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 H_2O, CH_4 etc) by $O(^1D)$ reactions.

In 'natural' troposphere, CH_4 is oxidized to CO and CO_2, 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 O_3: nb problem in *inorganic* chemistry of making NO_2
  - small stratospheric source as well
- Attack of OH
- Peroxy radical formation
- Loss of peroxy radicals
  - *So far*, in this discussion, one NO_2 makes one O_3, and that is the end of involvement of NO_x: limited oxidation.

Summary of chemistry of troposphere
- With emphasis on the OH and HO_2 radicals
  - *notes:* (i) backward links – later; (ii) NO "hinted at" here
- With emphasis on the CH_4

Cyclic radical reaction scheme
- Critical feature is oxidation of NO to NO_2 by RO_2 and HO_2
- Reactions of CH_3O can also yield HO_2, as can photolysis of HCHO (photochemically rather labile. Thus, ultimately, all H in CH_4 is available to convert NO to NO_2:
  H is catalysing the oxidation process! (And the carbon ends up as CO)

Higher hydrocarbons
- NO to NO_2 conversion continues (RO_2 and HO_2)
- Other carbonyl compounds - aldehydes and ketones - are generated

Acyl radicals

Derived from aldehydes (nb especially acetylperoxy)

Capable of converting NO to NO_2

Another important reaction of acyl radicals shortly (PAN)

Importance of NO_2 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 NO_2 production allows more O_3, and hence OH, to be formed

But note also addition of NO_2 to make $CH_3CO.O_2NO_2$ (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 $OH + CH_4 \rightarrow H_2O + CH_3$: Rate = $k[OH][CH_4] = k'[OH]$

For both chemical and physical loss

concentration = rate of release × time in atmosphere

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

For species roughly in steady state $\tau \sim$ (concentration)/(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 O_3, so also depends on daytime $h\nu$

Abstraction and addition reactions

Inorganic reactions $\rightarrow HNO_3$

Feedbacks in atmospheric chemistry

Biogeochemistry

Stratosphere: source and sinks of O_3; UV protection

Troposphere:

Chemistry - atmospheric composition (eg O_2)

CO_2 - 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