Organic Nitrate Production from Organic Peroxy Radical Reactions with NO

Quantifying the effects of VOC/NOx chemistry on tropospheric ozone production: Yields of organic nitrates from reaction of organic peroxy radicals with NO.

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Background

- The production of ozone and SOA in the troposphere is controlled by the chemistry of volatile organic compounds (VOCs) and nitrogen oxides (NOx).

- Understanding the sources and removal rate of NOx is critical input into understanding, predicting and mitigating poor air quality.

- The formation of organic nitrates, from atmospheric oxidation of VOCs, is a major NOx loss and limits ozone production (e.g., Zare et al., 2018). Hence the yields of these nitrates are required.

- There remain systematic uncertainties in the formation yields of organic nitrates across the full range of VOC types and atmospheric conditions.
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Background

- Organic nitrates are formed from the oxidation of VOCs in the atmosphere.
  - \( \text{OH} + \text{RH} (+ \text{O}_2) \rightarrow \text{RO}_2 \)
  - \( \text{RO}_2 + \text{NO} \rightarrow \text{RO} + \text{NO}_2 \)  \(\) Major channel (1-\(\alpha\))
  - \( \text{RO}_2 + \text{NO} \rightarrow \text{RONO}_2 \)  \(\) Minor channel (\(\alpha \approx 0-30\%\))
  - \( \text{NO}_2 + h\nu (+ \text{O}_2) \rightarrow \text{NO} + \text{O}_3 \)  \(\) Ozone formation

- The goal is to systematically quantify ‘\(\alpha\)’ across the range of atmospheric VOCs and T/P conditions.

  e.g., Calvert et al., 2015
Factors Affecting Nitrate Formation: e.g. Jenkin et al. (2019) and refs. therein.

1) Size of the parent molecule
2) Nature of carbon atom carrying the peroxy group (primary, secondary, tertiary)
3) Temperature
4) Pressure
5) Presence of functional groups (alcohols, ethers, carbonyls, esters, …)

This Study:
• Address #1-3 for alkanes (NCAR).
• Discuss preliminary results for #5 (NCAR and CU).
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CONCEPTUAL EXPERIMENT:

• Put VOC of interest, NO$_x$, an OH (Cl) source, and air into one of our chambers.

• Analyze contents of the chamber as a function of photolysis time (i.e., quantify loss of the precursor VOC and appearance of oxidation products).

• Nitrate identification and quantification (so far):
  IR and GC/FID at NCAR. For alkanes, some standards available. Some synthesized (e.g., alkyl bromide reaction with AgNO$_3$).

• Additional capabilities at CU (in progress):
  (HPLC-UV/Vis, CIMS, ESI-MS, GC-FID-ITMS)
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- **3-METHYL PENTANE**
  - A tertiary site, a secondary site, and two unique primary sites (one ‘degenerate’)

<table>
<thead>
<tr>
<th></th>
<th>Primary(1)</th>
<th>Primary(2)</th>
<th>Secondary</th>
<th>Tertiary</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative Yield (%)</td>
<td>6.5</td>
<td>2.9</td>
<td>37.5</td>
<td>53.0</td>
<td></td>
</tr>
<tr>
<td>Measured Yield (%)</td>
<td>1.2</td>
<td>0.5</td>
<td>6.6</td>
<td>9.4</td>
<td>17.7</td>
</tr>
<tr>
<td>Site of Attack (%)</td>
<td>6.6</td>
<td>3.3</td>
<td>39</td>
<td>51</td>
<td></td>
</tr>
<tr>
<td>Normalized Yield (%)</td>
<td>17</td>
<td>16</td>
<td>17</td>
<td>18</td>
<td></td>
</tr>
<tr>
<td>Leeds MCM</td>
<td>7.8</td>
<td>7.8</td>
<td>17.8</td>
<td>5.9</td>
<td>10.7</td>
</tr>
<tr>
<td>New GECKO-A</td>
<td>10.7</td>
<td>10.7</td>
<td>16.5</td>
<td>16.5</td>
<td>15.9</td>
</tr>
<tr>
<td>MechGen</td>
<td>16</td>
<td>16</td>
<td>16</td>
<td>16</td>
<td>16</td>
</tr>
</tbody>
</table>

- Overall yield (18%) larger than for n-pentane (12%).
- No significant difference between nitrate yield from various radicals ($1^\text{ry}$, $2^\text{ry}$, $3^\text{ry}$).
- Higher measured yield from tertiary site leads to overall higher yield cf. MCM.
### SUMMARY OF ALL ALKANE DATA – 298 K

<table>
<thead>
<tr>
<th>Molecule</th>
<th># of C’s</th>
<th>Primary</th>
<th>Secondary</th>
<th>Tertiary</th>
<th>Total Yield</th>
<th>MCM Total</th>
<th>New GECKO-A Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>n-Pentane</td>
<td>5</td>
<td>10%</td>
<td>12%</td>
<td>n/a</td>
<td><strong>12.0%</strong></td>
<td>12.5%</td>
<td>10.4%</td>
</tr>
<tr>
<td>Isopentane</td>
<td>5</td>
<td>10%</td>
<td>11%</td>
<td>14%</td>
<td><strong>12.8%</strong></td>
<td>7.5%</td>
<td>10.1%</td>
</tr>
<tr>
<td>Cyclohexane</td>
<td>6</td>
<td>n/a</td>
<td></td>
<td>18%</td>
<td><strong>18.0%</strong></td>
<td>8% (?!?)</td>
<td>16%</td>
</tr>
<tr>
<td>3-methyl pentane</td>
<td>6</td>
<td>16%</td>
<td>17%</td>
<td>18%</td>
<td><strong>17.7%</strong></td>
<td>10.7%</td>
<td>16%</td>
</tr>
<tr>
<td>2-methyl pentane</td>
<td>6</td>
<td>16%</td>
<td>18%</td>
<td>18%</td>
<td><strong>17.7%</strong></td>
<td>11.4%</td>
<td>16%</td>
</tr>
<tr>
<td>2,4-dimethyl-pentane*</td>
<td>7</td>
<td>18%</td>
<td>18%</td>
<td>18%</td>
<td><strong>17.9%</strong></td>
<td>n/a</td>
<td>20.8%</td>
</tr>
</tbody>
</table>
TEMPERATURE DEPENDENCE OF THE YIELDS
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What about oxygenated VOCs? Generally, nitrate production thought to be reduced for RO$_2$ near the functional group. (Jenkin et al., 2019 and refs. therein).

Consider these related molecules:

- n-pentane
- diethyl ether
- di-isopropyl ether
- C$_{14}$-C$_{20}$ ethers
- ethyl acetate
- larger esters
- 3-pentanone

Commonality: Similar size, most of the reactivity of Cl/OH occurs at the CH$_2$ group indicated by the red arrow.
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RESULTS: n-PENTANE:

- Three different peroxy radicals, 1-pentyl (1\(^\gamma\)), 2-pentyl (2\(^\gamma\)), 3-pentyl (also 2\(^\gamma\))

<table>
<thead>
<tr>
<th></th>
<th>1-Pentyl Nitrate (Primary)</th>
<th>2-Pentyl Nitrate (Secondary)</th>
<th>3-Pentyl Nitrate (Secondary)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Relative Yield (%)</td>
<td>8.6</td>
<td>53.1</td>
<td>38.4</td>
</tr>
<tr>
<td>Measured Yield (%)</td>
<td>1.0</td>
<td>6.4</td>
<td>4.6</td>
</tr>
<tr>
<td>Site of Attack (%)</td>
<td>9</td>
<td>54</td>
<td>37</td>
</tr>
<tr>
<td>Normalized Yield per (\text{RO}_2) formed (%)</td>
<td><strong>0.117</strong></td>
<td>0.120</td>
<td>0.127</td>
</tr>
<tr>
<td>Leeds MCM</td>
<td>.052</td>
<td>.129</td>
<td>.131</td>
</tr>
<tr>
<td>GECKO-A</td>
<td>0.069</td>
<td>0.107</td>
<td>0.107</td>
</tr>
</tbody>
</table>

Site of attack data from Jenkin et al., 2018
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Oxygenated VOCs: Diethyl Ether

\[
\begin{align*}
\text{Diethyl Ether} & \rightarrow \text{Diethyl Peroxy Radical} \\
\text{Diethyl Peroxy Radical} & + \text{NO} \rightarrow \text{Diethyl Nitrate} \\
\text{Diethyl Nitrate} & \rightarrow \text{Ethyl Acetate} \\
\text{Ethyl Acetate} & \rightarrow \text{Ethyl Formate}
\end{align*}
\]
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Oxygenated VOCs: Diethyl Ether

Also, two ‘promising’ GC peaks suggest even lower yield (< 1%)

Nitrate Yield < 4%
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Oxygenated VOCs: Diethyl Ether

Di-isopropyl Ether

NB: GECKO-A yields 7% and 14% for these two ethers.

CU: Looking at larger ethers….
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Oxygenated VOCs: Ethyl Acetate

Nitrate Yield < 8%

NB: Acetic Acid production too fast in GECKO-A. The two processes shown can be made competitive at 298 K. [Orlando et al., 2010]
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Oxygenated VOCs: 3-Pentanone

Chemical reaction diagram showing the process of producing organic nitrates from 3-pentanone and NO.
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Oxygenated VOCs: 3-Pentanone

Nitrate Yield ≈ 6% (tentative)

NB: This nitrate yield could correspond to 2-nitrooxy- and/or 1-nitrooxy-3-pentanone.

- Chemistry at –CH₂-site accounts for about 70% of the 3-pentanone loss (with mixed Cl/OH initiation).
- What happens following attack at CH₃?
Conclusions: