Tropospheric Oxidation &
Ozone Formation I

Required Reading: Jacob Chapters 11 & 12

Atmospheric Chemistry
ATOC-5151 / CHEM 5151
Prof. Jose-Luis Jimenez
Spring 2013
Lecture by Doug Day

Review Clicker Q

What are the most important sources of
tropospheric hydroxyl radicals (OH)?
(in no particular order)

a) CH₂O, HONO, HCl
b) O₃, HNO₃, CH₂O
c) HONO, CH₂O, O₃
d) CH₄, O₃, HONO
e) I don’t know
The Atmosphere as a Low T Flame

- Reaction rates of as f(T) for
  \[ \text{CH}_4 + \text{OH} \rightarrow \cdot \text{CH}_3 + \text{H}_2\text{O} \]
  \[ k = 2.65 \times 10^{-12} \exp^{-1800/T} \text{ cm}^3 \text{molec}^{-1} \text{s}^{-1} \]

- What are the relative lifetimes of CH\(_4\) at flame vs. ambient temperatures? Does this make sense?

Answer: Radical Concentrations

- Lifetimes of CH\(_4\)
  - in atmosphere ~ a few years
  - in a flame ~ a few μs
  - Ratio = 10\(^{13}\)!!

- We can’t explain that with the reaction rate
  - Ratio ~ 10\(^{3}\)
  - Key are radical concentrations
    - Atmosphere ~ 0.1 ppt
    - Flame ~ 1 ppth
    - Ratio ~ 10\(^{10}\)

Equilibrium Composition Of Isooctane-Air Mixtures

From Heywood, 1988, Internal Combustion Engine Fundamentals
Radicals

- Radical = species with an unpaired electron
  - High energy, high tendency to pair the electron to reduce the free energy
  - Often rapid reactions

<table>
<thead>
<tr>
<th>Radical</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>OH</td>
<td>•O:H</td>
</tr>
<tr>
<td>HO$_2$</td>
<td>•O:O:H</td>
</tr>
<tr>
<td>Cl</td>
<td>•Cl:</td>
</tr>
<tr>
<td>NO$_3$</td>
<td>•N:O:</td>
</tr>
<tr>
<td>NO$_2$</td>
<td>•N:O:</td>
</tr>
<tr>
<td>NO</td>
<td>•N:O:</td>
</tr>
<tr>
<td>R</td>
<td>•R</td>
</tr>
<tr>
<td>RO*</td>
<td>•O:R</td>
</tr>
<tr>
<td>RO$_2$*</td>
<td>•O:O:R</td>
</tr>
</tbody>
</table>

Adapted from Paul Ziemann

Dominant Oxidant Source in Troposphere

**Hydroxyl Radical (OH) Production from Ozone:**

Photodissociation of O$_3$:

O$_3$ + $hv$ $\rightarrow$ O$_2$ + O($^1$D)

O($^1$D) + H$_2$O $\rightarrow$ 2 OH.

NET: O$_3$ + $hv$ +H$_2$O $\rightarrow$ O$_2$ + 2OH.

Sources of Ozone:
- Stratospheric transport
- Tropospheric photochemical production
O(1D) in the Troposphere

Production & Losses of OH, O(1D)
(new reactions from homework #5)

\[
\begin{align*}
O_3 + hv &\rightarrow O(1D) + O_2 \quad (4) \\
O(1D) + H_2O &\rightarrow 2 OH \quad (5) \\
O(1D) + O_2 &\rightarrow O(^3P) \quad (6) \\
O(1D) + N_2 &\rightarrow O(^3P) \quad (7) \\
OH + NO_2 + M &\rightarrow HNO_3 \quad (8)
\end{align*}
\]

**Clicker Q:**
With increasing altitude O(1D) mixing ratio in the troposphere should:

- a) Decrease
- b) Increase
- c) No net effect
- d) Increase then decrease
- e) I don’t know

---

The Many Faces of Atmospheric Ozone

- In stratosphere: UV shield
- In middle/upper troposphere: greenhouse gas
- In lower/middle troposphere: precursor of OH, main atmospheric oxidant
- In surface air: toxic to humans and vegetation

---

From Jacob
The Atmosphere: Oxidizing Medium in Global Biogeochemical Cycles

Atmospheric oxidation is critical for removal of many pollutants, e.g.
- methane (major greenhouse gas)
- Toxic gases such as CO, benzene...
- Gases affecting the stratosphere such as HCFCs

The Troposphere was viewed as chemically inert until 1970

- “The chemistry of the troposphere is mainly that of a large number of atmospheric constituents and of their reactions with molecular oxygen...Methane and CO are chemically quite inert in the troposphere” [Cadle and Allen, Atmospheric Photochemistry, Science, 1970]

- Lifetime of CO estimated at 2.7 years (removal by soil) leads to concern about global CO pollution from increasing car emissions [Robbins and Robbins, Sources, Abundance, and Fate of Gaseous Atmospheric Pollutants, SRI report, 1967]

**FIRST BREAKTHROUGH:**

- Measurements of cosmogenic $^{14}$CO place a constraint of ~ 0.1 yr on the tropospheric lifetime of CO [Weinstock, Science, 1969]

**SECOND BREAKTHROUGH:**

- Tropospheric OH $\sim 1 \times 10^6$ cm$^{-3}$ predicted from O(1D)+H$_2$O, results in tropospheric lifetimes of ~0.1 yr for CO and ~2 yr for CH$_4$ [Levy, J. Geophys. Res. 1973]

**THIRD BREAKTHROUGH:**

- Methylchloroform observations provide indirect evidence for OH at levels of 2-5x10$^5$ cm$^{-3}$ [Singh, Geophys. Res. Lett. 1977]

...but direct measurements of tropospheric OH had to wait until the 1990s
Why was tropospheric OH difficult to figure out?

Production of O(1D) in troposphere takes place in narrow band [290-320 nm]

Until ~1990, prevailing view was that tropospheric ozone originated mainly from stratosphere
...but that cannot work.

- Estimate ozone flux $F_{O_3}$ across tropopause (strat-trop exchange)
  - Total O₃ col = 5x10¹³ moles
  - 10% of that is in troposphere
  - Res. time of air in strat = 1.4 yr
  - $F_{O_3} = 3x10^{13}$ moles yr⁻¹
- Estimate CH₄ source $S_{CH₄}$:
  - Mean concentration = 1.7 ppmv
  - Lifetime = 9 years
  - $S_{CH₄} = 3x10^{13}$ moles yr⁻¹
- Estimate CO source $S_{CO}$:
  - Mean concentration = 100 ppbv
  - Lifetime = 2 months
  - $S_{CO} = 9.7x10^{13}$ moles yr⁻¹

$S_{CO} + S_{CH₄} > 2F_{O_3} \Leftrightarrow$ OH would be titrated!

We need a much larger source of tropospheric ozone
Ozone Chemistry in the Stratosphere

\[ \text{O}_2 + h\nu \rightarrow \text{O} + \text{O} \]
\[ \text{O} + \text{O}_2 + \text{M} \rightarrow \text{O}_3 + \text{M} \]
\[ \text{O}_2 + h\nu \rightarrow \text{O}_2 + \text{O}(^1D) \]
\[ \text{O}(^1D) + \text{M} \rightarrow \text{O} + \text{M} \]
\[ \text{XO} + \text{O} \rightarrow \text{X} + \text{O}_2 \]

By contrast, in troposphere:

- no photons < 240 nm
- no oxygen photolysis;
- negligible O atom conc.
- no XO + O loss

Ozone Loss in Troposphere

\[ F_{\text{O}_3} = 540 \pm 140 \text{ Tg O}_3 \text{ yr}^{-1} \]
\[ D_{\text{O}_3} = 1000 \pm 200 \text{ Tg O}_3 \text{ yr}^{-1} \]

Ozone chemical loss is driven by photolysis frequency \( J(O_3 \rightarrow O(^1D)) \) at 300-320 nm:

\[ J = \int_{0}^{\infty} q(\lambda)\sigma(\lambda)I(\lambda)d\lambda \]

Closing the tropospheric ozone budget requires a tropospheric chemical source >> \( F_{\text{O}_3} \)
Stratospheric Ozone and Tropospheric OH

**Clicker Q:**

How would a thinning of the stratospheric ozone layer affect tropospheric OH concentrations?

- a) Decrease
- b) Increase
- c) No net effect
- d) Increase in regions and decrease in others
- e) I don’t know

**Ozone Production in Troposphere: CO**

Photochemical oxidation of CO catalyzed by hydrogen oxide radicals (HOₓ) in the presence of nitrogen oxide radicals (NOₓ)

\[
\begin{align*}
\text{HO}_x &= \text{H} + \text{OH} + \text{HO}_2 (+ \text{RO} + \text{RO}_2) \\
\text{NO}_x &= \text{NO} + \text{NO}_2
\end{align*}
\]

Oxidation of CO:

\[
\begin{align*}
\text{CO} + \text{OH} &\rightarrow \text{CO}_2 + \text{H} \\
\text{H} + \text{O}_2 + \text{M} &\rightarrow \text{HO}_2 + \text{M} \\
\text{HO}_2 + \text{NO} &\rightarrow \text{OH} + \text{NO}_2 \\
\text{NO}_2 + \text{hv} &\rightarrow \text{NO} + \text{O} \\
\text{O} + \text{O}_2 + \text{M} &\rightarrow \text{O}_3 + \text{M}
\end{align*}
\]

Net: \( \text{CO} + 2\text{O}_2 \rightarrow \text{CO}_2 + \text{O}_3 \)

*Note that neither \( \text{NO}_x \) nor \( \text{HO}_x \) are in the net reaction since they are acting as catalysts*
Ozone Production in Troposphere:
CO + Radical Termination Reactions

**CO oxidation:**
Radical formation/propagation, ozone formation reactions:

\[
\begin{align*}
CO + OH & \rightarrow CO_2 + H \\
H + O_2 + M & \rightarrow HO_2 + M \\
HO_2 + NO & \rightarrow OH + NO_2 \\
NO_2 + hv & \rightarrow NO + O \\
O + O_2 + M & \rightarrow O_3 + M \\
\end{align*}
\]

Net: \( CO + 2O_2 \rightarrow CO_2 + O_3 \)

**HOx-NOx Radical Termination steps:**

\[
\begin{align*}
HO_2 + HO_2 + M & \rightarrow H_2O_2 + O_2 + M \\
OH + NO_2 + M & \rightarrow HNO_3 + M
\end{align*}
\]

**Global Budget of Tropospheric Ozone (Tg O_3 yr^{-1})**

- IPCC (2007) average of 12 models

<table>
<thead>
<tr>
<th></th>
<th>Chem prod in troposphere</th>
<th>Chem loss in troposphere</th>
<th>Transport from stratosphere</th>
<th>Deposition</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>4700 ±700</td>
<td>4200 ±500</td>
<td>500 ±100</td>
<td>1000 ±200</td>
</tr>
</tbody>
</table>

- Ozone lifetime: 24 ± 4 days

- From Jacob
Carbon Monoxide in Atmosphere

Source: incomplete combustion
Sink: oxidation by OH (lifetime of 2 months)

<table>
<thead>
<tr>
<th>Sources</th>
<th>Range of estimates (Tg CO yr$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fossil fuel combustion/industry</td>
<td>1800–2700</td>
</tr>
<tr>
<td>Biomass burning</td>
<td>300–550</td>
</tr>
<tr>
<td>Vegetation</td>
<td>300–700</td>
</tr>
<tr>
<td>Oceans</td>
<td>60–160</td>
</tr>
<tr>
<td>Oxidation of methane</td>
<td>20–200</td>
</tr>
<tr>
<td>Oxidation of other hydrocarbons</td>
<td>400–1000</td>
</tr>
<tr>
<td>Sinks</td>
<td>200–600</td>
</tr>
<tr>
<td>Tropospheric oxidation by OH</td>
<td>2100–3000</td>
</tr>
<tr>
<td>Stratosphere</td>
<td>1400–2600</td>
</tr>
<tr>
<td>Soil uptake</td>
<td>~ 100</td>
</tr>
</tbody>
</table>

Observations of CO from Space
(AIRS Satellite Instrument)

From Jacob

AIRS Satellite CO data at 500 hPa (W.W. McMillan)
Spatial and Seasonal Cycles of CO

Seasonal Cycle at Mauna Loa, Hawaii:

Latitudinal Trends (March 2009):

Seasonal Cycle of Latitudinal Global Background:

http://www.esrl.noaa.gov/gmd/dv/iadv/graph.php?code=MLO&program=ccgg&type=lg
(select gas from drop-down)

CO & OH in the Troposphere

Clicker Q:
If the source of CO were to double, CO concentrations would:
(assume that CO is the only sink of OH)

a) Double
b) More than double
c) Less than double
d) Stay the same
e) I don’t know
CO Oxidation & O₃
Destruction vs. Production?
NOₓ!

Very Clean (very low NOₓ)

\[ CO + OH + M \rightarrow CO_2 + H \]
\[ H + O_2 + M \rightarrow HO_2 + M \]
\[ HO_2 + O_3 \rightarrow OH + 2O_2 \]

\text{Net:} \ CO + O_3 \rightarrow CO_2 + O_2

Net Ozone Destruction

Polluted (with NOₓ)

\[ CO + OH + M \rightarrow CO_2 + H \]
\[ H + O_2 + M \rightarrow HO_2 + M \]
\[ HO_2 + NO \rightarrow OH + NO_2 \]
\[ NO_2 + hv \rightarrow NO + O \]
\[ O + O_2 + M \rightarrow O_3 + M \]

\text{Net:} \ CO + 2O_2 \rightarrow CO_2 + O_3

Net Ozone Production

NOₓ Emissions (Tg N yr⁻¹) to Troposphere

- FOSSIL FUEL: 23.1
- BIOMASS BURNING: 5.2
- SOILS: 5.1
- LIGHTNING: 5.8
- STRATOSPHERE: 0.2
- BIOFUEL: 2.2
- AIRCRAFT: 0.5

From Jacob
Satellite Observations Of Tropospheric NO₂

SCIAMACHY data. May-Oct 2004
(R.V. Martin, Dalhousie U.)

Tropospheric NO₂ from the OMI Satellite Instrument
(March 2006)

www.temis.nl
Lightning flashes seen from space (2000)

NO$_x$ in the Troposphere

**Clicker Q:**
If the source of NO$_x$ were to double, NO$_x$ concentrations would:

- a) Double
- b) More than double
- c) Less than double
- d) Stay the same
- e) I don’t know
Peroxyacetyl Nitrate (PAN) as Reservoir for Long-range Transport of NO\textsubscript{x}

\[ CH_3C(O)O_2 + NO_2 + M \rightleftharpoons CH_3C(O)O_2NO_2 + M \]

Increasing Temperature

\[ \text{long-range transport at low temperatures} \]

\[ \text{PAN} \]

\[ \text{C}_2\text{H}_2 \quad \text{NO}_2 \quad \rightarrow \quad \text{HNO}_3 \]

\[ \text{deposition} \]

\[ \text{thermal decomposition during subsidence} \]

\[ \text{NO}_2 \rightarrow \text{HNO}_3 \]

\[ \text{deposition} \]

\[ \text{From Jacob} \]

NO\textsubscript{2} SOURCE REGION REMOTE ATMOSPHERE

Can Photolysis Compete with Thermal Unimolecular Rxn?

Clicker Q:
What is the lifetime of PAN at 10 km?

a) 1 day  
b) 1 week  
c) 1 month  
d) 1 year  
e) I don't know

Adapted from Jacob
Fuels for O$_3$ Production

- CO + NO$_x$
- Hydrocarbons (+ NO$_x$)
  - Methane (CH$_4$)
  - More complex hydrocarbons (non-methane HCs or VOCs)

Global Methane Sources, TG A$^{-1}$ [IPCC, 2007]

Sink: oxidation by OH (lifetime of 10 years)

From Jacob
Methane: #2 Anthropogenic Greenhouse Gas
Greenhouse radiative forcing of climate between 1750 and 2005 [IPCC, 2007]

Referenced to concentration

Referenced to emission

Carbon Monoxide and Climate?

Clicker Q:
How does carbon monoxide (CO) affect Earth’s radiative balance?

a) Directly
b) Indirectly
c) Both
d) Neither
e) I don’t know
Measurement of Methane from Space

Detect solar backscatter in vibrational band at 2.265-2.280 μm

Methane SCIAMACHY/ENVISAT 2003-2005

Global Distribution Of Methane

NOAA/GMD surface air measurements
Historical Trends in Methane

The last 1000 years

The last 30 years

The last 10 years

Oxidation of CH₄: High NOₓ Case

Net reaction if only HCO+H from CH₂O (+CO oxidation):

\[ CH₄ + 10O₂ → CO₂ + H₂O + 5O₃ + 2OH \]

\[ \text{NO} + \text{HO}_2 \rightarrow \text{NO}_2 + \text{OH} \]

\[ \text{NO}_2 \rightarrow \text{NO} + \text{O} \]

\[ \text{O} + \text{O}_2 \rightarrow \text{O}_3 \]

From S. Nizkorodov
Oxidation of CH₄: Low NOₓ Case

CH₄ + OH → CH₃ + O₂
- H₂O → CH₃O₂⁻ + O₂
- H₂O + OH

CH₃O₂⁻ + HO₂ → CH₂O + H₂O + O₂
or
CH₃O₂⁻ + HO₂ → CH₃OH + CH₂O + O₂
or
CH₃O₂⁻ + O₂ → CH₃OH + CH₂O + O₂
or
CH₃O₂⁻ + O₂ → CH₃OH + CH₂O + O₂

We already know what happens to CH₂O (it is converted to H₂, HO₂ and CO).

How about CH₃OOH and CH₃OH?
(see next slide)

Adapted from S. Nizkorodov

Oxidation of CH₃OOH and CH₃OH
(continuation of low-NOₓ CH₄ oxidation)

CH₃OOH + OH → CH₃O⁻ + H₂O + OH
or
CH₃OOH + O₂ → CH₃OH + CH₂O + O₂
or
CH₃OOH + O₂ → CH₃OH + CH₂O + O₂
or
CH₃OOH + O₂ → CH₃OH + CH₂O + O₂

Recall high-NOₓ net reaction:
CH₄ + 10O₂ → CO₂ + H₂O + 5O₂ + 2O

Adapted from S. Nizkorodov

Net reaction of CH₄ oxidation in low-NOₓ assuming:
a) CH₃OOH reacts only by reaction pathway "a"
b) CH₂O reacts only with OH (no photolysis; see last slides)

Net: CH₄ + 30H + 2O₂ → CO₂ + 3H₂O + HO₂

Adapted from S. Nizkorodov
Tropospheric Oxidation & Ozone Formation II

*Required Reading: Jacob Chapters 11 & 12*

Atmospheric Chemistry
ATOC-5151 / CHEM 5151
Prof. Jose-Luis Jimenez
Spring 2013
Lecture by Doug Day

Thermodynamics of CO Oxidation

**CO oxidation rxns:**

\[
\begin{align*}
CO + OH & \rightarrow CO_2 + H \\
H + O_2 + M & \rightarrow HO_2 + M \\
HO_3 + NO & \rightarrow OH + NO_2 \\
NO_2 + h\nu & \rightarrow NO + O \\
O + O_2 + M & \rightarrow O_3 + M \\
\end{align*}
\]

Net: \( CO + 2O_2 \rightarrow CO_2 + O_3 \)

Enthalpy of formation (at 298 K, 1 Atm)

<table>
<thead>
<tr>
<th>Compound</th>
<th>( \Delta H^\circ [\text{kJ mol}^{-1}] )</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO</td>
<td>-111</td>
</tr>
<tr>
<td>O_2</td>
<td>0</td>
</tr>
<tr>
<td>CO_2</td>
<td>-394</td>
</tr>
<tr>
<td>O_3</td>
<td>143</td>
</tr>
</tbody>
</table>

**Clicker Q:**

Is the calculation that 49% of the chemical energy given by CO combustion to CO_2 is stored in the formation of O_3?

a) Correct  
 b) Incorrect  
 c) Approximately  
 d) Not possible without further details.  
 e) I don’t know

\[
\begin{align*}
\text{CO (+0.5O_2)} & \rightarrow \text{CO}_2: \ \Delta H^\circ = -394 - (-111+0) = -293 \text{ kJ/mol} \\
1.5O_2 & \rightarrow \text{O}_3: \ \Delta H^\circ = +143 - 0 = +143 \text{ kJ/mol} \\
\end{align*}
\]

\[
\begin{align*}
\text{CO} & \rightarrow \text{O}_3: \ \text{Efficiency} = \frac{143}{293} = 0.49 \Rightarrow 49% \\
\end{align*}
\]
CH$_4$, NO$_x$, O$_3$ in the Troposphere

**Clicker Q:**
Additional sources of NO$_x$ in remote regions should result in blank in O$_3$ production from CH$_4$ oxidation.

a) a decrease
b) catalytic destruction
c) an increase
d) no change
e) I don’t know

Non-methane VOC Emissions

- **Isoprene, terpenes, oxygenates...**
  - ~ 600 Tg C yr$^{-1}$
- **Alkenes, aromatics, oxygenates...**
  - ~ 50 Tg C yr$^{-1}$
- **Alkanes, alkenes, aromatics...**
  - ~ 200 Tg C yr$^{-1}$

Largest global flux is from isoprene (300-500 Tg C yr$^{-1}$)

From Jacob
Lifetimes of Organics

- As always: enormous number of possibilities, but what is important?

Org + X → Products  (X is an oxidant)

<table>
<thead>
<tr>
<th>Organic</th>
<th>OH (1 x 10^6 cm⁻³)</th>
<th>O₃ (100 ppb)</th>
<th>NO₂ (50 ppt)</th>
<th>HO₂ (2 x 10^11, 8 ppt)</th>
<th>CI (1 x 10^9 cm⁻³)</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Butane</td>
<td>5 days</td>
<td>1,300 yr</td>
<td>205 days</td>
<td>5 days</td>
<td></td>
</tr>
<tr>
<td>trans-2-Butene</td>
<td>4.3 h</td>
<td>36 min</td>
<td>35 min</td>
<td>~4 days</td>
<td></td>
</tr>
<tr>
<td>Acrylone</td>
<td>14 days</td>
<td>≥ 400 days</td>
<td>≥ 188 days</td>
<td>~22 days</td>
<td></td>
</tr>
<tr>
<td>Toluene</td>
<td>2 days</td>
<td>≥ 400 days</td>
<td>138 days</td>
<td>20 days</td>
<td></td>
</tr>
<tr>
<td>HCHO</td>
<td>1.2 days</td>
<td>≥ 463 days</td>
<td>16 days</td>
<td>18/8/h²</td>
<td></td>
</tr>
</tbody>
</table>

Table from F-P&P 45

Alkanes + OH⁻

- OH⁻ has strong tendency to abstract H
  RH + OH⁻ → R⁻ + H₂O
  - We will focus on R⁻ soon

- Rate increases with size and complexity
  - Maximum rate?

- CH₄ is far slower than others
  - Focus on Non-Methane Hydrocarbons (NMHC) for urban smog
  - Why CH₄ survives and builds up to be a greenhouse gas

<table>
<thead>
<tr>
<th>Alkane</th>
<th>k (× 10⁻¹² cm³ molecule⁻¹ s⁻¹) at 298 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>0.00618</td>
</tr>
<tr>
<td>Ethane</td>
<td>0.254</td>
</tr>
<tr>
<td>Propane</td>
<td>1.12</td>
</tr>
<tr>
<td>n-Butane</td>
<td>2.44</td>
</tr>
<tr>
<td>2-Methylpropane</td>
<td>2.19</td>
</tr>
<tr>
<td>n-Pentane</td>
<td>4.0</td>
</tr>
<tr>
<td>2-Methylbutane</td>
<td>3.7</td>
</tr>
<tr>
<td>2,2-Dimethylpropane</td>
<td>0.85</td>
</tr>
<tr>
<td>n-Hexane</td>
<td>5.45</td>
</tr>
<tr>
<td>2-Methylpentane</td>
<td>5.3</td>
</tr>
<tr>
<td>3-Methylpentane</td>
<td>5.4</td>
</tr>
<tr>
<td>2,3-Dimethylbutane</td>
<td>5.8</td>
</tr>
<tr>
<td>n-Heptane</td>
<td>7.0</td>
</tr>
<tr>
<td>2,2-Dimethylpentane</td>
<td>3.4</td>
</tr>
<tr>
<td>2,2,3-Trimethylbutane</td>
<td>4.2</td>
</tr>
<tr>
<td>n-Octane</td>
<td>8.7</td>
</tr>
<tr>
<td>2,2,4-Trimethylpentane</td>
<td>3.6</td>
</tr>
<tr>
<td>2,2,3,3-Tetramethylbutane</td>
<td>1.08</td>
</tr>
<tr>
<td>n-Nonane</td>
<td>10.0</td>
</tr>
<tr>
<td>n-Decane</td>
<td>11.2</td>
</tr>
<tr>
<td>n-Dodecane</td>
<td>12.9</td>
</tr>
<tr>
<td>n-Tridecane</td>
<td>13.9</td>
</tr>
<tr>
<td>n-Tetradecane</td>
<td>16.0</td>
</tr>
<tr>
<td>n-Pentadecane</td>
<td>18.0</td>
</tr>
<tr>
<td>n-Hexadecane</td>
<td>21.0</td>
</tr>
<tr>
<td>Cyclopropane</td>
<td>0.094</td>
</tr>
<tr>
<td>Cyclobutane</td>
<td>1.5</td>
</tr>
<tr>
<td>Cyclopentane</td>
<td>5.02 (4.8)</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>7.21 (7.2)</td>
</tr>
<tr>
<td>Cycloheptane</td>
<td>13.0</td>
</tr>
<tr>
<td>Methylcyclohexane</td>
<td>19 (9.4)</td>
</tr>
</tbody>
</table>
Alkanes + Cl·

- Cl· also likes to abstract H
  \[ \text{RH} + \text{Cl}· \rightarrow \text{R}· + \text{HCl} \]
- Also forms an alkyl radical
- Reactions compared with collision rate?
- Importance vs. OH chemistry?

### Fates of Alkyl Radicals (R·)

- Radical nomenclature:
  - Alkyl: R·
  - Alkylperoxide: R-O-O· or RO₂·
  - Alkoxy: R-O· or RO·
- R· from oxidation of alkanes
  - Generated with all oxidants
  - Fate is similar for H-abstraction radicals from other organics
- Only fate is reaction with O₂
  \[ \text{R}· + \text{O}_2 + \text{M} \rightarrow \text{RO}_2· + \text{M} \]
- \( k \sim 1 \times 10^{-11} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1} \)
  - Lifetime of R· at ground level?
Alkylperoxy Radicals (RO$_2^\cdot$) I

- React mainly with NO, HO$_2^\cdot$, RO$_2^\cdot$, and NO$_3^-$
- RO$_2^\cdot$ + NO →
  - Fast: $k \sim 8 \times 10^{-12}$ cm$^3$ molec$^{-1}$ s$^{-1}$
  - Do not vary much with R
  - Products
    - Mainly → RO$^\cdot$ + NO$_2$
      - Again: this is how we make O$_3$ in the troposphere
    - Also → RONO$_2$ (alkyl nitrate)
      - Yields increase with RO$_2^\cdot$ size
- CH$_3$O$_2^\cdot$ + NO$_3^-$ → CH$_3$O$^\cdot$ + NO$_2$ + O$_2$
  - Fast $k \sim 2 \times 10^{-12}$, important @ night

<table>
<thead>
<tr>
<th>Table 6.5</th>
<th>Yields of RONO$_2$ in RO$_2^\cdot$ + NO Reactions at Room Temperature and 1 atm$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td>R</td>
<td>Branching ratio $= \frac{k_{29} \cdot k_{29a}}{k_{29a} + k_{29b}}$</td>
</tr>
<tr>
<td>Ethane</td>
<td>Ethyl</td>
</tr>
<tr>
<td></td>
<td>≤0.014</td>
</tr>
<tr>
<td>Propane</td>
<td>1-Propyl</td>
</tr>
<tr>
<td></td>
<td>0.020</td>
</tr>
<tr>
<td>2-Propyl</td>
<td>0.05</td>
</tr>
<tr>
<td>n-Butane</td>
<td>1-Butyl</td>
</tr>
<tr>
<td></td>
<td>≤0.04</td>
</tr>
<tr>
<td>2-Butyl</td>
<td>0.083</td>
</tr>
<tr>
<td>Isobutane</td>
<td>2-Methyl-1-propyl</td>
</tr>
<tr>
<td></td>
<td>0.075</td>
</tr>
<tr>
<td>n-Propene</td>
<td>1-Pentyl</td>
</tr>
<tr>
<td></td>
<td>0.06</td>
</tr>
<tr>
<td>2-Pentyl</td>
<td>0.13</td>
</tr>
<tr>
<td>3-Pentyl</td>
<td>0.12</td>
</tr>
<tr>
<td>Isopentane</td>
<td>2-Methyl-1-bulyl</td>
</tr>
<tr>
<td></td>
<td>0.040</td>
</tr>
<tr>
<td>2-Methyl-2-bulyl</td>
<td>0.044–0.056</td>
</tr>
<tr>
<td>2-Methyl-3-bulyl</td>
<td>0.074–0.15</td>
</tr>
<tr>
<td>3-Methyl-1-bulyl</td>
<td>0.043</td>
</tr>
<tr>
<td>n-Propene</td>
<td>0.51</td>
</tr>
</tbody>
</table>

Table from F-P&P 49

Alkylperoxy Radicals (RO$_2^\cdot$) II

- RO$_2^\cdot$ + HO$_2^\cdot$ → ROOH + O$_2$ (24a)
  → Carbonyl + H$_2$O + O$_2$ (24b)
  → ROH + O$_3$ (24c)
  - ROOH is hydroperoxide R-O-O-H
  - Mostly by (24a) for small R, other channels contribute for larger R
  - $k \sim 6 \times 10^{-12}$ cm$^3$ molec$^{-1}$ s$^{-1}$ @ room T
- RO$_2^\cdot$ + RO$_2^\cdot$ → 2RO$^\cdot$ + O$_2$ (25a)
  → ROH + RCHO + O$_2$ (25b)
  → ROOR + O$_2$ (25c)

<table>
<thead>
<tr>
<th>Table 6.6</th>
<th>Recommended Rate Constants and Branching Ratios at Room Temperature for the Self-Reactions of Some RO$_2^\cdot$ Radicals$^a$</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Branching ratios</strong></td>
<td></td>
</tr>
<tr>
<td><strong>RO$_2^\cdot$</strong></td>
<td><strong>$k_{24a}$ (cm$^3$ molec$^{-1}$ s$^{-1}$)</strong></td>
</tr>
<tr>
<td>CH$_3$O$_2^\cdot$</td>
<td>$3.7 \times 10^{-13}$</td>
</tr>
<tr>
<td>HCOCH$_2$CH$_2$O$_2^\cdot$</td>
<td>$2.3 \times 10^{-12}$</td>
</tr>
<tr>
<td>C$_2$H$_5$O$_2^\cdot$</td>
<td>$6.4 \times 10^{-14}$</td>
</tr>
</tbody>
</table>

Table from F-P&P 50

25
Critical parameter is the ratio of the corresponding reaction rates:

\[
\begin{align*}
    k (CH_3O_2 + NO) & \approx 7.7 \times 10^{-12} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} @ 298 \text{ K} \\
    k (CH_3O_2 + HO_2) & \approx 5.6 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} @ 298 \text{ K} \\
    k (CH_3O_2 + CH_3O_2) & \approx 4.7 \times 10^{-13} \text{ cm}^3 \text{ molecule}^{-1} \text{ s}^{-1} @ 298 \text{ K}
\end{align*}
\]

\[
\begin{align*}
    [NO]_{\text{urban}} & \approx 20 \text{ ppb} = 5 \times 10^{11} \text{ molecule cm}^{-3} \\
    [HO_2]_{\text{urban}} & \approx [CH_3O_2]_{\text{urban}} \approx 40 \text{ ppt} = 10^8 \text{ molecule cm}^{-3} \\
    \frac{\text{Rate}(CH_3O_2 + NO)}{\text{Rate}(RO_2 + CH_3O_2)}_{\text{urban}} & \approx 4000
\end{align*}
\]

\[
\begin{align*}
    [NO]_{\text{clean}} & \approx 1 \text{ ppt} \approx 2 \times 10^7 \text{ molecule cm}^{-3} \\
    [HO_2]_{\text{clean}} & \approx [CH_3O_2]_{\text{clean}} \approx 5 \text{ ppt} \approx 10^8 \text{ molecule cm}^{-3} \\
    \frac{\text{Rate}(CH_3O_2 + NO)}{\text{Rate}(RO_2 + CH_3O_2)}_{\text{clean}} & \approx 1
\end{align*}
\]

Conclusion: In urban atmosphere, reaction with NO dominates ("high NOx limit"). In remote troposphere, both pathways are similar.

### Alkoxy Radicals (RO·)

- **Three main fates**
  - Reaction with O₂
  - Decomposition
  - Intramolecular isomerization (where possible, it dominates as R size increases)
- Otherwise RO + O₂

Schemes from F-P&P
Summary of Alkane Oxidation

- Chemistry is all about electrons
- Species with unpaired electrons (radical) doing most of the work

**FIGURE 6.2** Summary of alkane oxidation by OH in air.

Alkenes + OH

- Remember that collision rate $\sim 2.5 \times 10^{10}$
- Very fast reactions, faster for larger alkenes
- Pressure dep., negative T dep.
  - Supports importance of addition to double b.
- Compare OH +
  - Propane: $1 \times 10^{-12}$
  - Propene: $26 \times 10^{-12}$
  - Heptane: $7 \times 10^{-12}$
  - Heptene: $40 \times 10^{-12}$

### Table 6.3: Rate Constants and Temperature Dependence for the Reactions of OH Radicals with Alkenes at 1 atm Total Pressure of Air

<table>
<thead>
<tr>
<th>Alkene</th>
<th>$k$, 10$^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$</th>
<th>$A$, (10$^{-12}$ cm$^3$ molecule$^{-1}$ s$^{-1}$)</th>
<th>$E_A$ / $R$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethene</td>
<td>8.72</td>
<td>1.96</td>
<td>-428</td>
</tr>
<tr>
<td>Propane</td>
<td>26.3</td>
<td>4.05</td>
<td>-504</td>
</tr>
<tr>
<td>1-Butenne</td>
<td>31.4</td>
<td>6.55</td>
<td>-467</td>
</tr>
<tr>
<td>2-Methylpropene</td>
<td>56.4</td>
<td>11.0</td>
<td>-487</td>
</tr>
<tr>
<td>3-Methylbutene</td>
<td>64.0</td>
<td>10.1</td>
<td>-504</td>
</tr>
<tr>
<td>1-Pentene</td>
<td>31.4</td>
<td>9.47</td>
<td>-504</td>
</tr>
<tr>
<td>2-Methyl-2-pentene</td>
<td>65</td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-Methyl-2-pentene</td>
<td>68</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyclopentene</td>
<td>67</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-Methyl-3-pentene</td>
<td>31.8</td>
<td>5.32</td>
<td>-533</td>
</tr>
<tr>
<td>2,3-Dimethylpentene</td>
<td>61</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,3-Dimethyl-2-pentene</td>
<td>89.9</td>
<td>19.2</td>
<td>-410</td>
</tr>
<tr>
<td>3-Hexene</td>
<td>37</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>62.7</td>
<td></td>
<td></td>
</tr>
<tr>
<td>1-Hexene</td>
<td>40</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-Methyl-2-pentene</td>
<td>68</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Cycloheptane</td>
<td>74</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,3-Dihexene</td>
<td>66.6</td>
<td>13.8</td>
<td>-448</td>
</tr>
<tr>
<td>2-Methyl-1,3-hexadiene (isoprene)</td>
<td>101</td>
<td>25.4</td>
<td>-410</td>
</tr>
<tr>
<td>Cyclopentane</td>
<td>55</td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-Cyclooctene</td>
<td>80</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Limonene</td>
<td>171</td>
<td></td>
<td></td>
</tr>
<tr>
<td>α-Phellandrene</td>
<td>313</td>
<td></td>
<td></td>
</tr>
<tr>
<td>β-Phellandrene</td>
<td>160</td>
<td></td>
<td></td>
</tr>
<tr>
<td>α-Farnesene</td>
<td>55.7</td>
<td>12.1</td>
<td>-444</td>
</tr>
<tr>
<td>β-Farnesene</td>
<td>78.9</td>
<td>23.8</td>
<td>-337</td>
</tr>
<tr>
<td>α-Terpinene</td>
<td>365</td>
<td></td>
<td></td>
</tr>
<tr>
<td>γ-Terpinene</td>
<td>177</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Terpinolone</td>
<td>225</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methyl vinyl ketone</td>
<td>18.5*</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methylcyclopentene</td>
<td>33.3*</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* $k = A e^{-E_A/RT}$; valid only for the 250–425 K range.
* From Atkinson (1993b).
* High pressure limiting rate constant ($k_0$) except for C$_3$H$_4$ and C$_5$H$_{11}$.
* See Fig. A.22 for structure of biologics.
Reactions of Alkenes

- E.g. HC$_3$-CH=CH-CH$_3$, 2-butene
- Double bond adds reactivity
  - For alkanes OH could abstract any H
    - No strong preference for reaction site
  - The double bond has extra electron density
    - Attacked by electrophilic radicals: OH, O$_3$, NO$_3$, Cl
    - “The double bond gets the whole molecule in trouble”
  - Alkenes “are more reactive” than alkanes

\[
\begin{align*}
\text{OH} + \text{C} = \text{C} &\implies \text{OH} + \text{C} = \text{C} \\
&\quad \text{(32, 33)}
\end{align*}
\]

What happens after OH addition?

- → Hydroxy group + alkyl radical
- Alkyl radical → Peroxy radical
- Peroxy radical → Alkoxy radical or (stable) nitrate
- Alkoxy radical → reaction with O$_2$, decomposition, isomerization

\[
\begin{align*}
\text{OH} + \text{CH}_3\text{CH} &= \text{CH}_2 &\rightarrow \text{CH}_3\text{CH} = \text{CH}_2\text{OH}, &\quad (34a) \\
&\implies \text{CH}_3\text{CH(OH)} = \text{CH}_2, &\quad (34b)
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{CH} = \text{CH}_2\text{OH} + \text{O}_2 &\rightarrow \text{CH}_3\text{CH} = \text{CH}_2\text{OH}, &\quad (35)
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{CH} = \text{CH}_2\text{OH} + \text{NO} &\rightarrow \text{CH}_3\text{CH} = \text{CH}_2\text{OH} + \text{NO}_2, &\quad (36a) \\
&\implies \text{CH}_3\text{CH} = \text{CH}_2\text{OH}, &\quad (36b)
\end{align*}
\]

\[
\begin{align*}
\text{CH}_3\text{CH} = \text{CH}_2\text{OH} &\rightarrow \text{CH}_3\text{CHO} + \text{CH}_2\text{OH}, &\quad (37)
\end{align*}
\]
Example of β-hydroxyalkyl Isomerization

- As for alkanes, larger alkoxy radicals isomerize:

\[
\begin{array}{c}
\text{CH}_3\text{CH}_2\text{CH} = \text{CH}_2 + \text{OH} \xrightarrow{\text{O}_2} \text{CH}_3\text{CH}_2\text{CH} - \text{CH}_2\text{OO}^* \\
\text{OH} \\
\text{CH}_3\text{CH}_2\text{CH} - \text{CH}_2\text{OH} \xrightarrow{1,6-\text{H shift}} \text{CH}_3\text{CH}_2\text{CH} - \text{CH}_2\text{O}' \\
\text{OH} \\
\text{'OOCH}_2\text{CH}_2\text{CH} - \text{CH}_2\text{OH} \\
\text{OH} \\
\text{'OCH}_2\text{CH}_2\text{CH} - \text{CH}_2\text{OH} \\
\end{array}
\]

\[
\text{H} \quad \text{C} - \text{CH}_2\text{CH(0H)}\text{CH}_2\text{OH} \quad \text{3,4-Dihydroxybutanal}
\]

O₃ + Alkenes

- Remember that collision rate ~2.5 x 10⁻¹⁰
- Much slower reactions than for OH
- Compare
  - OH + Propene: 2.6 x 10⁻¹¹
  - O₃ + Propene: 1 x 10⁻¹⁷
- But remember:
  - d[Org]/dt = - k[Oxidant][Org]
  - OH: 0.1 ppt
  - O₃: 100 ppb

So although ozonolysis of alkenes is a slow process, it is important in the atmosphere because of the large concentrations of O₃.

---

**TABLE 6-9** Rate Constants and Temperature Dependence* for the Gas-Phase Reactions of O₃ with Some Alkenes

<table>
<thead>
<tr>
<th>Alkene</th>
<th>k (10⁻¹⁰ cm³ molecule⁻¹ s⁻¹)</th>
<th>A (10⁻¹⁰ cm³ molecule⁻¹ s⁻¹)</th>
<th>Eₜ / Kcal</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethene</td>
<td>1.6</td>
<td>9.14</td>
<td>2900</td>
<td></td>
</tr>
<tr>
<td>Propene</td>
<td>10.1</td>
<td>5.51</td>
<td>1878</td>
<td></td>
</tr>
<tr>
<td>1-Butene</td>
<td>9.64</td>
<td>3.56</td>
<td>1744</td>
<td></td>
</tr>
<tr>
<td>2-Methyl-1-butene</td>
<td>11.3</td>
<td>2.70</td>
<td>1032</td>
<td></td>
</tr>
<tr>
<td>cis-2-Butene</td>
<td>125</td>
<td>3.22</td>
<td>968</td>
<td></td>
</tr>
<tr>
<td>trans-2-Butene</td>
<td>190</td>
<td>6.64</td>
<td>1039</td>
<td></td>
</tr>
<tr>
<td>1-Pentene</td>
<td>14.0</td>
<td>2.88</td>
<td>1003</td>
<td></td>
</tr>
<tr>
<td>Cyclohexene</td>
<td>57.6</td>
<td>1.8</td>
<td>390</td>
<td></td>
</tr>
<tr>
<td>cyclo-2-Methyl-1-pentene</td>
<td>450</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>trans-2-Methyl-1-pentene</td>
<td>560</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2,3-Dimethyl-2-butene</td>
<td>1130</td>
<td>3.03</td>
<td>294</td>
<td></td>
</tr>
<tr>
<td>1,3-Butadiene</td>
<td>6.3</td>
<td>13.4</td>
<td>2206</td>
<td></td>
</tr>
<tr>
<td>2-Methyl-1,3-butadiene</td>
<td>12.8</td>
<td>7.06</td>
<td>1913</td>
<td></td>
</tr>
<tr>
<td>Mesitycne</td>
<td>470</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2-Cycene</td>
<td>73.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3-Cycene</td>
<td>27.0</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Limonene</td>
<td>200</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>α-Phellandrene</td>
<td>2880</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>β-Phellandrene</td>
<td>47</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>α-Pinene</td>
<td>86.6</td>
<td>1.01</td>
<td>732</td>
<td></td>
</tr>
<tr>
<td>β-Pinene</td>
<td>15</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>α-Terpine</td>
<td>2.1 × 10⁶</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>γ-Terpine</td>
<td>40</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Terpinenol</td>
<td>1080</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methyl vinyl ketone</td>
<td>5.6</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Methacrolein</td>
<td>1.2</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* k = Ae⁻¹ ⁄ Tₜ⁴.  
† From Atkinson (1995); and Atkinson et al. (1997); for structures of hydrocarbons, see Fig. 6.22. 
‡ Average of Grecojean and Grecojean (1998a) and Neeb et al. (1998b).
Mechanism of $O_3 +$ Alkenes: First steps

- $O_3$ adds across the double bond

\[
O_3 + R_1C=CR_2C=C(R_3) \rightarrow R_1C=CR_2OOR_3R_4
\]

(42)

- The primary ozonide is not stable and breaks

\[
\begin{align*}
\text{Criegee intermediate} & : R_3R_4C=O + R_1R_2\tilde{C}OO\cdot \quad (-) \\
\text{Criegee intermediate} & : R_3R_4C=O + R_1R_2\tilde{C}OO\cdot \quad (-)
\end{align*}
\]

(43)

c breaks, a or b break

Fate of Excited Criegee Intermediates

- Contain excess energy (from broken bonds)
  - Stabilized by collision
  - Decompose in various ways
    - Some to radicals and some to stable products
- Example of Criegee from 1-propene $+$ $O_3$

\[
\begin{align*}
(H\tilde{CHO})^* + M & \quad \overset{0.37}{\rightarrow} \quad H\tilde{CHO} + M, \quad (45a) \\
& \quad \overset{0.12}{\rightarrow} \quad HCO + OH, \quad (45b) \\
& \quad \overset{0.38}{\rightarrow} \quad CO + H_2O, \quad (45c) \\
& \quad \overset{0.13}{\rightarrow} \quad CO_2 + H_2, \quad (45d) \\
& \quad \rightarrow \quad CO_2 + 2H, \quad (45e) \\
& \quad \rightarrow \quad HCOOH. \quad (45f)
\end{align*}
\]

“Stabilized Criegee Intermediate”
Fate of Stabilized Criegee Intermediates

- React with H₂O, SO₂, NO, NO₂, CO, aldehydes, and ketones
  - All reactions lead to stable products
  - Reaction with H₂O dominates

\[
R_1\text{HCOO}^\cdot + H_2O \rightarrow R_1\text{C(O)OH} + H_2O, \quad (48a)
\]

\[
H \quad \rightarrow \quad R_1\text{COOH} \rightarrow \text{RC(O)OH} + H_2O, \quad (48b)
\]

\[
\text{OH} \quad \rightarrow \quad R_1\text{CHO} + H_2O_2. \quad (48c)
\]

- Others more uncertain, SO₂ & NO may be important in urban atmospheres

Importance of OH generation

<table>
<thead>
<tr>
<th>Alkene</th>
<th>OH yield</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethene</td>
<td>0.12 ± 0.08</td>
</tr>
<tr>
<td>Propane</td>
<td>0.35 ± 0.18</td>
</tr>
<tr>
<td>1-Butene</td>
<td>0.45</td>
</tr>
<tr>
<td>1-Pentene</td>
<td>0.35</td>
</tr>
<tr>
<td>1-Hexene</td>
<td>0.32</td>
</tr>
<tr>
<td>1-Heptene</td>
<td>0.25</td>
</tr>
<tr>
<td>1-Octene</td>
<td>0.18 ± 0.03</td>
</tr>
<tr>
<td>cis-2-Butene</td>
<td>0.41 ± 0.17</td>
</tr>
<tr>
<td>trans-2-Butene</td>
<td>0.64 ± 0.24</td>
</tr>
<tr>
<td>Cyclopentene</td>
<td>0.61</td>
</tr>
<tr>
<td>Cyclohexene</td>
<td>0.08</td>
</tr>
<tr>
<td>1-Methycyclohexene</td>
<td>0.90 ± 0.10</td>
</tr>
<tr>
<td>2-Methylpropene</td>
<td>0.84</td>
</tr>
<tr>
<td>2-Methyl-1-butene</td>
<td>0.83</td>
</tr>
<tr>
<td>2-Methyl-2-butene</td>
<td>0.89</td>
</tr>
<tr>
<td>2,3-dimethyl-2-butene</td>
<td>0.15 – 1.00±</td>
</tr>
<tr>
<td>Limonene</td>
<td>0.80 ± 0.10</td>
</tr>
<tr>
<td>Myrcene</td>
<td>1.10</td>
</tr>
<tr>
<td>a-Pinene</td>
<td>0.70 – 0.80±</td>
</tr>
<tr>
<td>b-Pinene</td>
<td>0.35</td>
</tr>
<tr>
<td>Terpinolene</td>
<td>1.09</td>
</tr>
<tr>
<td>Camphene</td>
<td>≤ 0.10 ± 0.05</td>
</tr>
<tr>
<td>2,3-Butadiene</td>
<td>0.08 ± 0.04</td>
</tr>
<tr>
<td>Isoprene</td>
<td>≤ 0.10 ± 0.04</td>
</tr>
</tbody>
</table>

FIGURE 6.6 Calculated rates of HO₂ radical generation from various sources for a rural forested site in the southeastern United States (adapted from Paulson and Orlando, 1996). Especially important at night because no photolytic OH sources
Tropospheric Oxidation & + Ozone Formation III

*Required Reading: Jacob Chapters 11 & 12*

Atmospheric Chemistry
ATOC-5151 / CHEM 5151
Prof. Jose-Luis Jimenez
Spring 2013
Lecture by Doug Day

**NO₃ + Alkenes**

- NO₃ adds to double bond
- Excited adduct can:
  - Form epoxide
  - Stabilize, form peroxy radical, blah blah...

![Mechanism of the NO₃ reaction with 2,3-dimethyl-2-butene](FIGURE 6.8 Mechanism of the NO₃ reaction with 2,3-dimethyl-2-butene (adapted from Skov et al., 1994).)
NO$_3$ Reaction Rates

- Remember that collision rate $\sim 2.5 \times 10^{-10}$
- Reactions are quite fast for biogenic alkenes
  - Comparable rates to OH
- $d\text{[Org]}/dt = -k\text{[Oxidant][Org]}$
  - NO$_3$: 50 ppt @ night
  - OH: 0.1 ppt @ day
- NO$_3$ reactions with biogenic alkenes @ night are very important

<table>
<thead>
<tr>
<th>Alkene</th>
<th>$k$ (cm$^3$ molecule$^{-1}$ s$^{-1}$) at 298 K</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ethene</td>
<td>$2.1 \times 10^{-15}$</td>
</tr>
<tr>
<td>Propene</td>
<td>$9.5 \times 10^{-15}$</td>
</tr>
<tr>
<td>1-Butene</td>
<td>$1.4 \times 10^{-14}$</td>
</tr>
<tr>
<td>2-Methylpropene</td>
<td>$3.3 \times 10^{-13}$</td>
</tr>
<tr>
<td>cis-2-Butene</td>
<td>$3.5 \times 10^{-13}$</td>
</tr>
<tr>
<td>trans-2-Butene</td>
<td>$3.9 \times 10^{-13}$</td>
</tr>
<tr>
<td>2-Methyl-2-butenone</td>
<td>$9.6 \times 10^{-13}$</td>
</tr>
<tr>
<td>2,3-Dimethyl-2-butene</td>
<td>$5.7 \times 10^{-11}$</td>
</tr>
<tr>
<td>1,3-Butadiene</td>
<td>$1.0 \times 10^{-13}$</td>
</tr>
<tr>
<td>2-Methyl-1,3-butadiene</td>
<td>$6.8 \times 10^{-13}$</td>
</tr>
<tr>
<td>Cyclopentene</td>
<td>$5.3 \times 10^{-13}$</td>
</tr>
<tr>
<td>Cyclohexene</td>
<td>$5.9 \times 10^{-13}$</td>
</tr>
<tr>
<td>Cycloheptene</td>
<td>$4.8 \times 10^{-13}$</td>
</tr>
<tr>
<td>Camphene</td>
<td>$6.2 \times 10^{-13}$</td>
</tr>
<tr>
<td>2-Carene</td>
<td>$1.9 \times 10^{-11}$</td>
</tr>
<tr>
<td>3-Carene</td>
<td>$9.1 \times 10^{-12}$</td>
</tr>
<tr>
<td>Limonene</td>
<td>$1.2 \times 10^{-11}$</td>
</tr>
<tr>
<td>$\alpha$-Pinene</td>
<td>$5.9 \times 10^{-13}$</td>
</tr>
<tr>
<td>$\beta$-Pinene</td>
<td>$2.1 \times 10^{-12}$</td>
</tr>
<tr>
<td>$\alpha$-Phellandrene</td>
<td>$7.3 \times 10^{-11}$</td>
</tr>
<tr>
<td>$\beta$-Phellandrene</td>
<td>$8.0 \times 10^{-11}$</td>
</tr>
<tr>
<td>$\alpha$-Terpinene</td>
<td>$1.4 \times 10^{-10}$</td>
</tr>
<tr>
<td>$\gamma$-Terpinene</td>
<td>$2.9 \times 10^{-11}$</td>
</tr>
<tr>
<td>Terpinolene</td>
<td>$9.7 \times 10^{-11}$</td>
</tr>
<tr>
<td>Methyl vinyl ketone</td>
<td>$&lt;6 \times 10^{-10}$</td>
</tr>
<tr>
<td>Methaeroelein</td>
<td>$3.3 \times 10^{-13}$</td>
</tr>
</tbody>
</table>

Table from F-P&P

What about other organics?

- Similar types of radical chemistries
  - Aromatics: OH-addition
  - Aldehydes: aldehydic H-abstraction
  - Ketones and alcohols: alkyl chain H-abstraction
  - Carboxylic acids: OH-addition or H-abstraction
- Similar types of downstream chemistries
  - Gets really complicated quickly
- You should be able to understand it from what we have covered
  - If need to know for your research:
    - See the book for introduction
    - Then search the literature
General rules for atmospheric oxidation of VOCs

• Attack by OH is by H abstraction for saturated VOCs, by addition for unsaturated VOCs
• Reactivity increases with number of C-H bonds, number of unsaturated bonds
• Organic radicals other than peroxo react with O₂ (if they are small) or decompose (if they are large); O₂ addition produces peroxo radicals.
• Organic peroxo radicals (RO₂) react with NO and HO₂ (dominant), other RO₂ (minor); they also react with NO₂ but the products decompose rapidly (except in the case of peroxyacyl radicals which produce peroxyacylnitrates or PANs)
• RO₂+HO₂ produces organic hydroperoxides ROOH, RO₂+NO produces carbonyls (aldehydes RCHO and ketones RC(O)R’) and also organic nitrates by a minor branch
• Carboxyls and hydroperoxides can photolyze (radical source) as well as react with OH
• Unsaturated HCs also react with ozone, producing carbonyls and carboxylic acids
• RO₂+R’O₂ reactions produce a range of oxygenated organic compounds including carbonyls, carboxylic acids, alcohols, esters...

Big Picture of Organic Oxidation

Aumont, Szopa, and Madronich, ACP, 2005
Fully Explicit Chemistry

Complexity is enormous, but starting to be tackled directly

CARBON BUDGET
Fully explicit chemistry of n-heptane
Global Distribution of Isoprene Emissions

\[ E = f (T, h) \]

Isoprene Emission\[ \text{mg/m}^2\text{day} \]
- < 2
- 2 - 4
- 4 - 8
- 8 - 16
- 16 - 30
- 30 - 50
- 50 - 100
- 100 - 150
- > 150

MEGAN biogenic emission model (Guenther et al., 2006) From Jacob

Large Supply of Biogenic VOCs – unrecognized until the 1990s

Switches polluted areas in U.S. from NO\(_x\)-saturated to NO\(_x\)-limited regime recognized in Revised Clean Air Act of 1999

Anthropogenic VOCs

Isoprene (biogenic VOC)

EMISSION FLUX

\[ 10^{11} \text{ atoms N or C cm}^{-2} \text{ s}^{-1} \]

Jacob et al., J. Geophys. Res. [1993] From Jacob
Coupling of HO\textsubscript{x} and NO\textsubscript{x} Catalytic Cycles

Fig. 1. Schematic of photochemical production of two new O\textsubscript{3} molecules from the oxidation of one generic organic molecule at the overlap of the HO\textsubscript{x} (a) and NO\textsubscript{x} (b) catalytic cycles. Only the NO\textsubscript{x} termination channels are shown. HO\textsubscript{x} chain terminations are reactions among peroxy radicals and OH.

Dependence of Ozone Production on NO\textsubscript{x} and Volatile Organic Compounds (VOCs)

Take hydrocarbon RH as example of VOC

\[
P(O_3) = \frac{2k_4 P_{HOx}[RH]}{k_9[NO_2][M]}
\]

“NO\textsubscript{x}-saturated” or “VOC-limited” regime

\[
P(O_3) = 2k_7 \left( \frac{P_{HOx}}{2k_8} \right)^{1/2}[NO]
\]

“NO\textsubscript{x}-limited” regime

From Jacob
Ozone Concentrations vs. NO\textsubscript{x} and VOC:
Ozone “Isoplaths”
(for a typical urban airshed)

Ozone Production Rate:
NO\textsubscript{x} Dependence for VOC Regimes

Fig. 2. The instantaneous ozone production rate (P\textsubscript{O\textsubscript{3}}) and, by analogy the ozone exceedance probability, as a function of NO\textsubscript{x} is shown for three categories of organic reactivity (VOCR): high (red), mid (blue), and low (violet). The mid- and high-VOCR curves correspond to scaling the base VOCR by 2 and 3, respectively. If temperature serves as an adequate proxy for VOCR then the three curves will also describe high- (red), moderate- (blue), and low- (violet) temperature regimes.
Ozone Regulatory Strategies

In rural areas it is most effective to regulate:
(assume some vegetation)

a) VOCs
b) NO\textsubscript{x}
c) CO
d) Equally VOCs \& NO\textsubscript{x}
e) I don’t know

Diesel vs Gasoline

In a very polluted urban area in the U.S. reducing diesel traffic may likely:
(hint: diesel engines make more NO\textsubscript{x} than gasoline engines)

a) Reduce ozone
b) Increase ozone
c) Increase NO\textsubscript{x}
d) Decrease OH
e) I don’t know
"Weekend Effect"

NOx and NMHC are lower on weekends, but ozone is higher

Fig. 7. Average daily maximum ozone (8-h average), morning NOx, and morning NMHC in the summertime at El Cajon (~30 km east of San Diego).

Marr and Harley, 2002

2010 Ozone Data from Cal-Nex

(Pollack et al., 2012)

From Tolbert
Evaporative Emissions

Reducing evaporative loss of gasoline at pumping stations in a polluted desert city (like Phoenix) should:

a) Reduce ozone
b) Increase ozone
c) Reduce NO\textsubscript{x}
d) Have zero effect
e) I don’t know

Even in NO\textsubscript{x}-limited Regime, the Total O\textsubscript{3} Produced is VOC-dependent and \([O_3] = f(E_{NOx})\) is Strongly Nonlinear

Define ozone production efficiency (OPE) as the total number of O\textsubscript{3} molecules produced per unit NO\textsubscript{x} emitted.

Assuming NO\textsubscript{x} steady state, efficient HO\textsubscript{x} cycling, and loss of NO\textsubscript{2} by reaction with OH:

\[
OPE = \frac{P(O_3)}{L(NO_x)} = \frac{2k_1[HO_2][NO]}{k_3[NO_2][OH]} = \frac{2k_1[RH]}{k_3[NO_2]}
\]

OPE \(\propto\) as NO\textsubscript{x} \(\propto\) strong nonlinearity; in models, decreasing NO\textsubscript{x} emissions by 50% reduces ozone only by \(~15\%)
Ozone vs. \((\text{NO}_y - \text{NO}_x)\)

\(\text{NO}_x = \text{NO} + \text{NO}_2; \ \text{NO}_y = \text{all oxidized nitrogen species}; \ \text{NO}_z = \text{NO}_y - \text{NO}_x\)

Approximately how many HO_x cycles occurred for each NO_x molecule oxidized to NO_z in the August Observations:

a) 3.9  

b) 4.3  

c) 8.6  

d) 2.0  

e) I don’t know

Figure 1. Scatterplots and linear regressions (reduced-major-axis method) of \(\text{O}_3\) versus NO_x(NO_y concentrations at Harvard Forest, Massachusetts, for the weeks of May 6-12, 1990 (squares, solid line) and August 24-30, 1992 (circles, dotted line). Concentrations are hourly means at 1100-1700 EST.

Impact of Asian Emissions on Surface Ozone

Data from Dan Jaffe (University of Washington)

\(\text{O}_3\) measurements at Mt. Bachelor (44°N, 122°W, 2.7 km, in central Oregon)

- Asian emissions increase surface ozone in the western US by 5-7 ppbv, compared with observed concentrations of ~50 ppbv.
- Doubling Asian emissions from 2000 to 2006 increases surface ozone by ~10 ppbv over Asia, and by 1-2 ppbv in the west US.

Zhang et al., 2008
Intercontinental Ozone Pollution Influences

Surface O₃ enhancements from North American anthropogenic emissions
from European anthropogenic emissions
from Asian anthropogenic emissions

Lin Zhang, Harvard

PAN and Ozone Production Efficiency (OPE)

PAN formed in polluted regions in East Asia and transported to the eastern Pacific will:

a) Decrease OPE in the source region
b) Increase OPE in the source region
c) Increase OPE in globally
d) A & B
e) A & C

Adapted from Jacob
Conceptual Picture of Ozone Production in Transpacific Asian Pollution Plumes

Ozone: Local, Regional, Global -- Complex Sources, Multiple Effects

Slide provided by Megan Melamed IGAC