Tropospheric photochemistry 2: role of organic compounds

1. Sources of organic compounds in urban air
2. Terminology
3. Alkanes, alkenes, alkynes, and oxygenated compounds
4. Aldehydes and ketones as a source of \( \text{HO}_x \)
5. Formaldehyde photochemistry
6. Tropospheric chemistry v2.0
1. Sources of organic compounds in urban air

Both anthropogenic and biogenic emissions contribute to atmospheric levels of organic compounds.

VOC emissions in the US by source category (US EPA, 2007b)
2. Terminology

VOC – volatile organic carbon
NMHC - non-methane hydrocarbons
OVOC – oxygenated volatile organic carbon
Elemental (black) carbon – aerosol graphitic soot
Brown carbon – aerosol soot containing many compounds, including OVOC’s

Classes of organic compounds:
Alkanes
Alkenes
Alkynes
Aromatics
Oxygenates: alcohols, aldehydes, ketones, acids
3. Alkanes

also called paraffins or saturated hydrocarbons
linear, branched or cyclic
single bonds only
formula: \( C_nH_{2n+2} \) for a straight chain alkane

<table>
<thead>
<tr>
<th>alkane name</th>
<th>formula</th>
<th>structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Methane</td>
<td>( \text{CH}_4 )</td>
<td><img src="image" alt="Methane Structure" /></td>
</tr>
<tr>
<td>Ethane</td>
<td>( \text{C}_2\text{H}_6 )</td>
<td></td>
</tr>
<tr>
<td>Propane</td>
<td>( \text{C}_3\text{H}_8 )</td>
<td><img src="image" alt="Propane Structure" /></td>
</tr>
<tr>
<td>Butane</td>
<td>( \text{C}<em>4\text{H}</em>{10} )</td>
<td></td>
</tr>
<tr>
<td>...</td>
<td>...</td>
<td></td>
</tr>
<tr>
<td>Octane</td>
<td>( \text{C}<em>8\text{H}</em>{18} )</td>
<td><img src="image" alt="Octane Structure" /></td>
</tr>
</tbody>
</table>
4. Alkenes

also known as olefins
contain one or more double bonds, “unsaturated”
used as basis for polymers in both industry and life,
   ie. plastics like polyethylene,
   biogenics like terpenes (linked isoprene units, C₅H₈) or sesquiterpenes
formula (CₙH₂ₙ for straight chain alkenes with 1 double bond)

<table>
<thead>
<tr>
<th>alkene name</th>
<th>formula</th>
<th>structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethylene</td>
<td>C₂H₄</td>
<td></td>
</tr>
<tr>
<td>propene (propylene)</td>
<td>C₃H₆</td>
<td></td>
</tr>
<tr>
<td>butene (butylene)</td>
<td>C₄H₈</td>
<td></td>
</tr>
<tr>
<td>isoprene</td>
<td>CH₂=C(CH₃)CH=CH₂</td>
<td></td>
</tr>
<tr>
<td>2-methyl-1,3 butadiene</td>
<td></td>
<td></td>
</tr>
<tr>
<td>caryophyllene</td>
<td>C₁₅H₂₄</td>
<td></td>
</tr>
<tr>
<td>(a sesquiterpene)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>α-pinene</td>
<td>C₁₀H₁₆</td>
<td></td>
</tr>
<tr>
<td>β-pinene</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
5. Alkynes

one or more triple bonds
highly reactive
formula: \( C_nH_{2n-2} \) for straight chain alkynes with one triple bond

<table>
<thead>
<tr>
<th>alkyne name</th>
<th>formula</th>
<th>structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>ethyne (acetylene)</td>
<td>( C_2H_2 )</td>
<td><img src="image" alt="structure" /></td>
</tr>
<tr>
<td>propyne</td>
<td>( C_3H_4 )</td>
<td><img src="image" alt="structure" /></td>
</tr>
<tr>
<td>butyne</td>
<td>( C_4H_8 )</td>
<td><img src="image" alt="structure" /></td>
</tr>
</tbody>
</table>

... 
| octyne           | \( C_8H_{14} \) | ![structure](image) |
6. Oxygenated organic compounds (OVOC’s)

- Alcohol – eg. ethanol
  \[
  \text{H}_3\text{C} - \text{C} - \text{O} - \text{H}
  \]

- Aldehyde – eg. formaldehyde
  \[
  \text{H} - \text{C} - \text{H} - \text{C} - \text{H} - \text{O}
  \]

- Ketone – eg. acetone
  \[
  \text{H}_3\text{C} - \text{C} - \text{O} - \text{H}
  \]

- Alcohol – eg. carboxylic acid
  \[
  \text{H} - \text{C} - \text{C} - \text{O} - \text{H}
  \]
7. Role of organics (tropospheric photochemistry v1.0)

1. Photolysis of aldehydes, ketones is an HO$_x$ source
2. VOC’s accelerate NO $\rightarrow$ NO$_2$

In polluted air...
  $\Rightarrow$ more ozone formation
8. Aldehydes and ketones as HOX sources

direct natural and pollutant emissions
“secondary production” from atmospheric oxidation of organic compounds

indoor/outdoor pollutant, ppb levels
aldehydes and ketones photolyze in the uv/visible region of the solar spectrum

two photolysis pathways

Formaldehyde (CH₂O)

![Formaldehyde and Acetone Structures]

![Photolysis Wavelength Graph]

![Quantum Yield Graph]
9. Formaldehyde photochemistry

2 photolysis pathways:

\[ \text{HCHO} \xrightarrow{hv} \text{H} + \text{HCO} \quad 50\% \]

\[ \text{HCHO} \xrightarrow{hv} \text{H}_2 + \text{CO} \quad 50\% \]

also, reaction with OH:

\[ \text{HCHO} + \text{OH} \rightarrow \text{HCO} + \text{H}_2\text{O} \]

quickly followed by:

\[ \text{H} + \text{O}_2 \xrightarrow{M} \text{HO}_2 \quad \text{fast} \]

\[ \text{HCO} + \text{O}_2 \rightarrow \text{HO}_2 + \text{CO} \quad \text{fast} \]

overall:

\[ \text{HCHO} \xrightarrow{hv, \text{O}_2} 2\text{HO}_2 + \text{CO} \]

\[ \text{HCHO} \xrightarrow{hv} \text{H}_2 + \text{CO} \]

\[ \text{HCHO} + \text{OH} \xrightarrow{\text{O}_2} \text{HO}_2 + \text{CO} \]

Bottom line: lots of HO\(_x\)!

what happens to the HO\(_2\)?
10. Tropospheric photochemistry v 2.0