

Chemistry in the Troposphere: Photochemical Smog

Overview:

- The atmosphere is an *oxidizing* system
- Tendency of organic components to be oxidized (both natural and anthropogenic)
 - $2\text{C}_2\text{H}_6 + 7\text{O}_2 \rightarrow 4\text{CO}_2 + 6\text{H}_2\text{O}$
 - C_2H_6 called: Volatile Organic Compound
 - VOCs
- Ideally, we would like to have complete oxidation of the hydrocarbon, the VOC in as few steps as possible.
- Toxic intermediates are formed towards complete oxidation to $\text{CO}_2 + \text{H}_2\text{O}$
- Ozone (O_3) is formed as a byproduct of VOC oxidation
- Central role of the hydroxyl radical, OH^\bullet , in initiating oxidation
- Interaction between VOC oxidation and NO_x chemistry
- Conditions for photochemical smog formation
 - strong sunlight
 - $T > \sim 20^\circ\text{C}$
 - Polluted air, *i.e.*, greater than background levels of both VOCs and NO_x
 - (Note Table 3.3, text, p. 81)

Photochemical rate constants: J(X)

- Only two important tropospheric examples:
 - $O_3 + h\nu (\lambda < 325 \text{ nm}) \rightarrow O_2^* + O^*$
 - $NO_2 + h\nu (\lambda < 400 \text{ nm}) \rightarrow NO + O$
 - O^* is an excited state oxygen atom

To estimate photochemical *rate* constants we have to know:

- The strength (intensity) of the photon flux, I_0 : photons per second per cm^2 of the Earth's surface. I_0 is a function of λ and zenith angle, Z
- The efficiency of photon absorption yielding excited state molecules, *e.g.*, $\sigma \times [NO_2]$. σ is the absorption cross section
 - (cm^2 per molecule: compare Beer's law)
 - is a function of wavelength λ (nm)
- The efficiency with which the excited NO_2 molecules dissociate, ϕ , is the quantum yield of dissociation.
- ϕ is also a function of wavelength λ , and is dimensionless.

$$\phi = \frac{\text{\# of molecules dissociated}}{\text{\# of photons absorbed}}$$

$$(I_o \times \sigma \times \phi)_{\lambda, Z} = J, S^{-1}$$

- Must be summed over all λ relevant to the specific Zenith Angle
- Rate of photolysis (of NO_2) = $(I_o \times \sigma \times \phi) \times [NO_2]$

Tropospheric formation and reactions of OH radical

- Formation by photolysis of ozone
 - UV-B region (295-325 nm)
 - $\text{O}_3 + h\nu (\lambda < 325 \text{ nm}) \rightarrow \text{O}_2^* + \text{O}^*$
 - $\text{O}^* + \text{H}_2\text{O} \rightarrow 2\text{OH}^\bullet$
- The reaction $\text{O}_3 + \lambda\nu \rightarrow \text{O}_2 + \text{O}$ also occurs but does not lead anywhere because ground state O cannot react with H_2O (explain why)
- in darkness, concentration of OH falls to near zero (no photolysis of ozone) because OH is so reactive that it disappears in seconds

Tropospheric concentration of OH

- Global average = 9.7×10^5 molecules cm^{-3} (day/night; winter/summer; poles/tropics)
- Experimental measurements are difficult, but day-time maxima in southern Canada $\sim 10^5$ molecules cm^{-3} in winter and $\sim 10^7$ molecules cm^{-3} in summer with high ozone

Characteristic reactions of OH radicals

- Abstract hydrogen atoms
 - Prototype reaction:
 - $\text{CH}_4 + \text{OH}^\bullet \rightarrow \text{CH}_3^\bullet + \text{H}_2\text{O}$
- Add to double bonds
 - Prototype reactions:
 - $\text{H}_2\text{C}=\text{CH}_2 + \text{OH} \rightarrow \text{HOCH}_2\text{-CH}_2^\bullet$
 - $\text{O}=\text{S}=\text{O} + \text{OH} \rightarrow \text{HO-SO}_2^\bullet$
- Terminate with another odd-electron species
 - Prototype reaction:
 - $\text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3$

*Before considering oxidation of VOCs, we need to consider **NO_x** chemistry*

Please note that OH implies the free radical form, whereas OH indicates hydroxyl ion in solution.

The formation of ozone: the NO/NO₂ cycle

- Clean troposphere: no significant parallel VOC oxidation
- Formation of ozone:
 - $\text{NO}_2 + h\nu (\lambda < 400 \text{ nm}) \rightarrow \text{NO} + \text{O}$ (1)
 - $\text{O} + \text{O}_2 \rightarrow \text{O}_3$ (fast reaction) (2)
- Destruction of ozone:
 - $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$ (3)
- Net reaction = "null cycle", in which sunlight is degraded to **heat**
- Steady state: NO₂ formed and destroyed at equal rates
 - $k_3 \cdot [\text{NO}] \cdot [\text{O}_3] = J(\text{NO}_2) \cdot [\text{NO}_2]$
 - Reaction (2) is fast
 - *or* $[\text{O}_3] = J(\text{NO}_2) \cdot [\text{NO}_2] / k_3 \cdot [\text{NO}]$ [A]
- Steady state – not equilibrium! – achieved in minutes in strong sunlight. [O₃]_{ss} depends on solar intensity of solar radiation, therefore, it also depends on latitude, season, and time of day. Because they are rapidly inter-converted, the sum {[NO] + [NO₂]} is known as **NO_x**.

Question: What happens at night? Would we realize more NO₂ or less NO₂?

Consider Equation [A] in some more detail...

- Actual concentrations of O_3 in urban air are larger than Eq. [A] predicts, therefore, other sources must be present.
 - So-called “Ground Level Ozone”
- Photo dissociation of NO_2 is the only important reaction by which O_3 is formed in the troposphere.
- In the polluted troposphere, ozone is formed as a byproduct of VOC oxidation.
 - *Specifically NO is converted to NO_2 by reactions that do not consume O_3*
- Null Cycle
 - $NO_2 + h\nu (\lambda < 420 \text{ nm}) \rightarrow NO + O$
 - $O + O_2 \rightarrow O_3$
 - $NO + O_3 \rightarrow NO_2 + O_2$
- Therefore, in order to build up $[O_3]$, we need different oxidants for NO besides O_3
 - Peroxy radicals $R-O-O^\bullet$ are the culprit here
- Every NO molecule that is oxidized to NO_2 while bypassing Reaction (3) yields one additional ozone molecule, because the “extra” NO_2 is photolyzed to restore the steady state

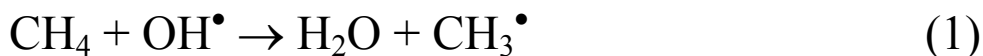
Peroxy radical R-O-O• chemistry

- RO_2 (or HO_2) + $\text{NO} \rightarrow \text{RO} + \text{NO}_2$
- Modified scheme
 - $\text{NO}_2 + h\nu (\lambda < 400 \text{ nm}) \rightarrow \text{NO} + \text{O}$ (1)
 - $\text{O} + \text{O}_2 \rightarrow \text{O}_3$ (2)
 - $\text{NO} + \text{RO}_2 \rightarrow \text{NO}_2 + \text{RO}$ (3)
 - Net Reaction: $\text{RO}_2 + \text{O}_2 \rightarrow \text{RO} + \text{O}_3$
- **Conclusion:**
 - If NO is oxidized by O_3 , then the steady state predicted by Equation [A] is valid. If NO is oxidized by peroxy radicals, there will be an excess of O_3 compared with Equation [A].
- Source of peroxy radicals
 - Addition of O_2 to a carbon-based radical
 - *Example:*
 - $\text{CH}_4 + \text{OH}^\bullet \rightarrow \text{CH}_3^\bullet + \text{H}_2\text{O}$
 - $\text{CH}_3^\bullet + \text{O}_2 \rightarrow \text{CH}_3\text{-O-O}^\bullet$

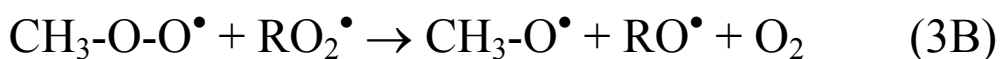
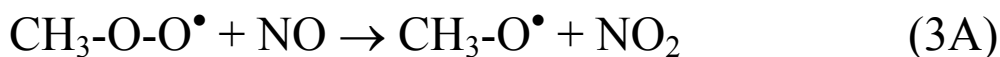
Summary:

- NO_x is indispensable to the formation of O_3 in the troposphere (the only other tropospheric source of ozone is downwards transport from the stratosphere) (not good)
- Background levels of NO_x are very low yielding low background levels of O_3 ; polluted urban air has higher levels of NO_x resulting in enhanced levels of O_3
- Peroxy radicals (R-O-O) are formed as intermediates in the oxidation of VOCs
- In polluted air (NO_x present), ROO radicals oxidize NO; O_3 is formed when the steady state process of NO: NO_2 is restored
- VOC oxidation in polluted air results in O_3

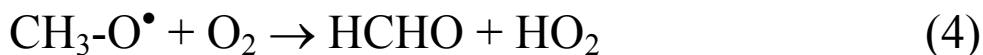
***Oxidation of Methane to Formaldehyde as a prototype
[only] VOC (simplified)***



OH^\bullet reactivity \gg RO_2 , HO_2 , NO_3



R = CH_3 or H



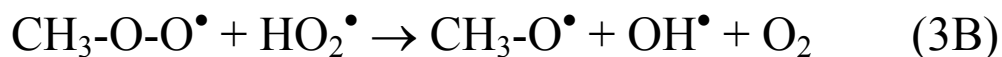
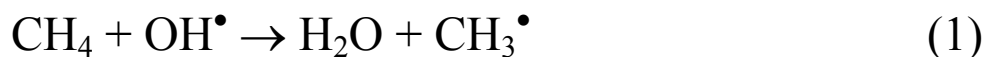
(HCHO is formaldehyde – a nasty air pollutant)

$\text{CH}_3\text{-O}^\bullet$ reacts much faster with O_2 than it abstracts H from CH_4

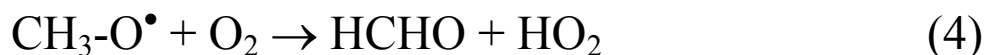
- Reactions 3A and 3B are in competition
 - Both always occur

What happens when Reaction 3B predominates?

- Low [NO_x]
- Unpolluted Air



Peroxy radicals self-annihilate instead of abstracting hydrogen atoms.



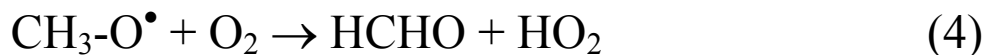
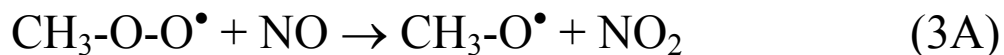
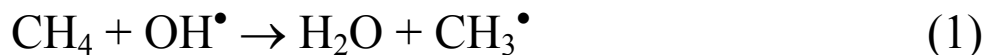
Net reaction I:



Under these conditions, methane production produces no ozone as a byproduct

What happens when Reaction 3A predominates

- High [NO_x]
- Polluted air



Net Reaction II:



- The Net Reaction is inconvenient to use because of the consideration of reactive intermediates in the equation.



- Need to end the cycles with non-reactive intermediates.
- Note
 - $\text{NO} \rightarrow \text{NO}_2$
 - $\text{OH} \rightarrow \text{HO}_2$
- Recycle
 - $\text{NO}_2 \rightarrow \text{NO}$
 - $\text{NO}_2 + \text{O}_2 + h\nu \rightarrow \text{NO} + \text{O}_3$
- Recycle
 - $\text{HO}_2 \rightarrow \text{OH}$
 - $\text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2$, then
 - $\text{NO}_2 + \text{O}_2 + h\nu \rightarrow \text{NO} + \text{O}_3$

New Net Reaction II (simplified):



Therefore, one mole of methane (oxidation) produces two moles of ozone as a byproduct

Volatile Organic Carbons (VOCs)

- Different VOCs react differently with OH[•].
- There is a greater potential to form ozone locally when the reaction between a VOC and OH[•] is fast.
- This is particularly true if the $t_{1/2}$ for the VOCs are less than a few hours.
- Alkenes and aromatics (H₂C=CH₂)
 - OH reacts by addition
- Alkanes
 - OH reacts by H abstraction
- Alkenes react more quickly than alkanes (important)
- Biogenic hydrocarbons (alkenes) are highly reactive.
- Can you think of a common source of VOCs?
 - Gasoline tanks (common)
 - Every time a gas tank is filled up, the volume of gasoline vapour above the gas at the bottom of the tank is displaced and released to the environment.

Photochemical Ozone Creation Potential (POCP)

- Developed by the Organization for Economic Cooperation and Development (OECD)
- An approximate approach to rank VOCs in terms of ozone forming potential based on the emission of equal masses of the VOC and ethylene

$$POCP = \frac{k(VOC)}{k(C_2H_2)} \times \frac{M(C_2H_2)}{M(VOC)} \times 100$$

@ 298 K, $k(\text{ethylene}) = 8.5 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1}$

Compound	k_{OH}	POCP
2-Butanone	8.9×10^{-13}	4
Toluene	6.0×10^{-12}	21
3-Methylpentane	5.7×10^{-12}	22
Cyclohexane	7.5×10^{-12}	29
<i>p</i> -Xylene	2.4×10^{-11}	74
Ethylene	8.5×10^{-12}	100
1-Hexene	3.7×10^{-11}	145
Styrene	5.5×10^{-11}	165
Propylene	2.6×10^{-11}	204
Isoprene	9.0×10^{-11}	1000

Sources of nitrogen oxides in the troposphere

- The primary pollutant is always NO:
 - $\text{N}_2 + \text{O}_2 \leftrightarrow 2\text{NO}$
 - $\Delta H^\circ = + 180 \text{ kJ}$ (as written)
- Natural background of NO_x is $< 1 \text{ ppb}_v$
 - Lightning.
 - All combustion processes $\uparrow [\text{NO}_x]$ above background
 - US data
 - Transportation 40-45%
 - Power generation, 30-35%
 - Industrial, 20%

Low [O₃] in major cities at night



- NO formation continues, but ozone formation shuts down
 - Result: $\downarrow [\text{O}_3]$

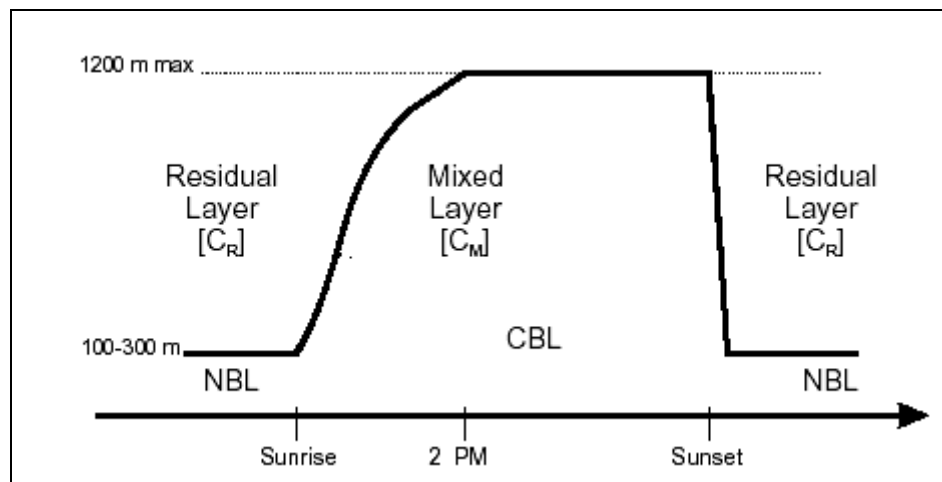
Low [O₃] in major cities during pollution episodes

- High NO emissions consume O₃
 - $\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$
- NO₂ consumes OH
 - $\text{NO}_2 + \text{OH} \rightarrow \text{HNO}_3 (\text{g})$
- Low OH means a low rate of VOC oxidation
 - Low production of O₃ as a byproduct

Highest O₃ occurs down-wind of city centre in the suburbs

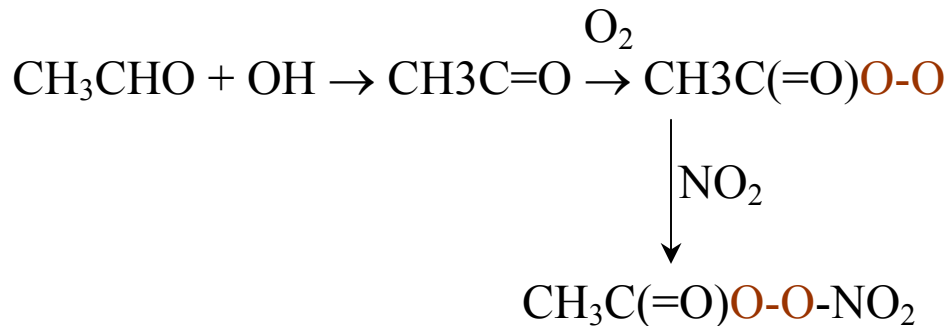
The problem of advection

- Vancouver or Los Angeles
 - Westerly airflow, "upwind" air is "clean". Excess ozone above the nocturnal boundary layer dissipates (because of winds) by morning, when mixing brings in clean air.
- Southwestern Ontario
 - Upwind air brings high $[O_3]$ from Detroit, Windsor, Ohio Valley.
 - Air above the nocturnal boundary is ozone-rich.
 - $[O_3]$ at ground level falls at night due to $NO + O_3$ reaction, but morning mixing raises $[O_3]$ because air is still ozone-rich. Data from CN Tower.



The effect of temperature

- Ozone episodes are promoted by high temperature.
 - PAN (peroxyacetyl nitrate) and related congeners act as storage reservoirs for NO_x.
 - Formation of PAN (text, p. 82)



- PAN has a large E_{act} for decomposition (113 kJ/mol)
 - CH₃C(=O)O-O-NO₂ → CH₃C(=O)O-O + NO₂
- Tying up NO₂ inhibits O₃ formation
 - NO₂ is the precursor
 - At high T, less NO₂ is tied up, so more O₃ forms

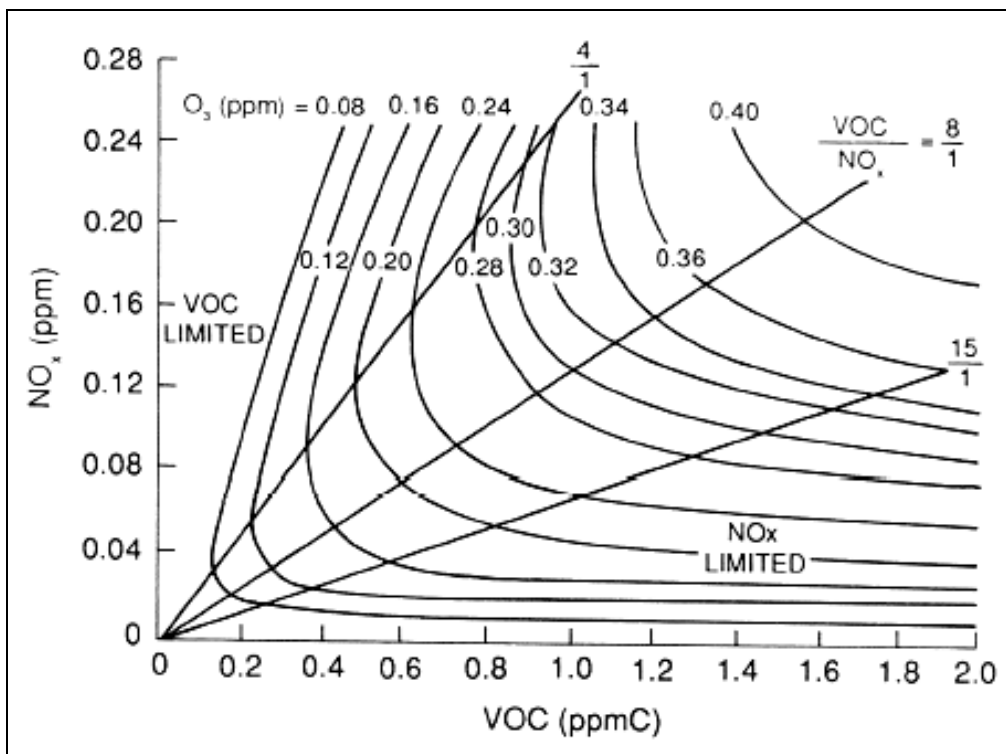
Tropospheric chemistry at night

- NO_3^\bullet (nitrate radical) initiates chain reactions
- It is much less reactive than OH
 - $\text{NO}_3^\bullet + \text{R-H} \rightarrow \text{HNO}_3 + \text{R}^\bullet \rightarrow \text{etc}$
 - NO_3^\bullet is indirectly made from NO_2
 - $\text{NO}_2 + \text{O}_3 \rightarrow \text{NO}_3^\bullet \leftrightarrow \text{N}_2\text{O}_5$
 - NO_3^\bullet is readily decomposed by sunlight
 - N_2O_5 is not decomposed by sunlight

“Researchers have determined that chemical processes at night remove atmospheric nitrogen oxides (NO_x) in the marine boundary layer off the New England coast, which has the effect of reducing ozone formation the next day. Nocturnal nitrate radical (NO_3) and dinitrogen pentoxide (N_2O_5) form nitric acid, which rapidly deposits on the surface, making these chemical species unavailable for ozone-forming the next day.”

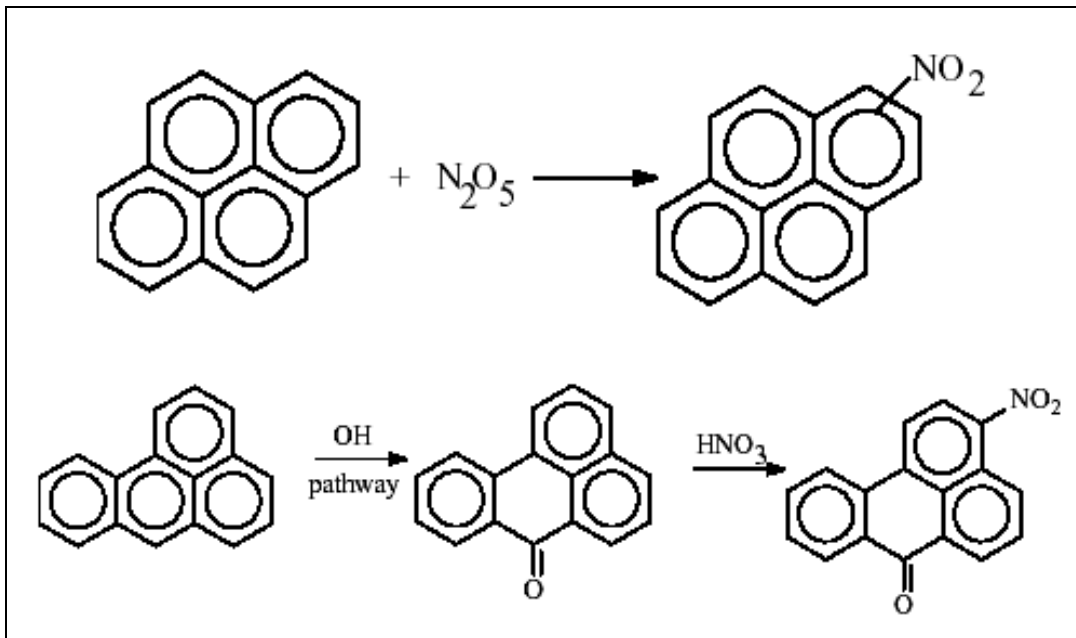
Emission controls

- Consideration: lower emissions of NO_x and VOCs by adjusting air-fuel ratios and using catalytic converters (text, pp. 85-89)
- The failure to control ground level ozone (US National Research Council Report, 1991) due to underestimation of VOC inventories, notably biogenic hydrocarbons, *e.g.*, isoprene, CH₂=C(CH₃)–CH=CH₂
 - Terpenes from trees
- Concept: either NO_x or VOCs can be the limiting reactant

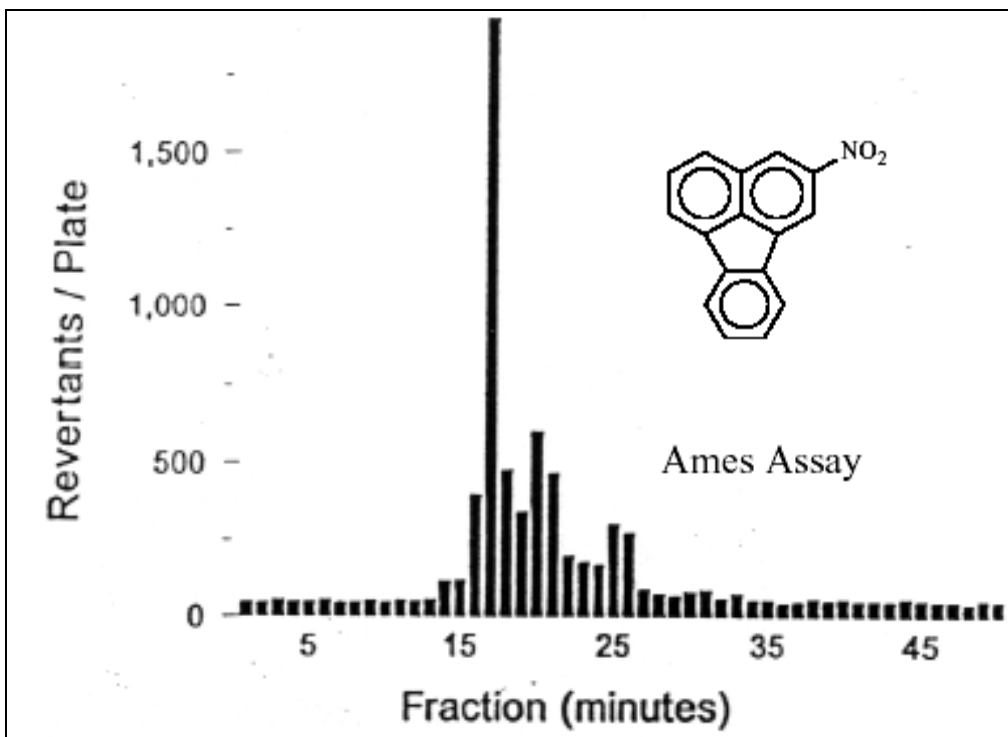
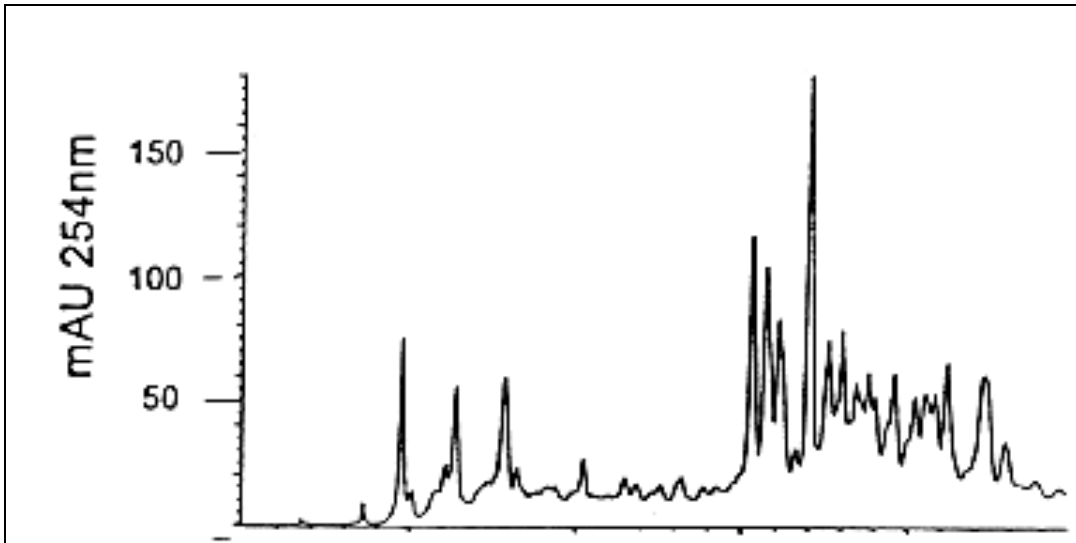


Problem compounds in urban/suburban air pollution

- Primary pollutants
 - VOCs
 - Polycyclic aromatic compounds (PAHs)
 - NO_x
 - Recall EPA priority airborne pollutants CO, SO₂
 - More later
- Secondary pollutants
 - Ozone
 - Aldehydes
 - Organic nitrates
 - Nitro-PAHs



- Mutagenic substances in urban air (Legsdins et al. , 1994)



Particles in the atmosphere (text, pp. 89-97)

- Particles will exhibit different settling rates depending on a number of variables
- Intuitively, very small and least dense particles will remain suspended in air the longest
- Concerns:
 - Light scattering – cooling
 - Contrails from airplanes – warming (9/11)
 - Condensation and Trail



- Daily, thousands of planes form tremendous amounts of ice particles, CO₂, NO_x and other gases, soot and aerosols at high altitudes.
- Aviation contributes to global warming in various ways.
- Adsorb polar substances *e.g.*, HNO₃ (g) → ultimate sink via wet or dry deposition
- Human toxicity for “respirable particles”
 - PM10, PM2.5 fractions (μm)
 - Text: Section 3.7 Level of understanding of the influence of particles

Particle Characteristics (in a Gas)

- Stokes’ Law

$$\text{Settling Rate} = \frac{g \times d^2 \times (\rho_{part} - \rho_{air})}{18\eta}$$

g=acceleration due to gravity

d=particle diameter

(Regular and irregularly shaped particles)

ρ=density of *particle* and *air*