

SECTION 2. TERMOLECULAR REACTIONS

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2.1 Introduction

Rate constants for association reactions (Table 2-1) of the type $A + B \leftrightarrow [AB]^* \xrightarrow{M} AB$ can be pressure dependent. The low-pressure-limiting rate constants are given in the form:

$$k_o(T) = k_o^{300} \left(\frac{T}{300} \right)^{-n} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1},$$

(where k_o^{300} has been adjusted for air as the third body), together with a recommended value of n . The limiting high-pressure rate constant is given in a similar form:

$$k_\infty(T) = k_\infty^{300} \left(\frac{T}{300} \right)^{-m} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}.$$

To obtain the effective second-order rate constant for a given condition of temperature and pressure (altitude), the following formula is used:

$$k_f([M], T) = \left(\frac{k_o(T)[M]}{1 + \frac{k_o(T)[M]}{k_\infty(T)}} \right) 0.6 \left\{ 1 + \left[\log_{10} \left(\frac{k_o(T)[M]}{k_\infty(T)} \right) \right]^2 \right\}^{-1}$$

The fixed value 0.6 that appears in this formula fits the data for all listed reactions adequately, although in principle this quantity may be different for each reaction, and also temperature dependent.

Thus, a compilation of rate constants of this type requires the stipulation of the four parameters, $k_o(300)$, n , $k_\infty(300)$, and m . These can be found in Table 2-1. The discussion that follows outlines the general methods we have used in establishing this table, and the notes to the table discuss specific data sources. Recent advances in theory have allowed direct calculation of rate constants for some reactions using RRKM/Master Equation methods.

2.2 Low-Pressure-Limiting Rate Constant, $k_o^x(T)$

Troe [259] has described a simple method for obtaining low-pressure-limiting rate constants. In essence this method depends on the definition:

$$k_o^x(T) \equiv \beta_x k_{o,sc}^x$$

Here sc signifies “strong” collisions, x denotes the bath gas, and β_x is an efficiency parameter ($0 < \beta_x < 1$), which provides a measure of energy transfer.

The coefficient β_x is related to the average energy transferred in a collision with gas x, $\langle \Delta E \rangle_x$, via:

$$\frac{\beta_x}{(1-\sqrt{\beta_x})} = \frac{\langle \Delta E \rangle_x}{F_E kT}$$

Notice that $\langle \Delta E \rangle$ is quite sensitive to β . F_E is the correction factor of the energy dependence of the density of states (a quantity of the order of 1.1 for most species of stratospheric interest).

For some of the reactions of possible stratospheric interest reviewed here, there exist data in the low-pressure limit (or very close thereto), and we have chosen to evaluate and unify this data by calculating $k_0^x(T)$ for the appropriate bath gas x and computing the value of β_x corresponding to the experimental value (Troe [259]). A compilation (Patrick and Golden [211]) gives details for many of the reactions considered here.

From the β_x values (most of which are for N_2 , i.e., β_{N_2}), we compute $\langle \Delta E \rangle_x$ according to the above equation. Values of $\langle \Delta E \rangle_{N_2}$ of approximately 0.3–1 kcal mole⁻¹ are generally expected. If multiple data exist, we average the values of $\langle \Delta E \rangle_{N_2}$ and recommend a rate constant corresponding to the β_{N_2} computed in the equation above.

Where no data exist we have sometimes estimated the low-pressure rate constant by taking $\beta_{N_2} = 0.3$ at $T = 300$ K, a value based on those cases where data exist.

2.3 Temperature Dependence of Low-Pressure Limiting Rate Constants: T^n

The value of n recommended here comes from measurements or, in some cases, a calculation of $\langle \Delta E \rangle_{N_2}$ from the data at 300 K, and a computation of $\beta_{N_2}(200\text{ K})$ assuming that $\langle \Delta E \rangle_{N_2}$ is independent of temperature in this range. This $\beta_{N_2}(200\text{ K})$ value is combined with the computed value of $k_0^{sc}(200\text{ K})$ to give the expected value of the actual rate constant at 200 K. This latter, in combination with the value at 300 K, yields the value of n.

This procedure can be directly compared with measured values of $k_0(200\text{ K})$ when those exist. Unfortunately, very few values at 200 K are available. There are often temperature-dependent studies, but some ambiguity exists when one attempts to extrapolate these down to 200 K. If data are to be extrapolated beyond the measured temperature range, a choice must be made as to the functional form of the temperature dependence.

There are two general ways of expressing the temperature dependence of rate constants. Either the Arrhenius expression

$$k_0(T) = A \exp(-E/RT)$$

or the form

$$k_0(T) = A' T^{-n}$$

is employed. Since neither of these extrapolation techniques is soundly based, and since they often yield values that differ substantially, we have used the method explained earlier as the basis of our recommendations.

2.4 High-Pressure-Limit Rate Constants, $k_\infty(T)$

High-pressure rate constants can often be obtained experimentally, but those for the relatively small species of atmospheric importance usually reach the high-pressure limit at inaccessibly high pressures. This leaves two sources of these numbers, the first being guesses based upon some model, and the second being extrapolation of fall-off data up to higher pressures.

Stratospheric conditions generally render reactions of interest much closer to the low-pressure limit and thus are fairly insensitive to the high-pressure value. This means that while the extrapolation is long, and the value of $k_\infty(T)$ not very accurate, a “reasonable guess” of $k_\infty(T)$ will then suffice. In some cases we have declined to guess since the low-pressure limit is effective over the entire range of stratospheric conditions.

2.5 Temperature Dependence of High-Pressure-Limiting Rate Constants: T^m

There are very few data upon which to base a recommendation for values of m . Values in Table 2-1 are often estimated, based on models for the transition state of bond-association reactions and whatever data are available.

2.6 Uncertainty Estimates

For three-body reactions (Table 2-1) uncertainties are assigned using a procedure that is analogous to that employed for bimolecular reactions. Values of $f(298\text{ K})$ are given for these rate constants at room temperature and assumed to be valid at all pressures. The additional uncertainty arising from the temperature extrapolation has in previous evaluations been expressed as an uncertainty in the temperature coefficients n and m . In this evaluation, those reactions that have been re-evaluated or added have uncertainties expressed with a g -factor as in Table 1-1. In future evaluations we will continue to update this format.

Table 2–1. Rate Constants for Termolecular Reactions

Reaction	Low-Pressure Limit ^a $k_0(T) = k_0^{300} (T/300)^{-n}$		High-Pressure Limit ^b $k_\infty(T) = k_\infty^{300} (T/300)^{-m}$		f	g	Notes
	k_0^{300}	n	k_∞^{300}	m			
O_x Reactions							
$O + O_2 \xrightarrow{M} O_3$	(6.0) (-34)	2.4	–	–	1.1	50	A1
O(¹D) Reactions							
$O(^1D) + N_2 \xrightarrow{M} N_2O$	(3.5±3.0) (-37)	0.6 ^{2.0} ±0.6	–	–			A2
HO_x Reactions							
$H + O_2 \xrightarrow{M} HO_2$	(5.7±0.5) (-32)	1.6±0.5	(7.5±4.0) (-11)	0±1.0			B1
$OH + OH \xrightarrow{M} H_2O_2$	(6.9) (-31)	1.0	(2.6) (-11)	0	1.5	100	B2
NO_x Reactions							
$O + NO \xrightarrow{M} NO_2$	(9.0±2.0) (-31)	1.5±0.3	(3.0±1.0) (-11)	0±1.0			C1
$O + NO_2 \xrightarrow{M} NO_3$	(2.5) (-31)	1.8	(2.2) (-11)	0.7	1.3	100	C2
$OH + NO \xrightarrow{M} HONO$	(7.0±1.0) (-31)	2.6±0.3	(3.6±1.0) (-11)	0.1±0.5			C3
$OH + NO_2 \xrightarrow{M} HONO_2$ (See Note)	(2.0) (-30)	3.0	(2.5) (-11)	0	1.3	100	C4
$HO_2 + NO_2 \xrightarrow{M} HO_2NO_2$	(1.8±0.3) (-31)	3.2±0.4	(4.7±1.0) (-12)	1.4±1.4			C5
$NO_2 + NO_3 \xrightarrow{M} N_2O_5$	(2.0) (-30)	4.4	(1.4) (-12)	0.7	1.2	100	C6
$NO_3 \xrightarrow{M} NO + O_2$	See Note						C7
Hydrocarbon Reactions							
$CH_3 + O_2 \xrightarrow{M} CH_3O_2$	(4.5±1.5) (-31)	3.0±1.0	(1.8±0.2) (-12)	1.7±1.7			D1
$C_2H_5 + O_2 \xrightarrow{M} C_2H_5O_2$	(1.5±1.0) (-28)	3.0±1.0	(8.0±1.0) (-12)	0±1.0			D2
$OH + C_2H_2 \xrightarrow{M} HOCHCH$	(5.5±2.0) (-30)	0.0±0.2	(8.3±1.0) (-13)	-2 ² ±1			D3
$OH + C_2H_4 \xrightarrow{M} HOCH_2CH_2$	(1.0±0.6) (-28)	0.8±2.0	(8.8±0.9) (-12)	0 ⁰ ±2			D4
$CH_3O + NO \xrightarrow{M} CH_3ONO$	(1.4±0.5) (-29)	3.8±1.0	(3.6±1.6) (-11)	0.6±1.0			D5
$CH_3O + NO_2 \xrightarrow{M} CH_3ONO_2$	(5.3) (-29)	4.4	(1.9) (-11)	1.8	1.1	0	D6
$C_2H_5O + NO \xrightarrow{M} C_2H_5ONO$	(2.8±1.0) (-27)	4.0±2.0	(5.0±1.0) (-11)	1.0±1.0			D7

Reaction	Low-Pressure Limit ^a $k_0(T) = k_0^{300} (T/300)^{-n}$		High-Pressure Limit ^b $k_{\infty}(T) = k_{\infty}^{300} (T/300)^{-m}$		f	g	Notes
	k_0^{300}	n	k_{∞}^{300}	m			
$C_2H_5O + NO_2 \xrightarrow{M} C_2H_5ONO_2$	(2.0±1.0) (-27)	4.0±2.0	(2.8±0.4) (-11)	1.0±1.0			D8
$CH_3O_2 + NO_2 \xrightarrow{M} CH_3O_2NO_2$	(1.5±0.8) (-30)	4.0±2.0	(6.5±3.2) (-12)	2.0±2.0			D9
$C_2H_5O_2 + NO_2 \xrightarrow{M} C_2H_5O_2NO_2$	(1.2)(-29)	4.0	(9.0)(-12)	0.0	1.3	50	D10
$CH_3C(O)O_2 + NO_2 \xrightarrow{M} CH_3C(O)O_2NO_2$	(9.7±3.8) (-29)	5.6±2.8	(9.3±0.4)(-12)	1.5±0.3			D11
$CH_3CH_2C(O)O_2 + NO_2 \xrightarrow{M} CH_3CH_2C(O)O_2NO_2$	(9.0) (-28)	8.9	(7.7) (-12)	0.2	2.0	100	D12
$CH_3C(O)CH_2 + O_2 \xrightarrow{M} CH_3C(O)CH_2O_2$	See Note						D13
FO_x Reactions							
$F + O_2 \xrightarrow{M} FO_2$	(4.4±0.4) (-33)	1.2±0.5	-	-			E1
$F + NO \xrightarrow{M} FNO$	(1.8±0.3) (-31)	1.0±10	(2.8±1.4) (-10)	0.0±1.0			E2
$F + NO_2 \xrightarrow{M} FNO_2$	(6.3±3.0) (-32)	2.0±2.0	(2.6±1.3) (-10)	0.0±1.0			E3
$FO + NO_2 \xrightarrow{M} FONO_2$	(2.6±2.0) (-31)	1.3±1.3	(2.0±1.0) (-11)	1.5±1.5			E4
$CF_3 + O_2 \xrightarrow{M} CF_3O_2$	(3.0±0.3) (-29)	4.0±2.0	(4.0±1.0) (-12)	1.0±1.0			E5
$CF_3O + NO_2 \xrightarrow{M} CF_3ONO_2$	3.1(-28)	2.0	1.5(-11)	2.8	1.1	50	E6
$CF_3O_2 + NO_2 \xrightarrow{M} CF_3O_2NO_2$	(2.2±0.5) (-29)	5.0±1.0	(6.0±1.0) (-12)	2.5±1.0			E7
$CF_3O + CO \xrightarrow{M} CF_3OCO$	(2.5±0.2) (-31)	-	(6.8±0.4) (-14)	-1.2			E8
$CF_3O \xrightarrow{M} CF_2O + F$	See Note						E9
ClO_x Reactions							
$Cl + O_2 \xrightarrow{M} ClOO$	(2.7±1.0) (-33)	1.5±0.5	-	-			F1
$Cl + NO \xrightarrow{M} ClNO$	(9.0±2.0) (-32)	1.6±0.5	-	-			F2
$Cl + NO_2 \xrightarrow{M} ClONO$	(1.3±0.2) (-30)	2.0±1.0	(1.0±0.5) (-10)	1.0±1.0			F3
$\xrightarrow{M} ClONO_2$	(1.8±0.3) (-31)	2.0±1.0	(1.0±0.5) (-10)	1.0±1.0			
$Cl + CO \xrightarrow{M} ClCO$	(1.3±0.5) (-33)	3.8±0.5	-	-			F4
$Cl + C_2H_2 \xrightarrow{M} ClC_2H_2$	((5.9±1.0) (-30)	2.1±1.0	(2.1±0.4) (-10)	1.0±0.5			F5
$Cl + C_2H_4 \xrightarrow{M} ClC_2H_4$	(1.6) (-29)	3.3	(3.1) (-10)	1.0	1.5	50	F6
$Cl + C_2Cl_4 \xrightarrow{M} C_2Cl_5$	(1.4) (-28)	8.5	(4.0) (-11)	1.2	1.2	50	F7

Reaction	Low-Pressure Limit ^a $k_0(T) = k_0^{300} (T/300)^{-n}$		High-Pressure Limit ^b $k_{\infty}(T) = k_{\infty}^{300} (T/300)^{-m}$		f	g	Notes
	k_0^{300}	n	k_{∞}^{300}	m			
$\text{ClO} + \text{NO}_2 \xrightarrow{\text{M}} \text{ClONO}_2$	(1.8±0.3) (-31)	3.4±0.2	(1.5±0.4) (-11)	1.9±0.5			F8
$\text{OCIO} + \text{NO}_3 \xrightarrow{\text{M}} \text{O}_2\text{ClONO}_2$	See Note						F9
$\text{ClO} + \text{ClO} \xrightarrow{\text{M}} \text{Cl}_2\text{O}_2$	(1.6) (-32)	4.5	(2.0) (-12)	2.4	1.1	25	F10
$\text{ClO} + \text{OCIO} \xrightarrow{\text{M}} \text{Cl}_2\text{O}_3$	(6.2±1.0) (-32)	4.7±0.6	(2.4±1.2) (-11)	0±1.0			F11
$\text{OCIO} + \text{O} \xrightarrow{\text{M}} \text{ClO}_3$	(1.9±0.5) (-31)	1.1±1.0	(3.1±0.8) (-11)	0±1.0			F12
$\text{CH}_2\text{Cl} + \text{O}_2 \xrightarrow{\text{M}} \text{CH}_2\text{ClO}_2$	(1.9±0.1) (-30)	3.2±0.2	(2.9±0.2) (-12)	1.2±0.6			F13
$\text{CHCl}_2 + \text{O}_2 \xrightarrow{\text{M}} \text{CHCl}_2\text{O}_2$	(1.3±0.1) (-30)	4.0±0.2	(2.8±0.2) (-12)	1.4±0.6			F14
$\text{CCl}_3 + \text{O}_2 \xrightarrow{\text{M}} \text{CCl}_3\text{O}_2$	(6.9±0.2) (-31)	6.4±0.3	(2.4±0.2) (-12)	2.1±0.6			F15
$\text{CFCl}_2 + \text{O}_2 \xrightarrow{\text{M}} \text{CFCl}_2\text{O}_2$	(5.0±0.8) (-30)	4.0±2.0	(6.0±1.0) (-12)	1.0±1.0			F16
$\text{CF}_2\text{Cl} + \text{O}_2 \xrightarrow{\text{M}} \text{CF}_2\text{ClO}_2$	(3.0±1.5) (-30)	4.0±2.0	(3±2) (-12)	1.0±1.0			F17
$\text{CCl}_3\text{O}_2 + \text{NO}_2 \xrightarrow{\text{M}} \text{CCl}_3\text{O}_2\text{NO}_2$	(5.0±1.0) (-29)	5.0±1.0	(6.0±1.0) (-12)	2.5±1.0			F18
$\text{CFCl}_2\text{O}_2 + \text{NO}_2 \xrightarrow{\text{M}} \text{CFCl}_2\text{O}_2\text{NO}_2$	(3.5±0.5) (-29)	5.0±1.0	(6.0±1.0) (-12)	2.5±1.0			F19
$\text{CF}_2\text{ClO}_2 + \text{NO}_2 \xrightarrow{\text{M}} \text{CF}_2\text{ClO}_2\text{NO}_2$	(3.3±0.7) (-29)	6.7±1.3	(4.1±1.9) (-12)	2.8±0.7			F20
BrO_x Reactions							
$\text{Br} + \text{NO}_2 \xrightarrow{\text{M}} \text{BrNO}_2$	(4.2±0.8) (-31)	2.4±0.5	(2.7±0.5) (-11)	0±1.0			G1
$\text{BrO} + \text{NO}_2 \xrightarrow{\text{M}} \text{BrONO}_2$	(5.2±0.4) (-31)	3.2±0.8	(6.9±0.4) (-12)	2.9±0.1			G2
IO_x Reactions							
$\text{I} + \text{NO} \xrightarrow{\text{M}} \text{INO}$	(1.8±0.5) (-32)	1.0±0.5	(1.7±1.0) (-11)	0±1.0			H1
$\text{I} + \text{NO}_2 \xrightarrow{\text{M}} \text{INO}_2$	(3.0±1.5) (-31)	1.0±1.0	(6.6±5.0) (-11)	0±1.0			H2
$\text{IO} + \text{NO}_2 \xrightarrow{\text{M}} \text{IONO}_2$	(5.9±2.0) (-31)	3.5±1.0	(9.0±1.0) (-12)	1.5±1.0			H3
SO_x Reactions							
$\text{HS} + \text{NO} \xrightarrow{\text{M}} \text{HSNO}$	(2.4±0.4) (-31)	3.0±1.0	(2.7±0.5) (-11)	$0_{\pm 2}^0$			I1
$\text{CH}_3\text{S} + \text{NO} \xrightarrow{\text{M}} \text{CH}_3\text{SNO}$	(3.2±0.4) (-29)	4.0±1.0	(3.9±0.6) (-11)	2.7±1.0			I2
$\text{O} + \text{SO}_2 \xrightarrow{\text{M}} \text{SO}_3$	$(1.3_{\pm 0.7}^{1.3}) (-33)$	-3.6±0.7					I3
$\text{OH} + \text{SO}_2 \xrightarrow{\text{M}} \text{HOSO}_2$	(3.0±1.0) (-31)	3.3±1.5	(1.5±0.5) (-12)	$0_{\pm 2}^0$			I4

Reaction	Low-Pressure Limit ^a $k_o(T) = k_o^{300} (T/300)^{-n}$		High-Pressure Limit ^b $k_{\infty}(T) = k_{\infty}^{300} (T/300)^{-m}$		f	g	Notes
	k_o^{300}	n	k_{∞}^{300}	m			
$\text{CH}_3\text{SCH}_2 + \text{O}_2 \xrightarrow{\text{M}} \text{CH}_3\text{SCH}_2\text{O}_2$	See Note						I5
$\text{SO}_3 + \text{NH}_3 \xrightarrow{\text{M}} \text{H}_3\text{NSO}_3$	(3.9±0.8) (-30)	3.0±3.0	(4.7±1.3) (-11)	0±1.0			I6
Metal Reactions							
$\text{Na} + \text{O}_2 \xrightarrow{\text{M}} \text{NaO}_2$	(3.2±0.3) (-30)	1.4±0.3	(6.0±2.0) (-10)	0±1.0			J1
$\text{NaO} + \text{O}_2 \xrightarrow{\text{M}} \text{NaO}_3$	(3.5±0.7) (-30)	2.0±2.0	(5.7±3.0) (-10)	0±1.0			J2
$\text{NaO} + \text{CO}_2 \xrightarrow{\text{M}} \text{NaCO}_3$	(8.7±2.6) (-28)	2.0±2.0	(6.5±3.0) (-10)	0±1.0			J3
$\text{NaOH} + \text{CO}_2 \xrightarrow{\text{M}} \text{NaHCO}_3$	(1.3±0.3) (-28)	2.0±2.0	(6.8±4.0) (-10)	0±1.0			J4

Shaded areas indicate changes or additions since JPL 97-4 and/or JPL 00-03.

The values quoted are suitable for air as the third body, M.

a Units are $\text{cm}^6/\text{molecule}^2\text{-s}$.

b Units are $\text{cm}^3/\text{molecule}\text{-s}$.

f(298 K) is the uncertainty factor at 298 K. To calculate the uncertainty at other temperatures, use the expression:

$$f(T) = f(298) \exp \left[g \left(\frac{1}{T} - \frac{1}{298} \right) \right]$$

Note that the exponent is absolute value

2.7 Notes to Table 2

- A1. O + O₂. Low pressure limit and T dependence are an average of Klais et al. [145], Huie et al. [127] and Lin and Leu [167]. These studies in N₂ and Ar are in the temperature range (200 < T/K < 268). The result is in agreement with the study of Hippler et al. [119] and the extrapolated recommendation fits their lower pressure N₂ data down to 100 K. High pressure studies by Croce de Cobos and Troe [72] are in agreement with this recommendation. Rawlins et al. [224] estimate values in Ar between 80 and 150 K from nascent vibrational distributions that are a factor of two higher than the recommendation extrapolated to 80 K. The temperature dependence of the rate constant determined from the experimental data is in excellent agreement with the value of n=2.36 determined from the calculations of Patrick and Golden [211].
- Kaye [139] has calculated isotope effects for this reaction, using methods similar to those discussed in the Introduction of this document (see Troe [259] and Patrick and Golden [211].) Isotope effects have been reported by Anderson et al. [8] and Gross and Billing [111]. Measurements of isotopic fractionation by Mauersberger and colleagues [288] and Thiemens and co-workers [236] reveal distinctly non-statistical effects. Various attempts at theoretical explanations exist [115], but the detailed knowledge of the potential energy surface required is unavailable.
- A2. O(¹D) + N₂. Low pressure limit from Kajimoto and Cvetanovic [138]. The T dependence is obtained by assuming a constant β. The rate constant is extremely low in this special system due to electronic curve crossing. Maric and Burrows [174] extract $(8.8 \pm 3.3) \times 10^{-37} \text{ cm}^6 \text{ s}^{-1}$ from a study of the photolysis of synthetic air, in agreement with the recommended value within mutual error limits.
- B1. H + O₂. Kurylo [151], Wong and Davis [290] and Hsu et al. [126] are averaged to obtain the low pressure limiting value at 300 K. The first two studies include T dependence, as does a study by Hsu et al. [125]. The recommended value is chosen with constant $\langle \Delta E \rangle_{\text{N}_2} \sim 0.05 \text{ kcal mol}^{-1}$. This very low number reflects rotational effects. The high pressure limit is from Cobos et al. [59]. The temperature dependence is estimated. Cobos et al. [59] estimate $m = -0.6$, which is within our uncertainty. High temperature measurements in Ar by Pirraglia et al. [216] are in good agreement. Measurements in the range 298 < T/K < 750 by Carleton et al. [51] agree within error limits. High temperature theoretical and experimental studies examining wide ranges of pressure and temperature [260], [24] are in good agreement with the recommendation.
- B2. OH + OH. Recommended values are from fits of measurements by Zellner et al. [297] in N₂, by Forster et al. [99] and Fulle et al. [105] in 1–150 bar He scaled to N₂. A study by Fagerstrom et al. [94] in 85–1000 mbar SF₆ gives slightly different values. A pressure independent bimolecular channel to H₂O + O with a rate $4.2 \times 10^{-12} \exp(-240/T)$ is observed (see Table 1–1). Zellner et al. used somewhat different values for this rate constant to make substantial corrections to their measured values. Changing to the accepted value will make large changes in the Zellner et al. values and it is unclear how to evaluate this. Trainor and von Rosenberg [258] report a value at 300 K that is lower than recommended by a factor of 2.7.
- C1. O + NO. Low pressure limit and n from direct measurements of Schieferstein et al. [237] and their re-analysis of the data of Whytock et al. [284]. Error limits encompass other studies. High pressure limit and m from Baulch et al. [26] and Baulch et al. [25], slightly modified. Hippler et al. [120] report higher values for the high pressure limiting rate constant. Atkinson et al. [14] use $F_c = \exp(-T/1850)$. This yields rate constants 10–20% higher than obtained from Table 2–1. Shock tube measurements by Yarwood et al. [293] in argon from 300–1300 K are consistent with the values in Table 2–1.
- C2. O + NO₂. Values of rate constants and temperature dependences from a combination of the study by Burkholder and Ravishankara [44] and that of Hahn et al. [112]. At 300K these studies almost overlap at the highest pressure of Burkholder and Ravishankara and the lowest pressure studied by Hahn et al.. The former values are larger by a factor of 2.2 under these conditions. This recommendation is in reasonable agreement with the evaluation of Baulch et al. [26], which fits the Hahn et al. values very well.
- C3. OH + NO. The low pressure limit rate constant has been reported by Anderson and Kaufman [6], Stuhl and Niki [254], Morley and Smith [185], Westenberg and de Haas [283], Anderson et al. [7], Howard and Evenson [124], Harris and Wayne [114], Atkinson et al. [16], Overend et al. [201], Anastasi and Smith [5], Burrows et al. [46] and Atkinson and Smith [11]. The general agreement is good, and the recommended values of both the rate constant and the temperature dependence are weighted averages. Studies by Sharkey et al. [242] and Donahue et al. [88] in the transition regime between low and high pressure limits are in agreement and serve to reduce the uncertainty. These latter studies yield a value for the high pressure limiting rate constant in

agreement with the results of Forster et al. [99], whose study reached pressures of 100 bar in He. The temperature dependence of the high pressure limiting rate constant is from the data of Anastasi and Smith [5] and Sharkey et al. (Both cis- and trans-HONO are expected to be formed.) Fulle et al. [106] report a high pressure limit in agreement with Forster et al. [99]. Pagsberg et al. [202] report low pressure values in SF₆ that are compatible (i.e. the ratio of collision efficiencies is about a factor of two.) with the recommendation. A study by Zabarnick [294] is noted.

- C4. OH + NO₂. This reaction has been the subject of detailed study. Golden and Smith [108] concluded that there were two pathways, one to HONO₂ (nitric acid) and the other to HOONO (pernitrous acid). They offered parameters in the format of this recommendation that were given in the note in JPL 00-3.[232] Donahue et al. [87] support the finding of two pathways in an analysis of isotopic effects. The low pressure limit and the high pressure limiting rate constants and their temperature dependences in JPL 00-3 are from a fit to the data of Anastasi and Smith [4] Wine et al. [286], Donahue et al. [88], Dransfield et al. [90], Brown et al. [39] and D'Ottone et al.[89]. (Brown et al. report that O₂ is about 30% less efficient than N₂ as a collider and suggest that air might therefore have a total efficiency of 0.94 relative to N₂) Data from Anderson et al. [7] Howard and Evenson [89], Burrows et al. [46], and Erler et al. [93] are in essential agreement. Data of Forster et al [99] and Fulle et al. [106] appear to be about 30% too high [118]. Experiments up to about 100 bar at 300 K and the finding of a double exponential decay of OH at 430 K and 100 bar implicate a second pathway [118]. Burkholder et al. [42] and Dransfield et al. [90] have searched for the isomer HOONO and have been unable to identify it. Nizkorodov and Wennberg [193] report 5% HOONO at 253K and 20 Torr of an N₂/He buffer gas . The presence of the HOONO isomer at 300 and 430 K can be accounted for with model transition states and RRKM calculations. However, this description of the reaction between HO and NO₂, requires that the data obtained at lower than 300 K represent the sum of the two pathways. Thus the fate of HOONO might have to be included in models. If this fate involves rapid loss due to reaction or photolysis, the effect of the second pathway is the diminution of the HONO₂ forming rate constant. However, evaluation of data, taking into account both pathways, indicates that the contribution of the HOONO forming reaction is quite small under atmospheric conditions. Thus, the recommendation is to use only the HONO₂ forming reaction. The following parameters relating to HOONO are provided for the purposes of model evaluation only and are not part of the Panel's recommendation for reaction C4.

Extrapolation of the model transition states used to fit the higher temperature results allows the formulation below.

Fits to individual product species in Table 2-1 format:

$$\text{HONO}_2: k_0(300) = 2.0 \times 10^{-30}; n = 3.0; k_\infty(300) = 2.5 \times 10^{-11}; m = 0$$

$$\text{HOONO}: k_0(300) = 1.0 \times 10^{-31}; n = 4.0; k_\infty(300) = 1.0 \times 10^{-10}; m = 0$$

For the HOONO case, the reverse reaction must be taken into account through the equilibrium constant. In the format of Table 3-1:

$$A = 4.66 \times 10^{-27}; B = 10028; K(298 \text{ K}) = 1.92 \times 10^{-12} \text{ and } f(298 \text{ K}) = 10$$

- C5. HO₂ + NO₂. Kurylo and Ouellette [152] have remeasured the 300-K rate constants. Kurylo and Ouellette [153] have also remeasured the temperature dependence. The recommended values are taken from this latter reference wherein their data were combined with that of Sander and Peterson [233]. The recommended k₀ (300 K) is consistent with Howard [123]. Other studies by Simonaitis and Heicklen [245] and Cox and Patrick [70] are in reasonable agreement with the recommendation, as is the value of Christensen et al. [56].
- C6. NO₂ + NO₃. Data with N₂ as the bath gas from Kircher et al. [143], Smith et al. [248], Burrows et al. [45], Wallington et al. [272] and Orlando et al. [199] ranging from 236 to 358 K were used to obtain k₀, k_∞, n and m. Values from Croce de Cobos et al. [71] are excluded due to arguments given by Orlando et al. [199], who point out that a reanalysis of these data using better values for the rate constant for NO₃ + NO → 2NO₂ yields a negative value for NO₂ + NO₃ + M. The study of Fowles et al. [100] is noted, but not used. Johnston et al. [130] have reviewed this reaction. Hahn et al. [112] have studied this reaction between 300 and 400 K at pressures from 30 to 900 bar. Their suggested parameterization yields values indistinguishable from those in this recommendation under most atmospheric conditions. (There are deviations of 30 to 50% at pressures less than a mbar and greater than 5 bar.)

A study of the reverse reaction has been carried out by Cantrell et al. [47]. These data are in excellent agreement with those obtained by Connell and Johnston [62] and Viggiano et al. [267]. The equilibrium

constant recommended in Table 3-1 is the one given in Cantrell et al. [47], who computed it from the ratio of the rate constant of Orlando et al. [199] and their rate constants for the reverse reaction.

- C7. $O_2 + NO$. Johnston et al. [130] and Davidson et al. [78] have suggested significant thermal decomposition of NO_3 . This has been disputed by Russell et al. [227]. Davis et al. [80] claim that the barrier to thermal dissociation is $47.3 \text{ kcal mol}^{-1}$. This would seem to rule out such a process in the atmosphere.
- D1. $CH_3 + O_2$. Low pressure limit from Selzer and Bayes [240]. (These workers determined the rate constants as a function of pressure in N_2 , Ar, O_2 , and He. Only the N_2 points were used directly in the evaluation, but the others are consistent.) Plumb and Ryan [218] report a value in He which is consistent within error limits with the work of Selzer and Bayes. Pilling and Smith [215] have measured this process in Ar (32–490 Torr). Their low pressure limiting rate constant is consistent with this evaluation, but their high pressure value is a little low. Cobos et al. [58] have made measurements in Ar and N_2 from 0.25 to 150 atmospheres. They report parameters somewhat different than recommended here, but their data are reproduced well by the recommended values. The work of Laguna and Baughcum [154] seems to be in the fall-off region. Results of Pratt and Wood [220] in Ar are consistent with this recommendation, although the measurements are indirect. Their T dependence is within our estimate. As can be seen from Patrick and Golden [211], the above value leads to a very small β , ~ 0.02 , and thus temperature dependence is hard to calculate. The suggested value accommodates the values of Keiffer et al. [140], who measured the process in Ar between 20 and 600 Torr and in the range $334 \leq T/K \leq 582$. Ryan and Plumb [230] suggest that the same type of calculation as employed by Patrick and Golden yields a reasonable value of β . We have not been able to reproduce their results. The high-pressure rate constant fits the data of Cobos et al. [58]. The temperature dependence is an estimate. (Data of van den Bergh and Callear [266], Hochenadel et al. [121], Basco et al. [23], Washida and Bayes [282], Laufer and Bass [156], and Washida [281] are also considered.) The fit to Keiffer et al. [140] is very good, suggesting that the temperature dependence for the high pressure limit is also reasonable. Kaiser [134] has determined values in reasonable agreement ($\pm 30\%$) with the recommended values.
- D2. $C_2H_5 + O_2$. A relative rate study by Kaiser et al. [136] yields $k_\infty = (9.2 \pm 0.9) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ and $k_0 = (6.5 \pm 2.0) \times 10^{-29} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ in He at 298 K and pressures between 3 and 1500 Torr. Their k_∞ agrees with the value calculated by Wagner et al. [269] ($k_\infty = 7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$) using variational RRKM theory. The extrapolation to the low-pressure limit is difficult due to the complex potential energy surface, but agrees with a Patrick and Golden-type calculation [211] using $\Delta H_0^0 = 32.4 \text{ kcal mol}^{-1}$. The recommended values use the calculated temperature dependence and a 2.5 times higher rate constant for air as the bath gas.
- D3. $OH + C_2H_2$. The rate constant for this complex process has been re-examined by Smith et al. [249] in the temperature range from 228 to 1400 K, and in the pressure range 1 to 760 Torr. Their analysis, which is cast in similar terms to those used here, is the source of the rate constants and temperature dependences at both limits. The negative value of m reflects the fact that their analysis includes a 1.2 kcal/mol barrier for the addition of OH to C_2H_2 . The data analyzed include those of Pastrana and Carr [210], Perry et al. [213], Michael et al. [181], and Perry and Williamson [214]. Other data of Wilson and Westenberg [285], Breen and Glass [35], Smith and Zellner [252], and Davis et al. [79] were not included. Studies by Liu et al. [168] and Lai et al. [155] are in general agreement with the recommendation. Calculations of k_0 via the methods of Patrick and Golden [211] yield values compatible with those of Smith et al. [249].
- D4. $OH + C_2H_4$. Experimental data of Tully [262], Davis et al. [79], Howard [122], Greiner [109], Morris et al. [186], and Overend and Paraskevopoulos [200] in helium, Atkinson et al. [17] in argon, and Lloyd et al. [169] and Cox [64] and Klein et al. [146] in nitrogen/oxygen mixtures, have been considered in the evaluation. This well-studied reaction is considerably more complex than most others in this table. The parameters recommended here fit exactly the same curve proposed by Klein et al. [146] at 298 K. Discrepancies remain and the effect of multiple product channels is not well understood. Kuo and Lee [150] report very strong temperature dependence for the low-pressure limit ($n=4$). Calculations of the type in Patrick and Golden [211] yield the recommended value. The high-pressure limit temperature dependence has been determined by several workers. Almost all obtain negative activation energies, the Zellner and Lorenz [298] value being equivalent to $m = +0.8$ over the range ($296 < T/K < 524$) at about 1 atmosphere. Although this could theoretically arise as a result of reversibility, the equilibrium constant is too high for this possibility. If there is a product channel that proceeds with a low barrier via a tight transition state, a complex rate constant may yield the observed behavior. The actual addition process ($OH + C_2H_4$) may even have a small positive barrier. The recommended limits encompass the reported values. A new high temperature measurement has been reported by Diau and Lee [84].

- D5. $\text{CH}_3\text{O} + \text{NO}$. The recommended values are taken from the results of Frost and Smith [103] in argon. Temperature dependences are from their higher temperature results. The low pressure rate constant is consistent with the measurement of McCaulley et al. [179] and Daele et al. [73] in helium and half the value from Troe-type calculations. A bimolecular (chemical activation) path also exists, forming $\text{HNO} + \text{CH}_2\text{O}$ (Frost and Smith [103]). Studies by Ohmori et al. [195] and Dobé et al. [86] are in general agreement with Frost and Smith with respect to both the addition and bimolecular pathways. (See the note in Table 1-1 for the bimolecular pathway.)
- D6. $\text{CH}_3\text{O} + \text{NO}_2$. The recommended values are from the work of Wollenhaupt and Crowley [289]. Agreement is good with earlier work at 298 K from the study of Frost and Smith [102] in argon (corrected by Frost and Smith [104] and that of Biggs et al [28] in He. Low pressure results agree within a factor of two with the measurements of McCaulley et al. [178] in helium. A minor bimolecular (chemical activation) pathway is also observed. (See Table 1-1.)
- D7. $\text{C}_2\text{H}_5\text{O} + \text{NO}$. High-pressure data at 298 K in Ar from Frost and Smith [103] and low-pressure measurements in He by Daele et al. [74] are scaled to N_2 and fit with an expression summing the bimolecular and termolecular channels. The low pressure value agrees with theory. The bimolecular channel with an estimated rate of about 10^{-12} needs to be verified by direct studies. The temperature dependence is estimated.
- D8. $\text{C}_2\text{H}_5\text{O} + \text{NO}_2$. High-pressure rate constant at 298 K from Frost and Smith [102]. Other values estimated from similar reactions.
- D9. $\text{CH}_3\text{O}_2 + \text{NO}_2$. Parameters from a reasonable fit to the temperature- and pressure-dependent data in Sander and Watson [235] and Ravishankara et al. [221]. These references report $F_c = 0.4$, and their parameters are a somewhat better fit at all temperatures than those recommended here. We do not adopt them since they are not much better in the stratospheric range, and they would require both a change in our $F_c = 0.6$ format and the adoption of a quite large negative activation energy for k_∞ . A study of the reverse reaction by Zabel et al. [295] also uses $F_c = 0.4$. The values recommended herein, taken with the value of the equilibrium constant in Table 3-1, fit the data in Zabel et al. [295] very well. Destriau and Troe [83] have fit the above data with k_∞ independent of temperature and $F_c = 0.36$. Bridier et al. [37] are in good agreement with this recommendation at one atmosphere and 298 K.
- D10. $\text{C}_2\text{H}_5\text{O}_2 + \text{NO}_2$. The only experimental study is that of Elfers et al. [91] who measured the rate constant relative to the $\text{C}_2\text{H}_5\text{O}_2 + \text{NO}$ reaction between 10 and 1000 mbar. Elfers et al. used a value of $k = 8.9 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ for the reference reaction. By comparison the recommended rate constant for the reference reaction from Table 1-1 of this evaluation is $1.1 \times 10^{-11} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 254 K. There are three data points. An evaluation of the Elfers et al. work by Destriau and Troe [83] cast the data in the format used in the IUPAC evaluation [14]. The parameters in Table 2-1 are adjusted to agree with the data corrected for the change in the reference reaction, using the simpler formula employed in this recommendation.
- D11. $\text{CH}_3\text{C(O)O}_2 + \text{NO}_2$. The recommended parameters are from the data of Bridier et al. [36], who report in the format represented here, but using $F_c = 0.3$. Their values are: $k_0^{300} = (2.7 \pm 1.5) \times 10^{-28}$,
 $k_\infty^{300} = (12.1 \pm 2.0) \times 10^{-12}$, with $n = 7.1 \pm 1.7$ and $m = 0.9 \pm 0.15$. Studies of the decomposition of $\text{CH}_3\text{C(O)O}_2\text{NO}_2$ [PAN] by Roberts and Bertman [226], Grosjean et al. [110], and Orlando et al. [198] are in accord with Bridier et al. [36]. In the former study it was shown that PAN decomposition yields only peroxyacetyl radical and NO_2 ; no methyl nitrate.
- D12. $\text{CH}_3\text{CH}_2\text{C(O)O}_2 + \text{NO}_2$. This reaction, forming peroxypropionyl nitrate (PPN), has been studied in the reverse direction by Schurath and Wipprecht [238], Mineshos and Glavas [182], Grosjean et al. [110] and Kirchner et al. [144]. The measured values are very similar to those for $\text{CH}_3\text{C(O)O}_2 + \text{NO}_2$ forming peroxyacetyl nitrate (PAN). Group additivity considerations indicate that the equilibrium constant for both PAN and PPN will be the same (both sides of the equilibrium for PPN differ from those for PAN by the group C-(C)(CO)(H)₂.) Therefore, the recommended value for the association reaction is taken from the decomposition studies multiplied by the same equilibrium constant as for PAN. Conservative error limits are estimated.
- D13. $\text{CH}_3\text{COCH}_2 + \text{O}_2$. Cox et al. [69] reported a value of $k = (1.5 \pm 0.3) \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$ at 298 K and 1 atm of SF_6 in which a pulse radiolysis study was modeled. This should be close to the high-pressure limit, but Cox et al point out that it is a bit low. (Using group additivity to calculate the entropy change yields about $10^{14.3} \text{ s}^{-1}$ for the decomposition A-factor. This compares with almost 10^{15} s^{-1} for $\text{C}_2\text{H}_5\text{O}_2$ decomposition.)
- E1. $\text{F} + \text{O}_2$. A study by Pagsberg et al. [206] reports k_0 in argon = $4.38 \times 10^{-33} (T/300)^{-1.2}$. This is in good agreement with earlier values of Smith and Wrigley [251], Smith and Wrigley [250], Shamonina and Kotov [241],

Arutyunov et al. [9] and slightly lower than the values of Chen et al. [54] and Chegodaev et al. [53]. Wallington and Nielsen [278], Wallington et al. [277] and Ellerman et al. [92] confirm the value of Pagsberg et al. [206]. Lyman and Holland [172] report a slightly lower value in Ar at 298K. We assume that $\beta_{\text{Ar}} = \beta_{\text{N}_2}$ at all temperatures. Pagsberg et al. [206], also determined the equilibrium constant and thus $\Delta H_f(\text{FO}_2)$. See F + O₂, Table 2–1. A calculation such as described in Patrick and Golden [211], using the new value yields: $k_0 = 1.06 \times 10^{-33} (\text{T}/300)^{-1.5}$ using $\beta_{\text{N}_2} = 0.3$ (i.e., $\langle \Delta E \rangle = 2 \text{ kJ mol}^{-1}$). This is not good agreement.

- E2. F + NO. A study by Pagsberg et al [203], taking into account data from Zetzsch [299], Skolnik et al. [246], Kim et al. [142], Pagsberg et al. [205] and Wallington et al. [275], reports rate constants for this reaction in several bath gases. Converting their values to the form used in this compilation yields the recommended parameters.
- E3. F + NO₂. A study by Pagsberg et al. [204], taking into account the experimental data of Fasano and Nogar [95] and Zetzsch [299], was used to determine both the high and low pressure limits at 300 K. Converting their values to the form used in this compilation yields the recommended parameters. Treatment of the data for this system requires knowledge of the relative stabilities of FNO₂ and FONO. Patrick and Golden [211] assumed that the difference between these would be the same as between the ClNO₂ isomers. Theoretical work by Dixon and Christie [85], Lee and Rice [159] and Amos et al. [3] indicates that FNO₂ is 35–40 kcal mol⁻¹ more stable than FONO, and therefore the measured rate refers to FNO₂ formation. The value of n = 2 is from Patrick and Golden, but consistent with Pagsberg et al. The value of m is a rough estimate from similar reactions, but is also consistent with Pagsberg et al.
- E4. FO + NO₂. Low pressure limit from strong collision calculation and $\beta = 0.33$. T dependence from resultant $\langle \Delta E \rangle = 0.523 \text{ kcal mol}^{-1}$, high-pressure limit and T dependence estimated. A theoretical study by Rayez and Destriau [225] indicates that the product is the single isomer FONO₂. Bedzhanyan et al. [27] report a value extracted from a complex mixture of bath gases.
- E5. CF₃ + O₂. Caralp et al. [49] have measured the rate constant in N₂ between 1 and 10 Torr. This supplants the value from Caralp and Lesclaux [48]. Kaiser et al. [137] have extended the pressure range to 580 Torr. They both recommend different parameters, but the data are well represented by the currently recommended values. Data of Ryan and Plumb [229] are in agreement.
- E6. CF₃O + NO₂. Fockenberget al. [98] report values in nitrogen with 250 < T/K < 302 and 7 < p/mbar < 107. They report large error limits. Their values, including two sigma errors, using the previous format are: $k_0 = (3.1 \pm 3.0) \times 10^{-28}$, n = (2.0 ± 2.0) $k_\infty = (1.5 \pm 0.5) \times 10^{-28}$, m = (2.8 ± 2.0). The reaction products agree with those reported by Chen et al. [55], who used photolysis of CF₃NO to prepare CF₃O₂ and subsequently CF₃O in 700 Torr of air at 297 + 2 K. They considered two product channels: (a) CF₃ONO₂ obtained via three-body recombination and (b) CF₂O + FNO₂ obtained via fluorine transfer. Both products were observed and found to be thermally stable in their reactor. They report $k_a/(k_a+k_b) > 90\%$ and $k_b/(k_a+k_b) < 10\%$, thus the formation of CF₃ONO₂ is the dominant channel at 700 Torr and 297 K.
- E7. CF₃O₂ + NO₂. Based on experiments in O₂ of Caralp et al. [50], who suggest a somewhat different fitting procedure, but the values recommended here fit the data just as well. Destriau and Troe [83] use yet a different fitting procedure that does not represent the data quite as well as that recommended here. Reverse rate data are given by Köppenkastrup and Zabel [148].
- E8. CF₃O + CO. Values taken from Turnipseed et al. [263]. The numbers were obtained for Ar as the bath gas and are assumed to hold for N₂ as well. The temperature dependence of the high-pressure rate constant was determined over the range 233 < T/K < 332 in SF₆. No temperature dependence of the low-pressure-limiting rate constant was reported. Wallington and Ball [273] report values in good agreement with Turnipseed et al.
- E9. CF₃O + M. The activation energy for thermal decomposition of CF₃O to CF₂O + F has been reported to be 31 kcal mol⁻¹ by Kennedy and Levy [141]. Thermochemical data yield $\Delta H^\circ(298) = 23 \text{ kcal mol}^{-1}$. This implies an intrinsic barrier of about 8 kcal mol⁻¹ to elimination of F from CF₃O. Electronic structure calculations by Li and Francisco [166] support this observation. Adopting the A-factor for unimolecular dissociation, A = 3 × 10¹⁴ s⁻¹ and E = 31 kcal mol⁻¹ from Kennedy and Levy, $k_\infty(298 \text{ K})$ is about 6 × 10⁻⁹ s⁻¹. This corresponds to a lifetime of about 6 years; therefore, thermal decomposition of CF₃O is unimportant throughout the atmosphere.
- F1. Cl + O₂. Nicovich et al. [189] measure $k_0 = (9 \pm 3) 10^{-33} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ at T = 187 ± 6 K in O₂. Using the methods described in Patrick and Golden [211], but adjusting the thermochemistry of ClO₂ such that $S_{298 \text{ K}}^\circ = 64.3 \text{ cal mol}^{-1} \text{ K}^{-1}$ and $\Delta H_{f,298} = 23.3 \pm 0.6 \text{ kcal mol}^{-1}$ (Cl + O₂, Table 3), we calculate $k_0 = 5.4 \times 10^{-33} \text{ cm}^6 \text{ molecule}^{-2} \text{ s}^{-1}$ at T = 185 K. The collisional efficiency of the bath gas is taken from the

formula $[\beta/(1-\beta^{1/2})] = \langle \Delta E \rangle / F_E kT$ and $\langle \Delta E \rangle \sim 0.5 \text{ kcal mol}^{-1}$ (i.e., $\beta_{185} = 0.42$ and $\beta_{300} = 0.30$). Since O_2 may be particularly efficient for this process, we use this calculation with broader error limits. The value from the calculation at 300 K (i.e., $2.7 \times 10^{-33} \text{ cm}^6 \text{ molecules}^{-2} \text{ s}^{-1}$) compares with an older value of Nicholas and Norrish [187] of 1.7×10^{-33} in an $N_2 + O_2$ mixture. The temperature dependence is from the calculation. Baer et al. [18] report a value at 298 K in good agreement with the value recommended here, but the temperature dependence is strikingly different, as noted by the authors.

- F2. Cl + NO. Low-pressure limit is from Lee et al. [158], Clark et al. [57], Ashmore and Spencer [10], and Ravishankara et al. [222]. Temperature dependence is from Lee et al. [158] and Clark et al. [57].
- F3. Cl + NO₂. Low-pressure limit and T dependence from Leu [164]. (Assuming similar T dependence in N₂ and He.) Leu [164] confirms the observation of Niki et al. [192] that both ClONO and ClNO₂ are formed, with the former dominating. This has been explained by Chang et al. [52], with detailed calculations in Patrick and Golden [211]. The temperature dependence is as predicted in Patrick and Golden [211]. Leu's results are in excellent agreement with those reported in Ravishankara et al. [223]. The latter work extends to 200 Torr, and the high-pressure limit was chosen to fit these measurements. The temperature dependence of the high-pressure limit is estimated. A turbulent flow study by Seeley et al. [239] that extends results to 250 Torr of Ar is in agreement with earlier work.
- F4. Cl + CO. From Nicovich et al. [190], who measured the process in N₂ for $185 \leq T/K \leq 260$.
- F5. Cl + C₂H₂. The recommended values are taken from the work of Kaiser [133] and Kaiser and Wallington [132], which extends the pressure range to 0.3–6000 Torr. The data are in reasonable agreement with earlier measurements of Brunning and Stief [40] and Wallington et al. [271], although the derived temperature dependence is much less than obtained by Brunning and Stief [40]. These values are compatible with earlier studies of Poulet et al. [219], Atkinson and Aschmann [12], Lee and Rowland [157] and Wallington et al. [279]. Using FTIR, Zhu et al. [300] reported branching of 16% and 84% to the trans and cis adduct isomers, respectively, at 700 Torr N₂ and 295 K.
- F6. Cl + C₂H₄. Values at 300K are from a relative rate study by Wallington et al. [271]. A relative rate study by Kaiser and Wallington [132] extends the pressure range to 0.3–6000 Torr and is compatible with earlier studies. Temperature dependence of k_o is taken from Kaiser and Wallington [135]. The temperature dependence of k_∞ is estimated. Values are in reasonable agreement with studies by Maricq et al. [175], Lee and Rowland [157], Iyer et al. [129], Atkinson and Aschmann [12], Atkinson and Aschmann [13] and Wallington et al. [280]. A study in He by Stutz et al. [255] is noted, as is a comment on it by Kaiser and Wallington [135]. Knyasev et al. [147] have done an extensive experimental and theoretical analysis. Their values agree with this recommendation.
- F7. Cl + C₂Cl₄. Recommendation is from the flash-photolysis study of Nicovich et al. [191] done at 231–390 K in 3–700 Torr N₂. A study by Thuner et al. is in agreement [257].
- F8. ClO + NO₂. The low-pressure-limit recommendation and uncertainties are based on temperature-dependent values from Zahniser et al. [296], Lee et al. [161], Birks et al. [31], Leu et al. [165], Wallington and Cox [274], Cox et al. [65] and Molina et al. [183]. All of these data were collected in N₂ bath gas, except for several points from Lee et al. [161] collected in O₂.
The high-pressure-limit recommendation is based on the RRKM calculations of Smith and Golden. There are several pressure-dependent data sets in the literature, such as Percival et al. [212], Handwerk and Zellner [113], Dasch et al. [77] and Cox and Lewis [68]; however, they are too disparate to extract unambiguous values. These data are all reproduced within two-sigma error limits by the current recommendation.
- F9. OClO + NO₃. Friedl et al. [101], studied this system at $1 \leq P/\text{Torr} \leq 5$ for helium and $220 \leq T/K \leq 298$. They deduced values for the rate constant consistent with their data of $k_o \approx 10^{-31}$ and $k_\infty \approx 10^{-11}$. They also suggest a value for the equilibrium constant: $K/\text{cm}^3 \text{ molecule}^{-1} = 1 \times 10^{-28} \exp(9300/T)$. However, Boyd et al. [34] have raised the question of possible heterogeneous effects in this system, and further work is needed.
- F10. ClO + ClO. The recommendation is based on a simultaneous fit to data from Bloss et al. (183–245 K) [33], (which supersedes earlier work of Sander et al. (194–247 K) [231]), Nickolaisen et al. (260–390 K) [188] and Troler et al. (200–263 K) [261]. The latter data have been corrected for the effect of Cl₂ as third body, as suggested by Nickolaisen et al. With this adjustment all the data are in reasonable agreement. Error limits are from the statistical fit. The k_o value for N₂ is not in accord with a Patrick and Golden-type calculation [211]. This may be due to uncertainty in the ClOCl thermochemistry, which is based on the equilibrium constants reported by Nickolaisen et al. and Cox and Hayman [67] (See Table 3.). Other previous rate constant measurements, such as those of Hayman et al. [116], Cox and Derwent [66], Basco and Hunt [22], Walker

[270], and Johnston et al. [131], range from $1\text{--}5 \times 10^{-32} \text{ cm}^6 \text{ s}^{-1}$, with N_2 or O_2 as third bodies. The major dimerization product is chlorine peroxide (Birk et al. [30], DeMore and Tschuikow-Roux [82], Slanina and Uhlik [247], Stanton et al. [253] and Lee et al. [160]).

- F11. $\text{ClO} + \text{OCIO}$. Data are from Burkholder et al. [43], who measured the rate constant in N_2 at $200 \leq T/\text{K} \leq 260$ and densities from $(1.1\text{--}10.9) \times 10^{18} \text{ molecules cm}^{-3}$. They also measured the equilibrium constant. Parr et al. [208] also report a value for the rate constant in reasonable agreement with the recommendation.
- F12. $\text{O} + \text{OCIO}$. The recommendation is based on data of Colussi et al. [61] and Colussi [60], who measured the pressure dependence between 248 and 312 K. Their results are consistent with calculations. A zero-pressure rate constant of $(1.6 \pm 0.4) \times 10^{-13} \text{ cm}^3 \text{ s}^{-1}$ is reported for the chemical activation channel producing $\text{ClO} + \text{O}_2$, and their value of $\Delta H_1^0(\text{ClO}_3) = 52 \text{ kcal mol}^{-1}$ is derived at 298 K. A low-pressure study by Gleason et al. [107] suggests a direct abstraction as well. See Table 1-1.
- F13. $\text{CH}_2\text{Cl} + \text{O}_2$. Measured by Fenter et al. [96] over the range $298 \leq T/\text{K} \leq 448$ and $1 \leq P/\text{Torr} \leq 760$ in nitrogen. Two different techniques were employed: laser photolysis/photoionization mass spectrometry in the range 1–10 Torr and laser photolysis/UV absorption for the range 20–760 Torr. A study by Bilde et al. [29] in N_2 relative to the reaction $\text{CH}_2\text{Cl} + \text{Cl}_2 \rightarrow \text{CH}_2\text{Cl}_2 + \text{Cl}$ is in excellent agreement.
- F14. $\text{CHCl}_2 + \text{O}_2$. Measured by Fenter et al. [96] over the range $298 \leq T/\text{K} \leq 383$ and $1 \leq P/\text{Torr} \leq 760$ in nitrogen. Two different techniques were employed: laser photolysis/photoionization mass spectrometry in the range 1–10 Torr and laser photolysis/UV absorption for the range 20–760 Torr. A study by Nottingham et al. [194], in He, is in agreement.
- F15. $\text{CCl}_3 + \text{O}_2$. The recommendation incorporates studies by Fenter et al. [97], Danis et al. [76] and Luther et al. [171]. Experimental data of Ryan and Plumb [230] have been considered in the evaluation. A study by Nottingham et al. [194], in He, is in agreement. A Patrick and Golden-type calculation using the thermochemistry of Russell et al. [228] yields $k_0^{300} = 1.5 \times 10^{-30}$, with $\beta = 0.3$. A value of $k_\infty^{300} = 5 \times 10^{-12}$ has been reported by Cooper et al. [63]. The value of the high-pressure-limiting rate constant recommended here is slightly below that of Luther et al., but within their error limits. If we use their value the fit to lower-pressure data in the atmospherically important regions is less good.
- F16. $\text{CFCl}_2 + \text{O}_2$. Values for both low- and high-pressure limits at 300 K are from Caralp and Lesclaux [48]. Temperature dependences are rough estimates based on calculations and similar reactions.
- F17. $\text{CF}_2\text{Cl} + \text{O}_2$. Values estimated from other reactions in this series.
- F18. $\text{CCl}_3\text{O}_2 + \text{NO}_2$. Based on experiments in O_2 of Caralp et al. [50], who suggest a somewhat different fitting procedure, but the values recommended here fit the data as well. Destriau and Troe [83] use yet a different fitting procedure that does not represent the data quite as well as that recommended herein. Reverse rate data are given by Köppenkaströp and Zabel [148].
- F19. $\text{CFCl}_2\text{O}_2 + \text{NO}_2$. Based on experiments in O_2 of Caralp et al. [50], who suggest a somewhat different fitting procedure, but the values recommended here fit the data as well. Destriau and Troe [83] use yet a different fitting procedure that does not represent the data quite as well as that recommended herein. Reverse rate data are given by Köppenkaströp and Zabel [148].
- F20. $\text{CF}_2\text{ClO}_2 + \text{NO}_2$. A study by Wu and Carr [291] supersedes the earlier work of Moore and Carr [184] and is recommended here. Reverse rate data are given by Köppenkaströp and Zabel [148] and Xiong and Carr [292].
- G1. $\text{Br} + \text{NO}_2$. The recommended values are from a study by Kreutter et al. [149]. Their k_0 value agrees with the measurement of Mellouki et al. [180] at 300 K. A Patrick-and-Golden-type calculation using the known structure of the more stable BrNO_2 isomer and the measured equilibrium by Kreutter et al. [149] underpredicts k_0 by an order of magnitude. Participation by other electronic states and isomers such as BrONO as suggested in JPL 97-4, in keeping with the chlorine analog, has been shown in studies by Broske and Zabel [38] and Orlando and Burkholder [196].
- G2. $\text{BrO} + \text{NO}_2$. Values from a study by Thorn et al. [256] that is in excellent agreement with Sander et al. [234] are recommended. Error limits are from a reanalysis of the data. Danis et al. [75] give slightly lower values for the low-pressure-limiting rate constant and a smaller temperature dependence as well. This latter study may be hampered by heterogeneous effects. A theoretical study by Rayez and Destriau [225] suggests that the bond-dissociation energy in BrONO_2 is higher than that in ClONO_2 , thus rationalizing the relative values of the low-

pressure-limiting rate constants for these two processes. This is confirmed by a more detailed study by Parthiban and Lee. [209] as well as by Orlando and Tyndall [197], who measured BrONO₂ decomposition and thus an equilibrium constant.

- H1. I + NO. Evaluation taken from IUPAC [128]. The data is from van den Bergh et al. [264] and Basco and Hunt [21]. Although IUPAC recommends $F_c = 0.75$, any differences will be insignificant, since this reaction is in the low pressure limit under atmospheric conditions.
- H2. I + NO₂. Evaluation taken from IUPAC [128]. The data is from van den Bergh et al. [264], Mellouki et al. [180], Buben et al. [41] and van den Bergh and Troe [265]. IUPAC uses $F_c = 0.63$, which is the same as the universal value adopted here of $F_c = 0.6$. (No evidence of possible isomers [INO₂ or IONO] is reported.)
- H3. IO + NO₂. Data taken from Daykin and Wine [81]. They suggest $k_o = 7.7 \times 10^{-31} (T/300)^{-5.0}$, $k_\infty = 1.5 \times 10^{-11}$ and $F_c = 0.4$. The values recommended here fit the data as well.
- I1. HS + NO. Data and analysis are from the work of Black et al. [32]. The temperature dependence of k has been estimated.
- I2. CH₃S + NO. The recommended values are from the study by Balla et al. [19] at 296K in nitrogen. Temperature dependences are derived from the higher temperature results of the same study.
- I3. O + SO₂. The recommendation is taken from Atkinson et al. [15] and was transformed to the format used herein.
- I4. OH + SO₂. Values of the rate constant as a function of pressure at 298 K are from Leu [163], Paraskevopoulos et al. [207], and Wine et al. [287]. The value of the low-pressure limit is from Leu [163], corrected for fall-off. The high-pressure limit is from a fit to all the data. The value of n comes from the above data combined with calculations such as those of Patrick and Golden [211], except that the heat of formation of HOSO₂ is raised by 4 kcal mol⁻¹, as suggested by the work of Margitan [173]. The value of m is estimated. This is not a radical-radical reaction and is unlikely to have a positive value of m. The limit of $m = -2$ corresponds to a real activation energy of ~1 kcal mol⁻¹. Earlier data listed in Baulch et al. [26] and Baulch et al. [25] are noted. Work of Martin et al. [177], Barnes et al. [20], and Lee et al. [162] confirm the current evaluation.
- I5. CH₃SCH₂ + O₂. Wallington et al. [276] have employed a pulse radiolysis technique, allowing the derivation of $k = 5.7 \pm 0.4 \times 10^{-12}$ in 992 mbar of SF₆ at room temperature.
- I6. SO₃ + NH₃. Recommendation is from Lovejoy and Hanson [170], who studied this reaction from 10–400 Torr N₂ at 295 K. They observe that the adduct isomerizes rapidly to sulfamic acid and clusters efficiently with itself and sulfuric acid. Observed sulfamic acid dimerization rate constant exceeds 5×10^{-11} . Measurements of Shen et al. [243] made at 1–2 Torr He are much higher than those of Lovejoy and Hanson. Temperature dependences are rough estimates.
- J1. Na + O₂. A study by Plane and Rajasekhar [217] finds $k_o = (2.9 \pm 0.7) \times 10^{-30}$ at 300 K with $n = 1.30 \pm .04$. They also estimate k_∞ to be about 6×10^{-10} , with a small positive temperature dependence. Another study by Helmer and Plane [117] yields $k_o = (3.1 \pm 0.2) \times 10^{-30}$ at 300 K with $n = 1.52 \pm 0.27$. The recommended values are taken from these studies. They are consistent with values measured by Marshall et al. [176] at 600 K and those measured by Vinckier et al. [268] at higher temperature. The k_o value is about 60% higher than that of Silver et al. [244].
- J2. NaO + O₂. Ager and Howard [1] have measured the low- pressure limit at room temperature in several bath gases. Their value in N₂ is used in the recommendation. They performed a Troe calculation, as per Patrick and Golden [211], to obtain collision efficiency and temperature dependence. They obtained a high-pressure-limit rate constant by use of a simple model. The temperature dependence is estimated.
- J3. NaO + CO₂. Ager and Howard [1] have measured the rate constant for this process in the “fall-off” regime. Their lowest pressures are very close to the low-pressure limit. The temperature dependence is an estimate. Ager and Howard calculate the high-pressure rate constant from a simple model.
- J4. NaOH + CO₂. Ager and Howard [2] have measured the low-pressure-limiting rate constant. The temperature dependence is an estimate. Ager and Howard have calculated the high-pressure limit using a simple model.

2.8 References

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