SOA and volatile product formation from the nighttime oxidation of various terpenes, and the ICARUS database

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Overview

- Discuss the potential for the reactions of terpenes + NO$_3$ to produce organic nitrogen and secondary organic aerosol (SOA).
- Present the viewpoint that we should consider modeling VOC oxidation in terms of RO$_2$ fates.

- Discuss how the ICARUS database can help existing and new model mechanism development efforts.
Motivation

Field observations have shown a surprisingly prominent signal of a gaseous $C_{10}$ organonitrate (PNP) and its correlation with particulate nitrates.

PNP has never been observed in chamber studies of terpenes + NO$_3$ because the RO$_2$ fate distribution of the reaction is not similar to the atmosphere. Thus, the product formation is not representative.

We performed chamber studies to probe each RO$_2$ fate and more accurately simulate nighttime chemical regime.
Results – particle formation


~60 % PNP yield from RO$_2$+HO$_2$
Comparison of SOA yields under dry conditions

<table>
<thead>
<tr>
<th>Fate of α-pinene nRO₂</th>
<th>Day et al. JPCA 2022</th>
<th>DeVault et al. ACS ESC 2022</th>
<th>Kurten et al. JPC Lett. 2017</th>
<th>Nah et al. EST 2016</th>
<th>Bates et al., ACP 2021 (this work)</th>
</tr>
</thead>
<tbody>
<tr>
<td>RO₂ + HO₂</td>
<td>5.6 (± 4.6)</td>
<td></td>
<td>3.6 (± 0.4)</td>
<td>0 (± 5)</td>
<td>Low</td>
</tr>
<tr>
<td>RO₂ + NO₃</td>
<td>8.9 (± 4.4)</td>
<td></td>
<td>0</td>
<td>4 (± 8)</td>
<td>Low</td>
</tr>
<tr>
<td>RO₂ + RO₂</td>
<td>12.5 (± 3.7)</td>
<td>48</td>
<td>56 (± 7)</td>
<td></td>
<td>High</td>
</tr>
<tr>
<td>RO₂ + NO</td>
<td></td>
<td></td>
<td></td>
<td>13 (± 11)</td>
<td>Low</td>
</tr>
</tbody>
</table>

Model extrapolation out to field conditions

~ 11% (60-70% particulate nitrates)

(~ 1 ppb VOC, 20 ppb O₃, 1 ppt NO₃, 2 ppt HO₂)

Simulated nighttime in the chamber

~ 22%

~ 60-80% AP+NO₃, 20-40% AP+O₃

~ 1:1 nRO₂ + HO₂ and nRO₂ + RO₂ (Ayres et al 2015, Romer et al 2018)
Results – particulate organonitrates

- C_{20} organonitrile dimers from the RO_{2} + RO_{2} channel were major components of the SOA.
Uncertainties and discrepancies

- Very uncertain rate coefficients of functionalized \( nRO_2 \)s (and larger \( RO_2 \)s in general)
  - Day et al (JPCA 2022) assumed an \( RO_2 + RO_2 \) rate of \(~ 2 \times 10^{-15} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}\) based on smaller \( RO_2 \)s
  - Zhao, Thornton and Pye (PNAS, 2018) measured \(~ 1-2 \times 10^{-12} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}\)
  - We derive a rate of \( 1 \times 10^{-13} \text{ cm}^3 \text{ molec}^{-1} \text{ s}^{-1}\) from data constraints

- SOA composition – ROOR dimers or acetals/hemiacetals
  - Zhao, Thornton and Pye (PNAS, 2018) directly show rapid gas-phase formation of ROOR dimers.
  - DeVault, Ziola and Ziemann (ACS ESC 2022) suggested that dimers must be particle phase hemiacetals and acetals because iodometric assay of dried and reconstituted extracts yielded low peroxide content
  - We conclude that SOA formation is from ROOR dimers from the gas phase. But these can decompose in sample treatment or with time/aging.
Studies on other terpenes and humid conditions (RH 60%)  
Caveat: work in progress!

<table>
<thead>
<tr>
<th>Structure:</th>
<th>Species:</th>
<th>Emissions: (Tg y⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>α-pinene</td>
<td>66.1</td>
</tr>
<tr>
<td></td>
<td>β-ocimene</td>
<td>19.4</td>
</tr>
<tr>
<td></td>
<td>β-pinene</td>
<td>18.9</td>
</tr>
<tr>
<td></td>
<td>limonene</td>
<td>11.4</td>
</tr>
<tr>
<td></td>
<td>sabinene</td>
<td>9.0</td>
</tr>
<tr>
<td></td>
<td>myrcene</td>
<td>8.7</td>
</tr>
<tr>
<td></td>
<td>Δ-3-carene</td>
<td>7.1</td>
</tr>
<tr>
<td></td>
<td>camphene</td>
<td>4.0</td>
</tr>
<tr>
<td></td>
<td>γ-terpinene</td>
<td>&lt; 1</td>
</tr>
<tr>
<td></td>
<td>pinonaldehyde</td>
<td>N/A</td>
</tr>
</tbody>
</table>
Total gaseous organonitrates observed for the simulated nighttime reaction

- Inspired us to look deeper into relationship with double bonds
Some preliminary trends of ON

- Total gaseous ON signal in CIMS
  - Number of double bonds:
    - 1
    - 2
    - 3

- Fraction of terpene reacting with NO$_3^-$
  - Number of double bonds:
    - 0
    - 1
    - 2
    - 3

*Adjusted for fraction reacting with NO$_3^-$
Some preliminary trends of SOA

- SOA numbers under humid conditions will be subject to validation with additional experimental methods.
ICARUS chamber database to support mechanism development

- These data and hundreds more high-quality experiments are available at [https://icarus.ucdavis.edu](https://icarus.ucdavis.edu)

**Data users** – start by searching or browsing all experiments.

**Data contributors** – watch a 30 minute how-to video to start the process.
Search and discovery page

Search, browse, filter using PubChem-controlled chemical vocabulary

The image shows a user interface for searching and discovery experiments. The interface includes:

- A search bar for entering terms like "Toluene" or "Ozonolysis".
- A results section displaying experiments with columns for PI Name, Reactant(s), Other Fields, RO₂ Main Fate, and Supplemental Information.
- Options to select or unselect experiments and download selected entries.
- Filters for sorting and organizing the search results.

The interface allows users to search, browse, and filter experiments using controlled chemical vocabulary from PubChem.
Interactive data set plots

Select dataset to view
Turn on/off data
Change x-coordinates
Thanks for your attention