

Atmospheric Chemistry IV

Tropospheric chemistry I: homogeneous gas-phase chemistry

Troposphere: 90% of total atmospheric mass in troposphere, and bulk of minor trace gases
plus (briefly) concept of boundary layer (0.5–2.0 km highly turbulent mixing)

Ozone is as critically important in tropospheric chemistry as it is in stratospheric chemistry. In troposphere, it initiates oxidation through the formation of OH (from H₂O, CH₄ etc) by O(¹D) reactions.

In 'natural' troposphere, CH₄ is oxidized to CO and CO₂, and other minor constituents are also oxidized by processes involving initial attack by OH by day (night-time later).

Sources of atmospheric gases. (NB Handout #2 for Lecture I)

Sinks of atmospheric gases

Physical removal:

Dry deposition

Wet deposition

Washout (falling precipitation); rainout (clouds)

Solubility of natural and anthropogenic compounds

Chemical conversion: and possible formation of species that can be removed physically

Return later to question of lifetimes and transport

Oxidation and transformation

Initiation

Source of O₃: nb problem in *inorganic* chemistry of making NO₂
small stratospheric source as well

Attack of OH

Peroxy radical formation

Loss of peroxy radicals

So far, in this discussion, one NO₂ makes one O₃, and that is the end of involvement of NO_x: limited oxidation.

Summary of chemistry of troposphere

With emphasis on the OH and HO₂ radicals

notes: (i) backward links – later; (ii) NO “hinted at” here

With emphasis on the CH₄

Cyclic radical reaction scheme

Critical feature is oxidation of NO to NO₂ by RO₂ and HO₂

Reactions of CH₃O can also yield HO₂, as can photolysis of HCHO (photochemically rather labile. Thus, ultimately, all H in CH₄ is available to convert NO to NO₂:

H is catalysing the oxidation process! (And the carbon ends up as CO)

Higher hydrocarbons

NO to NO₂ conversion continues (RO₂ and HO₂)

Other carbonyl compounds - aldehydes and ketones - are generated

Acyl radicals

- Derived from aldehydes (nb especially acetylperoxy)
- Capable of converting NO to NO₂
- Another important reaction of acyl radicals shortly (PAN)

Importance of NO₂ in methane oxidation

- Emerged in previous schemes as conversion of NO to NO_x
- Now made explicit in cyclic diagram: cycle only closes if NO present
- Not only is cycle closed, but NO₂ production allows more O₃, and hence OH, to be formed
- But note also addition of NO₂ to make CH₃CO.O₂NO₂ (PAN)
- Significance of PAN as transporter of NO_x
- (More in connection with photochemical smog: lecture 5)

Atmospheric lifetimes of trace gases

Meaning of lifetime (residence time): chemical and physical

τ can be defined as time for concentration to fall to 1/e of initial value if all source terms removed: ie $\tau = 1/k'$ (explain k')

e.g. via $\text{OH} + \text{CH}_4 \rightarrow \text{H}_2\text{O} + \text{CH}_3 \cdot$ Rate = $k[\text{OH}][\text{CH}_4] = k'[\text{OH}]$

For both chemical and physical loss

concentration = rate of release \times time in atmosphere

$\therefore \tau = \text{concentration} / \text{rate} = 1 / (\text{rate constant})$

For species roughly in steady state $\tau \sim (\text{concentration})/(\text{rate of supply})$

Transport E-W (10-30 m s⁻¹), N-S and vertical much slower

Interhemispheric and intrahemispheric

Comparison lifetime and transport

The nitrate radical

- Night-time oxidant, but also derived from O₃, so also depends on daytime hv
- Abstraction and addition reactions
- Inorganic reactions \rightarrow HNO₃

Feedbacks in atmospheric chemistry

Biogeochemistry

Stratosphere: source and sinks of O₃; UV protection

Troposphere:

Chemistry - atmospheric composition (eg O₂)

CO₂ - temperature

Both these two factors influence total pressure

DMS - cloudiness

Thus composition, pressure, temperature, solar intensity and wavelength distribution all modulated

Leads to concept of Gaia: argument as to whether or not the loop is closed

In terms of physical chemistry, the question could be reformulated to asking if the entropy reduction extends outside the *immediate* system (biota) so that the surroundings can be considered as **part of** the system.

Atmospheric Chemistry IV : Slides

- 1 R 1 Regions of atmosphere
- 2 R 8 Methane oxidation path (concentrates on methane)
- 3 YG 62 Chemical feedbacks

Atmospheric Chemistry IV : Viewgraphs

- “0” Regions of atmosphere
- 1 Sources of tropospheric gases (CAI-2)
- 2 Sinks of atmospheric species
- 3 Initial oxidation steps: day
- 4 Chemistry of the troposphere: centred on OH radical
- 5 Cyclic processes - NO_x
- 6 The importance of NO_x (cyclic diagram); PAN as carrier of NO_x
- 7 Atmospheric lifetimes of trace gases
- 8 The nitrate radical
- 9 Atmospheric chemistry - elements and couplings