

Atmospheric Chemistry V

General content of this lecture

Heterogeneous processes and air pollution (to include S-chemistry)

Note presence of clouds in troposphere

Aerosols and droplets

Sizes, lifetimes^a, sources, effects^b

^asmall coagulate fast; large precipitate fast; thus mid-size have longest lifetime

^bradiation, **chemistry** (cf PSCs of lecture III)

Chemistry on and in aerosols and droplets: types of process

- (i) Condensation of single component ("homogeneous, homomolecular")
- eg $\text{H}_2\text{O} \rightarrow$ droplet;
- (ii) Reaction of gases to form particle ("homogeneous, heteromolecular")
- eg $\text{NH}_3 + \text{HNO}_3 \rightarrow \text{NH}_4\text{NO}_3$
- (iii) Reactions of gases on existing particle ("heterogeneous, heteromolecular");
- eg $\text{NH}_3 + \text{HNO}_3 \rightarrow \text{NH}_4\text{NO}_3$ on pre-existing particle (? more important for NH_4NO_3 than process (ii))
- eg $\text{HNO}_3 + \text{NaCl}$ (sea salt) $\rightarrow \text{NaNO}_3 + \text{HCl}$
- (iv) Reactions within particles themselves
- eg hydration of anhydrides such as $\text{N}_2\text{O}_5 \rightarrow \text{HNO}_3$
- eg oxidation of SO_2 to SO_4^{2-} (to discuss later)

Process (iii) - condensation of gases on pre-existing particles - is sometimes called *aerosol scavenging*. It affects bulk tropospheric chemistry by providing a sink for nitrogen and hydrogen species, eg, HNO_3 , NO_3 , N_2O_5 , H_2O_2 , HO_2 and organic nitrates and peroxides. "Rainout" removes these aerosols.

In process (iv), clouds offer a medium for aqueous-phase reactions, and have large influence on troposphere: Three reasons:

- (a) concentration in solution enhances rates (especially of 2nd order processes);
- (b) activation energies often less in solution than in gas phase; and, a **special** feature,
- (c) high solubility of certain key compounds such as HO_2 and N_2O_5 . Reactions of these species within droplet ensures that dissolution is irreversible and partitioning into aqueous phase is thus strongly favoured despite relatively small fractional volume of H_2O droplets (ca. 10^{-6})

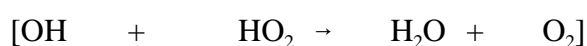
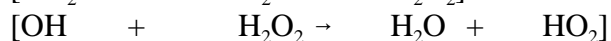
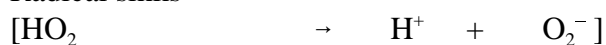
Examples of chemistry within droplets (the [..] represent the droplets)



(hydration of acid anhydride) most important. Rate limited by gas-phase diffusion and transfer through interface: reaction *within* the droplet is virtually "instantaneous".

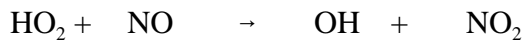
NOTE: Formation of an acid!

Radical sinks



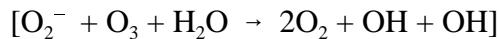
Thus oxidizing capacity of troposphere can be affected by droplet chemistry.

Because HO₂ is highly soluble, and NO is relatively *insoluble*, HO₂ and NO are separated by droplets, and inhibits the reaction



Remember that this reaction ultimately yields O₃ in the gas phase by NO₂ + hv, so that O₃ production is suppressed.

There are also reactions that destroy O₃, such as



Oxidation of sulphur compounds

Take in two steps: (i) formation of SO₂ and (ii) oxidation of SO₂

Lifetime of SO₂ is a few weeks, and variability by a factor of nearly 2000 suggests largely anthropogenic source. Important component of pollution.

Natural contributions to SO₂ are result of oxidation of H₂S, COS, DMS etc

Oxidation pathways discussed

Almost all SO₂ is oxidized to H₂SO₄ in form of aerosol, which is rapidly incorporated into water droplets: the S cycle is closed by wet precipitation of the acid. Homogeneous and heterogeneous oxidation pathways are possible, with the latter probably dominating: enhanced oxidation rates at high relative humidities or when liquid water is present indicate participation of liquid-phase processes.

Gas-phase and H₂O₂ and radical droplet mechanisms

Detail does not concern us - several strange intermediates, mechanisms recently elucidated. Note that heterogeneous steps start with HSO₃⁻ formation. Broad outline only - steps on handout - note cyclic nature (regeneration of OH in gas phase, SO₃⁻ in droplets)

Smoke and sulphur pollution: London smog

Existed since at least 12th century ⇒ beginning of 14th century – Edward I Law – execution ⇒ Victorian ‘pea soupers’ and Jack the Ripper

Bituminous coal: high S and high smoke (tars and hydrocarbons) → "London" **smog**

Irritant effects of SO₂

Potential (factor of 3-4) by soot particles: delivery into respiratory system

1952 smog disaster and legislation

Acid precipitation

Natural precipitation is slightly acid (CO_2), but $\text{pH} \geq \text{ca.}5.6$. Much lower pH have been observed in recent decades. For example, in some parts of Scandinavia, $[\text{H}^+]$ concentrations have increased by a factor of 200 in last two decades.

We have already examined two sources of acid: NO_x and $\text{SO}_2 \rightarrow \text{HNO}_3$ and H_2SO_4 .

Clear evidence that the sources are pollution and not biogenic: fossil fuel combustion.

Meteorological factors may lead to deposition in a small area of pollutants picked up over widespread urbanized or industrial regions: eg Swedish acid rain from Britain.

Granite vs. limestone bedrock

Effects of acid deposition: freshwater fish and land vegetation (forest decline)

Photochemical air pollution

Photochemical air pollution (*photochemical smog* or *Los Angeles smog*) is a grotesquely exaggerated form of 'natural' tropospheric chemistry, but concentrations of minor species are greatly elevated in the pollution phenomenon.

Los Angeles — clear and smoggy

What is observed: O_3 , NO_2 , particles, PAN etc

Effects: all toxic and damaging to human health; vegetation; buildings; visibility

Why especially Los Angeles? History - pre motor cars. 'Natural' photochemical smog. Smoky mountains. Other cities, including London.

Exhaust gases contain NO and unburnt hydrocarbons

Time evolution of pollutant concentrations: LAX and smog chamber

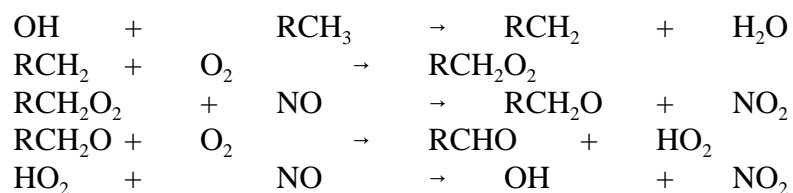
Problem

Inorganic chemistry CANNOT lead to oxidation of NO to NO_2 . Only possible reaction is $\text{NO} + \text{O}_3$, yet only source of O_3 is via NO_2 photolysis.

Note NO and O_3 anticorrelated – result of reaction.

Radical reaction scheme

Critical feature is oxidation of NO to NO_2 by RO_2 and HO_2 as discussed for natural troposphere (cf. Handout for Lect IV, #4.1, 4.2, 4.3, 4.4)



Initial addition of OH to alkenes yields similar chemistry *via* an OHRO₂ radical

Aldehydes will produce acyl and peroxyacyl radicals, and hence PAN.

Control strategies and their dangers

'lean burn' (→ high [NO], lowered [HC]) → local improvements (NO + O₃) but downwind increase (NO₂ + hv).

Chamber results illustrate effects of altering [HC] and [NO_x]. Reduction of [HC] reduces O₂ in all cases, but reduction of [NO_x] can lead to an *increase* (conditions on RHS of figure typical of urban ambient air)

Catalytic converters (but need for efficiency, otherwise aldehyde production may exacerbate problem).

Atmospheric Chemistry V : Slides

1. G 27 LAX street scene - clear
2. G 28 LAX street scene - smoggy
3. G 31 Observations - LAX
4. G 32 Observations - smog chamber

Atmospheric Chemistry V : Viewgraphs

- “0”. Regions of Earth's atmosphere
- 1. Sizes, lifetimes and effects of atmospheric particles
- 2. Chemistry on and in aerosols and droplets: types of process
- 3. Chemistry on and in aerosols and droplets: processes (iii) and (iv)
- 4. Droplet chemistry
- 5. Sulphur chemistry
- 6. Flow chart showing oxidation steps up to S(IV)
- 7. Concentration—time profiles for smog build-up
- 8. Concentration—time profiles for smog chamber
 - (a) basic outline
 - (b) effect of varying $[\text{NO}_x]$ for different $[\text{HC}]$
- 9. Photochemical smog reaction schemes
- 10. Attack of OH on alkenes, and oxidation scheme