allow for secondary removal of CH_3O_2 .
- 10
- (i) Flash-photolysis of Cl_2 in the presence of CH_4 - O_2 - N_2 mixtures over the pressure range 270 mbar to 930 mbar (200 Torr to 700 Torr). CH_3O_2 radicals were monitored by UV absorption. The values $k_{\text{obs}}/\sigma(210\text{ nm to }260\text{ nm})=1.17\times 10^5\text{ cm s}^{-1}$ and $\sigma(250\text{ nm})=4.8\times 10^{-18}\text{ cm}^2\text{ molecule}^{-1}$ were obtained. k_{obs}/k taken to be 1.35. At temperatures $>373\text{ K}$, the second-order decays of CH_3O_2 were affected by HO_2 radical reactions. The branching ratio was obtained from the effect of $[\text{HO}_2]$ on the CH_3O_2 decays.
- 15
- (j) Study of the photooxidation of CH_4 , initiated by Cl atoms generated from Cl_2 , in a slow-flow system under steady-state illumination. Analysis of HCHO, CH_3OH and HC(O)OH products by FTIR spectroscopy.
- 20
- (k) Photolysis of $\text{CH}_3\text{N}_2\text{CH}_3$ - O_2 and Cl_2 - CH_4 - O_2 mixtures, with analyses of reactants and products by FTIR spectroscopy.
- 25

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Preferred Values

$k = 3.5 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 1.03 \times 10^{-13} \exp(365/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–400 K.

5 $k_2 = 1.3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k_2 = 7.4 \times 10^{-13} \exp(-520/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 220–330 K.

Reliability

$\Delta \log k = \pm 0.12$ at 298 K.
10 $\Delta (E/R) = \pm 200$ K.
 $\Delta \log k_2 = \pm 0.15$ at 298 K.
 $\Delta (E_2/R) = \pm 300$ K.

Comments on Preferred Values

15 The room temperature measurements of k_{obs}/σ of Cox and Tyndall (1980), Sander and Watson (1980, 1981), McAdam et al. (1987), Kurylo and Wallington (1987), Jenkin et al. (1988), Simon et al. (1988) and Lightfoot et al. (1990) are in excellent agreement and lead to the recommended value of $k_{\text{obs}}/\sigma(250 \text{ nm}) = 1.24 \times 10^5 \text{ cm s}^{-1}$. The measurements of the absorption cross-section by Simon et al. (1990) form the basis of our recommendation of $\sigma(250 \text{ nm}) = 3.9 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$. Thus, we recommend
20 $k_{\text{obs}} = 4.8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K. Taking the branching ratio of $k_2/k = 0.37$ at 298 K yields the value of k at 298 K given above.

The temperature dependence of k reported by Lightfoot et al. (1990) is in

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excellent agreement with the studies of Sander and Watson (1981), Kurylo and Wallington (1987) and Jenkin and Cox (1991). Here we have recommended the E/R value of Lightfoot et al. (1990) on the basis of their more extensive temperature range, and the temperature-dependent branching ratio k_2/k . The
5 recommended Arrhenius equation follows from the recommended values of k_{298} and E/R .

There have been a number of measurements of the branching ratio, k_2/k , which have been carefully reanalysed by Tyndall et al. (1998). The values of k_2/k at 298 K range from 0.30 to 0.45. Tyndall et al. (1998) recommend the average of 0.37 ± 0.06 which is also accepted in the review of Tyndall et al. (2001).
10 This value is taken as our preferred value at 298 K, with enhanced error limits. The two studies (Lightfoot et al., 1990; Horie et al., 1990) of the temperature dependence of the branching ratio involve different temperature ranges. Here we have selected the results of Horie et al. (1990) over the more atmospherically relevant temperature range of 200 K to 330 K, modified to reproduce our
15 recommended value of k_2/k at 298 K. This has been combined with our recommended expression for k to obtain the preferred expression for k_2 . There is no convincing evidence for any contribution from channel (3) (Tyndall et al., 1998).

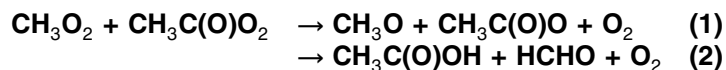
It should be noted that, from an analysis of their own data (Horie et al.,
20 1990) together with the results of Lightfoot et al. (1990), Anastasi et al. (1978), Kan et al. (1980), Parkes (1977), Niki et al. (1981) and Weaver et al. (1975), the equation $k_2/k = 1/(1 + [\exp(1330/T)]/33)$ was obtained by Horie et al. (1990) for the more extensive temperature range 223 K to 573 K. This equation shows slight non-Arrhenius behavior. Lightfoot et al. (1990) observed no pressure
25 dependence of the branching ratio, k_2/k , over the range 0.28 bar to 1 bar.

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II.A6.140



$$\Delta H^\circ(1) = -27.3 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -378 \text{ kJ}\cdot\text{mol}^{-1}$$

5

Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$k_1 = (8.8 \pm 1.5) \times 10^{-12}$	298	Roehl et al., 1996	PLP-UVAS (a)
$k_2 = (1.0 \pm 0.5) \times 10^{-12}$	298		
$8.5 \times 10^{-13} \exp[(726 \pm 25)/T]$	209–358	Maricq and Sente, 1996	PLP-UVAS (b)
$(1.0 \pm 0.2) \times 10^{-11}$	298		
$(8.2 \pm 0.6) \times 10^{-12}$	298	Villenave and Lesclaux, 1996	FP-UVAS (c)

Comments

- (a) Acetyl radicals were produced from the photolysis of $\text{Cl}_2\text{-CH}_3\text{CHO-O}_2$ mixtures. CH_3O_2 radicals were produced as secondary products, or through added CH_4 . k depends on $\sigma[\text{CH}_3\text{C(O)O}_2]$ for which values of $3.21 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ at 240 nm and $6.67 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ at 207 nm were obtained, relative to the UV spectrum of $\text{C}_2\text{H}_5\text{O}_2$

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$[\sigma(240\text{ nm})=4.36\times 10^{-18}\text{ cm}^2\text{ molecule}^{-1}]$. A value of $k_1/k=0.9$ was used in the data analysis.

(b) Technique as for (a) but with UV spectra recorded on a gated diode array spectrometer. $\sigma[\text{CH}_3\text{C}(\text{O})\text{O}_2]=6.5\times 10^{-18}\text{ cm}^2\text{ molecule}^{-1}$ at 206 nm and $2.9\times 10^{-18}\text{ cm}^2\text{ molecule}^{-1}$ at 250 nm. On the basis of the HCHO kinetics observed it was concluded that channel (2) was dominant over the entire temperature range covered (209 K to 358 K). A value of $k_1/k=0$ was used in the data analysis.

(c) CH_3O_2 radicals were generated simultaneously with $\text{CH}_3\text{C}(\text{O})\text{O}_2$ radicals from the flash photolysis of $\text{Cl}_2\text{-CH}_3\text{CHO-CH}_4\text{-O}_2$ mixtures. In the derivation of k , the branching ratio, $\alpha_c(=k_1/k)$ was assumed to be 0.65 but k was found to vary by less than 15% upon varying α between 0.5 and 1.0. Overall uncertainty was estimated to be 42% from error propagation analysis. A value of $k_1/k=0.65$ was used in the data analysis.

15 Preferred Values

$k = 1.1 \times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ at 298 K.

$k = 2.0 \times 10^{-12}\text{ exp}(500/T)\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ over the temperature range 200–350 K.

$k_1/k = 0.9$ at 298 K.

20 $k_2/k = 0.1$ at 298 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

$\Delta (E/R) = \pm 250\text{ K}$.

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$\Delta(k_1/k) = \Delta(k_2/k) = \pm 0.1$ at 298 K.

Comments on Preferred Values

The three cited studies, which all used UV spectroscopy with similar values of the relevant absorption cross-sections to monitor the progress of the reaction are, apparently, in good agreement. However, the values of k derived depend upon the value of k_1/k used in the data analysis and since the three studies used values ranging from 0 to 0.9 their close agreement must be, to some degree, fortuitous. Tyndall et al. (2001) show that, using our preferred value for k_1/k , the studies of Roehl et al. (1996), Maricq and Szenté (1996) and Villenave and Lesclaux (1996), give values of k in the range $(0.98\text{--}2)\times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$. We accept the analysis of Tyndall et al. (2001) and take the value of k which they recommend, based on the studies of Villenave and Lesclaux (1996) and Roehl et al. (1996), as our preferred value at 298 K. The temperature dependence is based on that observed for analogous reactions.

There is conflicting evidence on the branching ratios. At 298 K Moortgat et al. (1989) estimate that $k_1/k=0.5$, whilst Roehl et al (1996) find that $k_1/k=0.9$ and Maricq and Szenté (1996) conclude that, essentially, the reaction proceeds entirely by channel (2). Further information comes from a study of Crawford et al. (1999) on the $\text{HO}_2+\text{CH}_3\text{C}(\text{O})\text{O}_2$ reaction in which the yields of the products $\text{CH}_3\text{C}(\text{O})\text{OOH}$ and $\text{CH}_3\text{C}(\text{O})\text{OH}$ were monitored. Tyndall et al. (2001) have re-analysed the results reported by Crawford et al. (1999) and have shown that the product yields observed require that the $\text{CH}_3\text{O}_2+\text{CH}_3\text{C}(\text{O})\text{O}_2$ reaction, which could also contribute to the $\text{CH}_3\text{C}(\text{O})\text{OH}$ in the experiments of Crawford et al. (1999), must occur with k_1/k close to unity. Based on the studies of Moortgat et al. (1989), Horie and Moortgat (1992) and Roehl et al. (1996), Tyndall et al. (2001) recommend values of $k_1/k=0.9$ and $k_2/k=0.1$ at 298 K.

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These are adopted as our preferred values for the branching ratios. Moortgat et al. (1989) have reported values for the temperature dependence of k_1 and k_2 but they imply a difference in activation energy for the two channels of 32 kJ mol⁻¹ which is much greater than found for analogous peroxy radical reactions.

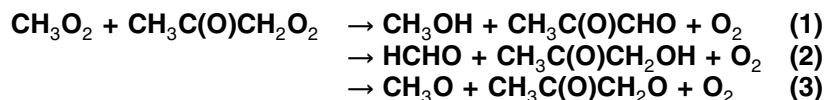
5 No recommendation is made for the temperature dependence of the branching ratio at this stage.

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II.A6.141



$$\Delta H^\circ(1) = -319.7 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -322.6 \text{ kJ}\cdot\text{mol}^{-1}$$

5

Rate coefficient data ($k=k_1+k_2+k_3$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(3.8 \pm 0.4) \times 10^{-12}$	298	Bridier et al., 1993	FP-UVA (a)
<i>Branching Ratios</i>			
$k_1/k = (0.5 \pm 0.1)$	298	Jenkin et al., 1993	P-FTIR (b)
$k_2/k = (0.2 \pm 0.1)$	298		
$k_3/k = (0.3 \pm 0.1)$	298	Bridier et al., 1993	FP-UVA (c)

Comments

- 10 (a) Flash photolysis of Cl₂ in the presence of CH₃C(O)CH₃-O₂-CH₄-N₂ mixtures at a total pressure of 1 bar (760 Torr). The overall rate coefficient k was derived from a kinetic analysis of absorption-time profiles measured at 230 nm and 260 nm.

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- (b) Steady-state photolysis of Cl_2 in the presence of $\text{CH}_3\text{C}(\text{O})\text{CH}_3\text{-N}_2$ mixtures at a total pressure of 930 mbar (700 Torr). Branching ratios were deduced from measurements of HCHO and $\text{CH}_3\text{C}(\text{O})\text{CHO}$ products by long-path FTIR spectroscopy and long-path UV-VIS diode-array spectroscopy.
- 5 (c) Derived from a kinetic analysis of the time-profiles obtained in the experiments described in Comment (a).

Preferred Values

$$k = 3.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$
$$k_1/k = 0.5 \text{ at } 298 \text{ K.}$$

10 $k_2/k = 0.2 \text{ at } 298 \text{ K.}$

$$k_3/k = 0.3 \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$

$$\Delta (k_1/k) = \Delta (k_2/k) = \Delta (k_3/k) = \pm 0.15 \text{ at } 298 \text{ K.}$$

15 *Comments on Preferred Values*

The preferred values of the rate coefficient and branching ratios are based on the measurements of Bridier et al. (1993) and Jenkin et al. (1993), and require independent confirmation to reduce the assigned error limits.

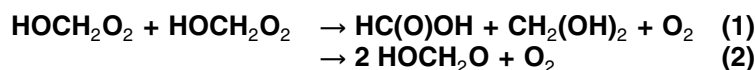
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- 5

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II.A6.142



Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$k_1 = 5.65 \times 10^{-14} \exp[(750 \pm 400)/T]$	275–323	Veyret et al., 1989	FP-UVA (a,b)
$k_1 = (7.0 \pm 2.1) \times 10^{-13}$	295		
$k_1 = (5.6 \pm 2.8) \times 10^{-13}$	298	Burrows et al., 1989	MM-IR-AS (a,c)
<i>Relative Rate Coefficients</i>			
$k_1 = (5.5 \pm 1.1) \times 10^{-12}$	298	Burrows et al., 1989	MM-IR-AS (a,c)

5 Comments

(a) k is defined by $-d[\text{HOCH}_2\text{O}_2]/dt = 2k[\text{HOCH}_2\text{O}_2]^2$.

(b) Flash photolysis of Cl_2 in the presence of HCHO or CH_3OH and O_2 , with time-resolved absorption spectroscopy for the detection of HO_2 and HOCH_2O_2 radicals. The rate coefficient k_1 was obtained from a computer fit of the absorption profiles of HOCH_2O_2 radicals at 250 nm. Channel (2) leads to the regeneration of HO_2 radicals and was thus not observable in this system.

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(c) Molecular modulation study of Cl_2 -HCHO- O_2 mixtures with diode laser infrared spectroscopy for the detection of HO_2 radicals and UV spectroscopy for HOCH_2O_2 radicals. The rate coefficient, k_2 , was obtained from a computer simulation of quantum yields for HC(O)OH formation.

5 Preferred Values

$k_1 = 7.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k_1 = 5.7 \times 10^{-14} \exp(750/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 270–330 K.

$k_2 = 5.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

10 Reliability

$\Delta \log k_1 = \pm 0.3$ at 298 K.

$\Delta (E_1/R) = \pm 750$ K.

$\Delta \log k_2 = \pm 0.3$ at 298 K.

Comments on Preferred Values

15 The parallel studies of Veyret et al. (1989) and Burrows et al. (1989) confirm that the interaction of HOCH_2O_2 radicals involves two channels. The two reports (Burrows et al., 1989; Veyret et al., 1989) of the rate coefficient, k_1 , at room temperature are in good agreement, and indicate that this channel is a factor of ~ 3 to 4 faster than that for the analogous interaction of CH_3O_2 radicals. The rate coefficient, k_2 , is even larger than k_1 , with a value ~ 50 times greater than that for the analogous reaction of CH_3O_2 radicals. Confirmation of the temperature coefficient of k_1 is needed, as well as a determination of the

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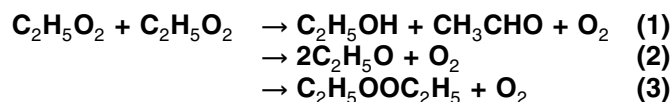
temperature coefficient of k_2 .

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II.A6.143



$$\Delta H^\circ(1) = -345.8 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -23.8 \text{ kJ}\cdot\text{mol}^{-1}$$

5

Rate coefficient data ($k=k_1+k_2+k_3$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.0 \pm 0.1) \times 10^{-13}$	298	Adachi et al., 1979	FP-UVA (a,b)
$2.7 \times 10^{-13} \exp(-470/T)$	302–373	Anastasi et al., 1983	MM-UVA (a,c)
5.6×10^{-14}	298		
8.1×10^{-14}	266–348	Cattell et al., 1986	MM-UVA (a,d)
$8.5 \times 10^{-14} \exp[-(110 \pm 40)/T]$	228–380	Wallington et al., 1988	FP-UVA (a,e)
5.9×10^{-14}	298		
$6.7 \times 10^{-14} \exp[(60 \pm 40)/T]$	248–460	Fenter et al., 1993	FP-UVA (a,f)
$(7.9 \pm 0.5) \times 10^{-14}$	298		
$2.49 \times 10^{-13} \exp(-518/T)$	220–330	Bauer et al., 1992	MM-UVA (a,g)
$+ 9.39 \times 10^{-16} \exp(960/T)$			
6.7×10^{-14}	298		
$(7.3 \pm 2.4) \times 10^{-14}$	295	Atkinson and Hudgens, 1997	PLP-UVA (a,h)
<i>Branching Ratios</i>			
$k_1/k_2 = 0.76$	298	Niki et al., 1982	P-FTIR (i)
$k_1/k_2 = 0.60$	298	Anastasi et al., 1983	MM-GC (c)
$k_1/k_2 = 0.49$	298	Wallington et al., 1989	P-FTIR (j)

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Comments

- (a) k is defined by $-d[\text{C}_2\text{H}_5\text{O}_2]/dt=2k[\text{C}_2\text{H}_5\text{O}_2]^2$ and is obtained from the overall decay constant k_{obs} corrected for secondary removal of $\text{C}_2\text{H}_5\text{O}_2$ radicals.
- 5 (b) k determined by simulation of $\text{C}_2\text{H}_5\text{O}_2$ radical decay using complex mechanism accounting for secondary removal of $\text{C}_2\text{H}_5\text{O}_2$ radicals.
- (c) Modulated photolysis of $(\text{C}_2\text{H}_5)_2\text{N}_2$ in the presence of O_2 at pressures of 7 mbar to 200 mbar (5 Torr to 150 Torr) and N_2 at pressures of 550 mbar to 730 mbar (410 Torr to 550 Torr). $k/\sigma(240\text{ nm})$ and $\sigma(240\text{ nm})$ were found to be temperature dependent. Branching ratios were determined from analysis of products, $\text{C}_2\text{H}_5\text{OH}$ and CH_3CHO , by GC. The data cited are derived from the rate coefficients k_1 and k_2 given in Table 6 of Anastasi et al. (1983).
- 10 (d) Modulated photolysis of $\text{Cl}_2\text{-C}_2\text{H}_6\text{-O}_2\text{-N}_2$ mixtures at pressures of 3 mbar to 1000 mbar (2 Torr to 760 Torr). $k_{\text{obs}}/\sigma(260\text{ nm})=(4.07\pm 0.04)\times 10^4\text{ cm s}^{-1}$ and $\sigma(260\text{ nm})=(3.20\pm 0.38)\times 10^{-18}\text{ cm}^2\text{ molecule}^{-1}$ were obtained, leading to $k_{\text{obs}}=(1.30\pm 0.16)\times 10^{-13}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$. Cited value of k obtained by taking $k_{\text{obs}}/k=1.6$.
- 15 (e) $k_{\text{obs}}=(1.41\pm 0.19)\times 10^{-13}\text{ exp}[-(110\pm 40)/T]\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ was obtained based on temperature independent value of $\sigma(250\text{ nm})=(3.89\pm 0.54)\times 10^{-18}\text{ cm}^2\text{ molecule}^{-1}$ and $k_{\text{obs}}/k=1.66$.
- 20 (f) Flash photolysis-UV absorption study of $\text{Cl}_2\text{-C}_2\text{H}_6\text{-O}_2\text{-N}_2$ mixtures at 1 bar (760 Torr) total pressure. Rate coefficients were derived from simultaneous computer analyses of several decay curves collected at different

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wavelengths. The value of $k_{\text{obs}}=(1.40\pm 0.11)\times 10^{-13}\text{ exp}[-(20\pm 40)/T]\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ was corrected at each temperature by dividing by $(1+\alpha)$, where $\alpha=\beta/(1+\beta)$ and $\beta=10.2\text{ exp}(-533/T)$.

- 5 (g) Molecular modulation study. $\text{C}_2\text{H}_5\text{O}_2$ radicals were generated from the photolysis of flowing mixtures of $\text{Cl}_2\text{-C}_2\text{H}_6\text{-O}_2\text{-N}_2$ at a total pressure of 133 mbar (100 Torr) and monitored by UV absorption. Values of k/σ were determined at 220 nm, 250 nm and 280 nm, leading to values of k_{obs} . The expression for k was derived by fitting the function $k_{\text{obs}}=A_1\text{exp}(B_1/T)+A_2\text{exp}(B_2/T)=2k_1+k_2$ to the observed values of k_{obs} over the temperature range 220–330 K, forcing the fit to a value of k_2/k of 0.65 at 298 K. The expressions for k_1 and k_2 obtained in this way gave $k_1/k_2=3.8\times 10^{-3}\text{ exp}(1478/T)$.
- 10 (h) Pulsed laser photolysis of $\text{Cl}_2\text{-C}_2\text{H}_6\text{-O}_2\text{-Ar}$ mixtures at (7.3 ± 1.0) mbar (5.5 Torr) total pressure with $\text{C}_2\text{H}_5\text{O}_2$ radicals being monitored by UV cavity ring-down spectroscopy at 265 nm and 270 nm. The measured value of k_{obs} was corrected for secondary reactions by taking $k_{\text{obs}}/k=1.7$.
- (i) Photolysis of $(\text{C}_2\text{H}_5)_2\text{N}_2\text{-O}_2$ mixtures and of $\text{Cl}_2\text{-C}_2\text{H}_6\text{-O}_2\text{-N}_2$ mixtures at a total pressure of 920 mbar (700 Torr). Products CH_3CHO , $\text{C}_2\text{H}_5\text{OH}$ and $\text{C}_2\text{H}_5\text{OOH}$ monitored by FTIR.
- 20 (j) Photolysis of $\text{Cl}_2\text{-C}_2\text{H}_6$ mixtures in 930 mbar (700 Torr) air. Products monitored by FTIR.

Preferred Values

$k = 6.4 \times 10^{-14}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$, independent of temperature over the range 250–450 K.

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$$k_2/k = 0.62 \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.12 \text{ at } 298 \text{ K.}$$

$$\Delta(E/R) = {}^{+300}_{-100} \text{ K}$$

$$5 \quad \Delta(k_2/k) = \pm 0.1 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The rate coefficients for this reaction have all been determined using UV absorption to monitor $\text{C}_2\text{H}_5\text{O}_2$, and hence the measured quantity is k/σ where σ is the absorption cross-section at the monitoring wavelength. The data for k_{298} are generally in good agreement. The most recent temperature coefficient reported by Fenter et al. (1993) ($E/R = -60 \text{ K}$) agrees with the earlier data of Cattell et al. (1986) ($E/R \approx 0 \text{ K}$) but less well with those of Anastasi et al. (1983) ($E/R = 470 \text{ K}$), Wallington et al. (1988) ($E/R = 110 \text{ K}$) or Bauer et al. (1992) ($E/R = -230 \text{ K}$). In view of the small temperature coefficients reported in most of these studies, together with the relatively large associated error limits, we have selected a temperature-independent rate coefficient k based on k_{298} . Thus, from the data of Adachi et al. (1979), Anastasi et al. (1983), Cattell et al. (1986), Wallington et al. (1988), Bauer et al. (1992) and Fenter et al. (1993), the average value of $k_{\text{obs}} = 1.03 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K is obtained. Taking $k_2/k = 0.62$ at 298 K (the mean of the data of Niki et al. (1982), Anastasi et al. (1983) and Wallington et al. (1989)) yields the recommended value of $k_{298} = 6.4 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$. The data of Wallington et al. (1989) show that $k_3/k \leq 0.06$. The rate coefficient of Atkinson and Hudgens (1997) is in agreement with the recommendations.

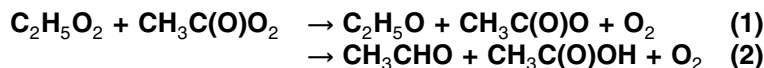
25 The differences between the values of the branching ratios reported by
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Anastasi et al. (1983) and Bauer et al. (1992) require further study.

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II.A6.144



$$\Delta H^\circ(1) = -23.6 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -398.5 \text{ kJ}\cdot\text{mol}^{-1}$$

5

Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.0 \pm 0.3) \times 10^{-11}$	298	Villenave and Lesclaux, 1996	FP-UVAS (a)
$5 \times 10^{-13} \exp[(1070 \pm 200)/T]$	220–440	Maricq and Szente, 2000	PLP-UVAS (b)
2.2×10^{-11}	295		

Comments

10 (a) Flash photolysis of $\text{Cl}_2\text{-C}_2\text{H}_6\text{-CH}_3\text{CHO-O}_2$ mixtures. $\text{CH}_3\text{C(O)O}_2$ and $\text{C}_2\text{H}_5\text{O}_2$ radical concentrations were determined by fitting absorption-time data at 207 nm and 240 nm, using cross-sections recommended in Lightfoot et al. (1992). Complex reaction mechanism with $\alpha_c (=k_1/k)$ assumed to be 0.82. The overall uncertainty was estimated as 54%.

15 (b) Pulsed laser photolysis at 351 nm of $\text{CH}_3\text{CHO-C}_2\text{H}_6\text{-Cl}_2\text{-O}_2\text{-N}_2$ mixtures at total pressures of 167 mbar to 192 mbar (125 Torr to 144 Torr). The reaction progress was monitored by time-resolved UV absorption over the
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5 range 200 nm to 300 nm. Values of k were derived by fitting the spectral profiles using a detailed model. The cross-sections for the principal absorbing radicals ($\text{CH}_3\text{C(O)O}_2$, $\text{C}_2\text{H}_5\text{O}_2$, and CH_3O_2) were taken from the studies of Maricq and Szente (1996) and Maricq and Wallington (1992). A satisfactory fit to the spectra could be obtained using values of $\alpha_c (=k_1/k)$ in the range 1.0–0.80.

Preferred Values

10 $k = 1.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 4.4 \times 10^{-13} \exp(1070/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 220–400 K.

Reliability

$$\Delta \log k = \pm 0.5 \text{ at } 298 \text{ K.}$$

$$\Delta (E/R) = \pm 500 \text{ K.}$$

Comments on Preferred Values

15 The two available experimental studies of this reaction report values of the rate coefficient at 298 K differing by a factor of 2. In both cases substantial error limits were assigned reflecting the difficulties in deconvoluting overlapping UV spectra and in accounting for complex secondary chemistry in deriving the rate coefficient. Villenave and Leclaux (1996) based their results on absorption measurements at only two wavelengths, whereas Maricq and Szente
20 (2000) used spectra covering the range 200 nm to 300 nm but, until more definitive measurements are available, the preferred value at 298 K is taken as the mean of the studies of Villenave and Lesclaux (1996) and of Maricq and Szente

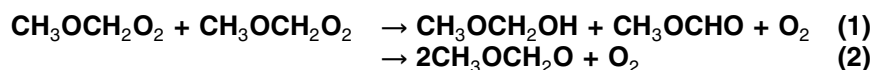
(2000), with substantial error limits. The only determination of the temperature dependence of k is that of Maricq and Szenté (2000) who obtained a value of E/R of -1070 K, which is consistent with values found for analogous reactions. The preferred expression for k is obtained by combining the temperature dependence found by Maricq and Szenté (2000) with an A -factor chosen to fit the preferred value of k at 298 K. Channel (1) is likely to be the main reaction channel at 298 K.

References

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Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.1 \pm 0.3) \times 10^{-12}$	298	Jenkin et al., 1993	MM-AS (a,b)
<i>Branching Ratios</i>			
$k_2/k = (0.67 \pm 0.11)$	295	Jenkin et al., 1993	P-FTIR (c)
$k_2/k = (0.67 \pm 0.13)$	298	Jenkin et al., 1993	P-FTIR (d)

5 Comments

- (a) k is defined by $-d[\text{CH}_3\text{OCH}_2\text{O}_2]/dt = 2k[\text{CH}_3\text{OCH}_2\text{O}_2]^2$ and has been derived from the measured overall second-order decay of $\text{CH}_3\text{OCH}_2\text{O}_2$ radicals (k_{obs}).
- (b) Molecular modulation study of Cl_2 - CH_3OCH_3 - O_2 - N_2 mixtures together with a pulsed radiolysis study of SF_6 - CH_3OCH_3 - O_2 mixtures. k_{obs} was found to be dependent on the total pressure over the range 23 mbar to 1013 mbar (17 Torr to 770 Torr) and on the composition of the reaction mixture. On the basis of a mechanism involving the generation of H atoms via the reaction $\text{CH}_3\text{OCH}_2\text{O} + \text{M} \rightarrow \text{CH}_3\text{OCHO} + \text{H} + \text{M}$, it was possible to derive the cited pressure-independent value of k .

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(c) FTIR spectroscopic study of the steady-state photolysis of Cl₂ in the presence of CH₃OCH₃-O₂-N₂ mixtures over the total pressure range 13 mbar to 930 mbar (10 Torr to 700 Torr). The branching ratio was determined from the yields of CH₃OCHO and CH₃OCH₂OOH. Minor amounts of CH₃OCH₂OH were also observed.

(d) Similar study to that described in Comment (c). The branching ratio and k were derived from a kinetic analysis of the effects of [O₂] and [Cl₂] on k_{obs} , based on a mechanism including the production of H atoms from the reaction CH₃OCH₂O+M → CH₃OCHO+H+M.

10 Preferred Values

$k = 2.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k_2/k = 0.67$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

15 $\Delta (k_2/k) = \pm 0.1$ at 298 K.

Comments on Preferred Values

The apparent effect of total pressure on k , the first reported for this type of reaction (Dagaut et al., 1989), has been shown to be an artifact by the more recent experiments of Jenkin et al. (1993). This comprehensive study on which the recommendation is based, has shown that the pressure effect was due to secondary chemistry involving H atoms which arise from the reaction

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CH₃OCH₂O+M→CH₃OCHO+H+M. A kinetic analysis of the molecular modulation system, allowing for secondary chemistry, yielded the preferred rate coefficient. At the same time the derived value of the branching ratio, k_2/k , is in excellent agreement with that obtained from a steady-state photolysis system with FTIR spectroscopic analyses (Jenkin et al., 1993).

References

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$$\Delta H^\circ = -71 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$2.8 \times 10^{-12} \exp[(530 \pm 100)/T]$	253–368	Moortgat et al., 1989	FP-UVAS (a,b)
$(1.6 \pm 0.3) \times 10^{-11}$	298		
$(1.36 \pm 0.19) \times 10^{-11}$	298	Roehl et al., 1996	PLP-UVAS (a,c)
$3.0 \times 10^{-12} \exp[(504 \pm 114)/T]$	209–358	Maricq and Szente, 1996	PLP-UVAS (a,d)
1.5×10^{-11}	298		

Comments

(a) k is defined by $-d[\text{CH}_3\text{C(O)O}_2]/dt = 2k [\text{CH}_3\text{C(O)O}_2]^2$.

(b) k was determined using absorption cross-sections for $\text{CH}_3\text{C(O)O}_2$ and CH_3O_2 radicals approximately 20% higher than later consensus values. $\text{CH}_3\text{C(O)O}_2$ radicals were produced by photolysis of Cl_2 - CH_3CHO - O_2 mixtures.

(c) k was determined using an absorption cross-section of $\sigma = 6.67 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ at 207 nm for $\text{CH}_3\text{C(O)O}_2$. Source of $\text{CH}_3\text{C(O)O}_2$ radicals as in (b). Detailed analysis of secondary chemistry.

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(d) Based on $\sigma(\text{CH}_3\text{C(O)O}_2) = 6.5 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ at 206 nm. Source of $\text{CH}_3\text{C(O)O}_2$ radicals as in (b). Detailed analysis of secondary chemistry.

Preferred Values

$k = 1.6 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 2.9 \times 10^{-12} \exp(500/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–370 K.

Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta (E/R) = \pm 200 \text{ K}$.

Comments on Preferred Values

All three studies (Moortgat et al., 1989; Roehl et al., 1996; Maricq and Szente, 1996), taking account of the complex secondary chemistry following recombination of $\text{CH}_3\text{C(O)O}_2$ radicals and of the magnitude and overlap of the UV absorptions due to acetylperoxy, methylperoxy and hydroperoxy radicals, now give results in good agreement for k and its temperature dependence. The recommendation is thus based on the data of Moortgat et al. (1989), Roehl et al. (1996) and Maricq and Szente (1996).

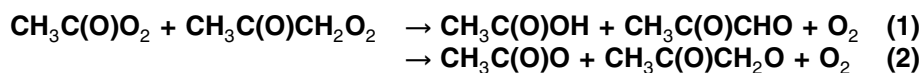
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$$\Delta H^\circ(1) = -369 \text{ kJ}\cdot\text{mol}^{-1}$$

5

Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(5.0 \pm 2.0) \times 10^{-12}$	298	Bridier et al., 1993	FP-UVAS (a)
$k_1 \leq 4 \times 10^{-12}$	298		
<i>Branching Ratios</i>			
$k_2/k = 0.5 \pm 0.2$	298	Jenkin et al., 1993	P-FTIR-AS (b)

Comments

- 10 (a) Flash photolysis of Cl_2 in the presence of $\text{CH}_3\text{C(O)CH}_3$ - CH_3CHO - N_2 mixtures at a total pressure of 1 bar (760 Torr). The rate coefficient k was derived from a kinetic analysis of absorption-time profiles measured at 210 nm, 220 nm, 230 nm and 245 nm, using the value of $k_2/k=0.5$ determined by Jenkin et al. (1993).

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- 5 (b) Steady-state photolysis of Cl_2 in the presence of $\text{CH}_3\text{C}(\text{O})\text{CH}_3\text{-N}_2$ mixtures at a total pressure of 930 mbar (700 Torr). The branching ratio was deduced from measurements of the concentrations of the HCHO and $\text{CH}_3\text{C}(\text{O})\text{CHO}$ products by long-path FTIR spectroscopy and long-path UV-VIS diode-array spectroscopy.

Preferred Values

$$k = 5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

$$k_2/k = 0.5 \text{ at } 298 \text{ K.}$$

Reliability

10 $\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$

$$\Delta (k_2/k) = \pm 0.2 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

15 The preferred values of the rate coefficient and the branching ratio are from the studies of Bridier et al. (1993) and Jenkin et al. (1993), and require independent confirmation.

References

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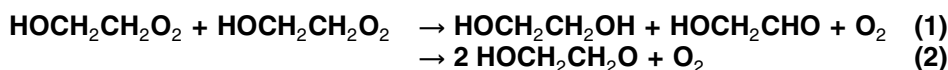
Jenkin, M. E., Cox, R. A., Emrich, M., and Moortgat, G. K.: J. Chem. Soc.

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Faraday Trans., 89, 2983, 1993.

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Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(2.2 \pm 0.3) \times 10^{-12}$	296	Murrells et al., 1991	PLP/MM-UVAS (a,b)
$(2.1 \pm 0.3) \times 10^{-12}$	298	Jenkin and Hayman, 1995	MM-UVAS (a,c)
$7.8 \times 10^{-14} \exp[(1000 \pm 80)/T]$	300–470	Boyd and Lesclaux, 1997	PLP-UVAS (a,d)
$(2.2 \pm 0.3) \times 10^{-12}$	298		
<i>Branching Ratios</i>			
$k_2/k = 0.5 \pm 0.1$	298	Barnes et al., 1993	P-FTIR (e)
$k_2/k = 0.55$	298	Boyd and Lesclaux, 1997	PLP-UVAS (f)

Comments

- (a) k is defined by $-d[\text{HOCH}_2\text{CH}_2\text{O}_2]/dt=2k[\text{HOCH}_2\text{CH}_2\text{O}_2]^2$.
- (b) Separate pulsed laser photolysis and molecular modulation studies using the photolysis of H_2O_2 to produce HO radicals in the presence of ethene

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and air at a pressure of 1 bar (760 Torr). $\text{HOCH}_2\text{CH}_2\text{O}_2$ radicals were monitored by UV absorption at 250 nm with $\sigma_{250}=4.7 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ (mean value). $k_{\text{obs}}/\sigma_{250}=6.7 \times 10^5 \text{ cm s}^{-1}$. k was calculated from the laser photolysis experiments with $k_2/k=0.36$.

- (c) Identical technique to that in Comment (a). $k_{\text{obs}}/\sigma_{250}=(7.1 \pm 0.6) \times 10^5 \text{ cm s}^{-1}$. k calculated using $k_2/k=0.5$ and, in addition, using data from Murrells et al. (1991).
- (d) Pulsed laser photolysis of H_2O_2 at 248 nm in the presence of ethene and O_2 . $\text{HOCH}_2\text{CH}_2\text{O}_2$ radicals were monitored by absorption at 250 nm.
- (e) Analysis of products by FTIR in the photolysis of $\text{HOCH}_2\text{CH}_2\text{I}$ or H_2O_2 - C_2H_4 mixtures in O_2+N_2 . Pressure 150 mbar to 900 mbar (114 Torr to 680 Torr). Mean value given from both systems, which were in excellent agreement, and independent of total pressure or O_2 concentration.
- (f) Based on HO_2 radical formation from the $\text{HOCH}_2\text{CH}_2\text{O} + \text{O}_2$ reaction, measured by UV absorption at 220 nm.

Preferred Values

- $k = 2.2 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 7.8 \times 10^{-14} \exp(1000/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250–450 K.
- $k_2/k = 0.5$ at 298 K.

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Reliability

$\Delta \log k = \pm 0.1$ at 298 K.

$\Delta (E/R) = \pm 300$ K.

$\Delta(k_2/k) = 0.5$ at 298 K.

5 Comments on Preferred Values

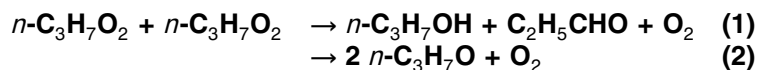
All the recent studies of this reaction provide consistent and seemingly reliable values for the rate coefficient and for the branching ratio (Murrells et al., 1991; Boyd and Lesclaux, 1997). The preferred value of k at 298 K is a mean of the values reported by Murrells et al. (1991), Jenkin and Hayman (1995) and
10 Boyd and Lesclaux (1997), and for the branching ratio the value of Barnes et al. (1993) is accepted. The temperature dependence of k from the work of Boyd and Lesclaux (1997), is recommended but with wider error limits on E/R . A measurement of the temperature dependence of the branching ratio would be of value.

15 References

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20 Murrells, T. P., Jenkin, M. E., Shalliker, S. J., and Hayman, G. D.: J. Chem. Soc. Faraday Trans., 87, 2351, 1991.

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II.A6.149



Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(3.3 \pm 0.3) \times 10^{-13}$	298	Adachi and Basco, 1982	FP-UVAS (a,b)

5 Comments

- (a) k is defined by $-d[n\text{-C}_3\text{H}_7\text{O}_2]/dt = 2k[n\text{-C}_3\text{H}_7\text{O}_2]^2$ and has been derived from the measured overall second order decay of $n\text{-C}_3\text{H}_7\text{O}_2$ radicals k_{obs} by correcting for secondary removal of the $n\text{-C}_3\text{H}_7\text{O}_2$ radicals.
- (b) The monitoring wavelength for $n\text{-C}_3\text{H}_7\text{O}_2$ radicals was 260 nm, with
10 $\sigma = 3.15 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$. The rate coefficient was derived from $k_{\text{obs}} = (3.84 \pm 0.33) \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ on the basis of a mechanism with 12 secondary reactions.

Preferred Values

$k = 3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

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Reliability

$\Delta \log k = \pm 0.5$ at 298 K.

Comments on Preferred Values

The recommended rate coefficient is the rounded-off value from the study of Adachi and Basco (1982). The room temperature rate coefficient requires substantiation along with a determination of the temperature coefficient.

The recommended value of k_{298} is in line with the rate coefficients of the analogous reactions of the CH_3O_2 and $\text{C}_2\text{H}_5\text{O}_2$ radicals. On the other hand, our recommended rate coefficient for the self-reaction of the $i\text{-C}_3\text{H}_7\text{O}_2$ radical is considerably lower ($k_{298}=1.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) and that reported (Anastasi et al., 1978) for the $t\text{-C}_4\text{H}_9\text{O}_2$ radical is even lower still ($k_{298}=2.3 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$). This trend is in keeping with that observed in the liquid phase for the RO_2 radical interactions (Bennett et al., 1970), i.e., $k(\text{primary RO}_2) > k(\text{secondary RO}_2) > k(\text{tertiary RO}_2)$.

References

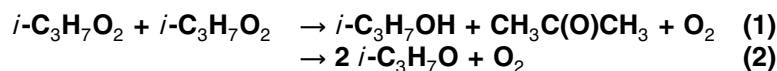
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6917

II.A6.150



$$\Delta H^\circ(1) = -352.1 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -33.0 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.43 \times 10^{-12} \exp[-(2243 \pm 69)/T]$	300–373	Kirsch et al., 1978	MM-UVAS (a,b)
8.10×10^{-16}	300		
$(1.3 \pm 0.4) \times 10^{-15}$	298	Adachi and Basco, 1989	FP-UVAS (a,c)
$(5.3 \pm 0.5) \times 10^{-14}$	298	Munk et al., 1986	PR-UVAS (a,d)
<i>Branching Ratios</i>			
$k_1/k_2 = 1.39 \pm 0.04$	302	Kirsch et al., 1979	P-GC (e)
$k_2/k_1 = 56.3 \exp(-1130/T)$	302–372	Cowley et al., 1982	P-GC (f)

Comments

(a) k is defined by $-d[i\text{-C}_3\text{H}_7\text{O}_2]/dt = 2k[i\text{-C}_3\text{H}_7\text{O}_2]^2$ and has been derived from the observed overall second-order decay of $i\text{-C}_3\text{H}_7\text{O}_2$ radicals k_{obs} by correcting for secondary removal of the $i\text{-C}_3\text{H}_7\text{O}_2$ radicals.

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- (b) Molecular modulation study of the photolysis of 2,2'-azopropane in the presence of O₂ and N₂ at total pressures up to 950 mbar (710 Torr). *i*-C₃H₇O₂ radicals were monitored by absorption at 265 nm. The rate coefficient, *k*, has been calculated from the experimental value of $k_{\text{obs}} = (2.37 \pm 0.17) \times 10^{-12} \exp[-(2243 \pm 60)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and the branching ratio $k_2/k_1 = 1.39$ at 302 K determined in the subsequent study (Kirsch et al. 1979).
- (c) Flash photolysis of 2,2'-azopropane in the presence of O₂ and added N₂ at total pressures up to 960 mbar (720 Torr). *i*-C₃H₇O₂ radicals were monitored by absorption at 240 nm, for which $\sigma(240 \text{ nm}) = 4.86 \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$. The rate coefficient, *k*, has been calculated from the experimental value of $k_{\text{obs}} = (2.03 \pm 0.58) \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K, on the basis of a proposed mechanism of 12 elementary reactions including secondary consumption of *i*-C₃H₇O₂ radicals.
- (d) Pulsed radiolysis of H₂ at 1 bar in the presence of C₃H₆; *i*-C₃H₇ radicals were generated from the reaction of H atoms with C₃H₆. The absorption spectrum of the *i*-C₃H₇O₂ radical was observed on the addition of O₂ and the decay of *i*-C₃H₇O₂ radicals monitored by UV absorption at 253 nm, and found to obey second-order kinetics. It is not clear if the reported value of the rate coefficient is k_{obs} or *k*.
- (e) Steady-state photolysis of 2,2'-azopropane in the presence of O₂ and added N₂ at total pressures up to 670 mbar (500 Torr). Ratio of rate coefficients based on analyses of CH₃COCH₃ and (CH₃)₂CHOH by GC.
- (f) Extension of the experiments by Kirsch et al. (1979), to obtain k_2/k_1 at 333 K and 372 K. The Arrhenius equation calculated from these data and a value of k_2/k_1 at 302 K was reported by Kirsch et al. (1979).

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Preferred Values

$k = 1.0 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 1.6 \times 10^{-12} \exp(-2200/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 300–400 K.

$k_1/k = 0.44$ at 298 K.

$k_1/k = 3.7 \times 10^{-2} \exp(740/T)$ over the temperature range 300–400 K.

$k_2/k = 0.56$ at 298 K.

$k_2/k = 2.0 \exp(-380/T)$ over the temperature range 300–400 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

$\Delta (E/R) = \pm 300 \text{ K}$.

$\Delta (k_1/k) = \Delta (k_2/k) = \pm 0.15$ at 298 K.

Comments on Preferred Values

The recommended rate coefficient, *k*, at 298 K is the average of the rate coefficients from the data of Kirsch et al. (1978) and Adachi and Basco (1982), which are in reasonable agreement. We have not taken into account the rate coefficient reported by Munk et al. (1986), for which experimental details are lacking. The recommended temperature dependence of *k* is based on the results of Kirsch et al. (1978), which have been rounded-off and adjusted to the recommended value of k_{298} .

The measurements of the branching ratio and its temperature dependence (Kirsch et al., 1979; Cowley et al., 1982) appear to be reliable and have been adopted here, but require further confirmation.

The value of k_{298} is considerably lower than that for the analogous reaction

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of the $n\text{-C}_3\text{H}_7\text{O}_2$ radical, which is consistent with the trend observed in studies of the interactions of alkylperoxy radicals in solution (Bennett et al., 1970) i.e., $k(\text{primary RO}_2) > k(\text{secondary RO}_2) > k(\text{tertiary RO}_2)$.

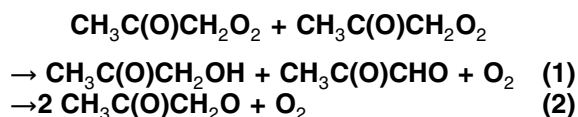
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 10 Kirsch, L. J., Parkes, D. A., Waddington, D. J., and Woolley, A.: *J. Chem. Soc. Faraday Trans.*, 1, 75, 2678, 1979.
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6921

II.A6.151



$$\Delta H^\circ(1) = -314 \text{ kJ}\cdot\text{mol}^{-1}$$

5

Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$\leq 8.3 \times 10^{-12}$	298	Cox et al., 1990	PR-UVA (a,b)
$(8.0 \pm 0.2) \times 10^{-12}$	298	Bridier et al., 1993	FP-UVA (a,c)
<i>Branching Ratios</i>			
$k_2/k = (0.75 \pm 0.1)$	298	Bridier et al., 1993	FP-UVA (d)
$k_2/k = (0.50 \pm 0.05)$	298	Emrich and Warneck, 2003	UVP-GC (e)

Comments

- (a) k is defined by $-d[\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}_2]/dt = 2k[\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}_2]^2$.
- 10 (b) Derived value of $k_{obs} = (8.3 \pm 1.6) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K is an upper limit due to secondary reactions producing possible enhanced decay of $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}_2$ radicals.

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- (c) Flash photolysis of Cl_2 in the presence of $\text{CH}_3\text{C}(\text{O})\text{CH}_3\text{-O}_2\text{-N}_2$ mixtures at a total pressure of 1013 mbar (760 Torr). The rate coefficient, k , was derived from a kinetic analysis of absorption-time profiles at 230 nm and 260 nm, taking account of the information on the mechanism of the overall reaction obtained from the product study of Jenkin et al. (1993).
- (d) Technique as in Comment (c). The branching ratio was obtained on the basis of absorption due to radicals formed in channel (2) and subsequent reactions.
- (e) Continuous photolysis of Cl_2 at 330 nm, in the presence of $\text{CH}_3\text{C}(\text{O})\text{CH}_3\text{-O}_2\text{-NO}_2\text{-N}_2$ mixtures at a total pressure of 1020 mbar (765 Torr). The branching ratio, k_2/k , was determined from the observed formation of peroxyacetyl nitrate (PAN), which is generated in the system from chemistry subsequent to the thermal decomposition of $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}$, using simulations with an explicit chemical mechanism. PAN was measured by GC coupled with indirect analysis, which involved conversion to NO in a heated molybdenum catalytic converter, followed by detection of NO by its chemiluminescent reaction with O_3 .

Preferred Values

$$k = 8.0 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$
$$k_2/k = 0.63 \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.3 \text{ at } 298 \text{ K.}$$
$$\Delta (k_2/k) = \pm 0.2 \text{ at } 298 \text{ K.}$$

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Comments on Preferred Values

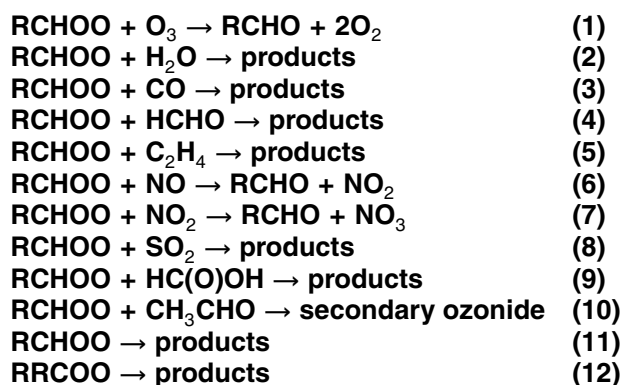
The rate coefficients for $\text{CH}_3\text{C}(\text{O})\text{CH}_2\text{O}_2$ radical decay obtained in the two studies (Cox et al., 1990; Bridier et al., 1993) are in good agreement, and the more rigorous analysis carried out by Bridier et al. (1993) on the basis of the product study of Jenkin et al. (1993) provides the basis for the preferred rate coefficient. The value of k_2/k reported more recently by Emrich and Warneck (2003) is somewhat lower than that derived by Bridier et al. (1993), but the two determinations are in reasonable agreement, given the complexity of the chemical systems and the indirect nature of the determinations. The preferred branching ratio is the mean of the values reported in those two studies. Further verification of the overall rate coefficient and branching ratio is required, as are studies as a function of temperature.

References

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II.A6.152



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R=H or CH₃**Rate coefficient data**

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Criegee intermediate	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>				
$k_2/k_8 = (6.1 \pm 0.3) \times 10^{-5}$	CH ₃ CHOO	295	Calvert et al., 1978	(a)
$k_1:k_3:k_4:k_5:k_6 = 2.5 \times 10^{-3}:$ $1.8 \times 10^{-3}:2.5 \times 10^{-1}:$ $2.5 \times 10^{-3}:1.0$	CH ₂ OO	296	Su et al., 1980	RR-FTIR (b)
$k_2/k_8 = (2.3 \pm 1) \times 10^{-4}$	CH ₂ OO	298	Suto et al., 1984	(c)
$k_7/k_8 = (1.4 \pm 0.4) \times 10^{-2}$	CH ₂ OO	298	Manzanares et al., 1987	(d)
$k_2/k_8 = (8.3 \pm 3.6) \times 10^{-4}$	CH ₂ OO	298	Becker et al., 1993	RR-FTIR/TDLS (e)
$k_2/k_8 = (4.1 \pm 2.2) \times 10^{-4}$	(CH ₃) ₂ COO	298	Becker et al., 1993	RR-FTIR/TDLS (f)
$k_2/k_9 = 7.1 \times 10^{-5}$	CH ₂ OO	298	Neeb et al., 1997	RR-FTIR/HPLC (g)
<i>Absolute Rate Coefficients</i>				
$k_{10} = 1.0 \times 10^{-12}$	CH ₃ CHOO	~298	Fenske et al., 2000	FT-FTIR (h)
$k_{11} = 76 \text{ s}^{-1}$	CH ₃ CHOO	~298	Fenske et al., 2000	(i)
$k_{12} = 6.4 \text{ s}^{-1}$ (measured at ~ 130 mbar)	(CH ₃) ₂ COO	298	Kroll et al., 2001	LIF (j)

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Comments

- 5 (a) Derived from a re-analysis of the data of Cox and Penkett (1972) from a study of the aerosol formation from SO₂ in the presence of O₃-O₂-*cis*-2-C₄H₈ mixtures at atmospheric pressure. In this system the Criegee intermediate involved is believed to be CH₃CHOO.
- 10 (b) FTIR study of the C₂H₄-O₃ reaction in the presence of O₂-N₂ mixtures at a total pressure of 920 mbar and with added CO, HCHO, or SO₂. Relative rate coefficients derived from a computer simulation of reactant consumption and product formation, based on a mechanism of 20 elementary reactions.
- (c) Flow system involving C₂H₄-O₃-SO₂-H₂O mixtures in which H₂SO₄ aerosol concentrations were monitored by scattered UV light. Relative rate coefficients obtained from the dependencies of the aerosol formation on the concentrations of O₃, SO₂ and H₂O.
- 15 (d) Similar study to that of Comment (c), with the inclusion of the effect of added NO₂ on the formation of the H₂SO₄ aerosol.
- (e) Study of the C₂H₄-O₃ reaction in the presence of 1 bar of synthetic air with and without added SO₂; H₂O₂ yields were measured by tunable diode laser absorption spectroscopy or by FTIR spectroscopy.
- 20 (f) Same study as for Comment (e) with (CH₃)₂C=C(CH₃)₂ as the reactant.
- (g) Reaction carried out in a 570 L spherical glass reactor. Hydroxymethyl hydroperoxide (HMHP) concentrations monitored by HPLC and formic acid concentration by FTIR. Formation of HC(O)OH from HMHP shown to be due, in part, to heterogeneous processes. k_2/k_9 was derived

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by fitting [HC(O)OH] and [HMHP] as a function of time to a reaction scheme and using values of $k(\text{O}_3 + \text{C}_2\text{H}_4) = 1.6 \times 10^{-18} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, $k(\text{CH}_3\text{OO} + \text{H}_2\text{O}) = 1 \times 10^{-17} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and assuming that 47% of the Criegee biradicals are stabilized.

- 5 (h) Reaction studied in an atmospheric pressure flow-tube. An excess of acetaldehyde was added to the reaction mixture through a sliding injector such that all thermalised CH₃CHOO, post-injector, was converted to secondary ozonide (SOZ). SOZ was detected by FTIR. The temperature of the study was not reported.
- 10 (i) Unimolecular decomposition rate coefficient obtained relative to the reaction with acetaldehyde from a numerical analysis of the flow-tube data.
- (j) HO observed by LIF in flow-tube experiments. The unimolecular rate coefficient was calculated by assuming that at 100 Torr pressure the observed formation of HO, over timescales of ~ 100-1000 ms, is due to the thermal decomposition of stabilised dimethylcarbonyl oxide.
- 15

Preferred Values

No recommendation for rate data.

Comments on Preferred Values

- 20 Vibrationally excited Criegee intermediates, [RCHOO][‡], are produced from the reactions of O₃ with alkenes (Atkinson and Carter, 1984). These species decompose unimolecularly to give molecular or radical products or undergo collisional deactivation to yield thermally equilibrated Criegee intermediates,

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RCHOO. Here we consider the kinetic and other information relating to the bimolecular reactions that have been proposed for these thermally equilibrated Criegee intermediates.

Studies have been made of the reactions of RCHOO with aldehydes (Su et al., 1980; Fenske et al., 2000; Cox and Penkett, 1972; Hanst et al., 1958; Kan et al., 1981; Niki et al., 1975, 1981; Neeb et al., 1995), SO₂ (Calvert et al., 1978; Su et al., 1980, Cox and Penkett, 1972; Kerr and Calvert, 1984; Hatakeyama et al., 1986), H₂O (Cox and Penkett, 1972; Akimoto et al., 1979; Kan et al., 1981), carboxylic acids (Neeb et al., 1995; Neeb et al., 1996) and methanol (Neeb et al., 1996), but detailed kinetic data are often lacking. Relative rate coefficients have been derived by Calvert et al. (1978), Su et al. (1980) and Suto et al. (1985) based on experimental measurements of the rates of consumption of molecular reactants relative to consumption of SO₂ in systems involving RCHOO Criegee intermediates. The only compound, other than SO₂, common to any of these studies is H₂O, for which the derived relative rate coefficients differ by a factor of ~4. Notwithstanding this discrepancy, these relative rate measurements are the only experimental basis on which to assess the rates of these reactions. It is apparent from these measurements that the reactions of the Criegee intermediates, RCHOO, with O₃, CO and alkenes are not important under atmospheric conditions. The reactions with H₂O, RCHO, NO₂ and SO₂ need to be considered, although for most tropospheric conditions the only effective reaction of the Criegee intermediates is likely to be that with H₂O.

Previous reviewers (Kerr and Calvert, 1984; Atkinson and Lloyd, 1984) have made the reasonable assumption that the reaction of RCHOO with NO could also be significant, based on estimates of the energetics of the proposed reaction pathway RCHOO+NO→RCHO+NO₂. Unfortunately, there is no direct experimental evidence for this reaction and very little information upon which to base an estimate of its rate coefficient. Atkinson and Lloyd (1984) have

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estimated the relative rate coefficients for RCHOO reacting with NO and SO₂, corresponding to $k_6/k_8=10^2$, whereas Kerr and Calvert (1984) propose $k_6/k_8=1$. Experimental data on this ratio of rate coefficients are badly needed.

In the absence of direct kinetic measurements of the absolute rate coefficients for any of the RCHOO bimolecular reactions (excepting the recent measurement of Fenske et al. (2000) for CH₃CHOO + CH₃CHO which cannot be used with any of the relative-rate measurements made to date), both Atkinson and Lloyd (1984) and Kerr and Calvert (1984) have suggested that k_6 should be equated to the rate coefficient for the structurally analogous reactions, RO₂+NO→RO+NO₂, with $k_6=7\times 10^{-12}$ cm³ molecule⁻¹ s⁻¹ at 298 K. While this seems a reasonable proposition, it is desirable to obtain experimental verification. At present it is difficult to see how any direct measurements could be made with RCHOO systems involving O₃-alkene reactions owing to the complex chemistry involved. In this regard the study of Hatakeyama et al. (1981) involving the generation of CH₂OO Criegee intermediates from the reaction of CH₂(³B₁) with O₂ are of considerable interest.

In deriving the relative rate coefficients listed above, it has been necessary in some cases to compare data obtained from different O₃-alkene systems and to assume that all the RCHOO Criegee intermediates have equal reactivity, e.g., CH₂OO and CH₃CHOO. Again, while this seems to be a reasonable assumption, it requires experimental verification.

There is little direct experimental evidence on the products of the Reactions (1) to (9). Where the products are stated these have largely been suggested on the basis of analogy with related reactions.

Recent work of Neeb et al. (1997) shows that the reaction of the CH₂OO Criegee intermediate with H₂O leads initially to hydroxymethyl hydroperoxide (HOCH₂OOH). The HOCH₂OOH may then decompose to HC(O)OH and H₂O but the extent to which this occurred by heterogeneous processes in the sys-

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tem used by Neeb et al. (1997) is uncertain. Hydroperoxides have been found in a number of other O₃-alkene studies (Simonaitis et al., 1991; Martinez et al., 1981; Winterhalter et al., 2000) and are suggested to arise in a similar way, by direct interaction of the Criegee intermediate with H₂O. In addition to the expected formation of carboxylic acids from the reactions of the Criegee intermediates with H₂O, recent studies of the reactions of O₃ with *trans*-2-butene (Becker et al., 1993; Simonaitis et al., 1991; Martinez et al., 1981), isoprene (Neeb et al., 1997; Simonaitis et al., 1991) and monoterpenes (Simonaitis et al., 1991; Martinez et al., 1981; Winterhalter et al., 2000) have reported varying amounts of H₂O₂ product. Since the yields of H₂O₂ were considerably enhanced by the presence of H₂O, it was proposed that H₂O₂ was formed in a direct reaction involving Criegee intermediates. Thus these observations may be rationalised in terms of the reactions depicted in Fig. 6. For the reaction of CH₂OO with H₂O, H₂O₂ formation is a minor pathway.

Reaction of R₁R₂COO Criegee intermediates with aldehydes leads to the formation of the corresponding ozonides (Fenske et al., 2000; Niki et al., 1977, 1983, 1987). However, the formation of ethene ozonide has not been observed in the reaction of CH₂OO with HCHO or in the O₃-ethene reaction (Su et al., 1980; Kan et al., 1981; Niki et al., 1981, 1983). The proposal that the reaction of the CH₂OO Criegee intermediate with HCHO leads to HOCH₂OCHO (Su et al., 1980; Kan et al., 1981; Niki et al., 1981, 1983; Horie and Moortgat, 1991) has now been shown to be incorrect. The spectrum observed in the CH₂OO-HCHO reaction and assigned to HOCH₂OCHO is now known to belong to HOOCH₂OCHO (Neeb et al., 1995; Thamm et al., 1996), which is formed by the reaction of the CH₂OO Criegee intermediate with HC(O)OH.

Tobias and Ziemann (2001) have determined rate coefficients for the reactions of the CH₃(CH₂)₁₁CHOO Criegee intermediate with acids, aldehydes and alcohols relative to the reaction with H₂O. The following rate coefficient ratios

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were obtained (H₂O=1): methanol, 22; 2-propanol, 50; formaldehyde, 2700; and heptanoic acid, 17000.

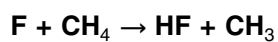
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Appendix 7: X + VOC

II.A7.165



$\Delta H^\circ = -131.5 \text{ kJ}\cdot\text{mol}^{-1}$

5 Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$5.5 \times 10^{-10} \exp[-(580 \pm 150)/T]$	250–350	Wagner et al., 1971	DF-MS
7.9×10^{-11}	298		
7.2×10^{-11}	298	Kompa and Wanner, 1972	(a)
$(6.0 \pm 6.0) \times 10^{-11}$	298	Clyne et al., 1973	DF-MS
$(5.72 \pm 0.30) \times 10^{-11}$	298	Fasano and Nogar, 1982	(b)
$(5.3 \pm 0.3) \times 10^{-11}$	294	Moore et al., 1994	(c)
<i>Relative Rate Coefficients</i>			
$9.0 \times 10^{-11} \exp(-137/T)$	253–348	Foon and Reid, 1971	RR (d)
5.7×10^{-11}	298		
$1.3 \times 10^{-10} \exp(-215/T)$	180–410	Persky, 1996	RR (e)
6.2×10^{-11}	298		

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Comments

- (a) Flash photolysis of WF_6 . Overall rate coefficient was obtained by monitoring the decay of the HF chemical laser emission.
- (b) Infrared multiphoton dissociation of SF_6 in a mixture of CH_4 , D_2 and Ar. First-order decay of [F] was monitored by chemiluminescence from either HF or DF. Dependence of decay rate on mixture composition gave values for k and for $k(\text{F}+\text{D}_2)$.
- (c) Time-resolved vibrational chemiluminescence from HF monitored following the production of F atoms in the presence of CH_4 by pulsed laser photolysis of F_2 at 266 nm. Rate coefficient values were also reported at 218 K, 179 K and 139 K, with the values increasing at temperatures below about 200 K.
- (d) Competitive fluorination-consumption technique. Value of k derived from measured ratio $k/k(\text{F}+\text{H}_2)=0.82 \exp(313/T)$ and $k(\text{F}+\text{H}_2)=1.1 \times 10^{-10} \exp(-450/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current evaluation).
- (e) Competitive study using DF-MS technique. Value of k derived from measured ratio $k/k(\text{F}+\text{D}_2)=1.21 \exp(420/T)$, the kinetic isotope effect $k(\text{F}+\text{H}_2)/k(\text{F}+\text{D}_2)=1.04 \exp(185/T)$ (Persky, 1973) and $k(\text{F}+\text{H}_2)=1.1 \times 10^{-10} \exp(-450/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current evaluation).

Preferred Values

$$k = 6.3 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$
$$k = 1.3 \times 10^{-10} \exp(-215/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ over the temperature range } 180\text{--}410 \text{ K.}$$

180–410 K.

Reliability

$$\Delta \log k = \pm 0.15 \text{ at } 298 \text{ K.}$$
$$\Delta (E/R) = \pm 200 \text{ K.}$$

Comments on Preferred Values

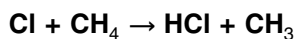
The preferred value at room temperature is based on the room temperature values reported in Wagner et al. (1971), Kompa and Wanner (1972), Clyne et al. (1973), Fasano and Nogar (1982), Moore et al. (1994), Foon and Reid (1971) and Persky (1973). The preferred temperature dependence is that reported by Persky (1973). Results reported in this study are preferred over the temperature dependences reported in the much earlier studies of Wagner et al. (1971) and Foon and Reid (1971).

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II.A7.166



$$\Delta H^\circ = 7.6 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$7.94 \times 10^{-12} \exp[-(1260 \pm 35)/T]$	218–401	Watson et al., 1976	FP-RF (a)
$(1.13 \pm 0.1) \times 10^{-13}$	298		
$7.93 \times 10^{-12} \exp[-(1272 \pm 51)/T]$	218–322	Manning and Kurylo, 1977	FP-RF
$(1.04 \pm 0.1) \times 10^{-13}$	296		
$6.51 \times 10^{-12} \exp[-(1229 \pm 27)/T]$	200–299	Whytock et al., 1977	FP-RF (b)
$(1.13 \pm 0.07) \times 10^{-13}$	299		
$(1.08 \pm 0.07) \times 10^{-13}$	298	Michael and Lee, 1977	DF-RF
$1.06 \times 10^{-11} \exp[-(1415 \pm 100)/T]$	268–423	Lin et al., 1978	DF-MS
$(9.6 \pm 0.9) \times 10^{-14}$	296		
$8.2 \times 10^{-12} \exp[-(1320 \pm 20)/T]$	200–300	Zahniser et al., 1978	DF-RF (c)
$(9.9 \pm 1.5) \times 10^{-14}$	298		
$7.4 \times 10^{-12} \exp[-(1291 \pm 68)/T]$	220–298	Keyser, 1978	DF-RF (d)
$(1.01 \pm 0.02) \times 10^{-13}$	298		
$3.2 \times 10^{-12} \exp[-(1063 \pm 34)/T]$	221–298	Ravishankara and Wine, 1980	PLP-RF (e)
$(9.65 \pm 0.55) \times 10^{-14}$	298		
$8.06 \times 10^{-12} \exp[-(1300 \pm 113)/T]$	233–338	Heneghan et al., 1981	(f)
$(9.60 \pm 0.50) \times 10^{-14}$	298		

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$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
$(9.93 \pm 0.13) \times 10^{-14}$	298	Dobis and Benson, 1987	(f)
$(9.17 \pm 0.75) \times 10^{-14}$	294	Sawerysyn et al., 1987	DF-MS
$(9.40 \pm 0.40) \times 10^{-14}$	298	Beichert et al., 1995	DF-RF
$7.0 \times 10^{-12} \exp[-(1270 \pm 60)/T]$	181–291	Seeley et al., 1996	(g)
$(9.9 \pm 0.3) \times 10^{-14}$	298		
$(1.00 \pm 0.10) \times 10^{-13}$	298	Matsumi et al., 1997	PLP-LIF
$3.7 \times 10^{-13} (T/298)^{2.6} \exp(-385/T)$	292–800	Pilgrim et al., 1997	PLP (h)
$(9.3 \pm 0.9) \times 10^{-14}$	292		
$(1.07 \pm 0.03) \times 10^{-13}$	297	Mellouki, 1998	PLP-RF
$6.5 \times 10^{-12} \exp[-(1235 \pm 34)/T]$	218–298	Wang and Keyser, 1999	DF-RF
$(1.01 \pm 0.06) \times 10^{-13}$	298		

Comments

- (a) These values were derived using the original data, but correcting for the presence of C_2H_6 (see Addenda to Watson, 1977).
- 5 (b) Non-linear Arrhenius behaviour was observed over the entire temperature range (200 K to 500 K) of measurements. Data for the temperature range 200 K to 299 K are well represented by the Arrhenius expression given in the table (Whytock et al., 1977).
- 10 (c) Non-linear Arrhenius behaviour was observed over the entire temperature range (200 K to 504 K) of measurements. Data for the temperature range 200 K to 300 K are well represented by the Arrhenius expression given in

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the table (Zahniser et al., 1978).

- (d) Non-linear Arrhenius behaviour was observed over the entire temperature range (220 K to 423 K) of measurements. Data for the temperature range 220 K to 298 K are well represented by the Arrhenius expression given in
- 5 the table (Keyser, 1978).
- (e) Non-linear Arrhenius behaviour was observed. At temperatures at and below 240 K the apparent bimolecular rate constant was dependent upon the chemical composition of the reaction mixture. Ravishankara and Wine (1980) suggested that this was due to a non-equilibration of the $^2\text{P}_{1/2}$ and
- 10 $^2\text{P}_{3/2}$ spin states of atomic chlorine at high values of the pseudo-first order rate constant, k' , i.e., if the mixture did not contain an efficient spin equilibrators, e.g. Ar or CCl_4 , the bimolecular rate constant decreased at high CH_4 concentrations, i.e., high values of k' . The Arrhenius expression for k between 221 K and 298 K was derived from the data shown in their Table II (excluding the high CH_4 concentration data in the He- Cl_2 - CH_4 system).
- 15 (f) Very low pressure reactor system with MS detection of reactants and products.
- (g) Turbulent flow tube technique at pressures near 80 mbar (60 Torr). The Cl atom decay was monitored by RF.
- 20 (h) Pulsed laser photolysis of CF_2Cl_2 at 193 nm. Time evolution of HCl product was monitored by continuous wave infrared long-path absorption at the R(3) line of the fundamental vibrational transition. Non-linear Arrhenius behavior was observed between 292 K and 800 K and was described by the modified Arrhenius expression given in the table.

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Preferred Values

$k = 1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

$k = 6.6 \times 10^{-12} \exp(-1240/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 200–300 K.

5 Reliability

$\Delta \log k = \pm 0.06$ at 298 K.

$\Delta (E/R) = \pm 200$ K.

Comments on Preferred Values

The preferred Arrhenius expression is derived from a least-squares fit to the
10 experimental data between 200 K and 300 K reported in the studies of Wat-
son et al. (1976), Manning and Kurylo (1977), Whytock et al. (1977), Michael
and Lee (1977), Lin et al. (1978), Zahniser et al. (1978), Keyser (1978), Ravis-
hankara and Wine (1980), Heneghan et al. (1981), Dobis and Benson (1987),
15 Sawerysyn et al. (1987), Beichert et al. (1995), Seeley et al. (1996), Matsumi
et al. (1997) and Pilgrim et al. (1997). The data used were restricted to the 200
K to 300 K temperature range because of the curvature in the Arrhenius plot
at higher temperatures reported in the studies of Whytock et al. (1977), Zah-
niser et al. (1978), Keyser (1978), Ravishankara and Wine (1980) and Pilgrim
20 et al. (1997). Therefore, for some studies only a subset of the data reported in
the study was used. Results of the most recent studies of Mellouki et al. (1998)
and Wang and Keyser (1999) are in excellent agreement with the preferred
values. Results of relative rate studies were not used in this evaluation in the
derivation of the preferred values. In general, the relative rate data (Lin et al.,
1978; Watson, 1977; Pritchard et al., 1954; Pritchard et al., 1955; Knox, 1955)

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used in previous evaluations are in good agreement with the preferred values
at room temperature, but are significantly lower than the preferred values at low
temperatures.

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II.A7.167



Low-pressure rate coefficients

Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(3.15 \pm 0.30) \times 10^{-21} T^{-3.5}[\text{Ar}]$	210–361	Brunning and Stief, 1985	FP-RF (a)
$6.9 \times 10^{-30} [\text{Ar}]$	298		
<i>Relative Rate Coefficients</i>			
$(5.2 \pm 0.7) \times 10^{-30} [\text{air}]$	295	Wallington et al., 1990	RR (b)
$5.4 \times 10^{-30} (T/300)^{-2.092}[\text{air}]$	252–370	Kaiser, 1992	RR (c)
5 $(6.1 \pm 0.2) \times 10^{-30} [\text{air}]$	297	Kaiser and Wallington, 1996	RR (d)

Comments

- (a) The concentration of the bath gas Ar was varied over the range $(2.7-120) \times 10^{17} \text{ molecule cm}^{-3}$. Some experiments with N_2 were also conducted. Falloff extrapolations were made using $F_c=0.6$.
- 10 (b) Cl atoms were generated by photolysis of Cl_2 in the presence of C_2H_2 and C_2H_6 (or $\text{C}_2\text{H}_5\text{Cl}$). The decays of C_2H_2 , C_2H_6 (or $\text{C}_2\text{H}_5\text{Cl}$) were followed by FTIR spectroscopy. The measured rate coefficient ratios have been placed

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on an absolute basis using a rate coefficient of $k(\text{Cl}+\text{C}_2\text{H}_6)=5.7\times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$. Measurements were conducted over the pressure range 0.013 mbar to 7.6 bar. Falloff extrapolations were made with $F_c = 0.6$.

- 5 (c) Mixtures of C_2H_2 , C_2H_6 , Cl_2 and diluent (air, N_2 , or SF_6) were irradiated by a UV fluorescent lamp. C_2H_2 and C_2H_6 concentrations were determined by GC. The reaction was studied at pressures between 0.03 bar and 1.7 bar. The measured rate coefficient ratios are placed on an absolute basis using the rate coefficient $8.68 \times 10^{-11} \exp(-113/T)\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ for the reaction $\text{Cl}+\text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_5+\text{HCl}$. Falloff extrapolations were made with a temperature independent $F_c=0.6$.
- 10 (d) Mixtures of Cl_2 , C_2H_2 , CH_4 , CH_3Cl , C_2H_6 and $\text{C}_2\text{H}_5\text{Cl}$ and the diluent gases air and N_2 were irradiated with a UV fluorescent lamp. After irradiation C_2H_2 , CH_4 and CH_3Cl were monitored by GC (0.4 mbar to 13 mbar). CH_3Cl , C_2H_6 and $\text{C}_2\text{H}_5\text{Cl}$ were determined by FTIR (13 mbar to 920 mbar). The following values were used for the reference abstraction reactions: $1.0\times 10^{-13}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ ($\text{Cl}+\text{CH}_4$), $4.9\times 10^{-13}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ ($\text{Cl}+\text{CH}_3\text{Cl}$), $5.7 \times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ ($\text{Cl}+\text{C}_2\text{H}_6$) and $8.05\times 10^{-12}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ ($\text{Cl}+\text{C}_2\text{H}_5\text{Cl}$). The results were analyzed together with previous determinations performed between 0.13 bar and 7.9 bar and extrapolated with $F_c=0.6$ (Wallington et al., 1990).
- 15
- 20

Preferred Values

$k_0 = 6.1 \times 10^{-30} (T/300)^{-3} [\text{N}_2]\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ over the temperature range 200–300 K.

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Reliability

$\Delta \log k_0 = \pm 0.3$ at 298 K.

$\Delta n = \pm 1$.

Comments on Preferred Values

- 5 The preferred values are based on the room temperature measurements of Kaiser and Wallington (1996) which have been evaluated with $F_c=0.6$. The temperature dependence is a compromise of the results from Brunning and Stief (1985) and Kaiser (1992).

High-pressure rate coefficients

10 Rate coefficient data

$k_\infty/\text{cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.52 \pm 0.15) \times 10^{-4} T^{-2.63}$	210–361	Brunning and Stief, 1985	FP-RF (a)
4.7×10^{-11}	298		
<i>Relative Rate Coefficients</i>			
$(2.3 \pm 0.7) \times 10^{-10}$	295	Wallington et al., 1990	RR (b)
$2.13 \times 10^{-10} (T/300)^{-1.045}$	252–370	Kaiser, 1992	RR (c)
$(2.0 \pm 0.1) \times 10^{-10}$	297	Kaiser and Wallington, 1996	RR (d)

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Comments

(a) to (d) See comments (a) to (d) for k_0 .

Preferred Values

$k = 5.2 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and 1 bar of air.

5 $k_\infty = 2.0 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 200–400 K.

Reliability

$\Delta \log k_\infty = \pm 0.3$ at 298 K.

$\Delta n = \pm 1$.

10 Comments on Preferred Values

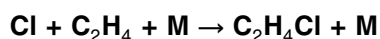
The preferred values are based on the data of Kaiser and Wallington (1996) which cover the broadest pressure range (0.13 bar to 7.9 bar). They have been evaluated with $F_c=0.6$. Relative rate coefficients near 1 bar from Lee and Rowland (1977), Atkinson and Aschmann (1985) and Wallington et al. (1988) are
15 in good agreement with the preferred values. A branching ratio of 0.19 ± 0.05 for formation of *cis*- and *trans*-isomers of the CHCl adduct was determined by Zhu et al. (1994) around 1 bar of N_2 and 295 K.

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Low-pressure rate coefficients

Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.4 \pm 0.2) \times 10^{-29} (T/298)^{-2.0} [\text{N}_2]$	218–297	Maricq et al., 1993	(a)
$(1.0 \pm 0.2) \times 10^{-29} [\text{He}]$	293	Stutz et al., 1997	(b)
<i>Relative Rate Coefficients</i>			
$(1.6_{-0.3}^{+1}) \times 10^{-29} [\text{air}]$	295	Wallington et al., 1990	RR (c)
$(1.7 \pm 0.3) \times 10^{-29} (T/298)^{-3.28} [\text{air}]$	297–383	Kaiser and Wallington, 1996	RR (d)
$(1.42 \pm 0.05) \times 10^{-29} [\text{air}]$	297		
$1.0 \times 10^{-29} [\text{He}]$	297	Kaiser and Wallington, 1998	RR (d,e)
$1.85 \times 10^{-29} [\text{N}_2]$			

Comments

(a) IR absorption measurements of C_2H_6 and HCl after laser photolysis of Cl_2 in $\text{Cl}_2\text{-C}_2\text{H}_4\text{-O}_2\text{-N}_2$ mixtures. Measurements at 39 mbar of N_2 , here evaluated without falloff corrections. k also measured at 170 mbar and 297 K.

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(b) Fast-flow discharge study detecting Cl by resonance fluorescence at 135 nm. Similar results by relative rate measurements.

(c) Measurements of k performed by a relative rate technique. Cl atoms were generated by photolysis of Cl_2 in the presence of C_2H_4 , and C_2H_6 (or $\text{C}_2\text{H}_5\text{Cl}$). Decay of C_2H_4 , C_2H_6 (or $\text{C}_2\text{H}_5\text{Cl}$) monitored by FTIR spectroscopy. Using a value of $5.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the rate coefficient for the $\text{Cl} + \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_5 + \text{HCl}$ reaction, the relative data were placed on an absolute basis. The reaction was studied over the pressure range 13 mbar to 4000 mbar and the measured rate coefficients fitted with $F_c = 0.6$.

(d) Mixtures of Cl_2 , C_2H_4 , CH_4 , CH_3Cl , CCl_3H , C_2H_6 and $\text{C}_2\text{H}_5\text{Cl}$ and the diluent gases air and N_2 were irradiated with a UV fluorescent lamp. After irradiation, C_2H_4 and the above reference compounds were determined by GC or FTIR techniques. The experiments were performed at total pressures of 0.26 mbar to 130 mbar. The following values were used for the reference abstraction reactions: $1.0 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ($\text{Cl} + \text{CH}_4$), $4.9 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ($\text{Cl} + \text{CH}_3\text{Cl}$), $1.1 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ($\text{Cl} + \text{CCl}_3\text{H}$), $5.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ($\text{Cl} + \text{C}_2\text{H}_6$) and $8.05 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ ($\text{Cl} + \text{C}_2\text{H}_5\text{Cl}$). The results were analyzed together with previous determinations conducted at 130 mbar to 4000 mbar of air (Wallington et al., 1990) and extrapolated with $F_c = 0.6$.

(e) Falloff extrapolation with $F_c = 0.4$.

Preferred Values

$k_0 = 1.85 \times 10^{-29} (T/300)^{-3.3}$ [air] cm³ molecule⁻¹ s⁻¹ over the temperature range 250–300 K.

Reliability

- 5 $\Delta \log k_0 = \pm 0.5$ at 298 K.
 $\Delta n = \pm 1$.

Comments on Preferred Values

- 10 The preferred values are based on the most detailed results from Kaiser and Wallington (1996, 1998) which agree with the results from Maricq et al. (1993) and Stutz et al. (1997) (only for the bath gas He, but not N₂). The given value of k_0 corresponds to a falloff extrapolation with $F_c=0.4$.

High-pressure rate coefficients

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
$3.05^{+2}_{-0.4} \times 10^{-10}$	295	Wallington et al., 1990	RR (a)
$(3.2 \pm 0.15) \times 10^{-10}$	297	Kaiser and Wallington, 1996	RR (b)
5.7×10^{-10}	297	Kaiser and Wallington, 1998	RR (c)

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Comments

- (a) See comment (c) for k_0 .
(b) See comment (d) for k_0 .
(c) See comments (d) and (e) for k_0 .

5 Preferred Values

$k = 1.1 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and 1 bar of air.
 $k_\infty = 6 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 250–300 K.

Reliability

- 10 $\Delta \log k_\infty = \pm 0.3$ at 298 K.
 $\Delta n = \pm 1$.

Comments on Preferred Values

- 15 The falloff extrapolation of the data from Wallington et al. (1990) is consistent with results in the intermediate falloff range from Maricq et al. (1993), Lee and Rowland (1977), Iyer et al. (1983), Atkinson and Aschmann (1985), Atkinson and Aschmann (1987) and Wallington et al. (1988). Measurements of the reverse decomposition of C₂H₄Cl in the falloff range at 400–480 K have been reported by Knyazev et al. (1999).

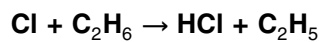
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II.A7.169



$$\Delta H^\circ = -8.7 \text{ kJ}\cdot\text{mol}^{-1}$$

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Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
$(6.0 \pm 1.5) \times 10^{-11}$	298	Davis et al., 1970	FP-RF (a)
$7.29 \times 10^{-11} \exp[-(61 \pm 44)/T]$	222–322	Manning and Kurylo, 1977	FP-RF
$(5.93 \pm 0.44) \times 10^{-11}$	296		
$(5.95 \pm 0.28) \times 10^{-11}$	298	Ray et al., 1980	DF-MS
$9.01 \times 10^{-11} \exp[-(133 \pm 15)/T]$	220–604	Lewis et al., 1980	DF-RF
$(5.48 \pm 0.30) \times 10^{-11}$	298		
$8.20 \times 10^{-11} \exp[-(86 \pm 10)/T]$	203–343	Dobis and Benson, 1991	(b)
$(6.10 \pm 0.11) \times 10^{-11}$	298		
$(7.05 \pm 1.4) \times 10^{-11}$	298	Kaiser et al., 1992	PLP-IRA
$(5.9 \pm 0.6) \times 10^{-11}$	297	Stickel et al., 1992	PLP-TDLS
$(5.53 \pm 0.21) \times 10^{-11}$	298	Beichert et al., 1995	DF-RF
$(5.75 \pm 0.45) \times 10^{-11}$	298	Tyndall et al., 1997	FP-RF
$8.6 \times 10^{-11} \exp[-(135 \pm 26)]$	292–600	Pilgrim et al., 1997	PLP (c)
$(5.5 \pm 0.2) \times 10^{-11}$	292		
$(6.5 \pm 0.3) \times 10^{-11}$	297	Mellouki, 1998	PLP-RF
$(5.85 \pm 0.55) \times 10^{-11}$	298	Hitsuda et al., 2001	PLP-LIF
<i>Relative Rate Coefficients</i>			
$(6.0 \pm 1.3) \times 10^{-11}$	296	Hooshiyar and Niki, 1995	RR (d)
$(5.4 \pm 1.2) \times 10^{-11}$	298	Beichert et al., 1995	RR (e)
$(5.5 \pm 1.2) \times 10^{-11}$	297	Tyndall et al., 1997	RR (f)
$(5.7 \pm 0.5) \times 10^{-11}$	298	Finlayson-Pitts et al., 1999	RR (g)

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Comments

- (a) Reported value has been reduced by 10% as discussed previously (CO-DATA, 1980).
- (b) Very low pressure reactor study. Cl atoms were generated by microwave discharge of Cl_2 -He mixtures, with MS analysis of reactants and products.
- (c) Cl atoms generated from pulsed laser photolysis of CF_2Cl_2 at 193 nm. Time evolution of HCl product was monitored by continuous wave infrared long-path absorption at the R(3) line of the fundamental vibrational transition.
- (d) Cl atoms generated by photolysis of Cl_2 in N_2 at 1 bar pressure. Relative disappearance rates of organics studied were measured by GC. Rate coefficient ratio $k/k(\text{Cl}+n\text{-C}_4\text{H}_{10})=0.294\pm 0.023$ is placed on an absolute basis by use of $k(\text{Cl}+n\text{-C}_4\text{H}_{10})=2.05\times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, this evaluation).
- (e) Cl atoms generated by photolysis of Cl_2 in air at 1 bar pressure. Relative disappearance rates of organics studied were measured by GC. Rate coefficient ratio $k/k(\text{Cl}+n\text{-C}_4\text{H}_{10})=0.261\pm 0.013$ is placed on absolute basis by use of $k(\text{Cl} + n\text{-C}_4\text{H}_{10})=2.05\times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, this evaluation).
- (f) Cl atoms generated by photolysis of Cl_2 in air or N_2 at a total pressure of 156 mbar to 666 mbar (117–500 Torr). Relative disappearance rates of organics studied were measured by GC or FTIR. Rate coefficient ratio $k/k(\text{Cl}+n\text{-C}_4\text{H}_{10})=0.267\pm 0.037$ is placed on absolute basis by use of $k(\text{Cl}+n\text{-C}_4\text{H}_{10})=2.05\times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, this evaluation).

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(g) Cl atoms generated by photolysis of Cl₂, SOCl₂, or CCl₃COCl in air or N₂ at 1 bar pressure. Rate coefficient ratio $k/k(\text{Cl}+n\text{-C}_4\text{H}_{10}) = 0.277 \pm 0.025$ is placed on absolute basis by use of $k(\text{Cl}+n\text{-C}_4\text{H}_{10})=2.05 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, this evaluation).

5 Preferred Values

$k = 5.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 8.3 \times 10^{-11} \exp(-100/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 220–600 K.

Reliability

10 $\Delta \log k = \pm 0.06$ at 298 K.
 $\Delta (E/R) = \pm 100$ K.

Comments on Preferred Values

The 298 K rate coefficient is the average of the room temperature absolute rate coefficients of Davis et al. (1970), Manning and Kurylo (1977), Ray et al. (1980), Lewis et al. (1980), Dobis and Benson (1991), Kaiser et al. (1992),
15 Stickel et al. (1992), Beichert et al. (1995), Tyndall et al. (1997), Pilgrim et al. (1997), Mellouki (1998) and Hitsuda et al. (2001). The temperature dependence is the average of those from the temperature-dependent studies of Manning and Kurylo (1977), Lewis et al. (1980), Dobis and Benson (1991) and
20 Pilgrim et al. (1997). The room temperature relative rate values of Hooshiyar and Niki (1995), Beichert et al. (1995), Tyndall et al. (1997) and Finlayson-Pitts et al. (1999) are in good agreement with the preferred value, while those of

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Atkinson and Aschmann (1985) and Wallington et al. (1988) are 20% to 30% higher than the preferred value.

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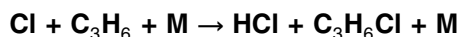
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II.A7.170



Low-pressure rate coefficients

Rate coefficient data

$k_0/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
$(4.0 \pm 0.4) \times 10^{-28} [\text{N}_2]$	298	Kaiser and Wallington, 1996	RR (a)

Comments

(a) Cl atoms were generated by photolysis of Cl_2 in the presence of C_3H_6 and C_2H_6 at 1 mbar to 900 mbar of N_2 . C_3H_6 consumption was determined by FTIR or GC analysis, the major products being 3-chloropropene and 1,2-dichloropropane. At low pressure (below 12 mbar) 3-chloropropene is the major product indicating that abstraction of H by Cl from the CH_3 group in C_3H_6 is the dominant channel. At pressures higher than 12 mbar, the primary product observed is 1,2-dichloropropane, indicating that addition of a Cl atom to the double bond is the major channel. The limiting rate coefficients were obtained using $F_c=0.6$. A rate coefficient for the reference reaction $\text{Cl} + \text{C}_2\text{H}_6 \rightarrow \text{C}_2\text{H}_5 + \text{HCl}$ of $5.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ was employed (Kaiser and Wallington, 1996; this evaluation).

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Preferred Values

$$k_0 = 4.0 \times 10^{-28} [\text{N}_2] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k_0 = \pm 0.5 \text{ at } 298 \text{ K.}$$

5 Comments on Preferred Values

The preferred value is based on the only value reported (Kaiser and Wallington, 1996). Due to this and to the uncertainty of the extrapolated k_0 , a large error limit is assigned.

High-pressure rate coefficients

10 Rate coefficient data

$k_\infty/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
$(2.54 \pm 0.09) \times 10^{-10}$	296	Atkinson and Aschmann, 1985	RR (a)
$(2.94 \pm 0.13) \times 10^{-10}$	295	Wallington et al., 1988	RR (b)
$(2.68 \pm 0.13) \times 10^{-10}$	298	Kaiser and Wallington, 1996	RR (c)

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Comments

5 (a) Cl atoms generated by the photolysis of Cl_2 - n - C_4H_{10} - C_3H_6 -air at 1 bar. The reaction was studied relative to the reaction $\text{Cl} + n\text{-C}_4\text{H}_{10} \rightarrow \text{products}$ for which a rate coefficient $2.05 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ is used (this evaluation). C_3H_6 and $n\text{-C}_4\text{H}_{10}$ were analyzed by GC.

10 (b) Cl atoms were formed by photolysis of Cl_2 in the presence of C_3H_6 and C_2H_6 or $n\text{-C}_4\text{H}_{10}$ at atmospheric pressure of synthetic air. The decay rate of C_3H_6 was measured relative to that of $n\text{-C}_4\text{H}_{10}$ and placed on an absolute basis using rate coefficients of $2.05 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the reference reactions (this evaluation).

(c) See comment (a) for k_0 . Rate coefficient at 933 mbar (700 Torr) pressure of N_2 or air.

Preferred Values

$$k = 2.7 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K and } 1 \text{ bar of air.}$$

$$15 k_\infty = 2.8 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k_\infty = \pm 0.3 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

20 The preferred value at 1 bar of air is an average of earlier results from Atkinson and Aschmann (1985) and Wallington et al. (1988a), and the more recent

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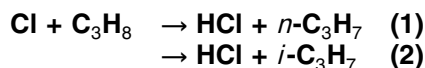
determination by Kaiser and Wallington (1996). At room temperature and atmospheric pressure, the addition of Cl atoms to the double bond accounts for approximately 90% of the reaction (Kaiser and Wallington, 1996). The H atom abstraction occurs from the C-H bonds of the methyl group (Kaiser and Wallington, 1996).

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II.A7.171



$$\Delta H^\circ(1) = -8.3 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -22.5 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.36 \times 10^{-10} \exp[(44 \pm 25)/T]$	220–607	Lewis et al., 1980	DF-RF (a)
$(1.51 \pm 0.06) \times 10^{-10}$	298		
$(1.23 \pm 0.10) \times 10^{-10}$	298	Beichert et al., 1995	DF-RF (b)
$(1.38 \pm 0.03) \times 10^{-10}$	292–700	Pilgrim et al., 1997	PLP (c)
$(1.31 \pm 0.03) \times 10^{-10}$	297	Mellouki, 1998	PLP-RF (d)
$(1.33 \pm 0.03) \times 10^{-10}$	298	Hitsuda et al., 2001	PLP-LIF (e)
<i>Relative Rate Coefficients</i>			
$(1.40 \pm 0.28) \times 10^{-10}$	296	Atkinson and Aschmann, 1985	RR (f)
$(1.45 \pm 0.28) \times 10^{-10}$	295	Wallington et al., 1988	RR (g)
$(1.34 \pm 0.28) \times 10^{-10}$	296	Hooshiyar and Niki, 1995	RR (h)
$(1.44 \pm 0.26) \times 10^{-10}$	298	Beichert et al., 1995	RR (i)
$(1.43 \pm 0.25) \times 10^{-10}$	297	Tyndall et al., 1997	RR (j)

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Comments

- (a) Rate constant was measured at three temperatures: 220 K, 298 K and 607 K. Within experimental uncertainty, these three values were the same. Authors gave as an alternative rate expression the simple mean of the three values: $k=(1.58\pm 0.13)\times 10^{-10}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$.
- (b) Both relative and absolute rate studies of reactions of Cl atoms with C₁-C₄ alkanes. Direct measurement of ratio $k/k(\text{Cl}+\text{C}_2\text{H}_6)$ is in good agreement with the ratio of the absolute values.
- (c) Cl atoms were generated from pulsed laser photolysis of CF₂Cl₂ at 193 nm. Time evolution of HCl product was monitored by continuous wave infrared long-path absorption..
- (d) Experiments carried out in 60 Torr (80 mbar) He bath gas. O₂ added to prevent reformation of Cl atoms via R+Cl₂ which was used as Cl precursor (355 nm photolysis).
- (e) 193 nm photolysis of HCl as Cl source. Detection of both Cl(²P_{1/2}) and Cl(²P_{3/2}) using VUV-LIF. The rate constants for Cl(²P_{1/2}) were found to be ≈ 30% of those for the Cl(²P_{3/2}) ground state. The rate constant for Cl(²P_{3/2}) with fully deuterated propane was found to be $0.86\times 10^{-10}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$.
- (f) Cl atoms were generated by photolysis of Cl₂ in air at 1 bar pressure. Relative disappearance rates of organics studied were measured by GC. Rate coefficient ratio $k/k(\text{Cl}+n\text{-C}_4\text{H}_{10})=0.681\pm 0.025$ is placed on absolute basis by use of $k(\text{Cl}+n\text{-C}_4\text{H}_{10})=2.05\times 10^{-10}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ (IUPAC, this evaluation).
- (g) Cl atoms were generated by photolysis of Cl₂ in air at 987 mbar (740 Torr) pressure. Relative disappearance rates of organics studied were measured by GC. Rate coefficient ratio $k/k(\text{Cl}+n\text{-C}_4\text{H}_{10})=0.711\pm 0.019$ is placed on absolute basis by use of $k(\text{Cl}+n\text{-C}_4\text{H}_{10})=2.05\times 10^{-10}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ (IUPAC, this evaluation).
- (h) Cl atoms were generated by photolysis of Cl₂ in N₂ at 1 bar pressure. Relative disappearance rates of organics studied were measured by GC. Rate coefficient ratio $k/k(\text{Cl}+n\text{-C}_4\text{H}_{10})=0.656\pm 0.009$ is placed on absolute basis by use of $k(\text{Cl}+n\text{-C}_4\text{H}_{10})=2.05\times 10^{-10}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ (IUPAC, this evaluation).
- (i) Cl atoms were generated by photolysis of Cl₂ in air at 1 bar pressure. Relative disappearance rates of organics studied were measured by GC. Rate coefficient ratio $k/k(\text{Cl}+\text{C}_2\text{H}_6)=2.44\pm 0.26$ is placed on absolute basis by use of $k(\text{Cl}+\text{C}_2\text{H}_6)=5.9\times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ (IUPAC, this evaluation).
- (j) Cl atoms were generated by photolysis of Cl₂ in air or N₂ at a total pressure of 156 mbar to 666 mbar (117 Torr to 500 Torr). Relative disappearance rates of organics studied were measured by GC or FTIR. Rate coefficient ratio $k/k(\text{Cl}+\text{C}_2\text{H}_6)=2.42\pm 0.10$ is placed on absolute basis by use of $k(\text{Cl}+\text{C}_2\text{H}_6)=5.9\times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ (IUPAC, this evaluation).

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Preferred Values

$k = 1.4 \times 10^{-10}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$, independent of temperature over the range 200–700 K.

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Reliability

$\Delta \log k = \pm 0.06$ at 298 K.

$\Delta (E/R) = \pm 100$ K.

Comments on Preferred Values

5 The preferred value at room temperature is the mean of the absolute values reported by Lewis et al. (1980), Beichert et al. (1995), Pilgrim et al. (1997), Mellouki (1998) and Hitsuda et al. (2001) and the relative values reported by Atkinson and Aschmann (1985), Wallington et al. (1988), Hooshiyar and Niki (1995), Beichert et al. (1995) and Tyndall et al. (1997). The temperature independence is based on the results of Lewis et al. (1980) over the range 220 K to 607 K and those of Pilgrim et al. (1997) over the range 292 K to 700 K. Tyndall et al. (1997) studied the mechanism of the reaction at 298 K and reported the yield of 1-propyl radicals to be $43 \pm 3\%$ and that of 2-propyl radicals to be $57 \pm 3\%$.

15 References

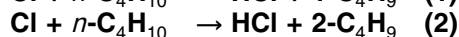
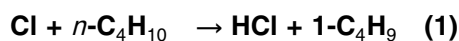
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Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$2.15 \times 10^{-10} \exp[(12 \pm 26)/T]$	298–598	Lewis et al., 1980	DF-RF (a)
$(2.25 \pm 0.10) \times 10^{-10}$	298		
$(1.8 \pm 0.2) \times 10^{-10}$	298	Nesbitt and Leone, 1982	(b)
$(2.11 \pm 0.18) \times 10^{-10}$	298	Beichert et al., 1995	DF-RF (c)
$(2.15 \pm 0.15) \times 10^{-10}$	298	Tyndall et al., 1997	FP-RF (d)
$(1.91 \pm 0.10) \times 10^{-10}$	298	Qian et al., 2002	PLP-TDLS (e)
$(2.05 \pm 0.15) \times 10^{-10}$	298	Hitsuda et al., 2001	PLP-LIF (f)
<i>Branching ratios</i>			
$k_1/k = 0.29 \pm 0.02$	298	Tyndall et al., 1997	GC
$k_2/k = 0.71 \pm 0.02$	298	Tyndall et al., 1997	GC

5 Comments

(a) Rate constant was measured at three temperatures: 298 K, 422 K and 598 K. Within experimental uncertainty, these three values were the same.

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Authors gave as an alternative rate expression the simple mean of the three values: $k = (2.20 \pm 0.10) \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$.

(b) Laser photodissociation of Cl_2 with time-resolved monitoring of infrared emission of HCl ($\nu=1$) product.

5 (c) Both relative and absolute rate studies of reactions of Cl atoms with C_1 to C_4 alkanes. Direct measurement of ratio $k/k(\text{Cl}+\text{C}_2\text{H}_6)$ is in very good agreement with the ratio of the absolute values.

10 (d) Both relative and absolute rate studies of reactions of Cl atoms with C_2H_6 , C_3H_8 and $n\text{-C}_4\text{H}_{10}$. Measurements of $k/k(\text{Cl}+\text{C}_2\text{H}_6)$ over the temperature range 298 K to 540 K support the essentially zero temperature dependence for k reported by Lewis et al. (1980). GC measurements at 298 K show that the reaction $\text{Cl}+n\text{-C}_4\text{H}_{10}$ yields $29 \pm 2\%$ 1-butyl radicals and $71 \pm 2\%$ 2-butyl radicals.

15 (e) 193 nm Laser photolysis of $(\text{ClOC})_2$ to form Cl. Kinetics of reaction derived from HCl formation profiles, measured using infra red diode laser absorption spectroscopy.

(f) 193 nm photolysis of HCl as Cl source. Detection of both $\text{Cl}(^2\text{P}_{1/2})$ and $\text{Cl}(^2\text{P}_{3/2})$ using VUV-LIF. The rate constants for $\text{Cl}(^2\text{P}_{1/2})$ was found to be $\approx 30\%$ of that for $\text{Cl}(^2\text{P}_{3/2})$ ground state.

20 Preferred Values

$k = 2.05 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, independent of temperature over the range 290–600 K.

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Reliability

$\Delta \log k = \pm 0.06$ at 298 K.

$\Delta (E/R) = \pm 100$ K.

Comments on Preferred Values

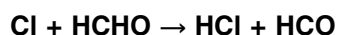
5 The preferred value at room temperature is the mean of the values reported by Beichert et al. (1995), Tyndall et al. (1997), Qian et al. (2002) and Hitsuda et al. (2001). The temperature independence is based on the results of Lewis et al. (1980) over the range 298 K to 598 K and is supported by the relative measurements of Tyndall et al. (1997) over the range 298 K to 540 K. Tyndall et al. (1997) studied the mechanism of the reaction at 298 K and reported the yield of 1-butyl radicals to be $29 \pm 2\%$ and that of 2-butyl radicals to be $71 \pm 2\%$.

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$$\Delta H^\circ = -61.9 \text{ kJ}\cdot\text{mol}^{-1}$$

5

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(7.48 \pm 0.50) \times 10^{-11}$	200–500	Michael et al., 1979	FP-RF
$1.09 \times 10^{-10} \exp[-(131 \pm 98)/T]$	223–323	Anderson and Kurylo, 1979	FP-RF
$(7.18 \pm 0.61) \times 10^{-11}$	293		
$(7.40 \pm 0.7) \times 10^{-11}$	298	Fasano and Nogar, 1981	PLP-CL
<i>Relative Rate Coefficients</i>			
$(7.6 \pm 0.6) \times 10^{-11}$	298	Niki et al., 1978	RR (a)
$(6.8 \pm 1.4) \times 10^{-11}$	295	Poulet et al., 1981	RR (b)

Comments

10 (a) Competitive photo-chlorination between HCHO and C_2H_6 using FTIR. The measured rate coefficient ratio $k/k(\text{Cl}+\text{C}_2\text{H}_6)=1.3 \pm 0.1$ is placed on an absolute basis by use of $k(\text{Cl}+\text{C}_2\text{H}_6)=5.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, this evaluation).

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(b) DF-MS study. Value of k derived from measured ratio of $k/k(\text{Cl}+\text{C}_2\text{H}_6)=1.16\pm 0.12$ and $k(\text{Cl}+\text{C}_2\text{H}_6)=5.9\times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ (IUPAC, this evaluation).

Preferred Values

5 $k = 7.3 \times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ at 298 K.
 $k = 8.2 \times 10^{-11}\text{ exp}(-34/T)\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ over the temperature range 200–500 K.

Reliability

$\Delta \log k = \pm 0.06$ at 298 K.
10 $\Delta (E/R) = \pm 100\text{ K}$.

Comments on Preferred Values

The preferred temperature dependence is based on a least-squares fit to the 200 K to 500 K data of Michael et al. (1979) and the 223 K to 323 K data of Anderson and Kurylo (1979). The preferred 298 K rate coefficient
15 is based on these absolute studies (Michael et al., 1979; Anderson and Kurylo, 1979) and the room temperature data of Niki et al. (1978), Fasano and Nogar (1981) and Poulet et al. (1981), all of which are in good agreement. Kinetic isotope effects have been determined in relative rate studies as $k(\text{Cl}+\text{HCHO})/k(\text{Cl}+\text{DCDO})=1.30$ and $k(\text{Cl}+\text{H}^{13}\text{CHO})/k(\text{Cl}+\text{DCDO})=1.22$
20 (Beukes et al., 2000).

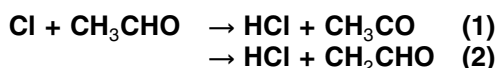
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$$\Delta H^\circ(1) = -57.8 \text{ kJ}\cdot\text{mol}^{-1}$$

$$\Delta H^\circ(2) = -37.3 \text{ kJ}\cdot\text{mol}^{-1}$$

5 Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(6.6 \pm 1.4) \times 10^{-11}$	210–343	Payne et al., 1990	FP-RF
$(7.3 \pm 0.7) \times 10^{-11}$	295	Tyndall et al., 1999	PLP-RF (a)
$(7.5 \pm 0.8) \times 10^{-11}$	298	Kegley-Owen et al., 1999	PLP-TDLAS (b)
<i>Relative Rate Coefficients</i>			
$(7.9 \pm 1.2) \times 10^{-11}$	298	Niki et al., 1985	RR (c)
$(8.1 \pm 0.8) \times 10^{-11}$	295 ± 2	Wallington et al., 1988	RR (d)
$(6.1 \pm 0.5) \times 10^{-11}$	298	Bartels et al., 1989	RR (e)
$(8.8 \pm 1.0) \times 10^{-11}$	298	Tyndall et al., 1999	RR (a)
<i>Branching Ratios</i>			
$k_2/k < 0.01$	298	Niki et al., 1985	(c)
$k_2/k < 0.07$	298	Bartels et al., 1989	(e)

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Comments

- (a) In the absolute study, Cl atoms were generated from the 308 nm photolysis of Cl_2 . 1 Torr (1.3 mbar) of O_2 added to total pressure of 20–90 Torr (27–120 mbar) N_2 or He to scavenge CH_3CO and reduce regeneration of Cl, some correction was however still necessary. In the relative rate study, broad band irradiation of Cl_2 was the source of Cl atoms. Experiments were carried out in 700 Torr N_2 , with analysis of CH_3CHO and reference compound (C_2H_6 and C_2H_4) with FTIR. $k(\text{Cl}+\text{CH}_3\text{CHO})/k(\text{Cl}+\text{C}_2\text{H}_6)=1.49\pm 0.1$, $k(\text{Cl}+\text{CH}_3\text{CHO})/k(\text{Cl}+\text{C}_2\text{H}_4)=0.90\pm 0.05$. The data have been placed on an absolute basis using $k(\text{Cl}+\text{C}_2\text{H}_6)=5.9\times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, this evaluation).
- (b) Cl atoms were generated from the 308 nm photolysis of Cl_2 at total pressures of 10–50 Torr (13–67 mbar) N_2 . Kinetic parameters were derived by monitoring HCl formation ($\nu = 0$) by infra-red tuneable diode laser absorption spectroscopy. N_2O was added to quench vibrationally excited HCl, O_2 was added to reduce secondary regeneration of Cl via reaction of CH_3CO with Cl_2 .
- (c) Cl atoms were generated by photolysis of Cl_2 at 930 mbar (700 Torr) total pressure of N_2 . Relative decay rates of CH_3CHO and C_2H_6 measured, and the measured rate coefficient ratio is placed on an absolute basis by use of $k(\text{Cl}+\text{C}_2\text{H}_6)=5.9\times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, this evaluation). The branching ratio was determined from FTIR spectroscopic product analysis.
- (d) Cl atoms were generated from the photolysis of Cl_2 in $\text{Cl}_2\text{-N}_2\text{-CH}_3\text{CHO-C}_2\text{H}_6$ mixtures and the relative decay rates of CH_3CHO and C_2H_6 measured. The measured rate coefficient ratio is placed on an absolute basis

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by use of $k(\text{Cl}+\text{C}_2\text{H}_6)=5.9\times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ (IUPAC, this evaluation).

(e) DF-MS study. Relative decay rates of CH_3CHO and C_2H_6 were monitored, and the measured rate coefficient ratio is placed on an absolute basis by use of $k(\text{Cl}+\text{C}_2\text{H}_6)=5.9\times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ (IUPAC, this evaluation). The branching ratio was derived from the products observed by MS.

Preferred Values

$k = 7.9 \times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$, independent of temperature over the range 210–340 K.
 $k_2/k < 0.01$ at 298 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.
 $\Delta (E/R) = \pm 300\text{ K}$.

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of the absolute rate coefficients of Tyndall et al. (1999) and Kegley Owen et al. (1999) and the relative rate coefficients of Niki et al. (1985), Wallington et al. (1988) and Tyndall et al. (1999). The lack of a temperature dependence of the rate coefficient is consistent with the data of Payne et al. (1990). The branching ratio is derived from the data of Niki et al. (1985). The relative rate measurement of Scollard et al. (1993) was carried out relative

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to $\text{CH}_3\text{C}(\text{O})\text{CH}_3$, which is not considered sufficiently well defined to derive an accurate relative rate coefficient. Deuterium kinetic isotope effects were determined to be: $k(\text{Cl}+\text{CH}_3\text{CHO})/k(\text{Cl}+\text{CH}_3\text{CDO})=1.34\pm 0.02$, $k(\text{Cl}+\text{CH}_3\text{CHO})/k(\text{Cl}+\text{CD}_3\text{CDO})=1.32\pm 0.02$, $k(\text{Cl}+\text{CD}_3\text{CHO})/k(\text{Cl}+\text{CH}_3\text{CDO})=1.35\pm 0.02$, $k(\text{Cl}+\text{CD}_3\text{CHO})/k(\text{Cl}+\text{CD}_3\text{CDO})=1.39\pm 0.02$ (Beukes, 2000).

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Cl + C₂H₅CHO → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
$(1.17 \pm 0.10) \times 10^{-10}$	295 ± 2	Wallington et al., 1988	RR (a)
$(1.45 \pm 0.08) \times 10^{-10}$	298 ± 3	Thévenet et al., 2000	RR(b)
$(1.20 \pm 0.07) \times 10^{-10}$	298 ± 3		(c)
$(1.25 \pm 0.06) \times 10^{-10}$	298 ± 3		(d)
$(1.41 \pm 0.10) \times 10^{-10}$	298 ± 3		(e)

5 Comments

- (a) Cl atoms were generated by the photolysis of Cl₂ in Cl₂-air mixtures, and the decay rates of C₂H₅CHO and C₂H₆ monitored by GC. The measured rate coefficient ratio is placed on an absolute basis by use of $k(\text{Cl}+\text{C}_2\text{H}_6)=5.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, this evaluation).
- 10 (b) Cl atoms were generated by the photolysis of Cl₂ in Cl₂-air mixtures, and the decay rates of C₂H₅CHO and C₂H₆ monitored by GC. The measured rate coefficient ratio of $k(\text{Cl}+\text{C}_2\text{H}_5\text{CHO})/k(\text{Cl}+\text{C}_2\text{H}_6)=2.4 \pm 0.08$ is placed on an absolute basis by use of $k(\text{Cl}+\text{C}_2\text{H}_6)=5.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, this evaluation).

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- (c) Method as (b) but C₃H₈ as reference gas. The measured rate coefficient ratio of $k(\text{Cl}+\text{C}_2\text{H}_5\text{CHO})/k(\text{Cl}+\text{C}_3\text{H}_8)=0.85 \pm 0.05$ is placed on an absolute basis by use of $k(\text{Cl}+\text{C}_3\text{H}_8)=1.4 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, this evaluation).
- 5 (d) Method as (b) but *n*-C₄H₁₀ as reference gas. The measured rate coefficient ratio of $k(\text{Cl}+\text{C}_2\text{H}_5\text{CHO})/k(\text{Cl}+n\text{-C}_4\text{H}_{10})=0.61 \pm 0.03$ is placed on an absolute basis by use of $k(\text{Cl}+n\text{-C}_4\text{H}_{10})=2.05 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, this evaluation).
- 10 (e) Method as (b) but *n*-hexane as reference gas. The measured rate coefficient ratio of $k(\text{Cl}+\text{C}_2\text{H}_5\text{CHO})/k(\text{Cl}+n\text{-hexane})=0.44 \pm 0.02$ is placed on an absolute basis by use of $k(\text{Cl}+n\text{-hexane})/k(\text{Cl}+n\text{-butane})=1.56$ (average value from Tyndall et al., 1999, and Hooshiyar and Niki, 1995) and $k(\text{Cl}+n\text{-butane})=2.05 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, this evaluation).

Preferred Values

15 $k = 1.3 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

Comments on Preferred Values

20 The preferred value uses data from the relative rate studies of Wallington et al. (1988) and Thévenet et al. (2000), and is an average of the rate constants obtained in experiments in which, C₂H₆, C₃H₈ and *n*-C₄H₁₀ were used

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as reference gases, which have well defined rate coefficients for reaction with Cl.

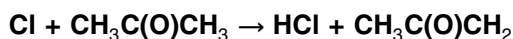
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$$\Delta H^\circ = -20.3 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(3.06 \pm 0.38) \times 10^{-12}$	298 ± 2	Notario et al., 2000	PLP-RF (a)
<i>Relative Rate Coefficients</i>			
$(2.6 \pm 0.2) \times 10^{-12}$	295 ± 2	Wallington et al., 1990	RR (b)
$(1.7 \pm 0.3) \times 10^{-12}$	294 ± 1	Olsson et al., 1997	RR (c)
$3.1 \times 10^{-11} \exp [(815 \pm 150) / T]$	215–298	Orlando et al., 2000	RR (d)
5 $(2.0 \pm 0.3) \times 10^{-12}$	298		

Comments

(a) Experiments carried out at pressures of 15 or 60 Torr (20 or 80 mbar) He using the 355 nm photolysis of Cl_2 as Cl-atom source. Addition of 0.4 Torr (0.53 mbar) O_2 (to scavenge organic radicals and prevent secondary formation of Cl) resulted in similar rate coefficients.

10

(b) Cl atoms were generated by the photolysis of Cl_2 -air (or N_2)- $\text{CH}_3\text{C}(\text{O})\text{CH}_3$ - $\text{C}_2\text{H}_5\text{Cl}$ mixtures. From the relative decays of CH_3COCH_3 and $\text{C}_2\text{H}_5\text{Cl}$, a rate coefficient ratio of

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$k(\text{Cl}+\text{CH}_3\text{C}(\text{O})\text{CH}_3)/k(\text{Cl}+\text{C}_2\text{H}_5\text{Cl})=0.295\pm 0.015$ was obtained. Combined with a measurement of $k(\text{Cl}+\text{C}_2\text{H}_5\text{Cl})/k(\text{Cl}+\text{C}_2\text{H}_6)=0.15\pm 0.01$ (Shi et al., 1993) and $k(\text{Cl}+\text{C}_2\text{H}_6)=5.9\times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ (IUPAC, this evaluation) the value cited in the table is obtained.

5 (c) Cl atoms were generated by pulsed laser photolysis of Cl_2 at 355 nm followed by competition between the reactions $\text{Cl}+\text{CH}_3\text{C}(\text{O})\text{CH}_3$ and $\text{Cl}+\text{ClONO}_2\rightarrow\text{Cl}_2+\text{NO}_3$. The formation of NO_3 with and without acetone in the reaction mixture was monitored by TDLS at 661.8 nm. The value recommended in Yokelson et al. (1995) for the value of the rate constant
10 of the reference reaction ($\text{Cl}+\text{ClONO}_2$) was used.

(d) Cl atoms were generated by the photolysis of Cl_2 - $\text{CH}_3\text{C}(\text{O})\text{CH}_3$ - CH_2Cl_2 mixtures. From the relative decays of $\text{CH}_3\text{C}(\text{O})\text{CH}_3$ and CH_2Cl_2 , temperature dependent rate coefficient ratios of $k(\text{Cl}+\text{CH}_3\text{C}(\text{O})\text{CH}_3)/k(\text{Cl}+\text{CH}_2\text{Cl}_2)=5.39$ (298 K), 5.83 (267 K), 6.26
15 (251 K), 6.69 (240 K), 7.21 (225 K) and 7.72 (215 K) were derived. These ratios were placed on an absolute basis using $k(\text{Cl}+\text{CH}_2\text{Cl}_2)=1.5\times 10^{-11}\text{ exp}(-1100/T)\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ (Orlando, 1999).

Preferred Values

$k = 2.5 \times 10^{-12}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ at 298 K.
20 $k = 3.9 \times 10^{-11}\text{ exp}(-815/T)\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ over the temperature range 215–300 K.

6985

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
 $\Delta (E/R) = \pm 300$ K.

Comments on Preferred Values

5 Because of the potential for errors in the experimental technique of Olsson et al. (1997) (the assumption that Cl atoms only react with ClONO_2 and acetone, the need for absolute concentration measurements of acetone and the experimental approach of sequential experiments in the presence and absence of acetone) these data are not considered when making the recommendation. For
10 room temperature, an average of the rate coefficients of Notario et al. (2000), Wallington et al. (1990) and Orlando et al. (2000) is taken. The temperature dependent expression adopts the value of $E/R=815$ K from Orlando et al. (2000) with expanded error limits. The pre-exponential factor has been adjusted to yield the recommended rate coefficient at 298 K.

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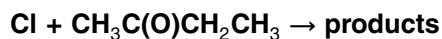
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6987

II.A7.177



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(3.24 \pm 0.38) \times 10^{-11}$	298 ± 2	Notario et al., 2000	PLP-RF (a)
<i>Relative Rate Coefficients</i>			
$(4.28 \pm 0.59) \times 10^{-11}$	295	Wallington et al., 1990	RR (b)

Comments

- (a) Experiments carried out at pressures of 15 or 60 Torr (20 or 80 mbar) He using the 355 nm photolysis of Cl_2 as Cl-atom source. Addition of 0.4 Torr (0.53 mbar) O_2 (to scavenge organic radicals and prevent secondary formation of Cl) resulted in similar rate coefficients.
- (b) Cl atoms were generated by the photolysis of Cl_2 in $\text{Cl}_2\text{-N}_2\text{-CH}_3\text{C}(\text{O})\text{C}_2\text{H}_5\text{-C}_2\text{H}_6$ mixtures at 930 mbar (700 Torr) total pressure, and the $\text{CH}_3\text{C}(\text{O})\text{C}_2\text{H}_5$ and C_2H_6 concentrations monitored by FTIR absorption spectroscopy. The measured rate coefficient ratio is placed on an absolute basis by use of $k(\text{Cl}+\text{C}_2\text{H}_6)=5.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, this evaluation).

6988

Preferred Values

$k = 3.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

5 Comments on Preferred Values

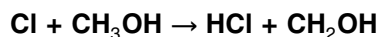
The preferred value is an average result from the studies of Wallington et al. (1990) and Notario et al. (2000). This result is supported by the value of $k = (3.8 \pm 0.3) \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ quoted in Niki et al. (1987) as unpublished results from that laboratory.

10 References

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15 10, 301, 1990.

6989

II.A7.178



$\Delta H^\circ = -29.8 \text{ kJ}\cdot\text{mol}^{-1}$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(6.33 \pm 0.70) \times 10^{-11}$	200–500	Michael et al., 1979	FP-RF
$(5.1 \pm 1.0) \times 10^{-11}$	298	Payne et al., 1988	DF-MS (a)
$(6.14 \pm 0.67) \times 10^{-11}$	298 ± 2	Dóbe et al., 1993	DF-EPR
$(5.1 \pm 0.4) \times 10^{-11}$	295 ± 2	Tyndall et al., 1999	PLP-RF
<i>Relative Rate Coefficients</i>			
$(4.73 \pm 0.42) \times 10^{-11}$	295 ± 2	Wallington et al., 1988	RR (b)
$(5.0 \pm 0.34) \times 10^{-11}$	298 ± 2	Nelson et al., 1990	RR (c)
5 $(5.5 \pm 0.6) \times 10^{-11}$	295	Tyndall et al., 1999	RR (d)

Comments

- (a) Reaction between Cl and CH₃OD was studied.
(b) Cl atoms were generated by the photolysis of Cl₂ in Cl₂-CH₃OH-C₂H₆-air (N₂) mixtures at 1 bar total pressure. Concentrations

6990

of CH₃OH and C₂H₆ were monitored by GC and a rate coefficient ratio $k(\text{Cl}+\text{CH}_3\text{OH})/k(\text{Cl}+\text{C}_2\text{H}_6)=0.802\pm 0.071$ determined. This rate coefficient ratio is placed on an absolute basis by use of $k(\text{Cl}+\text{C}_2\text{H}_6)=5.9\times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ (IUPAC, this evaluation).

5 (c) Cl atoms were generated from the photolysis of Cl₂ or C(O)Cl₂ in Cl₂ (or C(O)Cl₂)-N₂ (or O₂)-CH₃OH-cyclohexane mixtures at 1 bar pressure. Concentrations of CH₃OH and cyclohexane were measured by GC, and the rate coefficient ratio is placed on an absolute basis by use of $k(\text{Cl}+\text{cyclohexane})/k(\text{Cl}+n\text{-butane})=1.59$ (Ashmann and Atkinson, 1995)
10 and $k(\text{Cl}+n\text{-butane})=2.05\times 10^{-10}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ (IUPAC, this evaluation).

(d) Broad band irradiation of Cl₂ as source of Cl atoms. Experiments were carried out in 700 Torr N₂, with analysis of CH₃OH and reference compound (C₂H₅ and C₂H₄) with FTIR. $k(\text{Cl}+\text{CH}_3\text{OH})/k(\text{Cl}+\text{C}_2\text{H}_6)=0.94\pm 0.04$,
15 $k(\text{Cl}+\text{CH}_3\text{OH})/k(\text{Cl}+\text{C}_2\text{H}_4)=0.63\pm 0.03$. The data have been placed on an absolute basis using $k(\text{Cl}+\text{C}_2\text{H}_6)=5.9\times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ (IUPAC, this evaluation).

Preferred Values

$k = 5.5 \times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$, independent of temperature over the range
20 200–500 K.

Reliability

$\Delta \log k = \pm 0.10$ at 298 K.

$\Delta (E/R) = \pm 200$ K.

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Comments on Preferred Values

The preferred 298 K value is the unweighted average of the absolute rate coefficients of Michael et al. (1979), Payne et al. (1988), Dóbé et al. (1993) and Tyndall et al. (1999), and the relative rate studies of Nelson et al. (1990)
5 and Tyndall et al. (1999). The inclusion of the data of Payne et al. (1988) on Cl+CH₃OD is justified considering the strong body of evidence showing that the H-abstraction proceeds solely at the CH₂-group at room temperature (see Payne et al., 1988, Radford et al., 1981, Meier et al., 1984, Dóbé et al., 1994 and Jodkowsji et al., 1998). The relative rate study of Wallington et al. (1988)
10 has been superseded by a more recent study from the same group (Tyndall et al., 1999) and is not used in the evaluation. The zero temperature dependence is taken from the study of Michael et al. (1979) and is supported by time resolved measurement of relative HO₂ and CH₃O₂ concentrations formed in the photolysis of Cl₂ in the presence of CH₄ and CH₃OH and O₂ (Lightfoot et al.,
15 1990).

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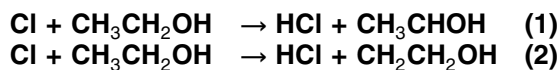
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6993

II.A7.179



Rate coefficient data ($k = k_1 + k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(9.4 \pm 1.4) \times 10^{-11} \exp[(45 \pm 32)/T]$	295–600	Taatjes et al., 1999	LP-IR (a)
$(1.09 \pm 0.9) \times 10^{-10}$	298		
<i>Relative Rate Coefficients</i>			
$(8.75 \pm 0.95) \times 10^{-11}$	295 ± 2	Wallington et al., 1988	RR (b)
$(1.06 \pm 0.06) \times 10^{-10}$	298 ± 2	Nelson et al., 1990	RR (c)
$(8.3 \pm 1.8) \times 10^{-11}$	295	Edelbüttel-Einhaus et al., 1992	RR (d)
$(9.4 \pm 0.8) \times 10^{-11}$	298	Taatjes et al., 1999	RR (e)
<i>Branching Ratios</i>			
$k_2/k_1 = 0.28 \exp -(350/T)$		Taatjes et al., 1999	
$k_1/k = 0.92$	298		
5 $k_2/k = 0.08$	298		

6994

Comments

- (a) Cl atoms were generated by the 193 nm pulsed photolysis of CF_2Cl_2 or CFCl_3 , and kinetic parameters were obtained by analysis of HCl product formation profiles using transient IR absorption spectroscopy. Bath gas was 10 Torr CO_2 to quench vibrationally excited HCl. Use of deuterated ethanol enabled site specific rate coefficients to be determined via measurement of HCl yields. Complementary FTIR product analysis confirmed the result.
- (b) Cl atoms were generated by photolysis of Cl_2 in Cl_2 - $\text{C}_2\text{H}_5\text{OH}$ - C_2H_6 -air (or N_2) mixtures at 1 bar total pressure. $\text{C}_2\text{H}_5\text{OH}$ and C_2H_6 were monitored by GC and a rate coefficient ratio $k(\text{Cl}+\text{C}_2\text{H}_5\text{OH})/k(\text{Cl}+\text{C}_2\text{H}_6)=1.483\pm 0.160$ determined. Placed on an absolute basis by use of $k(\text{Cl}+\text{C}_2\text{H}_6)=5.9\times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ (IUPAC, this evaluation).
- (c) Cl atoms were generated by photolysis of Cl_2 or $\text{C}(\text{O})\text{Cl}_2$ in Cl_2 (or $\text{C}(\text{O})\text{Cl}_2$)- N_2 (or O_2)-ethanol-cyclohexane mixtures at 1 bar pressure. Concentrations of ethanol and cyclohexane were measured by GC, and the rate coefficient ratio is placed on an absolute basis by use of $k(\text{Cl} + \text{cyclohexane})/k(\text{Cl} + n\text{-butane})=1.59$ (Aschmann and Atkinson, 1995) and $k(\text{Cl} + n\text{-butane})=2.05\times 10^{-10}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ (IUPAC, this evaluation).
- (d) Isothermal discharge flow reactor at 1 mbar pressure, with molecular beam sampling and analysis by mass spectrometry. $k/k(\text{Cl}+\text{C}_2\text{H}_6)$ measured to be 1.4 ± 0.3 . Placed on an absolute basis by use of $k(\text{Cl}+\text{C}_2\text{H}_6)=5.9\times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ (IUPAC, this evaluation). Supersedes earlier value reported from same laboratory (Khatoun et al., 1989)

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- (e) Cl atoms were generated by the photolysis of Cl_2 in O_2 or N_2 bath gas. Loss of $\text{C}_2\text{H}_5\text{OH}$ was measured relative to C_2H_6 using *in-situ* FTIR absorption spectroscopy. $k(\text{Cl}+\text{C}_2\text{H}_5\text{OH})/k(\text{Cl}+\text{C}_2\text{H}_6)$ was measured to be 1.6 ± 0.13 and is placed on an absolute basis by use of $k(\text{Cl}+\text{C}_2\text{H}_6)=5.9\times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ (IUPAC, this evaluation). The branching ratios were derived by product analysis.

Preferred Values

- $k = 9.6 \times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ at 298 K.
 $k_1 = 8.8 \times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ at 298 K.
 $k_2 = 0.8 \times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ at 298 K.
 $k = 8.2 \times 10^{-11}\text{ exp}(45/T)\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ over the temperature range 295–600 K.
 $k_2/k_1 = 0.28\text{ exp}(-350/T)$

Reliability

- $\Delta \log k = \pm 0.1$ at 298 K.
 $\Delta (E/R) = \pm 100\text{ K}$.

Comments on Preferred Values

- The preferred 298 K rate coefficient is the average of the single absolute rate measurement of Taatjes et al. (1999) and the relative rate studies of Wallington et al. (1988), Nelson et al. (1990), Edelbüttel-Einhaus et al. (1992) and Taatjes et al. (1999), which are in good agreement. The slight temperature dependence is taken from Taatjes et al. (1999) as are temperature dependent values for the

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branching ratios for k_1 and k_2 .

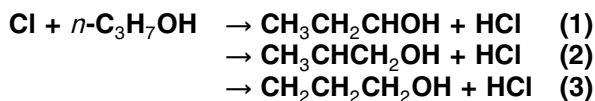
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II.A7.180



Rate coefficient data ($k=k_1+k_2+k_3$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
$(1.49 \pm 0.12) \times 10^{-10}$	295 ± 2	Wallington et al., 1988	RR (a)
$(1.53 \pm 0.07) \times 10^{-10}$	298 ± 2	Nelson et al., 1990	RR (b)
$2.68 \times 10^{-10} \exp[-(128 \pm 20)/T]$	273–342	Cheema et al., 2001	RR (c)
$(1.69 \pm 0.20) \times 10^{-10}$	298		
<i>Branching Ratios</i>			
$k_1/k = 0.56$	298	Cheema et al., 2001	RR (c)
$k_2/k = 0.30$	298		
$k_3/k = 0.14$	298		

5 Comments

- (a) Cl atoms were generated by photolysis of Cl_2 in Cl_2 - $n\text{-C}_3\text{H}_7\text{OH}$ - C_2H_6 -air (or N_2) mixtures at 990 mbar (740 Torr) total pressure. $n\text{-C}_3\text{H}_7\text{OH}$ and C_2H_6 were monitored by GC and a rate coefficient ratio $k(\text{Cl}+n\text{-C}_3\text{H}_7\text{OH})/k(\text{Cl}+\text{C}_2\text{H}_6)=2.518\pm 0.202$ determined. Placed on an absolute

6998

basis by use of $k(\text{Cl}+\text{C}_2\text{H}_6)=5.9\times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ (IUPAC, this evaluation).

- 5 (b) Cl atoms were generated by the photolysis of Cl_2 or $\text{C}(\text{O})\text{Cl}_2$ in Cl_2 (or $\text{C}(\text{O})\text{Cl}_2$)- N_2 (or O_2)-*n*-propanol-cyclohexane mixtures at 1 bar pressure. Decay rates of *n*-propanol and cyclohexane were measured by GC, and the rate coefficient ratio placed on an absolute basis by use of $k(\text{Cl}+\text{cyclohexane})/k(\text{Cl}+n\text{-butane})=1.59$ (Aschmann and Atkinson, 1995) and $k(\text{Cl}+n\text{-butane})=2.05\times 10^{-10}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ (IUPAC, this evaluation).
- 10 (c) The reaction was initiated in 100, 250 or 1000 cm^3 Pyrex vessels by photolysis of Cl_2 in presence of O_2 , NO , *n*- $\text{C}_3\text{H}_7\text{OH}$ - C_2H_6 and N_2 mixtures at 700 Torr total pressure. *n*- $\text{C}_3\text{H}_7\text{OH}$ and C_2H_6 were monitored by GC and rate coefficient ratios $k(\text{Cl}+n\text{-C}_3\text{H}_7\text{OH})/k(\text{Cl}+\text{C}_2\text{H}_6)$ determined at temperatures between 273 and 342 K. Placed on an absolute basis by use of
- 15 $k(\text{Cl}+\text{C}_2\text{H}_6)=8.3\times 10^{-11}\exp(-100/T)\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ (IUPAC, this evaluation). Product analysis in separate FTIR experiments combined with an assumed reaction scheme to give branching ratios.

Preferred Values

- $k = 1.6 \times 10^{-10}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ at 298 K.
- 20 $k = 2.5 \times 10^{-10}\exp(-130/T)\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ over the temperature range 270–350 K.

6999

Reliability

$\Delta \log k = \pm 0.15$ at 298 K.
 $\Delta (E/R) = \pm 100$ K.

Comments on Preferred Values

- 5 The preferred 298 K rate coefficient is based on the data of Wallington et al. (1988), Nelson et al. (1990) and Cheema et al. (2001). The temperature dependence is taken from the single study (Cheema et al., 2001) that varied the temperature. The branching ratios are expected to be approximately independent of temperature over the atmospheric temperature range, but until this
- 10 is confirmed, we make no recommendation.

References

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7000

II.A7.181

Cl + *i*-C₃H₇OH → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
$(8.80 \pm 0.35) \times 10^{-11}$	298 ± 2	Nelson et al., 1990	RR (a)

5 Comments

- (a) Cl atoms were generated by the photolysis of Cl₂ or C(O)Cl₂ in isopropyl alcohol-cyclohexane-O₂ (or N₂) mixtures at 1 bar pressure. The decay rates of isopropyl alcohol and cyclohexane were measured, and rate coefficient ratio placed on an absolute basis by use of $k(\text{Cl} + \text{cyclohexane})/k(\text{Cl} + n\text{-butane}) = 1.59$ (Aschmann and Atkinson, 1995) and $k(\text{Cl} + n\text{-butane}) = 2.05 \times 10^{-10} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, this evaluation).

Preferred Values

$k = 8.8 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

15 Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

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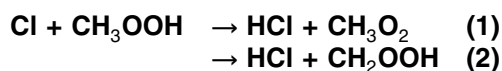
Comments on Preferred Values

Based on the sole study of Nelson et al. (1990).

References

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5 Nelson, L., Rattigan, O., Neavyn, R., Sidebottom, H., Treacy, J., and Nielsen, O. J.: Int. J. Chem. Kinet., 22, 1111, 1990.

II.A7.182



$$\Delta H^\circ(1) = -74 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
$(5.9 \pm 0.3) \times 10^{-11}$	295 ± 2	Wallington et al., 1990	RR (a)

Comments

(a) Cl atoms were generated by the photolysis of Cl_2 in $\text{Cl}_2\text{-N}_2\text{-CH}_3\text{OOH-C}_2\text{H}_6$ mixtures at 930 mbar (700 Torr) total pressure, and the CH_3OOH and C_2H_6 concentrations monitored by FTIR absorption spectroscopy. The measured rate coefficient ratio is placed on an absolute basis by use of $k(\text{Cl}+\text{C}_2\text{H}_6)=5.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, this evaluation).

Preferred Values

$$k = 5.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

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Reliability

$$\Delta \log k = \pm 0.5 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

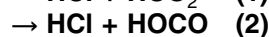
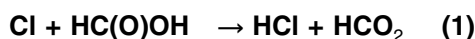
The sole study carried out to date is that of Wallington et al. (1990). The reaction may occur by the two pathways listed and the formation of HO radicals via decomposition of CH_2OOH may have led to secondary reactions involving HO radicals. Since the room temperature rate coefficient for the Cl atom reaction with H_2O_2 is two orders of magnitude lower than that for $\text{Cl}+\text{CH}_3\text{OOH}$ (IUPAC, current recommendation), it is expected that channel (2) will dominate. Wallington et al. (1990) concluded that secondary reactions involving HO radicals did not contribute >15% to the observed CH_3OOH consumption. The cited uncertainty limits on the preferred values reflect this possibility.

References

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7004

II.A7.183



$$\Delta H^\circ(2) = -52 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(1.83 \pm 0.12) \times 10^{-13}$	295 ± 2	Li et al., 2000	FP-IR (a)
<i>Relative Rate Coefficients</i>			
$(2.15 \pm 0.12) \times 10^{-13}$	295 ± 2	Wallington et al., 1990	RR (b,c)
$(1.83 \pm 0.10) \times 10^{-13}$	295 ± 2	Wallington et al., 1990	RR (b,d)

Comments

(a) Cl-atoms made in the flash photolysis of Cl_2 in He at 10 Torr. O_2 was added to convert HOCO to CO_2 , which was monitored by transient IR absorption spectroscopy to obtain kinetic data. A small correction (<10%) was applied to take HC(O)OH dimerisation into account.

(b) Cl atoms were generated by the photolysis of Cl_2 in Cl_2 -air-HC(O)OH- CH_3Cl (or CH_4) mixtures at 930 mbar (700 Torr) total pressure. HC(O)OH

7005

and CH_3Cl (or CH_4) were monitored by FTIR absorption spectroscopy during the experiments.

(c) Relative to $k(\text{Cl}+\text{CH}_3\text{Cl})$. Placed on an absolute basis by use of $k(\text{Cl}+\text{CH}_3\text{Cl})=4.9 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation).

(d) Relative to $k(\text{Cl}+\text{CH}_4)$. Placed on an absolute basis by use of $k(\text{Cl}+\text{CH}_4)=9.9 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, this evaluation).

Preferred Values

$$k = 1.9 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

Reliability

$$\Delta \log k = \pm 0.15 \text{ at } 298 \text{ K.}$$

Comments on Preferred Values

The preferred 298 K rate coefficient is the average of the absolute rate coefficient of Li et al. (2000) and the relative rate coefficients obtained by Wallington et al. (1990).

Tyndall et al. (1991) have observed that CO_2 is the sole carbon-containing product formed from this reaction in air or N_2 diluent, and conclude from comparison of the rate coefficients for the reactions of the Cl atom with HC(O)OH, $\text{CH}_3\text{C(O)OH}$ (Koch and Moortgat, 1990) and $\text{CD}_3\text{C(O)OH}$ (Koch and Moortgat, 1990) that reaction channel (2) dominates.

7006

References

IUPAC: <http://www.iupac-kinetic.ch.cam.ac.uk/>.

Koch, S. and Moortgat, G. K.: Chem. Phys. Lett., 173, 531, 1990.

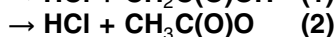
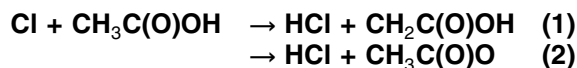
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5 Tyndall, G. S., Wallington, T. J., and Potts, A. R.: Chem. Phys. Lett., 186, 149, 1991.

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7007

II.A7.184



$$\Delta H^\circ(2) = 11 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
5 $(2.8 \pm 0.4) \times 10^{-14}$	298 ± 1	Koch and Moortgat, 1990	RR (a)

Comments

(a) Cl atoms were generated by the photolysis of Cl_2 in Cl_2 - $\text{CH}_3\text{C}(\text{O})\text{OH}$ - CH_4 - N_2 mixtures at 1 bar total pressure. The concentrations of $\text{CH}_3\text{C}(\text{O})\text{OH}$ and CH_4 were measured by IR absorption spectroscopy. The rate coefficient ratio $k(\text{Cl}+\text{CH}_3\text{C}(\text{O})\text{OH})/k(\text{Cl}+\text{CH}_4)=0.28\pm 0.04$ is placed on an absolute basis by use of $k(\text{Cl}+\text{CH}_4)=1.0\times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation). An analogous experiment using $\text{CD}_3\text{C}(\text{O})\text{OH}$ yielded a rate coefficient of $k(\text{Cl}+\text{CD}_3\text{C}(\text{O})\text{OH})=(7.5\pm 0.2)\times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$, indicating that the reaction proceeds mainly by channel (1).

15 Preferred Values

$$k = 2.8 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 298 \text{ K.}$$

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Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is based on the sole study of Koch and Moortgat (1990). The measured rate coefficient ratio of $k(\text{Cl}+\text{CH}_3\text{C}(\text{O})\text{OH})/k(\text{Cl}+\text{CD}_3\text{C}(\text{O})\text{OH})=3.7$ at 298 ± 1 K indicates that channel (1) dominates at 298 K.

References

Koch, S. and Moortgat, G. K.: Chem. Phys. Lett., 173, 531, 1990.

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7009

II.A7.185

Cl + CH₃ONO₂ → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
$(2.42 \pm 0.02) \times 10^{-13}$	298 ± 2	Nielsen et al., 1991	RR (a)
$(2.40 \pm 0.20) \times 10^{-13}$	295 ± 2	Sokolov et al., 1999	RR (b)

5 Comments

(a) Cl atoms were generated by the photolysis of Cl₂ in Cl₂-CH₃ONO₂-C₂H₆-N₂ mixtures at 1 bar pressure. Concentrations of methyl nitrate and ethane were measured by GC and the rate coefficient ratio is placed on an absolute basis by use of $k(\text{Cl}+\text{C}_2\text{H}_6)=5.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, this evaluation).

(b) Cl atoms were generated by the photolysis of Cl₂ in Cl₂-CH₃ONO₂-CH₃Cl or Cl₂-CH₃ONO₂-CH₄ mixtures at 700 Torr pressure of N₂. Concentrations of methyl nitrate and the reference compounds measured in situ using FTIR. Relative rates were $k(\text{Cl}+\text{CH}_3\text{ONO}_2)/k(\text{Cl}+\text{CH}_3\text{Cl})=0.50\pm 0.04$ and $k(\text{Cl}+\text{CH}_3\text{ONO}_2)/k(\text{Cl}+\text{CH}_4)=2.36\pm 0.15$. The rate coefficient ratios were placed on an absolute basis by use of $k(\text{Cl}+\text{CH}_3\text{Cl})=4.8 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recom-

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mentation) and $k(\text{Cl}+\text{CH}_4)=9.9\times 10^{-14}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ (IUPAC, this evaluation) and averaged to give the final number.

Preferred Values

$k = 2.4 \times 10^{-13}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ at 298 K.

5 Reliability

$\Delta \log k = \pm 0.15$ at 298 K.

Comments on Preferred Values

Based on the relative rate studies of Nielsen et al. (1991) and Sokolov et al. (1999). The reaction probably occurs via H-atom abstraction from the $-\text{CH}_3$ group (Nielsen et al., 1991).

References

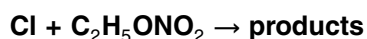
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Nielsen, O. J., Sidebottom, H. W., Donlon, M., and Treacy, J.: Chem. Phys. Lett., 178, 163 1991.

15 Sokolov, O., Hurley, M. D., Ball, J. C., Wallington, T. J., Nelson, W., Barnes, I., and Becker, K. H.: Int. J. Chem. Kinet., 31, 357, 1999.

7011

II.A7.186



Rate coefficient data

$k/\text{cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
$(5.5 \pm 0.8) \times 10^{-12}$	295 ± 2	Wallington et al., 1990a	RR (a)
5 $(3.95 \pm 0.15) \times 10^{-12}$	298 ± 2	Nielsen et al., 1991	RR (b)

Comments

(a) Cl atoms were generated by the photolysis of Cl_2 in Cl_2 -ethyl nitrate- $\text{C}_2\text{H}_5\text{Cl}$ -air mixtures at 1 bar pressure. Ethyl nitrate and $\text{C}_2\text{H}_5\text{Cl}$ were measured by GC, and a rate coefficient ratio of $k(\text{Cl} + \text{ethyl nitrate})/k(\text{Cl}+\text{C}_2\text{H}_5\text{Cl})=0.46\pm 0.03$ determined. Combined with $k(\text{Cl}+\text{C}_2\text{H}_5\text{Cl})/k(\text{Cl}+\text{C}_2\text{H}_6)=0.201\pm 0.027$ (Wallington et al., 1990b) and $k(\text{Cl}+\text{C}_2\text{H}_6)=5.9\times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ (IUPAC, this evaluation), the rate coefficient cited in the table is obtained.

15 (b) Cl atoms were generated by the photolysis of Cl_2 -ethyl nitrate- C_2H_6 - N_2 mixtures at atmospheric pressure. Concentrations of ethyl nitrate and ethane were measured by GC and the rate coefficient ratio placed on an absolute basis by use of $k(\text{Cl}+\text{C}_2\text{H}_6)=5.9\times 10^{-11}\text{ cm}^3\text{ molecule}^{-1}\text{ s}^{-1}$ (IUPAC, this evaluation).

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Preferred Values

$k = 4.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

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Comments on Preferred Values

The preferred 298 K rate coefficient is the average of the data of Wallington et al. (1990a) and Nielsen et al. (1991). The reaction probably proceeds by H atom abstraction from the C-H bonds (Nielsen et al., 1991).

References

- Nielsen, O. J., Sidebottom, H. W., Donlon, M., and Treacy, J.: Chem. Phys. Lett., 178, 163, 1991.
Wallington, T. J., Hinman, M. M., Andino, J. M., Siegl, W. O., and Japar, S. M.: Int. J. Chem. Kinet., 22, 665, 1990a.
15 Wallington, T. J., Andino, J. M., Ball, J. C., and Japar, S. M.: J. Atmos. Chem., 10, 301, 1990b.

7013

II.A7.187



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
$(3.17 \pm 0.47) \times 10^{-11}$	295 ± 2	Wallington et al., 1990a	RR (a)
5 $(2.28 \pm 0.14) \times 10^{-11}$	298 ± 2	Nielsen et al., 1991	RR (b)

Comments

- (a) Cl atoms were generated by the photolysis of Cl_2 in Cl_2 - n -propyl nitrate- $\text{C}_2\text{H}_5\text{Cl}$ -air mixtures at 1 bar pressure. n -Propyl nitrate and $\text{C}_2\text{H}_5\text{Cl}$ concentrations were measured by GC and a rate coefficient ratio of $k(\text{Cl}+n\text{-propyl nitrate})/k(\text{Cl}+\text{C}_2\text{H}_5\text{Cl})=2.67\pm 0.16$ determined. Combined with $k(\text{Cl}+\text{C}_2\text{H}_5\text{Cl})/k(\text{Cl}+\text{C}_2\text{H}_6)=0.201\pm 0.027$ (Wallington et al., 1990b) and $k(\text{Cl}+\text{C}_2\text{H}_6)=5.9\times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, this evaluation), the rate coefficient cited in the table is obtained.
- 10
15 (b) Cl atoms were generated by the photolysis of Cl_2 in Cl_2 - n -propyl nitrate- C_2H_6 - N_2 mixtures at 1 bar pressure. Concentrations of n -propyl nitrate and C_2H_6 were measured by GC, and the rate coefficient ratio is placed on an absolute basis by use of $k(\text{Cl}+\text{C}_2\text{H}_6)=5.9\times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, this evaluation).

7014

Preferred Values

$k = 2.7 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.

5 Comments on Preferred Values

The preferred 298 K rate coefficient is the average of the data of Wallington et al. (1990a) and Nielsen et al. (1991). The reaction probably proceeds by H-atom abstraction from the C-H bonds (Nielsen et al., 1991).

References

- 10 Nielsen, O. J., Sidebottom, H. W., Donlon, M., and Treacy, J.: Chem. Phys. Lett., 178, 163, 1991.
Wallington, T. J., Hinman, M. M., Andino, J. M., Siegl, W. O., and Japar, S. M.: Int. J. Chem. Kinet., 22, 665, 1990a.
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15 10, 301, 1990b.

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II.A7.188



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
5 $(5.8 \pm 1.1) \times 10^{-12}$	295 ± 2	Wallington et al., 1990a	RR (a)

Comments

- (a) Cl atoms were generated by the photolysis of Cl_2 in Cl_2 -isopropyl nitrate- $\text{C}_2\text{H}_5\text{Cl}$ -air mixtures at 1 bar pressure. Concentrations of isopropyl nitrate and $\text{C}_2\text{H}_5\text{Cl}$ were measured by GC, and a rate coefficient ratio of
10 $k(\text{Cl}+\text{isopropyl nitrate})/k(\text{Cl}+\text{C}_2\text{H}_5\text{Cl})=0.49\pm 0.06$ determined. Combined with $k(\text{Cl}+\text{C}_2\text{H}_5\text{Cl})/k(\text{Cl}+\text{C}_2\text{H}_6)=0.201\pm 0.027$ (Wallington et al., 1990b) and $k(\text{Cl}+\text{C}_2\text{H}_6)=5.9\times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, this evaluation), the rate coefficient cited in the table is obtained.

Preferred Values

- 15 $k = 5.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

7016

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

Comments on Preferred Values

The preferred 298 K rate coefficient is based on the sole study of Wallington
5 et al. (1990a).

References

- Wallington, T. J., Hinman, M. M., Andino, J. M., Siegl, W. O., and Japar, S. M.:
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10 10, 301, 1990b.

7017

II.A7.189



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Relative Rate Coefficients</i>			
$(8.54 \pm 0.20) \times 10^{-11}$	298	Nielsen et al., 1991	RR (a)

5 **Comments**

- (a) Cl atoms were generated by the photolysis of Cl₂ in Cl₂-*n*-butyl nitrate-
C₂H₆-N₂ mixtures at 1 bar pressure. Concentrations of *n*-butyl nitrate and
C₂H₆ were measured by GC, and the rate coefficient ratio placed on an
absolute basis by use $k(\text{Cl}+\text{C}_2\text{H}_6)=5.9 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC,
10 this evaluation).

Preferred Values

$k = 8.5 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

7018

Comments on Preferred Values

Based on the sole study of Nielsen et al. (1991), with expanded uncertainty limits.

References

- 5 Nielsen, O. J., Sidebottom, H. W., Donlon, M., and Treacy, J.: Chem. Phys. Lett., 178, 163, 1991.

7019

II.A7.190



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(3.7 \pm 1.7) \times 10^{-13}$	298	Tsalkani et al., 1988	DF-EPR
<i>Relative Rate Coefficients</i>			
5 $< 7 \times 10^{-15}$	295 ± 2	Wallington et al., 1990	RR (a)

Comments

- 10 (a) Cl atoms were generated by the photolysis of Cl_2 in Cl_2 -air- $\text{CH}_3\text{C}(\text{O})\text{OONO}_2$ - CH_4 mixtures at 930 mbar (700 Torr) total pressure, with the $\text{CH}_3\text{C}(\text{O})\text{OONO}_2$ and CH_4 concentrations being monitored by FTIR absorption spectroscopy. Upper limit to relative rate coefficient ratio placed on an absolute basis by use of $k(\text{Cl}+\text{CH}_4)=9.9 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, this evaluation).

Preferred Values

15 $k < 2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.

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Comments on Preferred Values

The preferred value is based on the relative rate coefficient measurement of Wallington et al. (1990), in which no reaction of $\text{CH}_3\text{C}(\text{O})\text{OONO}_2$ was observed in the presence of Cl atoms. In both the relative rate study of Wallington et al. (1990) and the absolute rate study of Tsalkani et al. (1988), the major impurity in the $\text{CH}_3\text{C}(\text{O})\text{OONO}_2$ samples would be the C_{12} or C_{13} alkane solvent, respectively. While this was of no consequence in the relative rate study of Wallington et al. (1990), the presence of $\sim 0.1\%$ tridecane in the $\text{CH}_3\text{C}(\text{O})\text{OONO}_2$ sample used by Tsalkani et al. (1988) could account for the Cl reaction rate observed; their $\text{CH}_3\text{C}(\text{O})\text{OONO}_2$ sample was $>99\%$ pure from IR measurements. The upper limit cited here is a factor of ~ 3 higher than measured by Wallington et al. (1990) to allow for greater uncertainties.

References

- Tsalkani, N., Mellouki, A., Poulet, G., Toupance, G., and Le Bras, G.: J. Atmos. Chem., 7, 409, 1988.
- Wallington, T. J., Andino, J. M., Ball, J. C., and Japar, S. M.: J. Atmos. Chem., 10, 301, 1990.

7021

II.A7.191

Cl + CH_3CN → products

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$\leq 2.0 \times 10^{-15}$	298	Kurylo and Knable, 1984	FP-RF
$3.46 \times 10^{-11} \exp[-(2785 \pm 115)/T]$	478–723	Poulet et al., 1984	DF-MS (a)
$(8.89 \pm 1.24) \times 10^{-15}$	295		
$(1.24 \pm 0.20) \times 10^{-14}$	296	Tyndall et al., 1996	PLP-RF
<i>Relative Rate Coefficients</i>			
$7.2 \times 10^{-12} \exp(-2200/T)$	370–413	Olbregts et al., 1984	RR (b)
$1.7 \times 10^{-11} \exp[-(2140 \pm 200)/T]$	274–345	Tyndall et al., 1996	RR (c)
$(1.22 \pm 0.15) \times 10^{-14}$	296		

Comments

- (a) Data were obtained over the range 295 K to 723 K, and a curved Arrhenius plot was observed.
- (b) Relative formation rates of products were monitored in a competitive chlorination system between CH_3CN and CHCl_3 . Placed on an absolute basis by use of $k(\text{Cl}+\text{CHCl}_3)=4.9 \times 10^{-12} \exp(-1240/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, current recommendation).

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(c) Relative decay rates of CH₃CN and the reference gas were monitored by FTIR. For the temperature dependent study the reference compound was CH₄. In a completely independent system, relative values at 296 K were also derived using as the reference compound CD₄, CF₃CCl₂H or CH₄.
5 Based on three independent determinations by both absolute and relative rate methods the authors derived the value $k = (1.15 \pm 0.20) \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 296 K and the Arrhenius expression $k = 1.6 \times 10^{-11} \exp[-(2140 \pm 200)/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 274–345 K.

Preferred Values

10 $k = 1.2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 1.6 \times 10^{-11} \exp(-2140/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 270–350 K.

Reliability

$\Delta \log k = \pm 0.3$ at 298 K.

15 $\Delta (E/R) = \pm 300 \text{ K}$.

Comments on Preferred Values

The preferred values are based on the results reported by Tyndall et al. (1996). The results of this study over a wide range of experimental conditions, using both relative and absolute rate methods, are preferred over results
20 of earlier studies by Kurylo and Knable (1984), Poulet et al. (1984) and Olbregts et al. (1984). In the study of Tyndall et al. (1996), the room temperature rate coefficient was found to be independent of pressure over the range 7 mbar to

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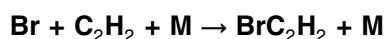
930 mbar (5 Torr to 700 Torr). Analysis of end products in smog-chamber experiments indicate that the reaction proceeds predominantly if not exclusively by H-abstraction (Tyndall et al., 1996, 2001). The atmospheric fate of the resultant CH₂CN radical is discussed by Tyndall et al. (2001).

5 References

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Olbregts, J., Brasseur, G., and Arijs, E.: J. Photochem., 24, 315, 1984.
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10 Tyndall, G. S., Orlando, J. J., Wallington, T. J., Sehested, J., and Nielsen, O. J.: J. Phys. Chem., 100, 660, 1996.
Tyndall, G. S., Orlando, J. J., Wallington, T. J., and Hurley, M. D.: J. Phys. Chem. A, 105, 5380, 2001.

7024

II.A7.192



Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(4.0 \pm 0.8) \times 10^{-15}$	210–393	Payne et al., 1986	FP-RF (a)
<i>Relative Rate Coefficients</i>			
$(4.5 \pm 0.9) \times 10^{-15}$	295	Wallington et al., 1989	RR (b)
$(3.90 \pm 0.16) \times 10^{-14}$ (1013 mbar air)	298	Barnes et al., 1989	RR (c)
$(4.93 \pm 0.20) \times 10^{-14}$ (1013 mbar air)	298		RR (d)
$(3.51 \pm 0.18) \times 10^{-14}$ (1013 mbar air)	313		
$(2.44 \pm 0.10) \times 10^{-14}$ (1013 mbar air)	333		
$(1.78 \pm 0.06) \times 10^{-14}$ (1013 mbar air)	353		
$(3.94 \pm 0.28) \times 10^{-14}$ (940 mbar air)	239	Ramacher et al., 2001	RR (e)
$(3.59 \pm 0.25) \times 10^{-14}$ (940 mbar air)	249		
$(3.72 \pm 0.26) \times 10^{-14}$ (940 mbar air)	261		
$(3.24 \pm 0.23) \times 10^{-14}$ (940 mbar air)	280		
$(2.55 \pm 0.18) \times 10^{-14}$ (940 mbar air)	296		

7025

Comments

- (a) Flash photolysis of CH_3Br ($\lambda > 195 \text{ nm}$) as Br source. Rate coefficient was independent of pressure between 20 and 133 mbar Ar.
- (b) CW photolysis of Br_2 in the presence of C_2H_2 in 986 mbar (740 Torr) N_2 and 2-methylpropane as reference reactant. Depletion of reactants followed by GC to derive $k(\text{Br} + \text{C}_2\text{H}_2)/k(\text{Br} + 2\text{-methylpropane}) = 2.96 \pm 0.11$. The rate coefficient was placed on an absolute basis using $k(\text{Br} + 2\text{-methylpropane}) = 1.52 \times 10^{-15} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 295 K (Russell et al., 1988).
- (c) CW photolysis of Br_2 (300–500 nm) in the presence of C_2H_2 in 33–1013 mbar (25–760 Torr) N_2/O_2 bath gas and CH_3CHO as reference reactant. At 298 K and a total pressure of 760 Torr air, $k(\text{Br} + \text{C}_2\text{H}_2)/k(\text{Br} + \text{CH}_3\text{CHO}) = (1.0 \pm 0.04) \times 10^{-2}$. Rate coefficient put on an absolute basis using $k(\text{Br} + \text{CH}_3\text{CHO}) = 3.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, this evaluation).
- (d) As (c) but using 2,2,4-trimethylpentane (TMP) as reference compound. Data put on absolute basis using $k(\text{Br} + \text{TMP}) = (4.16 \pm 0.33) \times 10^{-12} \text{ exp}(-1820/T)$ (Barnes et al., 1989), which itself was measured relative to $k(\text{Br} + 2\text{-methylpropane}) = 1.83 \times 10^{-10} \text{ exp}(-3452/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Russell et al., 1988).
- (e) Photolysis of Br_2 ($\lambda > 420 \text{ nm}$) in presence of C_2H_2 in 933–946 mbar (700–710 Torr) air, and C_2H_4 as reference reactant. Depletion of reactants followed by FTIR absorption spectroscopy. $k(\text{Br} + \text{C}_2\text{H}_2)/k(\text{Br} + \text{C}_2\text{H}_4) = (6.9 \pm 0.5) \times 10^{-2}$ at 239 K, $(7.9 \pm 0.5) \times 10^{-2}$ at 249 K, $(9.6 \pm 0.7) \times 10^{-2}$ at 261 K, $(13.5 \pm 0.9) \times 10^{-2}$ at 280 K and

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(19.3 ± 1.4) $\times 10^{-2}$ at 296 K. Rate coefficients placed on an absolute basis using $k(\text{Br} + \text{C}_2\text{H}_4) = 5.71 \times 10^{-13}$, 4.54×10^{-13} , 3.87×10^{-13} , 2.40×10^{-13} and $1.32 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 239 K, 249 K, 261 K, 280 K and 296 K, respectively (see Br+C₂H₄ data sheet). The reference value for $k(\text{Br} + \text{C}_2\text{H}_4)$ at 261 K is the average of the values obtained using HCHO and CH₃CHO as reference reactants.

Preferred Values

$k = 2.6 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and 1 bar air.
 $k = 6.35 \times 10^{-15} \exp(440/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (for ~1 bar air) over the temperature range 230–300 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
 $\Delta (E/R) = \pm 200 \text{ K}$.

Comments on Preferred Values

The measured rate coefficients reveal a strong dependence on total pressure (Barnes et al., 1989), temperature (Barnes et al., 1989, Ramacher et al., 2001) and the O₂ partial pressure (Barnes et al., 1989). This has been taken to indicate (Barnes et al., 1989) that the mechanism involves formation of a Br-C₂H₂ adduct, which can dissociate to reactants or react with O₂ to form a peroxy radical. For this reason, the effective rate coefficient is significantly higher in air than in an oxygen free bath gas at total pressures of up to an atmosphere. There is insufficient data to describe the temperature, pressure and [O₂] de-

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pendencies of the rate coefficient, and our recommendation is restricted to air as bath gas, and pressures close to 1 bar. The data presented by Ramacher et al. (2001) using C₂H₄ as reference reactant is preferred over measurements relative to 2,2,4-trimethylpentane for reasons discussed by these authors, and form the basis of our recommendation. The temperature dependence of the rate coefficient was derived by least squares fitting of the data listed. Further studies of the rate coefficient in air at low pressures and temperatures would be useful to aid modelling of the role of this reaction at high altitudes.

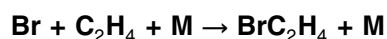
The formation of stable products when the reaction is initiated in air (in absence of NO_x) appears to be independent of temperature (Ramacher et al., 2001) and involves bimolecular reactions of the initially formed CHBr=CH radical with O₂ to form CO, HC(O)OH, HC(O)Br and CO₂ (for details see Barnes et al., 1989; Ramacher et al., 2001; Yarwood et al., 1991)

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$$\Delta H = -28 \text{ kJ}\cdot\text{mol}^{-1} \text{ (Bedjanian et al., 1999)}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$3.0 \times 10^{-33} \exp [(730 \pm 220/T)] [\text{He}]$	233–320	Bedjanian et al., 1999	DF-MS (a)
$(1.2 \pm 0.3) \times 10^{-15} \text{ (1.3 mbar He)}$	298		
<i>Relative Rate Coefficients</i>			
$< 2.5 \times 10^{-13}$	295	Wallington et al., 1989	RR (b)
$1.69 \times 10^{-13} \text{ (1013 mbar air)}$	298	Barnes et al., 1989	RR (c)
$(1.24 \pm 0.44) \times 10^{-14} \text{ (67 mbar air)}$	298		RR (d)
$(1.29 \pm 0.04) \times 10^{-13} \text{ (1013 mbar air)}$	313		
$(6.72 \pm 0.45) \times 10^{-14} \text{ (1013 mbar air)}$	333		
$(2.51 \pm 0.17) \times 10^{-14} \text{ (1013 mbar air)}$	353		
$(1.32 \pm 0.11) \times 10^{-13} \text{ (933 mbar air)}$	296	Yarwood et al., 1992	RR (e)
$(4.06 \pm 0.36) \times 10^{-13} \text{ (933 mbar air)}$	261	Ramacher et al., 2001	RR (f)
$(2.40 \pm 0.36) \times 10^{-13} \text{ (933 mbar air)}$	280		
$(1.22 \pm 0.18) \times 10^{-13} \text{ (933 mbar air)}$	296		
$(6.62 \pm 0.46) \times 10^{-13} \text{ (933 mbar air)}$	228	Ramacher et al., 2001	RR (g)
$(5.71 \pm 0.40) \times 10^{-13} \text{ (933 mbar air)}$	239		
$(4.54 \pm 0.32) \times 10^{-13} \text{ (933 mbar air)}$	249		
$(3.68 \pm 0.26) \times 10^{-13} \text{ (933 mbar air)}$	261		

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Comments

- (a) Experiments conducted at pressures of 0.7–2.7 mbar (0.5–2 Torr) He. Rate coefficient cited is at the low pressure limit, $k=k_0$. Br was detected as BrCl after titration with NOCl, and Br₂ was added to partly convert the BrC₂H₄ radical to BrC₂H₄Br, which was also detected. The kinetics of the title reaction were derived from fitting to an analytical expression that took loss of BrC₂H₄ by reaction with both Br₂ and Br into account.
- (b) CW photolysis of Br₂ in the presence of C₂H₄ in 986 mbar (740 Torr) air and CH₃CHO as reference reactant. The depletion of reactants was followed by GC to derive $k(\text{Br}+\text{C}_2\text{H}_4)/k(\text{Br}+\text{CH}_3\text{CHO}) < 0.067$. An absolute upper limit was calculated using $k(\text{Br}+\text{CH}_3\text{CHO}) = 3.8 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 295 K (IUPAC, this evaluation).
- (c) CW photolysis of Br₂ (300–500 nm) in the presence of C₂H₄ in 1013 mbar (760 Torr) N₂+O₂ bath gas and CH₃CHO as reference compound. Depletion of reactants monitored by GC. The tabulated rate coefficient in air was obtained by extrapolation of data obtained with O₂ partial pressures between 6.7 and 133 mbar (5 to 100 Torr) to 210 mbar O₂, and put on absolute basis using $k(\text{Br}+\text{CH}_3\text{CHO}) = 3.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, this evaluation).
- (d) CW photolysis of Br₂ (300–500 nm) in the presence of C₂H₄ in 33–1013 mbar (25–760 Torr) N₂+O₂ bath gas and 2,2,4-trimethylpenane (TMP) as reference compound. Depletion of reactants monitored by GC or FTIR spectroscopy. Data put on absolute basis using $k(\text{Br}+\text{TMP}) = (4.16 \pm 0.33) \times 10^{-12} (\exp -1820/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Barnes et al., 1989), which in turn was measured relative to $k(\text{Br} + 2\text{-methylpropane}) = 1.83 \times 10^{-10} \exp (-3452/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (Bierbach

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et al., 1996).

- (e) CW photolysis ($\lambda > 400$ nm) of Br_2 in presence of C_2H_2 and HCHO (reference reactant) in 933 mbar (700 Torr) air or $\text{N}_2 + \text{O}_2$ bath gas. The depletion of reactants was monitored by FTIR spectroscopy. A rate coefficient ratio of $k(\text{Br} + \text{C}_2\text{H}_4)/k(\text{Br} + \text{HCHO}) = 0.12 \pm 0.01$ was determined for 296 K and 933 mbar (700 Torr) air, and $k(\text{Br} + \text{C}_2\text{H}_4)$ was converted to an absolute value by use of $k(\text{Br} + \text{HCHO}) = 1.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, this evaluation).
- (f) CW photolysis ($\lambda > 420$ nm) of Br_2 in the presence of C_2H_4 and HCHO as reference reactant at total pressures of 933–946 (700–710 Torr) air. Depletion of reactants was monitored by FTIR spectroscopy. The following rate coefficient ratios were obtained: $k(\text{Br} + \text{C}_2\text{H}_4)/k(\text{Br} + \text{HCHO}) = 0.487 \pm 0.073$ at 261 K, 0.247 ± 0.037 at 280 K and 0.112 ± 0.017 at 296 K. The tabulated absolute rate coefficients were derived using $k(\text{Br} + \text{HCHO}) = 7.7 \times 10^{-12} \exp(-580/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, this evaluation).
- (g) As (f) but using CH_3CHO as reference reactant. The following rate coefficient ratios were obtained: $k(\text{Br} + \text{C}_2\text{H}_4)/k(\text{Br} + \text{CH}_3\text{CHO}) = 0.277 \pm 0.019$ at 228 K, 0.217 ± 0.015 at 239 K, 0.160 ± 0.011 at 249 K, and 0.119 ± 0.008 at 261 K. The absolute rate coefficients listed in the table were derived using $k(\text{Br} + \text{CH}_3\text{CHO}) = 1.8 \times 10^{-11} \exp(-460/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, this evaluation).

Preferred Values

$$k = 1.3 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} \text{ at } 296 \text{ K and } 1 \text{ bar air.}$$
$$k = 2.80 \times 10^{-13} \exp(224/T) \times B/[B + 8.5 \times 10^{12} \exp(-3200/T)] \text{ cm}^3 \text{ molecule}^{-1}$$

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s^{-1} where $B = 7.5 \times 10^{-12} [\text{O}_2] \text{ s}^{-1}$ and $[\text{O}_2]$ is in molecules cm^{-3} . The temperature range is 240–300 K.

Reliability

$$\Delta \log k = \pm 0.15 \text{ at } 298 \text{ K and } 1 \text{ bar air.}$$

Comments on Preferred Values

The measured rate coefficients reveal a strong dependence on total pressure (Barnes et al., 1989), temperature (Barnes et al., 1989; Ramacher et al., 2001) and the O_2 partial pressure (Barnes et al., 1989). This has been taken to indicate that the mechanism involves formation of a $\text{Br}-\text{C}_2\text{H}_4$ adduct, which can dissociate to reactants or react with O_2 to form a peroxy radical. For this reason, the effective rate coefficient is significantly higher in air than in an oxygen free bath gas at total pressures of up to an atmosphere. The 298 K recommendation is based on the average of the results of Yarwood et al. (1992) and Ramacher et al. (2001) which were both obtained relative to HCHO and which are in excellent agreement. As noted by both Barnes et al. (1989) and Ramacher et al. (2001) there is an inconsistency between the data sets of Barnes et al. (1989) obtained using CH_3CHO and 2,2,4-trimethylpentane/2-methylpropane as reference reactants, and the higher value of $k(298 \text{ K}) = 1.69 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ obtained in that study is considered less reliable. The data of Ramacher et al. (2001) listed in the Table above, which yield consistent results with HCHO and CH_3CHO as reference compounds and also using C_2HCl_3 as secondary standard, are used to derive the temperature dependence of the rate coefficient in one atmosphere air bath gas. The expression given describes the temperature dependence of the effective rate coefficient in one atmosphere of

air, and constrains the difference in the activation energies of the forward and reverse processes of adduct formation and dissociation according to Bedjanian et al. (1999) and assumes a temperature independent value of $7.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the rate coefficient for the reaction of the $\text{Br-C}_2\text{H}_4$ adduct with O_2 at one atmosphere. Further details are given by Ramacher et al. (2001). Note that extrapolation to conditions very different from one atmosphere pressure air could lead to large errors, and is not recommended. Further studies of the rate coefficient in air at low pressures and temperatures would be useful to aid modelling of the role of this reaction at high altitudes.

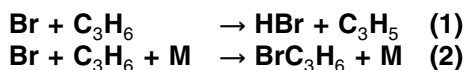
Identification of brominated aldehydes, alcohols and acids in product studies provides evidence for the formation and subsequent reaction of the $\text{BrC}_2\text{H}_4\text{O}_2$ peroxy radical in air (Barnes et al., 1989; Yarwood et al., 1992).

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$$\Delta H(1) = -2.9 \text{ kJ}\cdot\text{mol}^{-1} \text{ (Bedjanian et al., 1998)}$$

$$\Delta H(2) = -32.2 \text{ kJ}\cdot\text{mol}^{-1} \text{ (Bedjanian et al., 1998)}$$

Rate coefficient data = ($k=k_1+k_2$)

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$k_1 = 8.3 \times 10^{-12} \exp [-(2200 \pm 300/T)]$	263–363	Kondo et al., 1988	F-MS (a)
$k_1 = 8.15 \times 10^{-13} \exp [-(1250 \pm 160/T)]$	233–320	Bedjanian et al., 1998	DF-MS (b)
$k_1 = 1.2 \times 10^{-14}$	298		
$k_2 = 3.8 \times 10^{-33} \exp [(1200 \pm 50)/T] [\text{He}]$	233–320		
<i>Relative Rate Coefficients</i>			
$(4.2 \pm 0.5) \times 10^{-12}$	295	Wallington et al., 1989	RR (c)
$(2.9 \pm 0.3) \times 10^{-12}$	298	Barnes et al., 1989	RR (d)

Comments

- (a) Very low pressure reactor at $\approx 1 \times 10^{-3}$ mbar with bromine atoms detected directly using a mass spectrometer. The Arrhenius expression was derived from a calculated pre-exponential factor associated with a bent transition

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state, combined with the most reliable rate coefficient, which was that obtained at 363 K.

- (b) Experiments conducted at pressures of 0.7–2.7 mbar (0.5–2 Torr) He. Br was detected as BrCl after titration with NOCl. Consistent kinetic data for k_1 was derived by monitoring either Br, HBr or C_3H_5Br (formed in C_3H_5+Br). For determination of k_2 , Br_2 was added to partly convert the BrC_3H_6 radical to BrC_3H_6Br , which could be detected, and to regenerate Br. Values of k_2 at pressures of 0.7 to 2.7 mbar (0.5 to 2 Torr) He and 233 to 308 K were then derived by fitting to an analytical expression assuming a steady state for Br. An approximately linear dependence on He pressure was observed indicating that the derived values of k_2 are close to the low-pressure limit.
- (c) CW photolysis of Br_2 in the presence of C_3H_6 in 986 mbar (740 Torr) air and CH_3CHO as reference reactant. The depletion of reactants was followed by GC to derive $k(Br+C_3H_6)/k(Br+CH_3CHO)=1.10\pm 0.12$. An absolute rate coefficient was calculated using $k(Br+CH_3CHO)=3.8\times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 295 K (IUPAC, this evaluation).
- (d) CW photolysis of Br_2 (300–500 nm) in the presence of C_3H_6 in 1013 mbar (760 Torr) N_2+O_2 bath gas and CH_3CHO as reference compound. Depletion of reactants monitored by FTIR to derive $k(Br+C_3H_6)/k(Br+CH_3CHO)=0.75\pm 0.07$. An absolute rate coefficient was calculated using $k(Br+CH_3CHO)=3.9\times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K (IUPAC, this evaluation).

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Preferred Values

- $k_1 = 1.2 \times 10^{-14} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k_1 = 8.1 \times 10^{-13} \exp(-1250/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 230–320 K.
 $k = 3.6 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and 1 bar air.

Reliability

- $\Delta \log k_1 = \pm 0.2$ at 298 K.
 $\Delta (E_1/R) = \pm 500 \text{ K}$.
 $\Delta \log k = \pm 0.2$ at 298 K and one bar air.

Comments on Preferred Values

The reaction proceeds via both direct abstraction (k_1) and via a termolecular channel (k_2) involving formation of a BrC_3H_6 adduct that can redissociate to products or react with O_2 . The effective overall rate coefficient therefore displays a dependence on temperature, total pressure and the oxygen partial pressure (Barnes et al., 1989). The study of Bedjanian et al. (1998) is considered the more reliable measurement of k_1 as the work of Kondo et al. (1988) may have been influenced by the presence of excited states of Br. The recommended value for k_1 is therefore based on the work of Bedjanian et al. (1998), with expanded error limits.

In the absence of kinetic data for k_2 in the fall off regime it is not possible to derive a parameterisation of the rate coefficient for all atmospheric conditions. Instead, for the overall rate coefficient, we recommend an average of the results of the relative rate studies (Wallington et al., 1989; Barnes et al., 1989) at 298 K and note that the branching ratio to k_1 (i.e. to HBr formation) under atmospheric

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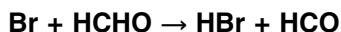
conditions is given by k_1/k . Pressure and temperature dependent studies in the fall-off regime are needed to model this reaction at high altitudes in the atmosphere where the pressure and temperature are lower. The structure of the radical product of the abstraction channel (1) is believed to be $\text{CH}_2=\text{CHCH}_2$ indicating that abstraction from the CH_3 group is most important (Kondo et al., 1988).

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$$\Delta H^\circ = 3.5 \text{ kJ}\cdot\text{mol}^{-1}$$

5 Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$1.44 \times 10^{-11} \exp[-(750 \pm 112)/T]$	223–480	Nava et al., 1981	FP-RF (a)
$(1.08 \pm 0.10) \times 10^{-12}$	298		
$2.97 \times 10^{-11} \exp[-(1015 \pm 70)/T]$	295–480	Poulet et al., 1981	DF-MS
$(9.4 \pm 0.8) \times 10^{-13}$	295		
<i>Relative Rate Coefficients</i>			
$5.0 \times 10^{-12} \exp[-(460 \pm 200)/T]$	250–296	Ramacher et al., 2000	RR(b)
1.08×10^{-12}	296		

Comments

(a) There appears to be curvature in the Arrhenius plot above room temperature; using the low-temperature values at 223, 254, and 298 K gives $E/R=584$ K.

10 (b) Br atoms were generated by photolysis of Br_2 in the presence of HCHO and CH_3CHO in 1 bar N_2 . Relative rates of decay of the two aldehydes

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were determined by an FTIR spectrometer system. The relative rates of decay were found to be independent of temperature over the range 250–296 K with the value $k(\text{Br}+\text{CH}_3\text{CHO})/k(\text{Br}+\text{HCHO})=3.60\pm 0.29$. This temperature-independent rate coefficient ratio is placed on an absolute basis by the use of $k(\text{Br}+\text{CH}_3\text{CHO})=1.8\times 10^{-11}\exp[-(460)/T]\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ (this evaluation)

Preferred Values

$k = 1.1 \times 10^{-12}\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ at 298 K.
 $k = 7.7 \times 10^{-12}\exp(-580/T)\text{cm}^3\text{molecule}^{-1}\text{s}^{-1}$ over the temperature range 220–300 K.

Reliability

$\Delta\log k = \pm 0.15$ at 298 K.

$\Delta(E/R) = \pm 200\text{K}$.

Comments on Preferred Values

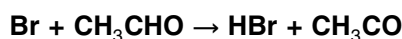
In the derivation of the preferred rate expression only data at and below room temperature were used. The room temperature value is the average of the absolute rate coefficients reported by Nava et al. (1981) and Poulet et al. (1981), and is in excellent agreement with the derived value given in Ramacher et al. (2000). The temperature dependence is derived from the low temperature results of Nava et al. (1981) ($E/R=584\text{K}$; see comment (a)), which is consistent with the relative rate data of Ramacher et al. (2000), and the A factor adjusted to yield the 298 K preferred values.

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References

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Ramacher, B., Orlando, J. J., and Tyndall, G. S.: Int. J. Chem. Kinet., 32, 460, 2000.

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$$\Delta H^\circ = 7.6 \text{ kJ}\cdot\text{mol}^{-1}$$

Rate coefficient data

$k/\text{cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$	Temp./K	Reference	Technique/Comments
<i>Absolute Rate Coefficients</i>			
$(3.5 \pm 0.5) \times 10^{-12}$	300	Islam et al., 1984	(a)
$1.51 \times 10^{-11} \exp[-(364 \pm 41)/T]$	255–400	Nicovich et al., 1990	LP-RF
4.45×10^{-12}	298		
$(3.5 \pm 0.3) \times 10^{-12}$	298	Szilagyi et al., 1998	F-RF
<i>Relative Rate Coefficients</i>			
$(3.7 \pm 0.1) \times 10^{-12}$	298	Niki et al., 1985	RR (b)
$2.6 \times 10^{-11} \exp[-(580 \pm 200)/T]$	250–296	Ramacher et al., 2000	RR(c)
4.0×10^{-12}	296		

Comments

(a) Very low pressure reactor study. Br atoms were generated by microwave discharge of Br_2 in helium, with mass spectrometric detection of reactants and products.

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(b) Br atoms were generated by photolysis of Br_2 at 350 nm to 600 nm in 930 mbar (700 Torr) total pressure of N_2 . The rate coefficient was determined relative to that for the reaction of Br atoms with HCHO, with $k(\text{Br}+\text{CH}_3\text{CHO})/k(\text{Br}+\text{HCHO})=3.39\pm 0.10$. This rate coefficient ratio is placed on an absolute basis by use of a rate coefficient of $k(\text{Br}+\text{HCHO})=1.1 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (IUPAC, this evaluation).

(c) Br atoms were generated by photolysis of Br_2 in the presence of HCHO and CH_3CHO in 1 bar N_2 . Relative rates of decay of the two aldehydes were determined by an FTIR spectrometer system. The relative rates of decay were found to be independent of temperature over the range 250–296 K with the value $k(\text{Br}+\text{CH}_3\text{CHO})/k(\text{Br}+\text{HCHO})=3.60\pm 0.29$. This temperature-independent rate coefficient ratio is placed on an absolute basis by the use of $k(\text{Br}+\text{HCHO})=7.7 \times 10^{-12} \exp[-580/T] \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ (this evaluation)

Preferred Values

$k = 3.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K.
 $k = 1.8 \times 10^{-11} \exp(-460/T) \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ over the temperature range 250–400 K.

Reliability

$\Delta \log k = \pm 0.2$ at 298 K.
 $\Delta E/R = \pm 200 \text{ K}$.

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Comments on Preferred Values

The room temperature value is the average of the rate coefficients reported by Islam et al. (1984), Nicovich et al. (1990), Szilagyi et al. (1998) and Niki et al. (1985), and is in excellent agreement with the relative rate value of Ramacher et al. (2000). The temperature dependence is derived from the results of Nicovich et al. (1990), which is consistent with the relative rate data of Ramacher et al. (2000), and the A factor adjusted to yield the 298 K preferred value. The preferred room temperature rate coefficient is consistent with the relative rate studies of Barnes et al. (1989) and Wallington et al. (1989) [which do not provide definitive data concerning the rate constant for the reaction of Br atoms with CH₃CHO].

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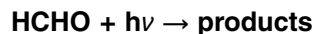
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Appendix 8: Organic Photochemistry

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Primary photochemical transitions

Reaction	$\Delta H_{298}^{\circ}/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
HCHO + $h\nu$ → H + HCO (1)	369.7	324
→ H ₂ + CO (2)	-1.9	

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Absorption cross-section data

Wavelength range/nm	Reference	Comments
240–360	Moortgat and Schneider, 1989	(a)
300–360	Cantrell et al., 1990	(b)
225–375	Meller and Moortgat, 2000	(c)

Quantum yield data ($\phi = \phi_1 + \phi_2$)

Measurement	Wavelength range/nm	Reference	Comments
$\phi, \phi_2/\phi$	253–353	Moortgat et al., 1983	(d)
ϕ_1	269–339	Smith et al., 2002	(e)

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Comments

- (a) Cross-sections measured at 220 K and 298 K at different concentrations of HCHO and extrapolated to zero concentration. This extrapolation procedure yielded virtually identical cross-sections with and without added N₂.
- 5 (b) High-resolution FT spectroscopy used to measure cross-sections as a function of temperature (223 to 293 K). Values at different concentrations of HCHO were extrapolated to zero concentration.
- 10 (c) Cross-section measurements with resolution of 0.025 nm at selected temperatures between 223–323 K. HCHO pressure kept below 0.65 mbar to avoid saturation effects. Error limits on $\sigma \pm 5\%$ and on temperature coefficients $< 8\%$. Results compared in detail with earlier work.
- 15 (d) Quantum yields of CO and H₂ were measured as a function of wavelength for HCHO in low concentration in air. Previous results (Moortgat and Warneck, 1979) showing the pressure and temperature dependences of ϕ_1 and ϕ_2 were confirmed.
- 20 (e) The relative quantum yield for the production of radical products, H and HCO, measured directly using an NO-chemical amplification method, with subsequent detection of NO₂ by CIMS. All yields were measured at a pressure of 50 Torr (66 mbar) and were normalized to a quantum yield of $\phi_2 = 0.753$ at 303.75 nm based on the recommendation of DeMore et al. (2000). The quantum yields were measured with sufficient wavelength resolution (± 0.62 nm, fwhm), to observe structure which had not been previously reported.

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Preferred Values

Absorption cross-sections at 298 and 223 K and Temperature Gradients of HCHO Averaged Over Intervals Used in Atmospheric Modelling

Wavelength*/nm	Wavelength Range, */nm	$10^{20}\sigma(298\text{ K})\text{ cm}^2$	$10^{20}\sigma(223\text{ K})\text{ cm}^2$	$10^{24}\Gamma\text{ cm}^2\text{ K}^{-1}$
226.0	224.7–227.3	0.0165		
228.6	227.3–229.9	0.0181		
231.3	229.9–232.6	0.0302		
234.0	232.6–235.3	0.0315		
236.7	235.3–238.1	0.0625		
239.6	238.1–241.0	0.0705		
242.5	241.0–243.9	0.1268		
245.4	243.9–246.9	0.1390		
248.5	246.9–250.0	0.2537		
251.7	250.0–253.3	0.2699	0.2642	0.76
254.9	253.3–256.4	0.4560	0.4427	1.78
258.1	256.4–259.7	0.4768	0.4363	5.40
261.5	259.7–263.2	0.7034	0.6933	1.35
265.0	263.2–266.7	0.7379	0.7008	4.97
268.5	266.7–270.3	1.1287	1.1074	2.86
272.2	270.3–274.0	1.2922	1.2631	3.88
275.9	274.0–277.8	1.8442	1.8865	-5.64
279.8	277.8–281.7	1.8592	1.8874	-3.76
283.7	281.7–285.7	2.5555	2.7238	-22.43
287.8	285.7–289.9	2.3095	2.3613	-6.90
292.0	289.9–294.1	2.6653	2.9321	-35.58
296.3	294.1–298.5	3.2939	3.2524	5.54

*Wavelengths are calibrated in air.

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Wavelength*/nm	Wavelength Range, */nm	$10^{20}\sigma(298\text{ K})\text{ cm}^2$	$10^{20}\sigma(223\text{ K})\text{ cm}^2$	$10^{24}\Gamma\text{ cm}^2\text{ K}^{-1}$
300.8	298.5–303.0	1.6046	1.5854	2.55
305.4	303.0–307.7	4.3944	4.4061	-1.56
310.1	307.7–312.5	1.6318	1.6737	-5.58
315.0	312.5–317.5	4.0853	4.0230	8.30
320.0	317.5–322.5	1.5290	1.4679	8.15
325.0	322.5–327.5	2.7908	2.7612	3.94
330.0	327.5–332.5	1.9889	1.9094	10.59
335.0	332.5–337.5	0.1959	0.1831	1.71
340.0	337.5–342.5	2.3872	2.2729	15.24
345.0	342.5–347.5	0.7586	0.7547	0.51
350.0	347.5–352.5	0.1947	0.2204	-3.43
355.0	352.5–357.5	0.9604		
360.0	357.5–362.5	0.0139		
365.0	362.5–367.5	0.0100		
370.0	367.5–372.5	0.0368		

*Wavelengths are calibrated in air.

To calculate the UV absorption spectrum at a given temperature T , the following equation is used:

$$\sigma(\lambda, T) = \sigma(\lambda, 298\text{ K}) + \Gamma(T - 298\text{ K})$$

**Absorption Cross-Sections at 298 K, σ (298 K), Averaged Over 1 nm Intervals
Centered at the Cited Wavelength, λ .**

λ/nm^*	$10^{21}\sigma(298\text{ K})\text{ cm}^2$	λ/nm^*	$10^{21}\sigma(298\text{ K})\text{ cm}^2$	λ/nm^*	$10^{21}\sigma(298\text{ K})\text{ cm}^2$
226	0.179	276	25.842	326	68.757
227	0.169	277	15.731	327	43.702
228	0.177	278	10.349	328	12.201
229	0.190	279	24.514	329	31.200
230	0.205	280	23.375	330	38.651
231	0.166	281	15.624	331	14.121
232	0.335	282	9.728	332	3.474
233	0.262	283	7.224	333	2.135
234	0.325	284	42.649	334	1.587
235	0.363	285	40.504	335	0.967
236	0.540	286	20.950	336	1.261
237	0.770	287	11.532	337	3.825
238	0.569	288	31.687	338	19.188
239	0.681	289	32.245	339	53.814
240	0.782	290	11.729	340	31.514
241	0.775	291	18.358	341	9.783
242	1.227	292	7.973	342	5.093
243	1.591	293	31.281	343	19.221
244	1.096	294	71.538	344	12.684
245	1.313	295	40.535	345	4.369
246	1.634	296	24.739	346	1.190
247	1.511	297	13.672	347	0.441
248	2.338	298	42.166	348	0.754
249	3.178	299	31.745	349	0.379

*Wavelengths are calibrated in air.

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λ/nm^*	$10^{21}\sigma(298\text{ K})\text{ cm}^2$	λ/nm^*	$10^{21}\sigma(298\text{ K})\text{ cm}^2$	λ/nm^*	$10^{21}\sigma(298\text{ K})\text{ cm}^2$
250	2.572	300	9.638	350	0.362
251	2.039	301	16.246	351	0.893
252	3.366	302	8.537	352	7.295
253	2.894	303	30.211	353	22.752
254	3.417	304	72.185	354	16.449
255	4.502	305	47.520	355	6.964
256	6.282	306	42.915	356	1.483
257	4.430	307	17.807	357	0.345
258	3.073	308	13.847	358	0.186
259	6.174	309	32.521	359	0.111
260	6.045	310	17.369	360	0.087
261	6.591	311	4.623	361	0.100
262	6.033	312	11.880	362	0.211
263	10.773	313	9.064	363	0.141
264	9.465	314	56.366	364	0.094
265	5.305	315	55.650	365	0.088
266	5.387	316	25.608	366	0.085
267	13.604	317	57.770	367	0.091
268	12.428	318	31.505	368	0.142
269	9.908	319	9.779	369	0.297
270	9.626	320	11.936	370	0.635
271	19.409	321	15.976	371	0.571
272	14.302	322	7.216	372	0.198
273	8.106	323	3.281	373	0.113
274	6.575	324	8.584	374	0.091
275	21.432	325	15.779	375	0.087

*Wavelengths are calibrated in air.

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Quantum yields in air at 1 bar and 298 K*

λ/nm	ϕ_1	ϕ_2
240.00	0.270	0.490
250.00	0.290	0.490
260.00	0.300	0.490
268.75	0.425	0.385
278.75	0.570	0.320
283.75	0.673	0.247
288.75	0.746	0.214
293.75	0.694	0.286
298.75	0.642	0.348
301.25	0.725	0.275
303.75	0.780	0.220
306.25	0.684	0.316
308.75	0.735	0.265
311.25	0.704	0.296
313.75	0.715	0.285
316.25	0.673	0.327
321.25	0.663	0.337
326.25	0.528	0.452
328.75	0.373	0.577
331.25	0.476	0.424
333.75	0.311	0.489
336.25	0.072	0.627
338.75	0.041	0.559

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λ/nm	ϕ_1	ϕ_2
340.00	0.00	0.560
350.00	0.00	0.210
360.00	0.00	0.030

ϕ_1 values between 240–330 nm independent of temperature and pressure

Comments on Preferred Values

The new cross-section measurements by Meller and Moortgat (2000) provide for the first time high-resolution data over the complete UV absorption band with minimised systematic error. These are the basis of the preferred values. The measured cross sections are 5–10% higher than the values previously recommended by IUPAC, which were based on cross-sections reported by Moortgat and Schneider (1989) for $\lambda \leq 300$ nm and of Cantrell et al. (1990) for $\lambda = 301$ nm to 356 nm. The temperature dependence over the range 250–356 nm reported by Meller and Moortgat (2000) exhibits the same general changes on band shape as previously recommended spectra, but differs in the shape of the individual rotational bands. Resolution should not exceed 1 nm to assure correct representation of the temperature dependent cross sections.

The recent quantum yield measurements of Smith et al. (2002) are in good agreement with those determined by Moortgat et al. (1983) upon which the earlier IUPAC recommended data for atmospheric pressure and 298 K was based, but show for the first time structure in the wavelength dependence of ϕ_1 . These results are also consistent with earlier measurements of the quantum yields by Horowitz and Calvert (1978), Clark et al. (1978), Tang et al. (1979) and Moortgat et al. (1983)

The preferred values for ϕ_1 are calculated from the relative values of Smith

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et al. (2002), using the value of $\phi_1=0.78$ at 302.5 nm. These values are independent of pressure and temperature in the atmospheric range. The values for ϕ_2 are obtained by the difference ($\phi_T-\phi_1$), where ϕ_T is the sum of the two channels (1) and (2) at 1 bar and 298 K, based on the data of Moortgat et al. (1983). Moortgat et al. (1979, 1983) show that for $\lambda>330$ nm, the quantum yields of CO and H₂ production are pressure and temperature dependent; quenching parameters are given in Moortgat et al. (1983).

Photodissociation of HCHO involves both S⁰ and T¹ excited states populated from the S¹ state produced initially by photo-excitation in the near UV. The structure observed by Smith et al. (2002) provides evidence for the complicated competition among the various dissociation pathways of singlet and triplet excited formaldehyde to give: H+HCO, H+H+CO and H₂+CO, which has been diagnosed from numerous studies of the photo-dissociation dynamics of excited HCHO molecules. These studies reveal that several parallel unimolecular decomposition pathways exist, yielding the two sets of chemically distinct products: H+HCO (1) and H₂+CO (2) (Green et al., 1992). Reaction (1) can occur via both S⁰ and T¹ states, while Reaction (2) occurs solely via S⁰. Not only do the molecular and radical product channels compete, but distinct S⁰ and T¹ pathways can lead to the same products, i.e. H + HCO (Chuang et al., 1987).

Recent experimental studies (Valachovic et al., 2000) of the radical channel have defined the energetics governing the competition between the S⁰ and T¹ pathways, which are consistent with earlier experiments (Chuang et al., 1987) and with ab initio calculations (Yamaguchi et al., 1998). The T¹ route dominates at higher energies. For the molecular channel, the S⁰ route, which is pressure quenched at energies below the radical threshold, may be replaced above the threshold by an 'abstraction' mechanism (v. Zee et al., 1993). This mechanism involves access to large H-HCO distances in the excited state just prior to bond breaking, which facilitate H-atom abstraction (Valachovic et al.,

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2000), producing H₂+CO. This may resolve some of the earlier discrepancies concerning the yields of molecular products at higher energies (Troe, 1984; Ho et al., 1982). Nevertheless, the branching ratios for $\lambda<300$ nm should be treated with caution.

The new recommended quantum yields result in increases of at least 8% in the calculated H/HCO production rate from formaldehyde photolysis in the troposphere.

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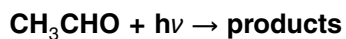
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II.A8.198



Primary photochemical transitions

Reaction	$\Delta H_{298}^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{CH}_3\text{CHO} + h\nu \rightarrow \text{CH}_4 + \text{CO}$ (1)	-19.5	
$\rightarrow \text{CH}_3 + \text{HCO}$ (2)	355.3	337
$\rightarrow \text{CH}_3\text{CO} + \text{H}$ (3)	373.8	320

5 Absorption cross-section data

Wavelength range/nm	Reference	Comments
202–365	Martinez et al., 1992	(a)

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Quantum yield data ($\phi = \phi_1 + \phi_2 + \phi_3$)

Measurement		Wavelength range/nm	Reference	Comments
ϕ_1	ϕ_2			
0.46	0.31	260	Meyrahn et al., 1982	(b)
0.42	0.32	265		
0.31	0.39	270		
0.16	0.51	275		
0.05	0.58	280		
0.02	0.57	285		
0.01	0.53	290		
0.005	0.48	295		
0.0	0.43	300		
0.0	0.37	305		
0.0	0.28	310		
0.0	0.10	320		
0.0	0.04	325		
0.0	0.00	330		

Comments

- 5 (a) Double beam spectrophotometric measurements with 10 cm path length. Data obtained at 0.1 nm intervals with 0.5 nm resolution. Argon-acetaldehyde mixtures used at a total pressure of 133 mbar and several acetaldehyde pressures in the range 1.3 mbar to 2.6 mbar. Cross-sections tabulated are averages over a 1 nm ($\lambda > 280$ nm) or 4 nm ($\lambda < 280$ nm) region

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centered on the corresponding wavelength (see Preferred Values).

- 5 (b) Quantum yields of CH_4 and CO determined from the photolysis of 100 ppm of CH_3CHO in air or N_2 at a total pressure of 1 bar. H_2 was found only in trace quantities and hence it was concluded that the photolytic channel giving $\text{CH}_3\text{CO} + \text{H}$ ($\lambda_{\text{threshold}} = 320$ nm) is negligible. Quantum yield data based on the assumption that $\phi_1 + \phi_2 + \phi_a = 1$, where ϕ_a refers to the quenching process $\text{CH}_3\text{CHO}^* + \text{M} \rightarrow \text{CH}_3 + \text{CHO} + \text{M}$. Quantum yield data at 1 bar pressure were found to be independent of the diluent, N_2 , or air. ϕ_{CO} both in N_2 and in air increased as the total pressure was lowered.

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Preferred Values

Absorption Cross-Sections at 298 K

λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$
202	0.056	297	4.38	334	0.363
206	0.053	298	4.41	335	0.350
210	0.049	299	4.26	336	0.238
214	0.048	300	4.16	337	0.222
218	0.052	301	3.99	338	0.205
222	0.065	302	3.86	339	0.219
226	0.096	303	3.72	340	0.150
230	0.151	304	3.48	341	0.074
234	0.241	305	3.42	342	0.042
238	0.375	306	3.42	343	0.031
242	0.564	307	3.36	344	0.026
246	0.818	308	3.33	345	0.021
250	1.128	309	3.14	346	0.019
254	1.524	310	2.93	347	0.015
258	1.994	311	2.76	348	0.016
262	2.44	312	2.53	349	0.010
266	3.05	313	2.47	350	0.008
270	3.42	314	2.44	351	0.007
274	4.03	315	2.20	352	0.006
278	4.19	316	2.04	353	0.005
280	4.50	317	2.07	354	0.005
281	4.69	318	1.979	355	0.004

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λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$
282	4.72	319	1.874	356	0.005
283	4.75	320	1.723	357	0.003
284	4.61	321	1.484	358	0.004
285	4.49	322	1.402	359	0.002
286	4.44	323	1.244	360	0.003
287	4.59	324	1.091	361	0.002
288	4.72	325	1.136	362	0.001
289	4.77	326	1.074	363	0.000
290	4.89	327	0.858	364	0.000
291	4.78	328	0.747	365	0.000
292	4.68	329	0.707		
293	4.53	330	0.688		
294	4.33	331	0.588		
295	4.27	332	0.530		
296	4.24	333	0.398		

Quantum yields in air at 1 bar and 298 K

λ/nm	ϕ_1	ϕ_2
260	0.46	0.31
270	0.31	0.39
280	0.05	0.58
290	0.01	0.53
295	0.00	0.48
300		0.43

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λ/nm	ϕ_1	ϕ_2
305		0.37
310		0.29
315		0.17
320		0.10
325		0.04
330		0.00

Comments on Preferred Values

The preferred absorption cross-sections are from the extensive measurements of Martinez et al. (1992). Over the wavelength region 260 nm to 320 nm these cross-sections are within 5% of the data of Calvert and Pitts (1966) and Weaver et al. (1976).

The preferred values for the quantum yields are those obtained by Meyrahn et al. (1982). Atkinson and Lloyd (1984) have evaluated the quantum yield data of Meyrahn et al. (1982) and of Horowitz and Calvert (1982), and derive values in very close agreement with those recommended here.

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II.A8.199



Primary photochemical transitions

Reaction		$\Delta H_{298}^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{C}_2\text{H}_5\text{CHO} \rightarrow \text{C}_2\text{H}_5 + \text{HCO}$	(1)	351.4	340
$\rightarrow \text{C}_2\text{H}_6 + \text{CO}$	(2)	-7.1	
$\rightarrow \text{C}_2\text{H}_4 + \text{HCHO}$	(3)	131.0	913
$\rightarrow \text{CH}_3 + \text{CH}_2\text{CHO}$	(4)	344.3	347

5 Absorption cross-section data

Wavelength range/nm	Reference	Comments
202–365	Martinez et al., 1992	(a)
280–330	Chen and Zhu, 2001	(b)

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Quantum yield data ($\phi = \phi_1 + \phi_2 + \phi_3 + \phi_4$)

Measurement	Wavelength range/nm	Reference	Comments
ϕ_1		Heicklen et al., 1986	(c)
0.89	294		
0.50	302		
0.26	325		
0.15	334		
ϕ_1		Chen and Zhu, 2001	(d)
0.85 ± 0.06	280		
1.01 ± 0.07	285		
0.95 ± 0.06	290		
0.98 ± 0.06	295		
0.92 ± 0.06	300		
0.95 ± 0.08	305		
0.98 ± 0.11	310		
0.91 ± 0.05	315		
1.08 ± 0.07	320		
1.07 ± 0.14	325		
0.84 ± 0.08	330		

Comments

- 5 (a) Absorption measurements as a function of $\text{C}_2\text{H}_5\text{CHO}$ pressure using a diode array spectrometer. Cross-sections are the average cross-section over a 1 nm ($\lambda > 280$ nm) or 4 nm ($\lambda < 280$ nm) region centered at the corresponding wavelength (see Preferred Values).

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- (b) Cross-sections determined from transmission of UV light at 5 nm intervals from tunable dye laser, as a function of C_2H_5CHO pressure. Overall uncertainty estimated to be 5–10% at all wavelengths. Results agree with those from Martinez et al. (1992) except at 280 and 330 nm, where values are 20–30% higher.
- (c) Laser flash photolysis of C_2H_5CHO in the presence of air and steady-state photolysis of C_2H_5CHO in the presence of O_2 at 263 K or 298 K, as a function of wavelength and of O_2 pressure. Quantum yields for radical channel from measurement of $C_2H_5O_2$ and HO_2 by UV absorption following laser photolysis. Quantum yields for CO and C_2H_6 were measured by GC. From the proposed mechanism it was deduced that $\phi_1 = (\phi_\infty - \phi[C_2H_6])$. The values of ϕ quoted are for 1 bar air.
- (e) Tunable dye laser photolysis of C_2H_5CHO with time resolved measurement of HCO concentration by cavity ring down spectroscopy at 613.8 nm. Absorbed flux was determined from photon fluence measurements using a calibrated Joulemeter. Absolute yields of HCO calculated from absorption cross sections, $\sigma(HCO)$ determined in situ from either photo-dissociation of HCHO or $Cl_2 + HCHO$ mixtures (at 310–330 nm). A weak dependence of ϕ on $P_{C_2H_5CHO}$ was observed but no dependence of ϕ on N_2 up to 1 bar. The values of ϕ quoted are for zero pressure, but the same values apply at 1 bar N_2 .

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Preferred Values

Absorption Cross-Sections at 298 K

λ/nm	$10^{20}\sigma/cm^2$	λ/nm	$10^{20}\sigma/cm^2$	λ/nm	$10^{20}\sigma/cm^2$
202	0.049	295	5.57	330	0.575
206	0.049	296	5.37	331	0.494
210	0.057	297	5.16	332	0.466
214	0.069	298	5.02	333	0.430
218	0.080	299	5.02	334	0.373
222	0.091	300	5.04	335	0.325
226	0.115	301	5.09	336	0.280
230	0.163	302	5.07	337	0.230
234	0.257	303	4.94	338	0.185
238	0.407	304	4.69	339	0.166
242	0.622	305	4.32	340	0.155
246	0.909	306	4.04	341	0.119

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λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$
250	1.287	307	3.81	342	0.076
254	1.745	308	3.65	343	0.045
258	2.25	309	3.62	344	0.031
262	2.88	310	3.60	345	0.025
266	3.43	311	3.53	346	0.019
270	4.12	312	3.50	347	0.016
274	4.59	313	3.32	348	0.014
278	5.17	314	3.06	349	0.013
280	5.16	315	2.77	350	0.010
281	5.21	316	2.43	351	0.008
282	5.35	317	2.18	352	0.007
283	5.57	318	2.00	353	0.005
284	5.78	319	1.864	354	0.004
285	5.86	320	1.831	355	0.002
286	5.82	321	1.777	356	0.001
287	5.72	322	1.662	357	0.001
288	5.59	323	1.577	358	0.000
289	5.52	324	1.488	359	0.000
290	5.56	325	1.300	360	0.000
291	5.68	326	1.129	361	0.000
292	5.81	327	0.996	362	0.000
293	5.88	328	0.828	363	0.000
294	5.80	329	0.685	364	0.000

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Quantum yields in air at 1 bar and 298 K

λ/nm	ϕ_1
280	0.85
285	0.90
290	0.95
295	1.00
300	1.00
305	1.00
310	1.00

Preferred Quantum Yields

No recommendation.

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Comments on Preferred Values

The preferred absorption cross-sections are from the measurements of Martinez et al. (1992). Over the wavelength region 260 nm to 320 nm these cross-sections are within 5% of the earlier data of Calvert and Pitts (1966), and the less precise measurements of Chen and Zhu (2001).

The quantum yields, ϕ_1 , reported by Chen and Zhu (2001) at wavelengths less than 310 nm and at 1 bar N_2 , agree well with those obtained for 1 bar air in the less direct study of Heicklen et al. (1986). However at wavelengths >310 nm the results of Chen and Zhu (2001) do not show the fall off observed by Heicklen et al. (1986) in air. This could be due to quenching by O_2 of the excited triplet state, which is believed to dissociate to give radical products (channel 1), or to

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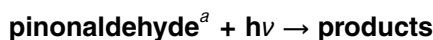
errors in the interpretation of the more complex chemistry in the presence of O₂. There are significant experimental uncertainties at the longer wavelengths associated with the weak absorption by propionaldehyde. Further work is needed to resolve this issue and we are unable to recommend values for ϕ_1 in this region.

References

- Calvert, J. G. and Pitts Jr., J. N.: Photochemistry, Wiley, New York, 1966.
Chen, Y. and Zhu, L.: J. Phys. Chem. A, 105, 9689, 2001.
Heicklen, J., Desai, J., Bahta, A., Harper, C., and Simonaitis, R.: J. Photochem., 34, 117, 1986.
Martinez, R. D., Buitrago, A. A., Howell, N. W., Hearn, C. H., and Joens, J. A.: Atmos. Environ., 26A, 785, 1992.

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II.A8.200



Absorption cross-section data

Wavelength range/nm	Reference	Comments
275–345	Hallquist et al., 1997	(b)

Quantum yield data

Measurement	Wavelength range/nm	Reference	Comments
$\phi(\text{average}) = 0.14 \pm 0.03$	sunlight	RADICAL, 2002	(c)
$\phi(\text{average}) \approx 0.4$	sunlight	Jaoui and Kamems, 2003	(d)

Comments

- (a) (3-acetyl-2,2-dimethyl-cyclobutyl)-acetaldehyde.
- (b) The UV spectrum was determined from long path (39.1 m) absorption measurements in a 0.48 m³ chamber. Measurements were made over the wavelength range 275–345 nm, at a resolution of 0.6 nm, using diode array spectroscopy. Cross sections were reported as averages over 5 nm intervals. Measurements were made at 300±1 K and low pressure (<0.1 mbar), and calibrated through measurement of the pressure change on admission

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of pinonaldehyde to the reaction vessel. Pinonaldehyde was synthesized from the ozonolysis of α -pinene. Its stated purity was 95%, based on GC-MS and NMR analyses.

- 5 (c) Natural sunlight photolysis of pinonaldehyde-cyclohexane-air mixtures in a 180 m³ outdoor chamber (the European Photoreactor, EUPHORE). The photolysis rate of pinonaldehyde was determined from its measured decay (HPLC), following correction for its removal by wall loss and dilution (which accounted for ca. 60% of its removal). Cyclohexane was included in the reaction mixtures as an HO scavenger. An average photodissociation quantum yield was determined from the observed photolysis rate relative to a theoretical rate, which was calculated using the absorption cross sections of Hallquist et al. (1997), the measured actinic flux and the assumption of a unit quantum yield.
- 10
- 15 (d) Natural sunlight photolysis of pinonaldehyde-air and pinonaldehyde-cyclohexane-air mixtures in a 190 m³ outdoor chamber, with GC-MS detection. The system was characterized by simulation using a detailed chemical mechanism, which also included pinonaldehyde removal by wall loss and dilution (which accounted for ~ 70-80% of its removal). An average photodissociation quantum yield was derived from the simulations, based on light absorption described by the cross sections of Hallquist et al. (1997) and the measured actinic flux. More than nine products were identified or tentatively identified and quantified using GC-MS.
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Preferred Values

Absorption Cross-Sections for pinonaldehyde at 300 K

λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$
277.5	12.19	312.5	6.84
282.5	12.96	317.5	4.90
287.5	13.48	322.5	3.07
292.5	12.94	327.5	1.72
297.5	12.17	332.5	0.72
302.5	10.62	337.5	0.29
307.5	8.94	342.5	0.08

Quantum Yields

- 5 No recommendation.

Comments on Preferred Values

The preferred absorption cross sections are from the study of Hallquist et al. (1997), which are the only measurements reported and appear to be reliable. As pointed out by Hallquist et al. (1997), the cross sections are consistent with additive contributions from the aldehyde and ketone groups in pinonaldehyde, based on cross sections reported for simple aldehydes and ketones.

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The studies of RADICAL (2002) and Jaoui and Kamens (2003) are indicative of removal of pinonaldehyde through photolysis, with average quantum yields which are substantially below unity at wavelengths >290 nm. Large corrections

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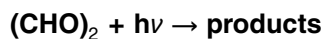
for pinonaldehyde wall loss and dilution were required in both studies, such that no firm quantum yield recommendation is made. Jaoui and Kamens (2003) identified a series of products which provided evidence for photolysis via both molecular and radical-forming channels. Further studies of the quantum yield and photolysis product channels are required.

References

- Hallquist, M., Wängberg, I., and Ljungström, E.: Environ. Sci. Technol., 31, 3166, 1997.
- Jaoui, M. and Kamens, R. M.: Atmos. Environ., 37, 1835, 2003.
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II.A8.201



Primary photochemical transitions

Reaction		$\Delta H_{298}^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$(\text{CHO})_2 + h\nu \rightarrow \text{H}_2 + 2\text{CO}$	(1)	-9.1	
$\rightarrow 2\text{HCO}$	(2)	298.1	401
$\rightarrow \text{HCHO} + \text{CO}$	(3)	-7.2	
$\rightarrow \text{H} + \text{CO} + \text{HCO}$	(4)	362.5	330

5 Absorption cross-section data

Wavelength range/nm	Reference	Comments
230–462	Plum et al., 1983	(a)

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Quantum yield data ($\phi = \phi_1 + \phi_2 + \phi_3 + \phi_4$)

Measurement	Wavelength range/nm	Reference	Comments
$\phi = 0.029 \pm 0.018$	325–470	Plum et al., 1983	(b)
$\phi(\text{HCO}) = 0.8 \pm 0.4$	308	Langford and Moore, 1984	(c)
$\phi(\text{HCO}) = 0.42 \pm 0.22$	193	Zhu et al., 1996	(d)
$\phi(\text{HCO}) = 0.54 \pm 0.24$	248		
$\phi(\text{HCO}) = 0.70 \pm 0.30$	308		
$\phi(\text{HCO}) = 1.50 \pm 0.6$	351		

Comments

- 5 (a) Conventional spectrophotometric study (Cary 17-D) using glyoxal pressures of ~4 mbar to 17 mbar.
- (b) Rate of photolysis of glyoxal in air mixtures at atmospheric pressure measured in an environmental chamber. The quantum yield for the photodissociation of glyoxal was obtained by comparison of the measured rate of removal of glyoxal with the rate of photolysis of NO_2 under similar experimental conditions.
- 10 (c) Laser photolysis of 5.3 mbar glyoxal in 1.3 bar N_2 at 295 K. HCO product determined by time-resolved laser resonance absorption. Quantum yield determined by comparing the HCO radical absorption observed with the same signals following HCHO and $(\text{CHO})_2$ photolyses.
- 15 (d) Excimer laser photolysis of flowing glyoxal- N_2 mixtures. [HCO] monitored by time-resolved cavity ring-down spectroscopy. Yields of HCO determined by comparison of absorption with signals from photolysis of
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formaldehyde- N_2 mixtures under similar conditions. Incident light intensities were measured by a Joulemeter calibrated by chemical actinometry. The HCO quantum yields were found to be independent of glyoxal pressure, total pressure (26 mbar to 470 mbar), and light intensity.

Preferred Values

Absorption Cross-Sections at 298 K

λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$
230.5	0.30	390	3.14	427	10.76
235	0.30	391	3.45	428	16.65
240	0.42	392	3.25	429	4.06
245	0.57	393	2.23	430	5.07
250	0.84	394	2.64	431	4.87
255	1.15	395	3.04	432	4.06
260	1.45	396	2.64	433	3.65
265	1.88	397	2.44	434	4.06
270	2.30	398	3.25	435	5.07
275	2.60	399	3.04	436	8.12
280	2.87	400	2.84	437	5.28
285	3.33	401	3.25	438	10.15
290	3.18	402	4.46	439	7.71
295	3.33	403	5.28	440	24.76
300	3.60	404	4.26	441	8.12
305	2.76	405	3.05	442	6.09
310	2.76	406	3.05	443	7.51
312.5	2.88	407	2.84	444	9.34
315	2.30	408	2.44	445	11.37
320	1.46	409	2.84	446	5.28
325	1.15	410	6.09	447	2.44
327.5	1.46	411	5.27	448	2.84

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λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$
330	1.15	412	4.87	449	3.86
335	0.30	413	8.32	450	6.09
340	0.00	414	7.51	451	10.96
345	0.00	415	8.12	452	12.18
350	0.00	416	4.26	453	23.95
355	0.00	417	4.87	454	17.05
360	0.23	418	5.89	455	40.60
365	0.30	419	6.70	456	10.14
370	0.80	420	3.86	457	1.63
375	1.03	421	5.68	458	1.22
380	1.72	422	5.28	459	0.41
382	1.57	423	10.55	460	0.41
384	1.49	424	6.09	461	0.20
386	1.49	425	7.31	462	0.00
388	2.87	426	11.77		

Comments on Preferred Values

Glyoxal exhibits two distinct absorption regions relevant for atmospheric photolysis. The first region consists of a series of discrete bands between 360–
5 460 nm super-imposed on a continuum. The second region shows a broad band with some structure with a maximum absorption near 300 nm. The preferred values for the absorption cross-sections are those determined by Plum et al. (1983). Zhu et al. (1996) have measured the cross-sections at 193 nm, 248 nm, 308 nm and 351 nm. Where comparison is possible with those of Plum
10 et al. (1983), there is good agreement at 308 nm, but at 248 nm and 351 nm the values obtained by Zhu et al. (1996) are substantially higher. Further measure-

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ments are desirable to resolve these differences.

There are insufficient data on quantum yields to recommend values as a function of wavelength under atmospheric conditions. The overall quantum efficiency in the first absorption region is low, but the results of Zhu et al. (1996) suggest that dissociation to 2 HCO radicals is significant at wavelengths less than the dissociation threshold (401 nm). The 'effective' quantum yield of $\phi=0.029$ reported by Plum et al. (1983) is valid only for the particular spectral distribution used in their study. They measured ($\phi\sigma$) integrated over the range 325 nm to 470 nm and this may be used to calculate the rate of photolysis of glyoxal under tropospheric conditions within that spectral region. The validity of this calculation has been supported by chamber studies of Klotz et al. (2000). Both Zhu et al. (1996) and Langford and Moore (1984) obtain a value of $\phi_2 \approx 0.4$ at 308 nm. The fall off in $\phi(\text{HCO})$ below 350 nm may be due to occurrence of molecular channels (1) and (3), which can now be rationalised theoretically.

References

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- Zhu, L., Kellis, D., and Ding, C.-F.: Chem. Phys. Lett., 257, 487, 1996.

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II.A8.202

HOCH₂CHO + hν → products

Primary photochemical transitions

Reaction	$\Delta H_{298}^{\circ}/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
HOCH ₂ CHO + hν → CH ₃ OH + CO (1)	-19.5	
→ HOCH ₂ + HCO (2)	355.3	337
→ HOCH ₂ CO + H (3)	373.8	320

Absorption cross-sections

Wavelength range/nm	Reference	Comments
205–335	Bacher et al., 2001	(a)

Quantum yield data ($\phi = \phi_1 + \phi_2 + \phi_3$)

Measurement	Wavelength range/nm	Reference	Comments
$0.5 < \phi < 1.0$	285 ± 25	Bacher et al., 2001	(b)

Comments

- (a) Diode array spectrophotometric measurements with 90 cm pathlength. Data obtained with 1 nm resolution. Beer-Lambert plot linear over range

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of glycolaldehyde pressure of 0.04–0.6 mbar. Cross-sections tabulated at 1 nm intervals. Peak cross section at 277 nm was $5.49 \times 10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$ with an error of $\pm 15\%$.

- 5 (b) Overall quantum yields for the photolysis of ~ 100 ppm of HOCH_2CHO in air at a total pressure of 1 bar, determined relative to a value of 0.3 determined for acetone in the same equipment. Products and mechanism of the steady state photolysis was deduced, which suggested that Reaction (2) was the main channel but with a significant contribution from Reaction (1).

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Preferred Values

Absorption Cross-Sections at 298 K

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
205	39.1	250	2.36	295	3.59
206	33.7	251	2.50	296	3.46
207	28.7	252	2.65	297	3.29
208	24.6	253	2.82	298	3.17
209	21.2	254	2.97	299	3.02
210	18.1	255	3.09	300	2.90
211	15.3	256	3.21	301	2.74
212	13.0	257	3.39	302	2.51
213	11.2	258	3.59	303	2.26
214	9.40	259	3.75	304	2.07
215	7.84	260	3.89	305	1.91
216	6.49	261	4.02	306	1.77
217	5.30	262	4.13	307	1.64

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λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$
218	4.26	263	4.24	308	1.50
219	3.37	264	4.40	309	1.36
220	2.65	265	4.60	310	1.25
221	2.13	266	4.75	311	1.15
222	1.65	267	4.85	312	1.03
223	1.36	268	4.92	313	0.884
224	1.12	269	4.99	314	0.771
225	0.933	270	5.05	315	0.689
226	0.783	271	5.14	316	0.597
227	0.691	272	5.23	317	0.516
228	0.637	273	5.36	318	0.455
229	0.637	274	5.40	319	0.396
230	0.649	275	5.41	320	0.329
231	0.644	276	5.39	321	0.285
232	0.680	277	5.42	322	0.249
233	0.723	278	5.37	323	0.213
234	0.785	279	5.34	324	0.185
235	0.833	280	5.34	325	0.147
236	0.880	281	5.37	326	0.128
237	0.939	282	5.37	327	0.105
238	1.03	283	5.25	328	0.087
239	1.11	284	5.12	329	0.084
240	1.20	285	5.01	330	0.068
241	1.28	286	4.93	331	0.058
242	1.38	287	4.80	332	0.043
243	1.50	288	4.67	333	0.040

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λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$
244	1.59	289	4.58	334	0.040
245	1.71	290	4.50	335	0.039
246	1.83	291	4.41		
247	1.95	292	4.19		
248	2.09	293	3.96		
249	2.22	294	3.76		

Quantum Yield: $\phi = 0.75 \pm 0.25$ for $\lambda = 260\text{--}310$ nm in 1 bar air

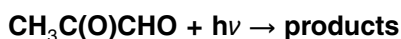
Comments on Preferred Values

The preferred absorption cross-sections are from the study of Bacher et al. (2001), which are the only measurements reported and appear to be reliable. The preferred value for the overall quantum yield is based on the work of Bacher et al. (2001). The value was determined relative to $\phi(\text{CH}_3\text{C}(\text{O})\text{CH}_3)=0.3$ in 1 bar air for the wavelength region 260–310 nm, which is consistent with the work of Gierczak et al. (1998) which forms the basis of the current IUPAC evaluation. The most likely decomposition channel was shown to be HCO production in channel (2), but there is insufficient information to recommend a branching ratio.

References

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 Gierczak, T., Burkholder, J. B., Bauerle, S., and Ravishankara, A. R.: Chem. Phys., 231, 229, 1998.

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Primary photochemical transitions

Reaction		$\Delta H_{298}^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{CH}_3\text{C(O)CHO} + h\nu$	$\rightarrow \text{CH}_4 + 2\text{CO}$ (1)	-24.7	393
	$\rightarrow \text{CH}_3\text{CO} + \text{HCO}$ (2)	304.2	
	$\rightarrow \text{CH}_3\text{CHO} + \text{CO}$ (3)	-5.2	

5 Absorption cross-section data

Wavelength range/nm	Reference	Comments
220–480	Meller et al., 1991	(a)
205–480	Staffelbach et al., 1995	(b)
290–440	Chen et al., 2000	(c)

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Quantum yield data ($\phi = \phi_1 + \phi_2 + \phi_3$)

Measurement	Wavelength range/nm	Reference	Comments
$\phi(2)$			
0.14	240–420	Staffelbach et al., 1995	(d)
1.0	260–320	Koch and Moortgat, 1998	(e)
1.10 ± 0.14	380		
0.47 ± 0.09	400		
0.21 ± 0.06	420		
0.08 ± 0.02	440		
0.82 ± 0.06	290	Chen et al., 2000	(f)
0.89 ± 0.10	300		
0.97 ± 0.08	320		
0.92 ± 0.10	380		
0.56 ± 0.09	400		
0.27 ± 0.04	420		
0.17 ± 0.02	440		

Comments

- 5 (a) Measured over the range 220 nm to 480 nm by conventional UV spectroscopy in a cell of path length 63 cm. Light was detected by a diode array camera and the spectral resolution was 0.07 nm. As well as using methylglyoxal prepared external to the cell, methylglyoxal was generated in situ by the Cl atom-initiated modulated photo-oxidation of hydroxyacetone and the cross-sections were measured over the range 390 nm to 460 nm in these in situ studies.
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- (b) Cross-sections measured in a 90 cm cell using a diode array spectrometer. The spectral resolution was estimated to be 0.6 nm. Pressures in the range 0.13 mbar to 8.0 mbar were used and measurements were made at 248 K, 273 K and 298 K.
- 5 (c) Cross-sections determined from transmission of UV light at 5 nm intervals from tunable dye laser, as a function of $\text{CH}_3\text{C}(\text{O})\text{CHO}$ pressure. Overall uncertainty estimated to be $\sim 10\%$ at all wavelengths, except at 280 and 330 nm, where uncertainties are 20–30% higher.
- 10 (d) Low concentrations of methylglyoxal in an O_2 (20%)/ N_2 (80%) mixture at 1 bar were photolysed with an Xe arc equipped with filters to isolate specific wavelength regions. Products (HCHO , $\text{CH}_3\text{C}(\text{O})\text{OH}$, $\text{CH}_3\text{C}(\text{O})\text{O}_2\text{H}$, CH_3OH , $\text{HC}(\text{O})\text{OH}$, CO , CO_2) were monitored by FTIR. Light intensity calibrated by photolysis of Cl_2 - CH_3OH - O_2 - N_2 mixture. Quantum yields were derived by modeling product yields taking into account a number of important secondary reactions. Average ϕ value quoted.
- 15 (e) Static photolysis of $\text{CH}_3\text{C}(\text{O})\text{CHO}$ in synthetic air. Quantum yields of molecular products CO and HCHO determined by GC. Pressure range 30–900 Torr (0.039–1.2 bar). For the short wavelength band ϕ was independent of pressure and wavelength; in the long wavelength band $\phi(\text{CO})$ showed Stern-Volmer pressure quenching and $\phi(\text{HCHO})$ increased with methylglyoxal pressure; zero pressure values of $\text{CH}_3\text{C}(\text{O})\text{CHO}$ are quoted here. The primary process was attributed to Reaction (2) at all wavelengths.
- 20 (f) Tunable dye laser photolysis of $\text{CH}_3\text{C}(\text{O})\text{CHO}$ with time resolved measurement of HCO concentration by cavity ring down spectroscopy at 613.8 nm. Absorbed flux was determined from photon fluence measurements us-
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ing a calibrated Joulemeter. Absolute yields of HCO calculated from absorption cross sections, $\sigma(\text{HCO})$, determined by in situ calibration using either photo-dissociation of HCHO (at 290–310 nm) or Cl_2 + HCHO mixtures (at 310–440 nm) to produce known amounts of HCO . A weak dependence of $\phi(\text{HCO})$ on $P_{\text{CH}_3\text{COCHO}}$ was observed and the values of ϕ quoted at selected wavelengths are for zero pressure, derived from Stern-Volmer plots. No dependence of $\phi(\text{HCO})$ on N_2 pressure up to 520 mbar was observed in the 270–390 nm region. Pressure quenching by N_2 was observed in the long wavelength band (380–440 nm) and expressions were reported for the wavelength-dependent zero pressure quantum yield $\phi(\text{HCO})_0 = (3.63 \pm 0.32) \times 10^{-7} [\exp(-(5693 \pm 533)/\lambda (\text{nm}))]$ and Stern-Volmer quenching constant by N_2 ($k_Q (\text{Torr}^{-1}) = (1.93 \pm 0.24) \times 10^4 [\exp(-(5639 \pm 497)/\lambda (\text{nm}))]$). Values of $\phi(2)$ for 1 bar air were obtained by extrapolation, and atmospheric photolysis rates were calculated.

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Preferred Values

Absorption cross-sections at 298 K at 5 nm intervals between 225 nm and 410 nm

λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$
225	1.268	320	1.511
230	1.477	325	0.938
235	1.803	330	0.652
240	2.071	335	0.482
245	2.304	340	0.323
250	2.612	345	0.300
255	2.859	350	0.394
260	3.280	355	0.560
265	3.618	360	0.695
270	4.159	365	1.077
275	4.413	370	1.475
280	4.877	375	1.911
285	4.719	380	2.429
290	4.838	385	3.221
295	4.362	390	4.029
300	3.754	395	4.732
305	3.361	400	5.664
310	2.365	405	6.923
315	1.891	410	8.459

7089

Absorption cross-sections at 298 K at 1 nm intervals between 401 nm and 475 nm

λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$
401	5.90	439	11.01
402	6.07	440	9.94
403	6.35	441	10.39
404	6.54	442	10.20
405	6.91	443	10.17
406	7.20	444	11.17
407	7.58	445	9.61
408	7.94	446	8.90
409	8.12	447	9.84
410	8.52	448	9.18
411	8.63	449	10.13
412	9.07	450	8.67
413	9.37	451	6.34
414	9.62	452	6.33
415	9.68	453	6.08
416	9.71	454	4.46
417	10.04	455	3.69
418	10.07	456	3.08
419	10.12	457	2.46

7090

λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$
420	10.21	458	1.81
421	10.34	459	1.28
422	10.51	460	0.914
423	10.45	461	0.795
424	10.15	462	0.642
425	10.34	463	0.479
426	10.24	464	0.332
427	9.84	465	0.268
428	10.01	466	0.227
429	9.94	467	0.187
430	10.41	468	0.160
431	10.53	469	0.133
432	9.79	470	0.108
433	10.64	471	0.099
434	10.54	472	0.089
435	10.81	473	0.077
436	11.13	474	0.067
437	9.99	475	0.062
438	10.59		

Quantum yields for zero pressure at 298 K

$\phi(2)_0 = (3.63 \pm 0.32) \times 10^{-7} [\exp(5693 \pm 533)/\lambda(\text{nm})]$ for $380 < \lambda < 440 \text{ nm}$

5 $\phi(2)_0 = 1.0$ for $280 < \lambda < 380 \text{ nm}$

7091

Comments on Preferred Values

The preferred values of the absorption cross-sections are taken from the work of Meller et al. (1991). The cross-sections of Staffelbach et al. (1995) and Chen et al. (2000) agree to within $<10\%$ with those of Meller et al. (1991) across
5 the whole range of the three studies. Staffelbach et al. (1995) also studied the cross-sections at three different temperatures, 248 K, 273 K, and 298 K. They found little variation in the cross-sections ($\leq 10\%$) over this temperature range.

The recent studies of Koch and Moortgat (1998) and Chen et al. (2000) provide for the first time information on the wavelength-resolved quantum yields
10 for methylglyoxal photolysis, and the latter study gives direct measurements of the initial product of photodissociation by Reaction (2), HCO. This demonstrates conclusively that Reaction (2) is the predominant dissociation channel over the wavelength range 280–440 nm. These results supercede the earlier work of
15 Staffelbach et al. (1995), Raber and Moortgat (1997) and Plum et al. (1983), which used broad-band excitation.

The results of Koch and Moortgat (1998) and Chen et al. (2000) are in good agreement for the zero pressure quantum yields, and for the absence of pressure dependence of $\phi(2)$ at $\lambda < 380 \text{ nm}$. At the longer wavelengths
20 ($380 < \lambda < 440 \text{ nm}$) both studies observed a fall off in $\phi(2)$ with wavelength, and a complex pressure dependence. Koch and Moortgat (1998) interpret their HCHO yields using a mechanism with a reaction of excited methylglyoxal with the ground state. The quenching by N_2 observed by Chen et al. (2000) in the long wavelength band (380–440 nm) did not exhibit Stern-Volmer behaviour, indicating the involvement of more than one excited precursor for HCO. There is
25 a difference of up to a factor of 4 in the extrapolated values for the quantum yields in the range $\lambda = 380\text{--}400 \text{ nm}$ at atmospheric pressure reported from the two studies.

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The preferred values are taken from Chen et al. (2000), since they were determined directly. The expression for the wavelength dependence of $\phi(2)_0$ (zero pressure) at $\lambda > 380$ nm is taken from their work. Values at higher pressures (of air) can be calculated using the expression for the wavelength dependence of the quenching constant obtained by approximating to the Stern Volmer relationship:

$$1/\phi(2) = 1/\phi(2)_0 + k_Q P[N_2 \text{ (Torr)}]$$

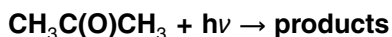
where $k_Q \text{ (Torr}^{-1}\text{)} = (1.93 \pm 0.24) \times 10^4 [\exp(-5639 \pm 497)/\lambda \text{ (nm)}]$. In view of the departure from linearity this leads to an estimated uncertainty up to $\pm 50\%$ in the overall quantum yield at 1 bar.

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7093

II.A8.204



Primary photochemical transitions

Reaction	$\Delta H_{298}^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{CH}_3\text{C(O)CH}_3 + h\nu \rightarrow \text{CH}_3\text{CO} + \text{CH}_3$ (1)	353.6	338
$\rightarrow 2\text{CH}_3 + \text{CO}$ (2)	399.5	299

Absorption cross-section data

Wavelength range/nm	Reference	Comments
202–355	Martinez et al., 1992	(a)
260–360	Hynes et al., 1992	(b)
215–350	Gierczak et al., 1998	(c)
240–350	Yujing and Mellouki, 2000	(d)

Quantum yield data ($\phi = \phi_1 + \phi_2$)

Measurement	Wavelength range/nm	Reference	Comments
$\phi_1 = 0.76\text{--}0.0033$	250–330	Meyrahn et al., 1986	(e)
$\phi = 1.0\text{--}0.016$	248–337	Gierczak et al., 1998	(f)
$\phi_1 = 1.0\text{--}0.062$	280–330	Emrich and Warneck, 2000	(g)
$\phi = 1.0, 0.28$	248, 308	Aloisio and Francisco, 2000	(h)

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Comments

- (a) Cross-sections are the average cross-section over a 1 nm ($\lambda > 280$ nm) or 4 nm ($\lambda < 280$ nm) region centered at the corresponding wavelength. $\sigma_{\max} = 5.07 \times 10^{-20}$ cm² molecule⁻¹ at 278 nm.
- 5 (b) Cross-sections measured as a function of temperature over the range 260 K to 360 K. Data were presented in graphical form and show a marked decrease in cross-section with decreasing temperature at longer wavelengths.
- 10 (c) Measurements made using a diode array spectrometer with a D₂ lamp source and temperature controlled cell with 200 cm path-length. Resolution 0.5 nm. Temperature range 235–298 K. Modest temperature dependence at $\lambda > 300$ nm. Tabulated cross sections at 1 nm intervals and parameterisation of temperature dependence given. $\sigma_{\max} = 4.94 \times 10^{-20}$ cm² molecule⁻¹ ($\pm 5\%$) at 278 nm.
- 15 (d) Commercial diode array spectrometer with a D₂ lamp source and 200 cm pathlength cell at 298 K. Resolution 0.04 nm. Tabulated cross sections at 1 nm intervals given. $\sigma_{\max} = 4.97 \times 10^{-20}$ cm² molecule⁻¹ ($\pm 5\%$) at 278 nm.
- 20 (e) Study of the quantum yield of formation of CO₂ and CO in the photolysis of dilute mixtures of acetone (0.13 mbar to 0.20 mbar) in air (990 mbar) at room temperature. In addition, the quantum yields of formation of peroxyacetyl nitrate (PAN) were measured when trace amounts of NO₂ (1.2×10^{-4} mbar) were added to the reactant mixtures. The listed values of ϕ_1 are the quantum yields of PAN, which were taken as a measure of the extent of primary process (1).
- 7095
- (f) Quantum yield determined using pulsed laser photolysis of static mixtures with measurement of the loss of acetone and formation of products. ϕ was determined as a function of pressure (30–1000 mbar air) and at nine discrete wavelengths in the stated range. At $\lambda > 270$ nm ϕ showed Stern-Volmer pressure quenching. The zero pressure quantum yield increased as wavelength decreased to a value of unity near 290 nm. At 308 nm ϕ was independent of temperature between 298 and 195 K. Expression given for the variation with pressure and wavelength of ϕ for 1 bar air.
- 5 (g) Quantum yields for peroxyacetyl nitrate (PAN) production from photodissociation of acetone (<1%) in air when trace amounts of NO₂ were added to the reactant mixtures. The quantum yields of PAN formation used to determine ϕ_1 at 10 nm intervals in the range given and at total pressures in the range 130–1000 mbar. Stern-Volmer pressure quenching observed at all wavelengths. Results interpreted in terms of the elementary processes involving the first excited singlet and triplet states of acetone, providing rate parameters for the competing processes as a function of excitation energy.
- 10 (h) Relative quantum yield for acetone photodissociation at the specified laser wavelengths with and without water present. At a total pressure of 133 mbar, H₂O up to 12 mbar suppressed the quantum yield, the effect being stronger at 308 nm.
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Preferred Values

Absorption cross-sections at 298 K

λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$
202	0.533	295	3.52	330	0.067
206	0.125	296	3.20	332	0.040
210	0.104	297	3.20	332	0.040
214	0.120	298	3.07	333	0.031
218	0.163	299	2.91	334	0.026
222	0.242	300	2.77	335	0.017
226	0.361	301	2.66	336	0.014
230	0.533	302	2.53	337	0.011
234	0.774	303	2.37	338	0.009
238	1.086	304	2.24	339	0.006
242	1.479	305	2.11	340	0.005
238	1.086	304	2.24	339	0.006
242	1.479	305	2.11	340	0.005
238	1.086	304	2.24	339	0.006
242	1.479	305	2.11	340	0.005
246	1.944	306	1.952	341	0.005
250	2.47	307	1.801	342	0.003
254	3.04	308	1.663	343	0.004
258	3.61	309	1.537	344	0.002
262	4.15	310	1.408	345	0.002
266	4.58	311	1.276	346	0.001
270	4.91	312	1.173	347	0.002
274	5.06	313	1.081	348	0.001

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λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$
278	5.07	314	0.967	349	0.001
280	5.05	315	0.858	350	0.001
281	5.01	316	0.777	351	0.000
282	4.94	317	0.699	352	0.001
283	4.86	318	0.608	353	0.000
284	4.76	319	0.530	354	0.001
285	4.68	320	0.467	355	0.000
286	4.58	321	0.407		
287	4.50	322	0.344		
288	4.41	323	0.287		
289	4.29	324	0.243		
290	4.19	325	0.205		
291	4.08	326	0.168		
292	3.94	327	0.135		
293	3.81	328	0.108		
294	3.67	329	0.086		

Temperature dependent cross-sections: 215–330 nm; 235–298 K

(Source: reference Gierczak et al., 1998)

$$\sigma(\lambda, T) = \sigma(\lambda, 298)(1 + c_1(\lambda)T + c_2(\lambda)T^2)$$

$$c_1(\lambda) = \sum a_i \cdot \lambda^i \quad c_2(\lambda) = \sum b_i \cdot \lambda^i$$

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i	a_i	b_i
0	13.1852	-0.0445238
1	-0.252309	0.000851385
2	0.00192398	-6.48766×10^{-6}
3	-7.30847×10^{-6}	2.46273×10^{-8}
4	1.3832×10^{-8}	-4.65788×10^{-11}
5	-1.04375×10^{-11}	3.51253×10^{-14}

Quantum Yields: 280–340 nm

(Source: Warneck, 2001)

$$1/\phi_{diss} = 1/\phi_s + Ap/T, \text{ where } p = \text{pressure in hPa}$$

$$A = 5.17 \times 10^{12} \exp(-8780.6/\lambda(\text{nm}))$$

$$\phi_s = (1-a)[1 + \exp((\lambda(\text{nm})-307.5)/3)]^{-1} + a, \text{ where } a=0.113$$

Comments on Preferred Values

The preferred absorption cross-sections are based on the measurements of Gierczak et al. (1998). They agree well with the room temperature measurements of Martinez et al. (1992) and Yujing and Mellouki (2000). Over the wavelength region 260 nm to 320 nm these cross-sections are within 5% of earlier recommendations based on the data of Calvert and Pitts (1966) and Meyrahn et al. (1986). The cross-sections reported by Hynes et al. (1992) at room temperature contain large error limits at 320 nm and 340 nm but are in reasonable agreement with those recommended here. The temperature dependence is based on the expression given by Gierczak et al. (1998).

The two recent studies (Gierczak et al., 1998; Emrich and Warneck, 2000) of the quantum yield for photodissociation of acetone have provided, for the first time, reliable

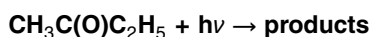
7099

wavelength and pressure dependence of ϕ and ϕ_1 . These studies are essentially in agreement. Gierczak et al. (1998) gave an empirical algorithm for the overall dissociation quantum yield in air as a function of wavelength and pressure. Warneck (2001) used the results of Emrich and Warneck (2000) to derive an algorithm consistent with the fundamental processes occurring in acetone photolysis under atmospheric conditions, which we adopt for the present recommendation. It is based on analysis of the wavelength dependence of the zero pressure quantum yields and temperature corrected Stern-Volmer quenching parameters. Dissociation occurs exclusively from the excited singlet state with an increasing fraction of decomposition via channel (2) at wavelengths below the threshold for this process at 299 nm.

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Primary photochemical transitions

Reaction		$\Delta H_{298}^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{CH}_3\text{C}(\text{O})\text{C}_2\text{H}_5 + h\nu$	$\rightarrow \text{CH}_3 + \text{C}_2\text{H}_5\text{CO}$ (1)	352.6	339
	$\rightarrow \text{C}_2\text{H}_5 + \text{CH}_3\text{CO}$ (2)	349.4	342
	$\rightarrow \text{CH}_3 + \text{C}_2\text{H}_5 + \text{CO}$ (3)	395.3	

5 Absorption cross-section data

Wavelength range/nm	Reference	Comments
202–355	Martinez et al., 1992	(a)
240–350	Yujing and Mellouki, 2000	(b)

Quantum yield data ($\phi = \phi_1 + \phi_2 + \phi_3$)

Measurement	Wavelength range/nm	Reference	Comments
ϕ_1 0.34 (1000 mbar) 0.89 (68 mbar)	275–380	Raber and Moortgat, 1987	(c)

7101

Comments

- (a) Conventional double-beam spectrophotometric measurements on mixtures of 2-butanone and argon at a resolution of 0.5 nm. The cross-sections are given as averages over a 1 nm ($\lambda > 280$ nm) or 4 nm ($\lambda < 280$ nm) region centered on the corresponding wavelength. $\sigma_{\text{max}} = 5.77 \times 10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$ at 278 nm.
- (b) Diode array spectrometer measurements on pure 2-butanone at a resolution of 0.04 nm. The cross-sections are given over 1 nm intervals. Precision based on observed standard deviation was within $\pm 5\%$. $\sigma_{\text{max}} = 5.65 \times 10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$ at 278 nm.
- (c) 2-butanone was photolyzed in synthetic air at several pressures in the range 68 mbar to 1 bar using a broad band radiation source (275 nm to 380 nm) and the product yields were monitored by FTIR. The quantum yield for photolysis of 2-butanone was found to be pressure dependent decreasing from 0.89 at 68 mbar to 0.34 at 1 bar. They also conclude that photolysis over the wavelength region used occurs to the extent of 80–90% by channel 2. These results were derived by modelling the secondary chemistry in the system.

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Preferred Values

Absorption cross-sections at 298 K

λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$
202	1.412	292	4.60	324	0.229
206	0.192	293	4.42	325	0.189
210	0.160	294	4.24	326	0.156
214	0.183	295	4.08	327	0.129
218	0.225	296	3.93	328	0.105
222	0.290	297	3.79	329	0.085
226	0.391	298	3.65	330	0.067
230	0.534	299	3.48	331	0.054
234	0.742	300	3.30	332	0.042
238	1.029	301	3.10	333	0.033
242	1.410	302	2.89	334	0.025
246	1.886	303	2.69	335	0.020
250	2.45	304	2.50	336	0.014
254	3.09	305	2.33	337	0.011
258	3.74	306	2.17	338	0.008
262	4.39	307	2.02	339	0.007
266	4.96	308	1.876	340	0.005
270	5.40	309	1.727	341	0.005
274	5.68	310	1.575	342	0.003
278	5.77	311	1.423	343	0.003
280	5.74	312	1.276	344	0.002
281	5.72	313	1.136	345	0.001
282	5.68	314	1.009	346	0.001

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λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$
283	5.62	315	0.896	347	0.000
284	5.54	316	0.794	348	0.001
285	5.44	317	0.697	349	0.000
286	5.35	318	0.611	350	0.000
287	5.26	319	0.531	351	0.000
288	5.17	320	0.457	352	0.001
289	5.06	321	0.389	353	0.000

Quantum Yields

$\phi = 0.34$ for $\lambda = 275\text{--}380$ nm at 1 bar

Comments on Preferred Values

- 5 The preferred absorption cross-sections are taken from the measurements of Martinez et al. (1992) over the wavelength region 220 nm to 350 nm. The values at the band maximum are 5% higher than the recent data of Yujing and Mellouki (2000), but 5% lower than those of McMillan, reported by Calvert and Pitts (1966). Raber and Moortgat (1987) have also given a spectrum which is in good agreement with these
- 10 cross-sections.

The only quantum yield measurements are those of Raber and Moortgat (1987), which forms the basis for the preferred quantum yield at 1 bar. This data needs further experimental support.

7104

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7105

II.A8.206



Primary photochemical transitions

Reaction	$\Delta H_{298}^{\circ}/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{CH}_2=\text{C}(\text{CH}_3)\text{CHO} + h\nu \rightarrow \text{CH}_2=\text{CCH}_3 + \text{HCO}$ (1)	320.5	373.1
$\rightarrow \text{C}_3\text{H}_6 + \text{CO}$ (2)	16.1	7428
$\rightarrow \text{H} + \text{CH}_2=\text{C}(\text{CH}_3)\text{CO}$ (3)		

5 Absorption cross-section data

Wavelength range/nm	Reference	Comments
250–395	Gierczak et al., 1997	(a)
235–400	Raber and Moortgat., 1996	(b)

Quantum yield data ($\phi = \phi_1 + \phi_2$)

Measurement	Wavelength range/nm	Reference	Comments
$\phi = 0.008$ (865 mbar)	308	Gierczak et al., 1997	(c)
$\phi = 0.005$ (33 mbar)	208		
$\phi = 0.005$ (865 mbar)	351		
$\phi = 0.003$ (33 mbar)	351		
$\phi < 0.05$ at 1 bar	275–370	Raber and Moortgat, 1996	(d)

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Comments

- (a) Measurements made using a diode array spectrometer with a D₂ lamp source and temperature controlled cell with 200 cm path-length. Resolution 0.5 nm. Temperature range 250–298 K. Tabulated cross sections at 1 nm intervals. $\sigma_{\max}=7.2\times 10^{-20}$ cm² molecule⁻¹ ($\pm 5\%$) at 331 nm and $\sigma=(2.21\pm 0.03)\times 10^{-17}$ cm² molecule⁻¹ at 213.86 nm (Zn lamp source). Small increase with decreasing temperature at λ max.
- (b) Measurements made at 298 K using a diode array spectrometer with a D₂ lamp source. $\sigma_{\max}=7.64\times 10^{-20}$ cm² molecule⁻¹ ($\pm 5\%$) at 330.7 nm.
- (c) Quantum yield determined using pulsed laser photolysis of static mixtures with measurement of the loss of CH₂=C(CH₃)CHO (methacrolein) by GC. ϕ was determined at pressures of 25 and 650 Torr (33 and 865 mbar) air, and at 308 and 351 nm. ϕ increased with pressure by a factor of ~ 2 over the range. Propene not observed as a product, in contrast to other studies.
- (d) Broad band photolysis of static mixtures (bath gas is air) with measurement of the loss of CH₂=C(CH₃)CHO and formation of products (C₂H₄, C₃H₆, C₂H₂, CO, CO₂, HCHO) by FTIR. Quantum yield from loss of CH₂=C(CH₃)CHO and formation of CO. Indication of a weak pressure effect with ϕ (50 Torr)/ ϕ (760 Torr) ~ 2 . No firm information on the relative importance of the photolysis channels could be obtained from the product yields.

7107

Preferred Values

Absorption cross-sections at 298 K

λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$
250	0.207	300	3.44	350	4.16
251	0.194	301	3.61	351	3.85
252	0.187	302	3.76	352	3.89
253	0.180	303	3.91	353	4.35
254	0.178	304	4.04	354	4.31
255	0.177	305	4.19	355	4.14
256	0.180	306	4.40	356	3.62
257	0.180	307	4.58	357	3.53
258	0.186	308	4.71	358	3.46
259	0.193	309	4.81	359	3.81
260	0.201	310	4.92	360	5.05
261	0.211	311	5.13	361	4.28
262	0.224	312	5.35	362	3.61
263	0.241	313	5.50	363	2.86
264	0.263	314	5.61	364	2.68
265	0.283	315	5.70	365	2.33
266	0.305	316	5.87	366	1.92
267	0.333	317	6.04	367	1.62
268	0.363	318	6.19	368	1.40
269	0.398	319	6.28	369	1.31
270	0.436	320	6.27	370	1.42
271	0.479	321	6.18	371	1.67
272	0.520	322	6.21	372	1.53

7108

λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$
273	0.567	323	6.34	373	1.43
274	0.616	324	6.58	374	1.08
275	0.673	325	6.74	375	0.977
276	0.732	326	6.73	376	1.000
277	0.793	327	6.68	377	1.07
278	0.863	328	6.83	378	1.35
279	0.936	329	7.07	379	2.18
280	1.01	330	7.15	380	1.30
281	1.09	331	7.16	381	0.984
282	1.18	332	7.03	382	0.555
283	1.26	333	6.69	383	0.456
284	1.35	334	6.41	384	0.364
285	1.45	335	6.08	385	0.331
286	1.56	336	5.97	386	0.246
287	1.67	337	6.25	387	0.205
288	1.79	338	6.38	388	0.181
289	1.90	339	6.37	389	0.161
290	2.03	340	6.24	390	0.147
291	2.16	341	6.02	391	0.156
292	2.28	342	5.98	392	0.159
293	2.40	343	6.58	393	0.153
294	2.52	344	6.79	394	0.149
295	2.68	345	6.53	395	0.123
296	2.85	346	6.11		
297	2.99	347	5.63		
298	3.13	348	5.22		
299	3.26	349	4.55		

7109

Quantum Yields

No recommendation

Comments on Preferred Values

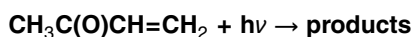
The preferred absorption cross-sections are based on the measurements of Gierzak et al. (1997). The peak cross-section agrees within 10% with the measurements of Raber and Moortgat (1996).

The two studies (Gierczak et al., 1997; Raber and Moortgat, 1996) of the quantum yield for photodissociation of $\text{CH}_2=\text{C}(\text{CH}_3)\text{CHO}$ are not in good agreement, although both indicate very low quantum efficiencies with $\phi < 0.05$. No firm recommendation can be given.

References

- Gierczak, T., Burkholder, J. B., Talukdar, R. K., Mellouki, A., Barone, S. B., and Ravishankara, A. R.: J. Photochem. Photobiol. A: Chem., 110, 1, 1997.
- Raber, W. H. and Moortgat, G. K.: in: 'Progress and Problems in Atmospheric Chemistry', edited by: Barker, J., pp. 318–373, World Scientific Publ. Co., Singapore, 1996.

7110



Primary photochemical transitions

Reaction	$\Delta H_{298}^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{CH}_3\text{C}(\text{O})\text{CH}=\text{CH}_2 + h\nu \rightarrow \text{CH}_2=\text{CHCO} + \text{CH}_3$ (1)		
$\rightarrow \text{C}_3\text{H}_6 + \text{CO}$ (2)	24.7	4842
$\rightarrow \text{C}_2\text{H}_3 + \text{CH}_3\text{CO}$ (3)	405	295.3

5 Absorption cross-section data

Wavelength range/nm	Reference	Comments
250–395	Gierczak et al., 1997	(a)
235–400	Raber and Moortgat, 1996	(b)

Quantum yield data ($\phi = \phi_1 + \phi_2$)

Measurement	Wavelength range/nm	Reference	Comments
$\phi = 0.16$ (33 mbar)	308	Gierczak et al., 1997	(c)
$\phi = 0.04$ (33 mbar)	337		
$\phi = 0.01$ (33 mbar)	351		
$\phi < 0.04$ (1 bar)	275–370	Raber and Moortgat, 1996	(d)

7111

Comments

- (a) Measurements made using a diode array spectrometer with a D_2 lamp source and temperature controlled cell with 200 cm path-length. Resolution 0.5 nm. Temperature range 250–298 K. Tabulated cross sections at 1 nm intervals $\sigma_{\text{max}} = 7.2 \times 10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$ ($\pm 5\%$) at 331 nm and $\sigma = (6.6 \pm 0.35) \times 10^{-18} \text{ cm}^2 \text{ molecule}^{-1}$ at 213.86 nm (Zn lamp source). Small temperature dependence at λ max (<2% increase at 250 K).
- (b) Measurements made at 298 K using a diode array spectrometer with a D_2 lamp source. $\sigma_{\text{max}} = 6.5 \times 10^{-20} \text{ cm}^2 \text{ molecule}^{-1}$ ($\pm 5\%$) at 330.7 nm.
- (c) Quantum yield determined using pulsed laser photolysis of static mixtures with measurement of the loss of $\text{CH}_3\text{C}(\text{O})\text{CH}=\text{CH}_2$ (methyl vinyl ketone) by GC. ϕ was determined at pressures of 25 and 650 Torr (33 and 850 mbar) air, and at 308, 337 and 351 nm. ϕ showed pressure quenching at 308 and 337 nm but not at 351 nm. Expression given for the variation with pressure (for air up to 1 bar) and wavelength of ϕ : $\phi_0(\lambda, P) < \exp[-0.055(\lambda-308)] / (5.5 + 9.2 \times 10^{-19} [M])$ where λ is in nm and M in molecule cm^{-3} .
- (d) Broad band photolysis of static mixtures (bath gas is air) with measurement of the loss of $\text{CH}_3\text{C}(\text{O})\text{CH}=\text{CH}_2$ and formation of products (C_3H_6 , CO, HCHO with minor amounts of CO_2 , $\text{HC}(\text{O})\text{OH}$, CH_3OH , $\text{CH}_3(\text{O})\text{OH}$ and $\text{C}_2\text{H}_3\text{C}(\text{O})\text{OH}$) by FTIR. Quantum yield from loss of $\text{CH}_3\text{C}(\text{O})\text{CH}=\text{CH}_2$ and formation of CO. Indication of a weak pressure effect with $\phi(50 \text{ Torr})/\phi(760 \text{ Torr}) \sim 2$. The relative importance of the photolysis channels could not be obtained accurately from the product yields.

7112

Preferred Values

Absorption cross-sections at 298 K

λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$
250	0.241	299	3.70	348	5.77
251	0.241	300	3.87	349	5.47
252	0.224	301	4.04	350	5.20
253	0.241	302	4.20	351	4.94
254	0.241	303	4.35	352	4.72
255	0.258	304	4.51	353	4.53
256	0.275	305	4.66	354	4.32
257	0.275	306	4.82	355	4.15
258	0.293	307	4.96	356	4.03
259	0.310	308	5.13	357	3.94
260	0.327	309	5.30	358	3.89
261	0.361	310	5.44	359	3.89
262	0.379	311	5.58	360	3.68
263	0.396	312	5.73	361	3.60
264	0.430	313	5.87	362	3.49
265	0.465	314	6.02	363	3.36
266	0.499	315	6.14	364	3.29
267	0.534	316	6.28	365	3.03
268	0.568	317	6.42	366	2.77
269	0.620	318	6.54	367	2.50
270	0.654	319	6.63	368	2.20
271	0.706	320	6.70	369	2.01
272	0.757	321	6.76	370	1.88

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λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$
273	0.809	322	6.83	371	1.74
274	0.878	323	6.85	372	1.58
275	0.929	324	6.88	373	1.48
276	0.998	325	6.95	374	1.39
277	1.08	326	7.02	375	1.31
278	1.15	327	7.09	376	1.26
279	1.24	328	7.16	377	1.24
280	1.33	329	7.23	378	1.20
281	1.41	330	7.28	379	1.20
282	1.50	331	7.30	380	1.05
283	1.60	332	7.26	381	0.981
284	1.70	333	7.18	382	0.912
285	1.81	334	7.04	383	0.878
286	1.91	335	6.94	384	0.929
287	2.03	336	6.85	385	0.757
288	2.15	337	6.70	386	0.637
289	2.29	338	6.56	387	0.534
290	2.43	339	6.47	388	0.447
291	2.55	340	6.44	389	0.396
292	2.67	341	6.42	390	0.344
293	2.81	342	6.35	391	0.310
294	2.93	343	6.35	392	0.293
295	3.08	344	6.30	393	0.275
296	3.24	345	6.23	394	0.241
297	3.39	346	6.14	395	0.207
298	3.56	347	6.08		

7114

Quantum Yields

$$\phi_0(\lambda, P) = \exp[-0.055(\lambda-308)] / (5.5 + 9.2 \times 10^{-19}[M])$$

where λ is in nm and M in molecule cm^{-3} .

Comments on Preferred Values

5 The preferred absorption cross-sections are based on the measurements of Gierzak et al. (1997). They agree well with the measurements of Raber and Moortgat (1996) within 10% over the range 290–365 nm.

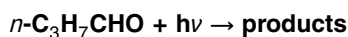
The two studies (Gierzak et al., 1997; Raber and Moortgat, 1996) of the quantum yield for photodissociation of $\text{CH}_3\text{C}(\text{O})\text{CH}=\text{CH}_2$ are essentially in agreement. Both show low efficiency for photolysis ($\phi < 0.1$) and a weak pressure dependence in ϕ (ϕ decreases with increasing pressure between 25 Torr (33 mbar) and 760 Torr (1 bar)).
10 Gierzak et al. (1997) also observe an increase at shorter wavelength. We recommend the empirical algorithm given by Gierzak et al. (1997) for the overall dissociation quantum yield in air as a function of wavelength and pressure, although this should
15 be considered an upper limit. The results of Raber and Moortgat (1996) indicate that the photolysis channel leading to propene (channel 2) accounts for 60% of the $\text{CH}_3\text{C}(\text{O})\text{CH}=\text{CH}_2$ loss, with the balance occurring by the two radical channels (1) and (3) with equal probability.

References

- 20 Gierczak, T., Burkholder, J. B., Talukdar, R. K., Mellouki, A., Barone, S. B., and Ravishankara, A. R.: J. Photochem. Photobiol. A: Chem., 110, 1, 1997.
Raber, W. H. and Moortgat, G. K.: in: 'Progress and Problems in Atmospheric Chemistry', edited by: Barker, J., pp. 318–373, World Scientific Publ. Co., Singapore, 1996.

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II.A8.208



Primary photochemical transitions

Reaction		$\Delta H_{298}^\circ / \text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}} / \text{nm}$
$n\text{-C}_3\text{H}_7\text{CHO} \rightarrow n\text{-C}_3\text{H}_7 + \text{HCO}$	(1)	355.7	336
$\rightarrow \text{C}_3\text{H}_8 + \text{CO}$	(2)	-3.2	
$\rightarrow \text{C}_2\text{H}_4 + \text{CH}_2\text{CHOH}$	(3)	~136	880
$\rightarrow \text{CH}_3 + \text{CH}_2\text{CH}_2\text{CHO}$	(4)		
5 $\rightarrow \text{C}_3\text{H}_6 + \text{HCHO}$	(5)	123.4	969

Absorption cross-section data

Wavelength range/nm	Reference	Comments
202–365	Martinez et al., 1992	(a)
240–350	Tadic et al., 2001	(b)

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Quantum yield data ($\phi = \phi_1 + \phi_2 + \phi_3 + \phi_4 + \phi_5$)

Measurement	Wavelength range/nm	Reference	Comments
$\phi = 0.48 \pm 0.02$ (100 Torr air)	275–380	Tadic et al., 2001	(c)
$\phi = 0.38 \pm 0.02$ (700 Torr air)	275–380		
$\phi_1 = 0.21$ (1 bar, air)	275–380		
$\phi_3 = 0.10$ (1 bar, air)	275–380		

Comments

- 5 (a) Absorption measurements as a function of C_3H_7CHO pressure using a diode array spectrometer. Cross-sections are the average cross-section over a 1 nm ($\lambda > 280$ nm) or 4 nm ($\lambda < 280$ nm) region centered at the corresponding wavelength.
- (b) Cross-sections determined from absorption measurements as a function of C_3H_7CHO pressure using a diode array spectrometer, with resolution of 0.25 nm.
- 10 (c) Broad band (275–280 nm) steady-state photolysis of C_3H_7CHO in the presence of air at 298 K. Products measured by FTIR were CO, C_2H_4 , CH_3CHO , CH_2CHOH and CO_2 . Quantum yields of CO and C_2H_6 were measured as a function of wavelength and pressure, to provide values of ϕ_1 and ϕ_3 . Overall quantum yields were pressure dependent over range 100–700 Torr, with the following Stern-Volmer expression: $1/\phi = 1.81 + (1.931 \times 10^{-3}) P[\text{Torr}]$.

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Preferred Values**Absorption cross-sections at 298 K**

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
202	0.0178	295	6.03	330	0.868
206	0.0316	296	5.87	331	0.734
210	0.0475	297	5.69	332	0.647
214	0.0623	298	5.56	333	0.602
218	0.0771	299	5.46	334	0.554
222	0.0850	300	5.42	335	0.485
226	0.102	301	5.43	336	0.417
230	0.133	302	5.44	337	0.346
234	0.202	303	5.43	338	0.285
238	0.316	304	5.32	339	0.242
242	0.488	305	5.08	340	0.215
246	0.724	306	4.79	341	0.191
250	1.05	307	4.50	342	0.144
254	1.45	308	4.29	343	0.093
258	1.93	309	4.15	344	0.059
262	2.52	310	4.07	345	0.041
266	3.09	311	4.00	346	0.031
270	3.81	312	3.92	347	0.026
274	4.34	313	3.82	348	0.023
278	5.02	314	3.69	349	0.018
280	5.18	315	3.46	350	0.015
281	5.22	316	3.17	351	0.014
282	5.30	317	2.85	352	0.012

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λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$
283	5.45	318	2.57	353	0.010
284	5.65	319	2.37	354	0.008
285	5.81	320	2.25	355	0.006
286	5.90	321	2.18	356	0.005
287	5.89	322	2.07	357	0.004
288	5.85	323	1.96	358	0.003
289	5.80	324	1.82	359	0.002
290	5.78	325	1.69	360	0.002
291	5.83	326	1.55	361	0.002
292	5.93	327	1.39	362	0.001
293	6.05	328	1.22	363	0.001
294	6.10	329	1.04	364	0.001

Quantum Yields

$\phi_3 = 0.10$; $\phi_1 = 0.21$ for 1 bar air, over the wavelength range 290–380 nm.

Comments on Preferred Values

- 5 The preferred absorption cross-sections are from the measurements of Martinez et al. (1992) The cross-section data of Tadic et al. (2001) are within 5% of the Martinez data over the wavelength region 260 nm to 350 nm.

10 The photolysis of long chain ($>C_4$) aldehydes undergo Norrish type I (ϕ_1) and Norrish type II (ϕ_3) dissociation in the first absorption band (260–340 nm). Channels 2, 4 and 5 are unimportant at wavelengths >280 nm. The indirect quantum yield measurements for the two channels, ϕ_1 and ϕ_3 reported by Tadic et al. (2001) for photolysis of $n\text{-C}_3\text{H}_7\text{CHO}$ appear reliable and are recommended here. Quantum yield measure-

7119

- 5 ments for the channel producing HCO (ϕ_1) from n -pentanal, obtained in the same study, agree with direct measurements for n -pentanal obtained by Cronin and Zhu (1998) using cavity ring-down detection of HCO. Weak pressure quenching of reported by Tadic et al. (2001) for photolysis of $n\text{-C}_3\text{H}_7\text{CHO}$ can be used to obtain quantum yields at lower atmospheric pressures, assuming constant branching ratio for channels 1 and 3.

References

- Cronin, T. J. and Zhu, L.: J. Phys. Chem. A, 102, 10 274, 1998.
 Martinez, R. D., Buitrago, A. A., Howell, N. W., Hearn, C. H., and Joens, J. A.: Atmos. Environ., 26A, 785, 1992.
 10 Tadic, J., Juranic, I., and Moortgat, G. K.: J. Photchem. Photobiol. A: Chem., 143, 169, 2001.

CH₃OOH + hν → products**Primary photochemical transitions**

Reaction		$\Delta H_{298}^{\circ}/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
CH ₃ OOH + hν → CH ₃ O + HO	(1)	185	645
→ CH ₃ + HO ₂	(2)	292	410
→ CH ₃ O ₂ + H	(3)	358	334

5 **Absorption cross-section data**

Wavelength range/nm	Reference	Comments
210–365	Vaghjiani and Ravishankara, 1989	(a)

Quantum yield data ($\phi = \phi_1 + \phi_2 + \phi_3$)

Measurement	Wavelength range/nm	Reference	Comments
$\phi_1 = 1.00 \pm 0.18$	248	Vaghjiani and Ravishankara, 1990	(b)

Comments

- 10 (a) CH₃OOH prepared by methylation of H₂O₂ and shown by ¹H NMR to be >97% pure [major impurity C₂H₅OC₂H₅]. A diode-array spectrometer was used to make

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5 relative absorption measurements over the whole wavelength range and the results were put on an absolute basis by measurement of the cross-sections at 213.9 nm (Zn line), and at 298.1 nm, 326.1 nm, 340.4 nm and 361.1 nm using Cd lines. The CH₃OOH concentration was determined by trapping the vapor at 77 K and titrating with Fe²⁺ or I⁻.

- (b) Direct measurement of products, HO by LIF, and O(³P) and H atoms by resonance fluorescence. Quantum yields for the formation of O(³P) and H atoms of <0.007 and 0.038±0.007, respectively, were obtained.

Preferred Values

Absorption cross-sections at 298 K

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
210	31.2	290	0.691
215	20.9	295	0.551
220	15.4	300	0.413
225	12.2	305	0.313
230	9.62	310	0.239
235	7.61	315	0.182
240	6.05	320	0.137
245	4.88	325	0.105
250	3.98	330	0.079
255	3.23	335	0.061
260	2.56	340	0.047
265	2.11	345	0.035
270	1.70	350	0.027
275	1.39	355	0.021
280	1.09	360	0.016
285	0.863	365	0.012

Quantum Yields

5 $\phi_1 = 1.0$ for $\lambda > 290$ nm.

7123

Comments on Preferred Values

The preferred absorption cross-section data are those of Vaghjiani and Ravishankara (1989), which are approximately 25% lower than the previously recommended data of Molina and Arguello (1979). The source of the discrepancy appears to lie in the determination of the concentrations of CH_3OOH in the absorption cell. Molina and Arguello (1979) used a bubbler containing Fe^{2+} solution, which Vaghjiani and Ravishankara (1989) showed does not give quantitative trapping.

On the basis of the results of Vaghjiani and Ravishankara (1990), who showed that $\phi_{\text{OH}} \sim 1.0$ at $\lambda=248$ nm, we recommend that the atmospheric photolysis of CH_3OOH ϕ_1 be taken to be unity for wavelengths >290 nm.

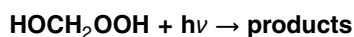
References

- Molina, M. J. and Arguello, G.: Geophys. Res. Lett., 6, 953, 1979.
Vaghjiani, G. L. and Ravishankara, A. R.: Geophys. Res., 94, 3487, 1989.
Vaghjiani, G. L. and Ravishankara, A. R.: J. Chem. Phys., 92, 996, 1990.

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7124

II.A8.210



Primary photochemical transitions

Reaction	$\Delta H_{298}^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{HOCH}_2\text{OOH} + h\nu \rightarrow \text{HOCH}_2\text{O} + \text{HO}$	~188	~637

5 Absorption cross-section data

Wavelength range/nm	Reference	Comments
205–360	Bauerle and Moortgat, 1999	(a)

Quantum yield data

No data

Comments

- 10 (a) HOCH_2OOH prepared by liquid phase reaction of HCHO with excess H_2O_2 . A diode-array spectrometer was used to make relative absorption measurements over the whole wavelength range. The HOCH_2OOH concentration was measured in situ by FTIR using a peak IR absorption coefficient of $\sigma = 7.4 \times 10^{-19} \text{ cm}^2 \text{ molecule}^{-1}$ at 1049 cm^{-1} . This cross section was determined in the same system by quantitative measurement of the decomposition products of HOCH_2OOH
- 15

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(HCOOH and HCHO) using the yields of these products. The decomposition channels were previously established by Neeb et al. (1997).

Preferred Values

Absorption cross-sections at 298 K

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
205	26.91	290	0.63
210	22.56	295	0.51
215	18.75	300	0.40
220	15.46	305	0.29
225	12.47	310	0.22
230	10.06	315	0.18
235	7.89	320	0.13
240	5.98	325	0.10
245	4.68	330	0.073
250	3.78	335	0.059
255	3.88	340	0.045
260	2.31	345	0.036
265	1.81	350	0.028
270	1.48	355	0.022
275	1.21	360	0.017
280	0.93	365	0.012
5 285	0.75		

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Quantum Yields

$\phi_1 = 1.0$ for $\lambda > 290$ nm.

Comments on Preferred Values

The preferred absorption cross-section data are those of Bauerle and Moortgat (1999) which are the only data reported for the absorption spectrum of HOCH₂OOH. The values are close to those recommended for CH₃OOH based on the measurements of Vaghjiani and Ravishankara (1990). The recommended quantum yields are based on an analogy with methyl hydroperoxide. Other channels may occur in photolysis at shorter wavelengths.

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II.A8.211



Primary photochemical transitions

Reaction		$\Delta H_{298}^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{CH}_3\text{ONO}_2 + h\nu \rightarrow \text{CH}_3\text{O} + \text{NO}_2$	(1)	170.1	703
$\rightarrow \text{HCHO} + \text{HONO}$	(2)	-68.4	
$\rightarrow \text{CH}_3\text{ONO} + \text{O}(^3\text{P})$	(3)	303.6	394

Absorption cross-section data

Wavelength range/nm	Reference	Comments
270–315	Roberts and Fajer, 1989	(a)
220–335	Rattigan et al., 1992	(b)
236–344	Talukdar et al., 1997	(c)

Quantum yield data ($\phi = \phi_1 + \phi_2 + \phi_3$)

Measurement	Wavelength range/nm	Reference	Comments
$\phi_1 = 0.9 \pm 0.2$	248	Talukdar et al., 1997	(d)
$\phi_1 = 1.3 \pm 0.3$	248		(e)
$\phi_2 < 0.05$	248		(d)
$\phi_3 < 0.1$	248		(d)

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Comments

- (a) Absorption cross-sections were measured in a 10.2 cm pathlength cell, using a single-beam spectrometer with a photometric accuracy of $\pm 0.5\%$. Numerical data for cross-sections are available from Roberts (1990).
- 5 (b) Cross-sections were measured with a dual-beam diode array spectrometer with a spectral resolution of 0.3 nm over the temperature range 238 K to 294 K. The temperature dependence of σ was found to obey the equation, $\ln\sigma(\lambda, T) = \ln\sigma(\lambda, 298 \text{ K}) + B(\lambda)(T - 298)$.
- 10 (c) Absorption cross-sections were measured with a diode-array spectrometer. Absorbances were measured in 80 nm blocks, which were assembled to construct the spectrum. Cross-sections were measured at 298 K and 6 other temperatures in the range 240 K to 360 K. The temperature dependence of σ was found to obey the equation $\ln\sigma(\lambda, T) = \ln\sigma(\lambda, 298 \text{ K}) + B(\lambda)(T - 298)$. The absorption cross-section at 213.86 nm (Zn line) was also measured. A value of $(1.67 \pm 0.08) \times 10^{-18} \text{ cm}^2$ molecule⁻¹ was obtained.
- 15 (d) Photolysis of methyl nitrate at 248 nm and 298 K in the presence of excess O₂ to scavenge radicals. Actinometry based on O₃ photolysis or N₂O photolysis in experiments carried out with 193 nm radiation. Yields of the products CH₃ONO, CH₂O, NO₂ and NO₃ were measured by UVA, NO₃ by time-resolved absorption at 662 nm, and H and O by resonance fluorescence. Channels leading to H, O, and NO₃ were found to make negligible contribution at 248 nm, but high yields of O were obtained at 193 nm. Small yields of HO observed were attributed to secondary reactions.
- 20 (e) Same technique as in (d), but NO was used to scavenge radicals instead of O₂.

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Preferred Values

Absorption cross-sections at 298 K

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
240	5.88	295	0.568
245	4.19	300	0.360
250	3.59	305	0.214
255	3.30	310	0.134
260	3.06	315	0.0633
265	2.77	320	0.0316
270	2.39	325	0.0144
275	2.00	330	0.00661
280	1.58	335	0.00274
285	1.19	340	0.00122
290	0.85		

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Temperature dependence of the absorption cross-sections over the range 240 K to 330 K

λ/nm	$10^3 B/K^{-1}$	λ/nm	$10^3 B/K^{-1}$
240	3.48	290	4.04
245	3.29	295	4.47
250	2.96	300	4.94
255	2.82	305	5.56
260	2.83	310	6.33
265	2.92	315	7.34
270	3.08	320	8.74
275	3.28	325	9.97
280	3.51	330	13.6
285	3.78		

The tabulated values of B may be used to calculate $\sigma(\lambda, T)$ using the relationship
 $\ln \sigma(\lambda, T) = \ln \sigma(\lambda, 298 \text{ K}) + B(\lambda)(T - 298)$.

Quantum Yields

5 $\phi_1 = 1.0$ for $\lambda \geq 248 \text{ nm}$.

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are average values from the data of Roberts and Fajer (1989), Rattigan et al. (1992) and Talukdar et al. (1997), which are in excellent agreement over the whole wavelength range of the measurements. They are also in reasonable agreement with the absorption spectrum reported by Calvert and Pitts (1966) and with the cross-sections reported by Maria et

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al. (1973). The results of Taylor et al. (1980) are consistently higher than the values from the other studies (Roberts and Fajer, 1989; Rattigan et al., 1992; Talukdar et al., 1997; Calvert and Pitts, 1966; Maria et al., 1973), by as much as a factor of two in the region 290 nm to 330 nm.

5 The two studies of the effect of temperature on the cross-sections are also in very good agreement with differences only appearing at wavelengths beyond 320 nm where the absorption cross-sections become very small and the precision of the measurements falls away. The preferred values of $B(\lambda)$ are those of Talukdar et al. (1997) averaged over 5 nm intervals around the given wavelength.

10 The preferred value of the quantum yield is based on the work of Talukdar et al. (1997) who concluded that the photodissociation of methyl nitrate at 248 nm produces NO_2 and CH_3O with a quantum yield of essentially unity. This is in accord with the general assumption (Roberts, 1990) that the lack of structure in the absorption spectrum of RONO_2 molecules indicates that the quantum yield for dissociation is unity, and is supported by the recently measured value for ethyl nitrate of $\phi_1 = (1.0 \pm 0.1)$ at 308 nm (Zhu and Ding, 1997).

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II.A8.212



Primary photochemical transitions

Reaction		$\Delta H_{298}^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{C}_2\text{H}_5\text{ONO}_2 + h\nu$	$\rightarrow \text{C}_2\text{H}_5\text{O} + \text{NO}_2$ (1)	171.7	697
	$\rightarrow \text{CH}_3\text{CHO} + \text{HONO}$ (2)	-91.3	
	$\rightarrow \text{C}_2\text{H}_5\text{ONO} + \text{O}({}^3\text{P})$ (3)	299.4	400

5 Absorption cross-section data

Wavelength range/nm	Reference	Comments
270–315	Roberts and Fajer, 1989	(a)
185–330	Turberg et al., 1990	(b)
265–340	Zhu and Ding, 1997	(c)
265–340	Clemishaw et al., 1997	(d)
265–340	Talukdar et al., 1997	(e)

Quantum yield data ($\phi = \phi_1 + \phi_2 + \phi_3$)

Measurement	Wavelength range/nm	Reference	Comments
$\phi_1 = 1.0 \pm 0.1$	308	Zhu and Ding, 1997	(f)

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Comments

- (a) Absorption cross-sections were measured in a 10.2 cm pathlength cell, using a single-beam spectrometer with a photometric accuracy of $\pm 0.5\%$. Numerical data for cross-sections are available from Roberts (1990).
- 5 (b) Absorption cross-sections were measured in cells of 2 cm and 10 cm pathlengths with a range of pressures of $\text{C}_2\text{H}_5\text{ONO}_2$. The spectral resolution was not specified.
- (c) Cross-sections measured at 10 nm intervals, between 238 K and 298 K, using cavity ring-down spectroscopy. Absorption cross-sections were obtained by measuring optical loss as a function of sample gas pressure (0.013 mbar to 18 mbar). The purity of ethyl nitrate was checked by FTIR and cavity ring-down spectroscopy.
- 10 (d) Absorption cross-sections were measured with a dual-beam diode array spectrometer, with a spectral resolution of approximately 0.6 nm, over the temperature range 233 K to 298 K. The purity of the ethyl nitrate was checked by NMR and FTIR.
- 15 (e) Absorption cross-sections were measured with a diode-array spectrometer at 298 K and six other temperatures in the range 240 K to 360 K. Absorbances were measured in 80 nm blocks which were assembled to construct the spectrum. Corrections were made for contributions to the spectrum from NO_2 present in the ethyl nitrate.
- 20 (f) Excimer laser used to photodissociate ethyl nitrate in a cavity ring-down spectrometer. Time-resolved spectra of products observed. Only NO_2 found as product, with undetectable yields of HONO and $\text{C}_2\text{H}_5\text{ONO}$. Quantum yield measurements were made at 278 K, 283 K, 288 K, 293 K and 298 K with ethyl nitrate pressures of 1.3 mbar to 13 mbar in a buffer gas of N_2 at total pressures of 16 mbar to 1 bar. ϕ_1 was found to be pressure and temperature independent.
- 25

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Preferred Values

Absorption cross-sections at 298 K and their temperature dependence over the ranges 233 K to 360 K and 235 nm to 340 nm

λ/nm	$10^{20}\sigma/\text{cm}^2$	$10^3 B/\text{K}^{-1}$	λ/nm	$10^{20}\sigma/\text{cm}^2$	$10^3 B/\text{K}^{-1}$
185	1710		265	3.6	2.9
190	1710		270	3.1	3.1
195	1490		275	2.7	3.3
200	1140		280	2.2	3.6
205	738		285	1.7	3.8
210	400		290	1.2	4.2
215	195		295	0.85	4.7
220	91		300	0.55	5.1
225	45		305	0.33	5.8
230	24		310	0.19	6.7
235	11.9	1.4	315	0.10	7.9
240	7.7	2.8	320	0.051	8.6
245	5.4	2.9	325	0.026	10.4
250	4.5	2.8	330	0.012	12.9
255	4.1	2.6	335	0.0049	14.1
260	3.9	2.6	340	0.0025	15.6

- The temperature variation of the absorption cross-section at a particular wavelength in the range 240 nm to 340 nm is expressed as $\ln \sigma(T) - \ln \sigma(298 \text{ K}) = B(T - 298)$.
- 5

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Quantum Yields

$\phi_1 = 1.0 \pm 0.1$ at 308 nm, independent of pressure over the temperature range 278–298 K.

Comments on Preferred Values

5 The preferred values of the cross-sections at 298 K are those obtained by Turberg et al. (1990) over the range 185 nm to 230 nm, where this is the only study, and for the range 235 nm to 340 nm averages are taken of the values from all of the five studies (Roberts and Fajer, 1989; Turberg et al., 1990; Zhu and Ding, 1997; Clemitshaw et al., 1997 and Talukdar et al., 1997) at the wavelengths where they overlap.

10 The temperature variation of the cross-sections has been studied by Zhu and Ding (1997), Clemitshaw et al. (1997) and Talukdar et al. (1997). These studies together cover the temperature range 233 K to 360 K and the wavelength range 235 nm to 340 nm. It is found in all of the studies that the temperature variation of σ can be expressed as $\ln \sigma(\lambda, T) - \ln \sigma(\lambda, 298 \text{ K}) = B(\lambda)(T - 298)$. The results from the three studies
15 (Zhu and Ding, 1997; Clemitshaw et al., 1997 and Talukdar et al., 1997) are in good agreement and the preferred values of B have been obtained by averaging values from the three studies (Zhu and Ding, 1997; Clemitshaw et al., 1997 and Talukdar et al., 1997).

The only direct measurement of the quantum yield is that of Zhu and Ding (1997).
20 Their finding that at 308 nm the sole photodissociation channel was that leading to NO_2 production with a quantum yield of unity is accepted for our preferred value of the quantum yield. It is in accord with the studies of Luke et al. (1998, 1989) who concluded that the measured rates of NO_2 production from ethyl nitrate photolysis in sunlight could be accounted for by assuming that $\phi_1 = 1$ throughout the region 290 nm
25 to 340 nm. This is also supported by the measured value of unity for the same channel in the 248 nm photolysis of methyl nitrate (Talukdar et al., 1997).

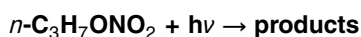
7137

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II.A8.213



Primary photochemical transitions

Reaction		$\Delta H_{298}^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$n\text{-C}_3\text{H}_7\text{ONO}_2 + h\nu$	$\rightarrow n\text{-C}_3\text{H}_7\text{O} + \text{NO}_2$ (1)	165.9	721
	$\rightarrow \text{C}_2\text{H}_5\text{CHO} + \text{HONO}$ (2)	-92.8	
	$\rightarrow \text{C}_3\text{H}_7\text{ONO} + \text{O}(^3\text{P})$ (3)		

5 Absorption cross-section data

Wavelength range/nm	Reference	Comments
270–330	Roberts and Fajer, 1989	(a)
185–330	Turberg et al., 1990	(b)
220–340	Clemitshaw et al., 1997	(c)

Comments

- 10 (a) Absorption cross-sections were measured in a cell of 10.2 cm pathlength using a single-beam spectrometer with a photometric accuracy of $\pm 0.5\%$. No NO_2 could be detected by FTIR in the *n*-propyl nitrate.
- (b) Absorption cross-sections were measured in 2 cm and 10 cm pathlength cells with a range of pressures of *n*- $\text{C}_3\text{H}_7\text{ONO}_2$ at an unspecified spectral resolution.

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- (c) Absorption cross-sections were measured with a dual-beam diode array spectrometer, with a spectral resolution of approximately 0.6 nm. The purity of the *n*-propyl nitrate was checked by NMR and FTIR.

Preferred Values

5 Absorption cross-sections at 298 K

λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$
185	1810	265	3.6
190	1800	270	3.2
195	1600	275	2.8
200	1260	280	2.3
205	855	285	1.8
210	489	290	1.3
215	244	295	0.95
220	105	300	0.57
225	50	305	0.34
230	27	310	0.19
235	15	315	0.10
240	8.9	320	0.053
245	6.0	325	0.031
250	4.8	330	0.022
255	4.4	335	0.018
260	4.0	340	0.016

Comments on Preferred Values

Clemmitshaw et al. (1997) have measured the absorption cross-sections at 298 K over the range 220 nm to 340 nm. In the wavelength region where their measurements overlap with those of Roberts and Fajer (1989) (270 nm to 320 nm), the two studies are in excellent agreement. Agreement with the results of Turberg et al. (1990) is also very good in the range 220 nm to 295 nm, but the results of Turberg et al. (1990) deviate significantly from those of both Clemmitshaw et al. (1997) and Roberts and Fajer (1989) at $\lambda > 295$ nm. This tendency to obtain higher values than others of the absorption cross-section at longer wavelengths is noticeable in the results of Turberg et al. (1990) in all of their studies of the higher nitrates and could be due to traces of NO₂ in their samples.

The preferred values of the absorption cross-section are those of Turberg et al. (1990) for the range 185 nm to 220 nm where theirs are the only measurements. Over the range 220 nm to 295 nm averages are taken of the results of Roberts and Fajer (1989), Turberg et al. (1990) and Clemmitshaw et al. (1997) where their studies overlap, and over the range 295 nm to 340 nm the preferred values are based on the results of Roberts and Fajer (1989) and Clemmitshaw et al. (1997).

There are no data on either the products of photodissociation or the quantum yields. However, the quantum yields for photodissociation of both ethyl and methyl nitrate to form NO₂ have been shown to be unity at 308 nm and 248 nm, respectively (see data sheets in this evaluation). Since the absorption spectra of organic nitrates are very similar, with structureless continua occurring in the same region of the spectrum, it seems likely that the photodissociation quantum yield for *n*-propyl nitrate will also be unity. Further support for this conclusion comes from direct measurements (Luke et al., 1989) of the rate of formation of NO₂ from the photolyses of *n*-C₃H₇ONO₂ in sunlight. These agreed well with the calculated rates of photolyses, based on measurements of the absorption cross-sections, solar irradiances, and an assumed value of $\phi_1 = 1$ throughout the wavelength region 290 nm to 340 nm (Luke et al., 1989).

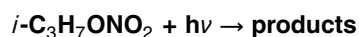
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II.A8.214



Primary photochemical transitions

Reaction		$\Delta H_{298}^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$i\text{-C}_3\text{H}_7\text{ONO}_2 + h\nu$	$\rightarrow 2\text{-C}_3\text{H}_7\text{O} + \text{NO}_2$ (1)	171.7	697
	$\rightarrow \text{CH}_3\text{C}(\text{O})\text{CH}_3 + \text{HONO}$ (2)	-105.9	
	$\rightarrow i\text{-C}_3\text{H}_7\text{ONO} + \text{O}$ (3)		

Absorption cross-section data

Wavelength range/nm	Reference	Comments
270–330	Roberts and Fajer, 1989	(a)
185–330	Turberg et al., 1990	(b)
220–340	Clemishaw et al., 1997	(c)
240–360	Talukdar et al., 1997	(d)

Comments

(a) Absorption cross-sections were measured in a 10.2 cm pathlength cell using a single-beam spectrophotometer with a photometric accuracy of $\pm 0.5\%$. Numerical data for cross-sections are available from Roberts (1990). Samples were checked by FTIR for the presence of NO_2 , which was not found.

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(b) Absorption cross-sections were measured in 2 cm and 10 cm pathlength cells, with a range of pressures of $i\text{-C}_3\text{H}_7\text{ONO}_2$, at a bandwidth of 1 nm.

(c) Absorption cross-sections were measured with a dual-beam diode array spectrometer, with a spectral resolution of approximately 0.6 nm. The purity of the i -propyl nitrate was checked by NMR and FTIR.

(d) Absorption cross-sections were measured with a diode-array spectrometer at 298 K and 6 other temperatures in the range 240 K to 360 K. Absorbances were measured in 80 nm blocks which were assembled to construct the spectrum.

Preferred Values

Absorption cross-sections at 298 K and their temperature dependence over the ranges 233 K to 360 K and 240 nm to 340 nm

λ/nm	$10^{20}\sigma/\text{cm}^2$	$10^3B/K^{-1}$	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^3B/K^{-1}$
185	1790		275	3.4	3.3
188	1810		280	2.8	3.6
190	1790		285	2.2	4.0
195	1610		290	1.6	4.4
200	1260		295	1.2	4.8
205	867		300	0.78	5.4
210	498		305	0.50	6.1
215	247		310	0.29	6.9
220	125		315	0.17	8.1
225	62		320	0.085	9.4
230	34		325	0.044	11.1
235	18		330	0.022	11.9
240	11	2.8	335	0.011	14.0
245	7.0	2.7	340	0.0053	13.9
250	5.4	2.5	345	0.0018	
255	4.9	2.5	350	0.00080	

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λ/nm	$10^{20}\sigma/\text{cm}^2$	$10^3B/K^{-1}$	λ/nm	$10^{20}\sigma/\text{cm}^2$	$10^3B/K^{-1}$
260	4.6	2.6	355	0.00029	
265	4.3	2.8	360	0.00018	
270	3.9	3.1			

The temperature variation of the absorption cross-section at a particular wavelength in the range 240 nm to 340 nm is expressed as $\ln \sigma(T) - \ln \sigma(298\text{ K}) = B(T - 298)$.

Comments on Preferred Values

Clemishaw et al. (1997) have measured the absorption cross-sections at 298 K over the range 220 nm to 340 nm and Talukdar et al. (1997) have measured both the cross-sections at 298 K over the range 240 nm to 360 nm and their temperature dependence at temperatures in the range 240 K to 360 K. The results of Clemishaw et al. (1997) and of Talukdar et al. (1997) are in excellent agreement with the earlier results of Roberts and Fajer (1989) and Turberg et al. (1990) at wavelengths where they overlap (in the range 220 nm to 330 nm), except for the results of Turberg et al. (1990) at wavelengths 310 nm which deviate increasingly from those of the other studies as the wavelength increases. This tendency, to obtain higher values than others, in this wavelength region, is noticeable in the results of Turberg et al. (1990) for all of the higher nitrates and could be due to traces of NO_2 present in their samples.

The preferred values of the absorption cross-sections at 298 K are those of Turberg et al. (1990) for the range 185 nm to 220 nm, where theirs are the only values. Over the range 220 nm to 305 nm averages are taken of the results of Roberts and Fajer (1989), Turberg et al. (1990), Clemishaw et al. (1997), and Talukdar et al. (1997), where their studies overlap, and over the range 310 nm to 360 nm the preferred values are based on the results of Roberts and Fajer (1989), Clemishaw et al. (1997) and Talukdar et al. (1997).

The preferred values of the constant B , which characterize the temperature de-

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pendence of the absorption cross-sections are those of Talukdar et al. (1997).

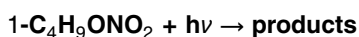
There are no data on either the products of photodissociation or the quantum yields. However, the quantum yields for the photodissociation of both ethyl and methyl nitrate to form NO₂ have been shown to be unity at 308 nm and 248 nm, respectively (see data sheets in this evaluation). Since the absorption spectra of organic nitrates are very similar structureless continua occurring at similar wavelengths, it seems likely that the photodissociation quantum yield for isopropyl nitrate will also be unity. Further support for this conclusion comes from measurements of the rate of formation of NO₂ from the photolyses of alkyl nitrates in sunlight (Luke et al., 1989). Thus the measured rate of formation of NO₂ matched well with calculated rates of photolyses based on measurements of the absorption cross-section, solar irradiances, and an assumed value of $\phi_1=1$ throughout the wavelength region 290 nm to 330 nm (Luke et al., 1989).

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II.A8.215



Primary photochemical transitions

Reaction	$\Delta H_{298}^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
1-C ₄ H ₉ ONO ₂ + hν → 1-C ₄ H ₉ O + NO ₂ (1)		
→ 1-C ₃ H ₇ CHO + HONO (2)		
→ <i>i</i> -C ₄ H ₉ ONO + O (3)		

Absorption cross-section data

Wavelength range/nm	Reference	Comments
270–315	Roberts and Fajer, 1989	(a)
185–320	Turberg et al., 1990	(b)
220–340	Clemitchaw et al., 1997	(c)

Comments

- (a) Absorption cross-sections were measured in a 10.2 cm pathlength cell using a single-beam spectrophotometer with a photometric accuracy of $\pm 0.5\%$. Data are presented graphically but an expression for σ as a function of λ is derived from a least squares fit to the data at $\lambda \geq 270$ nm. Purity of the butyl nitrate was checked by FTIR.

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- (b) Absorption cross-sections were measured in 2 cm and 10 cm pathlength cells in a Varian Carey 219 spectrophotometer using a bandwidth of 1 nm.
- (c) Absorption cross-sections were measured with a dual-beam diode array spectrometer, with a spectral resolution of approximately 0.6 nm. The purity of the 1-butyl nitrate was checked by NMR and FTIR.

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Preferred Values

Absorption cross-sections at 298 K

λ/nm	$10^{20} \sigma/\text{cm}^2$	λ/nm	$10^{20} \sigma/\text{cm}^2$
185	1810	265	3.9
190	1810	270	3.4
195	1620	275	3.0
200	1300	280	2.4
205	889	285	1.9
210	518	290	1.4
215	263	295	0.89
220	111	300	0.57
225	58	305	0.34
230	30	310	0.19
235	17	315	0.10
240	9.8	320	0.051
245	6.3	325	0.031
250	5.3	330	0.021
255	4.6	335	0.016
260	4.3	340	0.013

Comments on Preferred Values

- The results of Roberts and Fajer (1989), Turberg et al. (1990) and Clemitshaw et al. (1997) are in good agreement at wavelengths where the studies overlap (in the range 220 nm to 320 nm), except for the results of Turberg et al. (1990) at wavelengths ≥ 300 nm which deviate increasingly from those of the other studies as the wavelength increases. This tendency to obtain higher values than others, in this wavelength region,

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is noticeable in the results of Turberg et al. (1990) for all of the higher nitrates and could be due to traces of NO₂ present in their samples.

The preferred values of the absorption cross-sections are those of Turberg et al. (1990) for the range 185 nm to 220 nm, where theirs are the only values. Over the range 220 nm to 295 nm averages are taken of the results of Roberts and Fajer (1989), Turberg et al. (1990) and Clemitshaw et al. (1997), where their studies overlap, and over the range 300 nm to 400 nm the preferred values are based on the results of Roberts and Fajer and Clemitshaw et al. (1997).

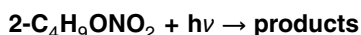
There are no data on either the products of photodissociation or the quantum yields. However, the quantum yields for the photodissociation of both ethyl and methyl nitrates to form NO₂ have been shown to be unity at 308 nm and 248 nm, respectively (see data sheets in this evaluation). Since the absorption spectra of alkyl nitrates are very similar structureless continua occurring at similar wavelengths, it seems likely that the photodissociation quantum yield for 1-butyl nitrate will also be unity. Further support for this conclusion comes from measurements of the rate of formation of NO₂ from the photolyses of alkyl nitrates in sunlight (Luke et al., 1989). Thus the measured rate of formation of NO₂ matched well with calculated rates of photolyses based on measurements of the absorption cross-sections, solar irradiances, and an assumed value of $\phi_1 = 1$ throughout the wavelength region 290 nm to 330 nm (Luke et al., 1989).

References

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 Turberg, M. P., Giolando, D. M., Tilt, C., Soper, T., Mason, S., Davies, M., Klingensmith, P., and Takacs, G. A.: J. Photochem. Photobiol., A51, 281, 1990.

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II.A8.216



Primary photochemical transitions

Reaction	$\Delta H_{298}^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$2\text{-C}_4\text{H}_9\text{ONO}_2 + h\nu \rightarrow 2\text{-C}_4\text{H}_9\text{O} + \text{NO}_2$	(1)	
$\rightarrow \text{CH}_3\text{C}(\text{O})\text{C}_2\text{H}_5 + \text{HONO}$	(2)	
$\rightarrow 2\text{-C}_4\text{H}_9\text{ONO} + \text{O}$	(3)	

Absorption cross-section data

Wavelength range/nm	Reference	Comments
250–320	Roberts and Fajer, 1989	(a)

Comments

- (a) Absorption cross-sections were measured in a cell of 10.2 cm pathlength using a single beam spectrophotometer with a photometric accuracy of $\pm 0.5\%$. The expression for σ as a function of λ was derived from a least-squares fit to the data at $\lambda \geq 270$ nm.

Preferred Values

Absorption cross-sections at 298 K

λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$
250	6.5	290	1.8
250	6.5	290	1.8
255	5.6	295	1.3
260	5.2	300	0.74
265	4.8	305	0.50
270	4.2	310	0.29
275	3.7	315	0.15
280	3.1	320	0.08
285	2.4		

Values at $\lambda \leq 265$ nm are taken from graphs in Roberts and Fajer (1989)

Values at $\lambda \geq 270$ nm are calculated from the expression given in Roberts and Fajer (1989) based on a least-squares fit to the data.

5 *Comments on Preferred Values*

The only available measurements of the absorption cross-sections are those of Roberts and Fajer (1989). Their measurements of cross-sections for other alkyl nitrates have agreed well with other studies, and their values are accepted as the preferred values for 2-butyl nitrate.

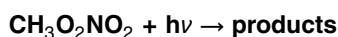
- 10 There are no data on either the products of photodissociation or the quantum yields. However, the quantum yields for the photodissociation of both ethyl and methyl nitrates to form NO_2 have been shown to be unity at 308 nm and 248 nm, respectively (see data sheets in this evaluation). Since the absorption spectra of alkyl nitrates are very similar structureless continua occurring at similar wavelengths, it seems likely

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- 5 that the photodissociation quantum yield for 2-butyl nitrate will also be unity. Further support for this conclusion comes from measurements of the rate of formation of NO_2 from the photolyses of alkyl nitrates in sunlight (Luke et al., 1989). Thus the measured rate of formation of NO_2 matched well with the calculated rates of photolyses based on measurement of the absorption cross-sections, solar irradiances, and an assumed value of $\phi = 1$ throughout the wavelength region 290 nm to 330 nm (Luke et al., 1989).

References

- Luke, W. T., Dickinson, R. R., and Nunnermacker, L. J.: J. Geophys. Res., 94, 14 905, 1989.
- 10 Roberts, J. M. and Fajer, R. W.: Environ. Sci. Technol., 23, 945, 1989.



Primary photochemical transitions

Reaction	$\Delta H_{298}^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{CH}_3\text{O}_2\text{NO}_2 + h\nu \rightarrow \text{CH}_3\text{O}_2 + \text{NO}_2$ (1)	86	1391
$\rightarrow \text{CH}_3\text{O} + \text{NO}_3$ (2)	135	886

5 Absorption cross-section data

Wavelength range/nm	Reference	Comments
202–280	Bridier et al., 1992	(a)

Comments

- 10 (a) Flash photolysis of Cl_2 in the presence of $\text{CH}_4\text{-O}_2\text{-NO}_2$ mixtures at a total pressure of 1 bar, with UV absorption to monitor the concentrations of CH_3O_2 radicals and $\text{CH}_3\text{O}_2\text{NO}_2$.

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Preferred Values

Absorption cross-sections at 298 K

λ/nm	$10^{20}\sigma/\text{cm}^2$	λ/nm	$10^{20}\sigma/\text{cm}^2$
200	500	265	20.0
205	360	270	16.0
210	240	275	13.0
215	150	280	10.5
210	240	275	13.0
215	150	280	10.5
220	105	285	6.2
225	80	290	3.9
230	68	295	2.4
235	60	300	1.4
230	68	295	2.4
235	60	300	1.4
240	53	305	0.85
245	46	310	0.53
250	39	315	0.39
255	32	320	0.24
260	26	325	0.15

Comments on Preferred Values

- 5 In view of the thermal instability of $\text{CH}_3\text{O}_2\text{NO}_2$, the measurement of the cross-sections for $\text{CH}_3\text{O}_2\text{NO}_2$ presents considerable experimental problems. Nevertheless, the measurements of Bridier et al. (1992) are in moderately good agreement with previous data (Cox and Tyndall, 1979; Morel et al., 1980; Sander and Watson, 1980) at

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wavelengths <255 nm and are taken as the preferred values in the range 200 nm to 280 nm. At longer wavelengths the agreement is less good and the experimental data from Cox and Tyndall (1979), which are the only values extending into the wavelength region of importance for the atmosphere ($\lambda \geq 290$ nm), show large scatter. The preferred values given in the table for wavelengths >280 nm are based on a comparison with the spectrum of HO₂NO₂.

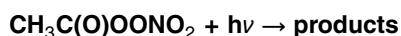
There are no data to indicate the relative importance of the two photodissociation channels, and neither can be precluded on energetic grounds in the absorbing wavelength region. By analogy with other molecules containing the -NO₂ chromophore (for example, HNO₃), it is likely that absorption around 270 nm is associated with an orbitally forbidden $n-\pi^*$ transition which leads to dissociation of the molecule. Thus it is probable that $\phi_1 + \phi_2 = 1$.

References

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 Cox, R. A. and Tyndall, G. S.: Chem. Phys. Lett., 65, 357, 1979.
 Morel, O., Simonaitis, R., and Heicklen, J.: Chem. Phys. Lett., 73, 38, 1980.
 Sander, S. P. and Watson, R. T.: J. Phys. Chem., 84, 1664, 1980.

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II.A8.218



Primary photochemical transitions

Reaction	$\Delta H_{298}^\circ/\text{kJ}\cdot\text{mol}^{-1}$	$\lambda_{\text{threshold}}/\text{nm}$
$\text{CH}_3\text{C}(\text{O})\text{O}_2\text{NO}_2 + h\nu \rightarrow \text{CH}_3\text{C}(\text{O})_2 + \text{NO}_2$ (1)	119	1004
$\rightarrow \text{CH}_3\text{CO}_2 + \text{NO}_3$ (2)	125	963

Absorption cross-section data

Wavelength range/nm	Reference	Comments
220–325	Libuda and Zabel, 1995	(a)
196–350	Talukdar et al., 1995	(b)

Quantum yield data ($\phi = \phi_1 + \phi_2$)

Measurement	Wavelength range/nm	Reference	Comments
$\phi(\text{NO}_2)$	248	Mazely et al., 1995	(c)

Comments

- (a) Longpath (39.1 m) UV absorption cell with diode array detector used. The concentration of the CH₃C(O)OONO₂ (PAN) was determined by FTIR (pathlength = 51.6 m) in the same cell. The UV spectral resolution was 0.6 nm.

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- (b) Diode array spectrometer with a resolution of 0.2 nm used with temperature controlled (± 1 K) absorption cells of pathlengths 100 cm and 25 cm. $\text{CH}_3\text{C}(\text{O})\text{OONO}_2$ concentrations were determined by pressure measurements. Cross-sections were measured at 250 K, 273 K and 298 K.
- 5 (c) Pulsed laser photolysis of PAN with LIF detection of NO_2 . The quantum yield for NO_2 formation was measured relative to the photodissociation of HNO_3 at 248 nm, assuming a value of $\phi(\text{NO}_2)$ from HNO_3 of unity at this wavelength (IUPAC, current recommendation, see HNO_3 photolysis data sheet). A value of $\phi(\text{NO}_2)=0.83\pm 0.09$ for the photolysis of PAN at 248 nm was obtained.

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Preferred Values

Absorption cross-sections at 298 K and the temperature coefficient B^a

λ/nm	$10^{20}\sigma/\text{cm}^2$	$10^3B/K^{-1}$	λ/nm	$10^{20}\sigma/\text{cm}^2$	$10^3B/K^{-1}$
196	429	2.02	274	2.45	5.55
198	398	1.73	276	2.07	5.76
200	361	1.36	278	1.74	5.98
202	325	1.07	280	1.46	6.20
204	292	0.86	282	1.21	6.43
206	261	0.75	284	1.01	6.67
208	226	0.71	286	0.81	6.90
210	196	0.75	288	0.648	7.15
212	168	0.84	290	0.537	7.39
214	143	0.97	292	0.447	7.63
216	122	1.12	294	0.369	7.86
218	104	1.29	296	0.297	8.08
220	89.7	1.47	298	0.245	8.27
222	77.7	1.64	300	0.189	8.44
224	67.6	1.81	302	0.152	8.61
226	59.3	1.98	304	0.125	8.76
228	52.0	2.14	306	0.0998	8.87
230	45.8	2.30	308	0.0816	9.01
232	40.4	2.46	310	0.0666	9.13
234	35.5	2.63	312	0.0538	9.30
236	31.4	2.80	314	0.0462	9.46

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λ/nm	$10^{20}\sigma/\text{cm}^2$	$10^3B/K^{-1}$	λ/nm	$10^{20}\sigma/\text{cm}^2$	$10^3B/K^{-1}$
238	27.9	2.96	316	0.0363	9.57
240	24.4	3.11	318	0.0300	9.75
242	21.5	3.25	320	0.0252	10.0
244	18.8	3.39	322	0.0199	10.2
246	16.6	3.52	324	0.0166	10.4
248	14.6	3.64	326	0.0140	10.6
250	12.9	3.76	328	0.0117	10.7
252	11.4	3.87	330	0.0106	10.9
254	10.0	3.98	332	0.00857	11.2
256	8.86	4.10	334	0.00676	11.5
258	7.8	4.23	336	0.00615	11.7
260	6.85	4.38	338	0.00526	11.9
262	6.01	4.53	340	0.00502	12.2
264	5.23	4.68	342	0.00360	12.4
266	4.54	4.82	344	0.00241	12.5
268	3.94	4.97	346	0.00231	
270	3.37	5.14	348	0.00247	
272	2.87	5.34	350	0.00165	

^aAbsorption cross-sections at temperatures in the range 250 K to 298 K are calculated using the equation $\ln[\sigma(T)/\sigma(298\text{ K})]=B(T-298)$.

Comments on Preferred Values

The preferred values of the absorption cross-sections at 298 K are based on the work of Libuda and Zabel (1995) and Talukdar et al. (1995), which agree to within a few percent at wavelengths below 290 nm and only slightly less well at longer wavelengths where the error limits on the measurements increase because of the difficulty

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of measuring the small cross-sections in that region of the spectrum.

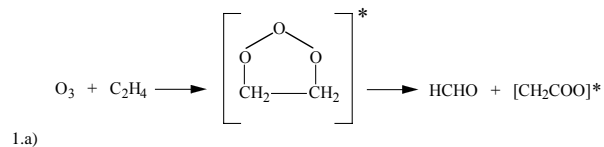
Talukdar et al. (1995) have also measured the cross-sections at three temperatures and expressed their results in the form $\ln[\sigma(T)/\sigma(298\text{ K})]=B(T-298)$ where B is a constant at a particular wavelength. The values of B and σ (298 K) obtained by Talukdar et al. (1995) are listed as our preferred values.

Measurements are still needed on the quantum yields and relative importance of the proposed primary processes as a function of wavelength. The NO_2 formation quantum yield measured by Mazely et al. (1995) at 248 nm suggests that pathway (1) dominates. It is therefore suggested that $(\phi_1 + \phi_2) = 1$ for absorption in the UV region and that channel (1) forming $\text{CH}_3\text{C}(\text{O})\text{O}_2$ and NO_2 is the dominant photochemical primary process.

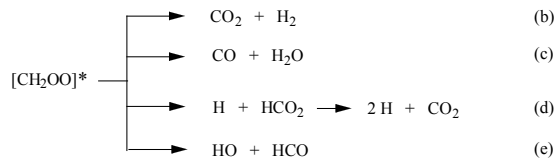
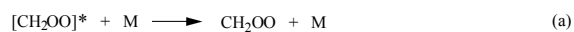
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- IUPAC: <http://www.iupac-kinetic.ch.cam.ac.uk/>.
 Libuda, H. G. and Zabel, F.: Ber. Bunsenges. Phys. Chem., 99, 1205, 1995.
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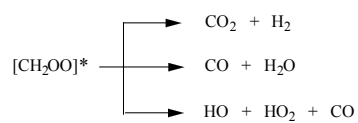
7162



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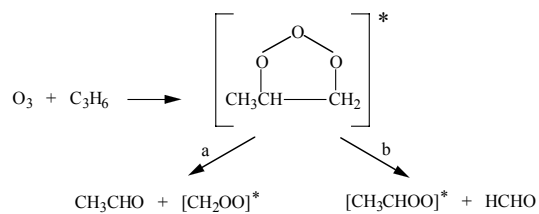
1.b)



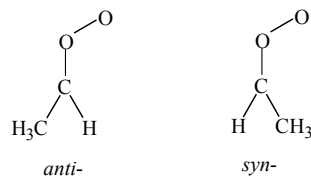
1.c)

Fig. 1. See text.

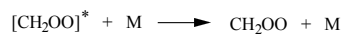
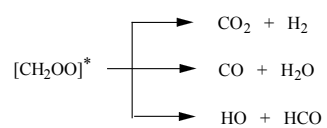
7163



2.a)



2.b)



2.c)

Fig. 2. (a), (b) and (c) – see text.

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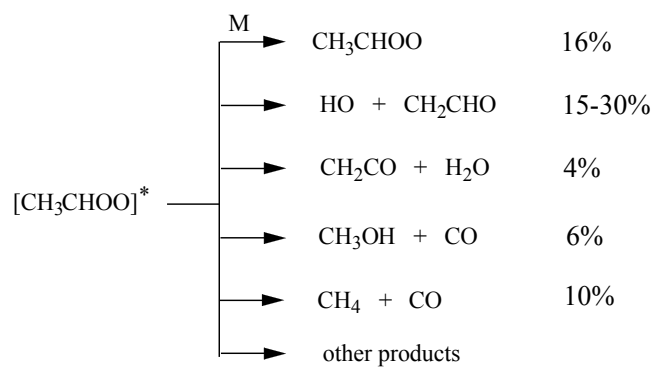


Fig. 3. See text.

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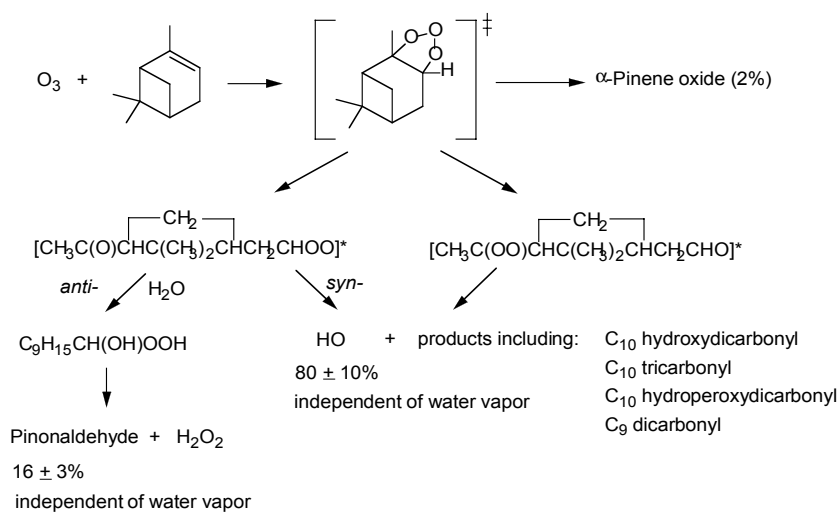


Fig. 4. See text.

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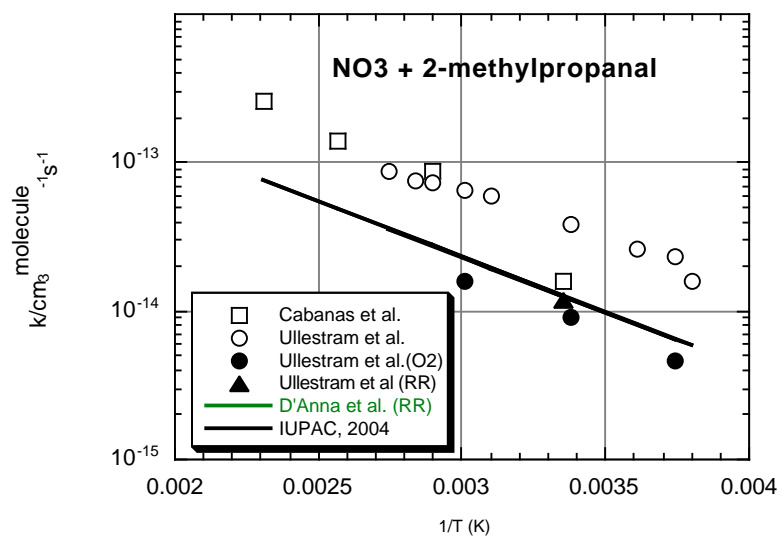


Fig. 5. See text.

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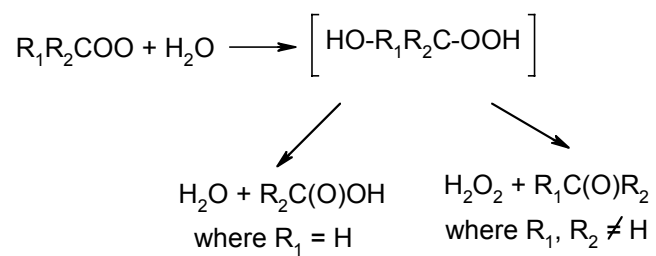


Fig. 6. See text.

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