Chemistry in the Troposphere: 
Photochemical Smog

Overview:

- The atmosphere is an *oxidizing* system
- Tendency of organic components to be oxidized (both natural and anthropogenic)
  - $2C_2H_6 + 7O_2 \rightarrow 4CO_2 + 6H_2O$
  - $C_2H_6$ 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 $CO_2 + H_2O$
- Ozone (O$_3$) is formed as a byproduct of VOC oxidation
- Central role of the hydroxyl radical, OH$^*$, in initiating oxidation
- Interaction between VOC oxidation and NO$_x$ chemistry
- Conditions for photochemical smog formation
  - strong sunlight
  - $T > \sim 20^\circ C$
  - 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:
  
  \[ \text{\( O_3 + hv \ (\lambda < 325 \text{ nm}) \rightarrow O_2^* + O^* \)} \]
  
  \[ \text{\( NO_2 + hv \ (\lambda < 400 \text{ nm}) \rightarrow NO + O \)} \]
  
  - \( O^* \) 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 \( \lambda \) and zenith angle, \( Z \)

- The efficiency of photon absorption yielding excited state molecules, e.g., \( \sigma \times \text{[NO2]} \). \( \sigma \) is the absorption cross section
  
  \[ \text{\( \sigma \) (cm\(^2\) per molecule: compare Beer's law)} \]
  
  \[ \text{\( \sigma \) is a function of wavelength \( \lambda \) (nm)} \]

- The efficiency with which the excited \( NO_2 \) molecules dissociate, \( \phi \), is the quantum yield of dissociation.

- \( \phi \) is also a function of wavelength \( \lambda \), and is dimensionless.

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

\[
\left( I_o \times \sigma \times \phi \right) = J, S^{-1}
\]

- Must be summed over all \( \lambda \) relevant to the specific Zenith Angle

- Rate of photolysis (of \( NO_2 \)) = \( \left( I_o \times \sigma \times \phi \right) \times \text{[NO}_2] \)
**Tropospheric formation and reactions of OH radical**

- Formation by photolysis of ozone
  - UV-B region (295-325 nm)
    - $\text{O}_3 + \text{hv} (\lambda < 325 \text{ nm}) \rightarrow \text{O}_2^* + \text{O}^*$
    - $\text{O}^* + \text{H}_2\text{O} \rightarrow 2\text{OH}^*$
- 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$_2$O (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 = $9.7 \times 10^5$ 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:
    - $\text{CH}_4 + \text{OH}^\cdot \rightarrow \text{CH}_3^\cdot + \text{H}_2\text{O}$
- Add to double bonds
  - Prototype reactions:
    - $\text{H}_2\text{C}=$CH$_2 + \text{OH} \rightarrow \text{HOCH}_2=$CH$_2^\cdot$
    - $\text{O}=$S=O + OH $\rightarrow$ HO–SO$_2^\cdot$
- 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:**
  - \( \text{NO}_2 + \text{hv} (\lambda < 400 \text{ nm}) \rightarrow \text{NO} + \text{O} \) \hspace{1cm} (1)
  - \( \text{O} + \text{O}_2 \rightarrow \text{O}_3 \) (fast reaction) \hspace{1cm} (2)

- **Destruction of ozone:**
  - \( \text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2 \) \hspace{1cm} (3)

- **Net reaction** = "null cycle", in which sunlight is degraded to heat

- **Steady state:** NO₂ formed and destroyed at equal rates
  - \( k_3.[\text{NO}].[\text{O}_3] = J(\text{NO}_2).[\text{NO}_2] \)
    - Reaction (2) is fast
      - or \( [\text{O}_3] = J(\text{NO}_2).[\text{NO}_2] / k_3.[\text{NO}] \) \hspace{1cm} [A]

- **Steady state – not equilibrium!** – achieved in minutes in strong sunlight. \([\text{O}_3]_{ss}\) 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 \([\text{NO}] + [\text{NO}_2]\) is known as NOₓ.

**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
  - \(NO_2 + hv (\lambda < 420 \text{ nm}) \rightarrow NO + O\)
  - \(O + O_2 \rightarrow O_3\)
  - \(NO + O_3 \rightarrow NO_2 + O_2\)

- Therefore, in order to build up \([O_3]\), we need different oxidants for \(NO\) besides \(O_3\)
  - Peroxy radicals \(R–O–O^*\) 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 $HO_2$) + NO $\rightarrow$ RO + NO$_2$
- Modified scheme
  - NO$_2$ + hv ($\lambda$ < 400 nm) $\rightarrow$ NO + O
  - O + O$_2$ $\rightarrow$ O$_3$
  - NO + RO$_2$ $\rightarrow$ NO$_2$ + RO

  ▪ Net Reaction: $RO_2$ + O$_2$ $\rightarrow$ RO + 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:
    - CH$_4$ + OH$^*$ $\rightarrow$ CH$_3^*$ + H$_2$O
    - CH$_3^*$ + O$_2$ $\rightarrow$ CH$_3$–O–O$^*$
Summary:

- NO\textsubscript{X} is indispensable to the formation of O\textsubscript{3} in the troposphere (the only other tropospheric source of ozone is downwards transport from the stratosphere) (not good)

- Background levels of NO\textsubscript{X} are very low yielding low background levels of O\textsubscript{3}; polluted urban air has higher levels of NO\textsubscript{X} resulting in enhanced levels of O\textsubscript{3}

- Peroxy radicals (R-O-O) are formed as intermediates in the oxidation of VOCs

- In polluted air (NO\textsubscript{X} present), ROO radicals oxidize NO; O\textsubscript{3} is formed when the steady state process of NO:NO\textsubscript{2} is restored

- VOC oxidation in polluted air results in O\textsubscript{3}
Oxidation of Methane to Formaldehyde as a prototype [only] VOC (simplified)

\[
\text{CH}_4 + \text{OH}^\cdot \rightarrow \text{H}_2\text{O} + \text{CH}_3^\cdot \quad (1)
\]

\[
\text{OH}^\cdot \text{ reactivity} \gg \text{RO}_2, \text{HO}_2, \text{NO}_3
\]

\[
\text{CH}_3^\cdot + \text{O}_2 \rightarrow \text{CH}_3\text{-O-O}^\cdot \quad (2)
\]

\[
\text{CH}_3\text{-O-O}^\cdot + \text{NO} \rightarrow \text{CH}_3\text{-O}^\cdot + \text{NO}_2 \quad (3A)
\]

\[
\text{CH}_3\text{-O-O}^\cdot + \text{RO}_2^\cdot \rightarrow \text{CH}_3\text{-O}^\cdot + \text{RO}^\cdot + \text{O}_2 \quad (3B)
\]

\[
\text{R} = \text{CH}_3 \text{ or H}
\]

\[
\text{CH}_3\text{-O}^\cdot + \text{O}_2 \rightarrow \text{HCHO} + \text{HO}_2 \quad (4)
\]

(HCHO is formaldehyde – a nasty air pollutant)

\[
\text{CH}_3\text{-O}^\cdot \text{ reacts much faster with } \text{O}_2 \text{ than it abstracts H from CH}_4
\]

- Reactions 3A and 3B are in competition
  - Both always occur
What happens when Reaction 3B predominates?

- Low [NOₓ]
- Unpolluted Air

\[
\text{CH}_4 + \text{OH}^\cdot \rightarrow \text{H}_2\text{O} + \text{CH}_3^\cdot \\
\text{(1)}
\]

\[
\text{CH}_3^\cdot + \text{O}_2 \rightarrow \text{CH}_3\text{-O-O}^\cdot \\
\text{(2)}
\]

\[
\text{CH}_3\text{-O-O}^\cdot + \text{HO}_2^\cdot \rightarrow \text{CH}_3\text{-O}^\cdot + \text{OH}^\cdot + \text{O}_2 \\
\text{(3B)}
\]


\[
\text{CH}_3\text{-O}^\cdot + \text{O}_2 \rightarrow \text{HCHO} + \text{HO}_2 \\
\text{(4)}
\]

Net reaction I:

\[
\text{CH}_4 + \text{O}_2 \rightarrow \text{HCHO} + \text{H}_2\text{O}
\]

*Under these conditions, methane production produces no ozone as a byproduct*
What happens when Reaction 3A predominates

- High [NO$_x$]
- Polluted air

\[
\text{CH}_4 + \text{OH}^\cdot \rightarrow \text{H}_2\text{O} + \text{CH}_3^\cdot \quad (1)
\]

\[
\text{CH}_3^\cdot + \text{O}_2 \rightarrow \text{CH}_3-\text{O}-\text{O}^\cdot \quad (2)
\]

\[
\text{CH}_3-\text{O}-\text{O}^\cdot + \text{NO} \rightarrow \text{CH}_3-\text{O}^\cdot + \text{NO}_2 \quad (3A)
\]

\[
\text{CH}_3-\text{O}^\cdot + \text{O}_2 \rightarrow \text{HCHO} + \text{HO}_2 \quad (4)
\]

Net Reaction II:

\[
\text{CH}_4 + 2\text{O}_2 + \text{OH} + \text{NO} \rightarrow \text{HCHO} + \text{NO}_2 + \text{H}_2\text{O} + \text{HO}_2
\]
• The Net Reaction is inconvenient to use because of the consideration of reactive intermediates in the equation.

\[ \text{CH}_4 + 2\text{O}_2 + \text{OH} + \text{NO} \rightarrow \text{HCHO} + \text{NO}_2 + \text{H}_2\text{O} + \text{HO}_2 \]

• Need to end the cycles with non-reactive intermediates.

• Note
  - \( \text{NO} \rightarrow \text{NO}_2 \)
  - \( \text{OH} \rightarrow \text{HO}_2 \)

• Recycle
  - \( \text{NO}_2 \rightarrow \text{NO} \)
  - \( \text{NO}_2 + \text{O}_2 + \text{hv} \rightarrow \text{NO} + \text{O}_3 \)

• Recycle
  - \( \text{HO}_2 \rightarrow \text{OH} \)
  - \( \text{HO}_2 + \text{NO} \rightarrow \text{OH} + \text{NO}_2 \), then
  - \( \text{NO}_2 + \text{O}_2 + \text{hv} \rightarrow \text{NO} + \text{O}_3 \)

New Net Reaction II (simplified):

\[ \text{CH}_4 + 4\text{O}_2 \rightarrow \text{HCHO} + 2\text{O}_3 + \text{H}_2\text{O} \]

*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 t½ 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

\[
POCP = \frac{k(VOC)}{k(C_2H_2)} \cdot \frac{M(C_2H_2)}{M(VOC)} \cdot 100
\]

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

<table>
<thead>
<tr>
<th>Compound</th>
<th>(k_{\text{OH}})</th>
<th>POCP</th>
</tr>
</thead>
<tbody>
<tr>
<td>2-Butanone</td>
<td>(8.9 \times 10^{-13})</td>
<td>4</td>
</tr>
<tr>
<td>Toluene</td>
<td>(6.0 \times 10^{-12})</td>
<td>21</td>
</tr>
<tr>
<td>3-Methylpentane</td>
<td>(5.7 \times 10^{-12})</td>
<td>22</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>(7.5 \times 10^{-12})</td>
<td>29</td>
</tr>
<tr>
<td>(p)-Xylene</td>
<td>(2.4 \times 10^{-11})</td>
<td>74</td>
</tr>
<tr>
<td>Ethylene</td>
<td>(8.5 \times 10^{-12})</td>
<td>100</td>
</tr>
<tr>
<td>1-Hexene</td>
<td>(3.7 \times 10^{-11})</td>
<td>145</td>
</tr>
<tr>
<td>Styrene</td>
<td>(5.5 \times 10^{-11})</td>
<td>165</td>
</tr>
<tr>
<td>Propylene</td>
<td>(2.6 \times 10^{-11})</td>
<td>204</td>
</tr>
<tr>
<td>Isoprene</td>
<td>(9.0 \times 10^{-11})</td>
<td>1000</td>
</tr>
</tbody>
</table>
Sources of nitrogen oxides in the troposphere

- The primary pollutant is always NO:
  - $\text{N}_2 + \text{O}_2 \leftrightarrow 2\text{NO}$
    - $\Delta H^o = +180 \text{ kJ}$ (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

$\text{NO}_2 + \text{hv (}\lambda < 400 \text{ nm)} \rightarrow \text{NO} + \text{O}$ daytime 1
$\text{O} + \text{O}_2 \rightarrow \text{O}_3$ 2
$\text{NO} + \text{O}_3 \rightarrow \text{NO}_2 + \text{O}_2$ day and night 3

- NO formation continues, but ozone formation shuts down
  - Result: $\downarrow [\text{O}_3]$
Low \([O_3]\) in major cities during pollution episodes

- High NO emissions consume \(O_3\)
  - \(NO + O_3 \rightarrow NO_2 + O_2\)
- \(NO_2\) consumes \(OH\)
  - \(NO_2 + OH \rightarrow HNO_3 (g)\)
- Low \(OH\) means a low rate of VOC oxidation
  - Low production of \(O_3\) as a byproduct

Highest \(O_3\) 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\textsubscript{x}.
  - Formation of PAN (text, p. 82)

\[
\begin{align*}
O_2 \\
\text{CH}_3\text{CHO} + \text{OH} & \rightarrow \text{CH}_3\text{C}=\text{O} \rightarrow \text{CH}_3\text{C}(=\text{O})\text{O}-\text{O} \\
& \downarrow \text{NO}_2 \\
& \text{CH}_3\text{C}(=\text{O})\text{O}-\text{O}-\text{NO}_2
\end{align*}
\]

- PAN has a large $E_{\text{act}}$ for decomposition (113 kJ/mol)
  - $\text{CH}_3\text{C}(=\text{O})\text{O}-\text{O}-\text{NO}_2 \rightarrow \text{CH}_3\text{C}(=\text{O})\text{O}-\text{O} + \text{NO}_2$

- Tying up NO\textsubscript{2} inhibits O\textsubscript{3} formation
  - NO\textsubscript{2} is the precursor
  - At high T, less NO\textsubscript{2} is tied up, so more O\textsubscript{3} forms
Tropospheric chemistry at night

- NO$_3^\cdot$ (nitrate radical) initiates chain reactions
- It is much less reactive than OH
  - NO$_3^\cdot$ + R–H $\rightarrow$ HNO$_3$ + R$^\cdot$ $\rightarrow$ etc
  - NO$_3^\cdot$ is indirectly made from NO$_2$
    - NO$_2$ + O$_3$ $\rightarrow$ NO$_3^\cdot$ $\leftrightarrow$ N$_2$O$_5$
- NO$_3^\cdot$ is readily decomposed by sunlight
- N$_2$O$_5$ 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$_2$O$_5$) 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\textsubscript{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, CH\textsubscript{2}=C(CH\textsubscript{3})–CH=CH\textsubscript{2}
  - Terpenes from trees

- Concept: either NO\textsubscript{X} or VOCs can be the limiting reactant
Problem compounds in urban/suburban air pollution

- Primary pollutants
  - VOCs
  - Polycyclic aromatic compounds (PAHs)
  - NO\textsubscript{x}
  - Recall EPA priority airborne pollutants CO, SO\textsubscript{2}
    - 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, NOₓ 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’s Law

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

  *g=* acceleration due to gravity
  
  *d=* particle diameter

  (Regular and irregularly shaped particles)

  *\rho=* density of particle and air