Atmos. Chem. Lecture 10, 10/9/13: Tropospheric Chemistry 1

- Troposphere: intro/background
  - Sources, cycling of HO\textsubscript{x}
  - Sources, cycling of NO\textsubscript{x}
  - Carbon monoxide oxidation

The troposphere

Earth’s surface

[Note: Additional material is discussed here during lecture.]
Early tropospheric chemistry research: LA Smog


"Photochemical and other reactions change normally harmless compounds into objectionable ones. On the other hand, substances irritating when released may soon be converted into harmless ones. A proper evaluation of the contribution of air pollutants to the smog nuisance must include not only the time and place of their emission, but also their fate in the air."

Haagen-Smit et al., *Ind. Eng. Chem.* 45:2086 (1953): ozone from HCs and NO$_x$

"The release of large quantities of hydrocarbons to the air and the simultaneous presence of nitrogen oxides from combustion processes explains the relatively high ozone content"

First laboratory simulations of tropospheric chemistry

"To study those reactions further a fumigation room was built from Plexiglas..."

| Table I. Eye irritation observed in the oxidation of olefins  
(With 0.4 p.p.m. of nitrogen dioxide and 0.2 p.p.m. of ozone under influence of sunlight) |
<table>
<thead>
<tr>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Olefins</td>
<td>Hydrocarbon concentration, P.P.M.</td>
<td>Degree of Eye irritation</td>
</tr>
<tr>
<td>Exohexene</td>
<td>1</td>
<td>Doubtful</td>
</tr>
<tr>
<td>Propene</td>
<td>2</td>
<td>None</td>
</tr>
<tr>
<td>1-Buten</td>
<td>0.6</td>
<td>Severe smog</td>
</tr>
<tr>
<td>3-Buten</td>
<td>0.2</td>
<td>Light smog</td>
</tr>
<tr>
<td>2-Octene</td>
<td>0.2</td>
<td>Medium smog</td>
</tr>
<tr>
<td>2-Buten</td>
<td>0.5</td>
<td>Medium smog</td>
</tr>
<tr>
<td>Isobutene</td>
<td>1</td>
<td>None</td>
</tr>
<tr>
<td>1-Butene</td>
<td>1</td>
<td>Medium smog</td>
</tr>
</tbody>
</table>

Haagen-Smit 1952
Early tropospheric chemistry research

Cadle and Allen, *Science* 167:3916 (1970): Troposphere is relatively inert; only photolysis or reactions with O or O$_2$ matter

“The chemistry of the troposphere is mainly that of a large number of atmospheric constituents and of their reactions with molecular oxygen”

Robbins and Robbins, “Sources, Abundance, and Fate of Gaseous Atmospheric Pollutants”, *SRI report*, 1967: Lifetime of CO estimated at 2.7 years (loss by soil)

Weinstock, *Science* 166:224 (1969): $^{14}$CO measurements → lifetime of 0.1 years, loss by OH


---

Ozone photochemistry

![Ozone photochemistry graph](image-url)

*Courtesy of James Hunter. Used with permission.*
Atmospheric OH

\[ \text{O}_3 + \text{hv} \rightarrow \text{O}^{(3\text{P})} + \text{O}_2 \]

\[ \rightarrow \text{O}^{(1\text{D})} + \text{O}_2 \]

\[ \text{O}^{(1\text{D})} + \text{M} \rightarrow \text{O}^{(3\text{P})} + \text{M} \]

\[ \text{O}^{(1\text{D})} + \text{H}_2\text{O} \rightarrow \text{OH} + \text{OH} \]

[Note: Additional material is discussed here during lecture.]

Measuring OH: Tracers

© John Wiley and Sons. All rights reserved. This content is excluded from our Creative Commons license. For more information, see http://ocw.mit.edu/help/faq-fair-use/.

Prinn et al, GRL 32, L07809 (2005)
**HO<sub>x</sub> cycle: Troposphere**

\[ \text{H}_2\text{O} \xrightarrow{\text{O(1D)}} \text{OH} \xrightarrow{} \text{HO}_2 \]

[Note: Additional material is discussed here during lecture.]

**Simple NO<sub>x</sub> cycle: Troposphere**

\[ \text{NO}_x \xrightarrow{} \text{O}_3 \xrightarrow{} \text{OH} \xrightarrow{\text{hv}} \text{HNO}_3 \]

Much more detail later...

<table>
<thead>
<tr>
<th>Source</th>
<th>Tg N·yr&lt;sup&gt;−1&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fossil fuel</td>
<td>21</td>
</tr>
<tr>
<td>Biomass burning</td>
<td>12</td>
</tr>
<tr>
<td>Soils</td>
<td>6</td>
</tr>
<tr>
<td>Lightning</td>
<td>3</td>
</tr>
<tr>
<td>NH₃ oxidation</td>
<td>3</td>
</tr>
<tr>
<td>Aircraft</td>
<td>0.5</td>
</tr>
<tr>
<td>Transport from stratosphere</td>
<td>0.1</td>
</tr>
</tbody>
</table>

© Princeton University Press. All rights reserved. This content is excluded from our Creative Commons license. For more information, see [http://ocw.mit.edu/help/faq-fair-use/](http://ocw.mit.edu/help/faq-fair-use/).
Global NO₂

From SCIAMACHY (SCanning Imaging Absorption spectrometer for Atmospheric Cartography)

http://www.temis.nl/airpollution/no2.html

Carbon monoxide: Sources, sinks

[Note: Additional material is discussed here during lecture.]

Global carbon monoxide

CO + HO\textsubscript{x} + NO\textsubscript{x} + hv

CO + OH (+O\textsubscript{2}) \rightarrow HO\textsubscript{2} + CO\textsubscript{2}

[Note: Additional material is discussed here during lecture.]
dependence of $[\text{HO}_2]$ on $P_{\text{HO}_x}$

Remote: Cape Grim, Tasmania

Polluted: Mace Head, Ireland

Penkett et al., JGR 102: 12805 (1997)

Carpenter et al., JGR 102: 25417 (1997)

© Academic Press. All rights reserved. This content is excluded from our Creative Common license. For more information, see http://ocw.mit.edu/help/faq-fair-use/.