Nighttime to daytime transition of the oxidation products of isoprene by NO$_3$ radicals

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Motivation on NO$_3$ + isoprene studies

- Biogenic volatile organic compounds (BVOC) emissions are 1 order of magnitude higher than the anthropogenic ones.
  - **Isoprene** represents about 50% of the total BVOC emissions.

- NO$_3$ can be the **major oxidant** during **nighttime**.
  - NO$_3$-induced oxidation of BVOC has been **poorly studied** compared to OH and O$_3$ oxidation.

- Better representation of organonitrates formation is essential for properly describing isoprene’s effect on NO$_x$, HO$_x$ as well as ozone formation.

- Contribution of organonitrates to secondary organic aerosol (SOA).

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Guenther et al., 2012; Goldstein & Galbally, 2007; Wennberg et al., 2018; Lee et al., 2016; Fry et al., 2018

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**NO$_3$ formation**

\[
NO + O_3 \rightarrow NO_2 + O_2 \\
NO_2 + O_3 \rightarrow NO_3 + O_2 \\
NO_3 + NO_2 + M \leftrightarrow N_2O_5 + M
\]
Experimental set up & conditions

Atmospheric simulation chamber SAPHIR at Forschungszentrum Jülich, Germany (Aug. 2018)
- Volume: 270 m$^3$, surface: 320 m$^2$
- FEP double wall
- Ambient pressure & temperature
- Shutter system for simulating dark conditions or daytime by exposing to sunlight

Various chemical conditions in order to change the fate of the peroxy radicals initially formed by NO$_3$+isoprene

- High/low RO$_2$ or HO$_2$
- Without or with seed particles
  - (NH$_4$)$_2$SO$_4$ with or without organic coating ($\beta$-caryophyllene)
- Nighttime to daytime transition
  - Photolysis
  - Photolysis + OH radicals
- Isoprene injections
- NO$_3$ formation by NO$_2$/O$_3$ injections

Photo: E. Tsiligiannis

Rohrer et al., 2005
Focus on this study

Instrumentation

Gas & particle phase measurements by I- Chemical Ionization Mass spectrometer (CIMS)

Detection limits:

- **Gas-Phase:** e.g., 4 pptv formic acid (1s, Bertram et al., 2011), 0.4 pptv malonic acid (15s, Lee et al., 2014)
- **Aerosol, FIGAERO:** e.g., 4 ng m$^{-3}$ formic acid and 2 ng m$^{-3}$ C$_9$ pinene acid (Lopez-Hilfiker et al., 2014)

Experiments

- Gas phase measurements of Organonitrates
- Effect of OH oxidation on the nighttime products

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Aug. 12</th>
<th>Aug. 12</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Nighttime $\rightarrow$ Photolysis</td>
<td>Nighttime $\rightarrow$ Photolysis + OH oxidation</td>
</tr>
<tr>
<td>Max Isoprene (ppbv)</td>
<td>3</td>
<td>2.5</td>
</tr>
<tr>
<td>O$_3$ (ppbv)</td>
<td>70-115</td>
<td>80-115</td>
</tr>
<tr>
<td>NO$_2$ (ppbv)</td>
<td>4-12</td>
<td>2-5</td>
</tr>
<tr>
<td>CO (ppbv)</td>
<td>120000</td>
<td>20</td>
</tr>
<tr>
<td>Seed aerosol</td>
<td>No</td>
<td>(NH$_4$)$_2$SO$_4$</td>
</tr>
<tr>
<td>Max J(NO$_2$)/10$^{-3}$ s$^{-1}$</td>
<td>4.8</td>
<td>4.8</td>
</tr>
<tr>
<td>T (°C)</td>
<td>14-36</td>
<td>20-28</td>
</tr>
<tr>
<td>H$_2$O (%)</td>
<td>0</td>
<td>1.6</td>
</tr>
</tbody>
</table>
Mass spectra overview

- **Monomers**: $C_5H_9NO_{4,5,6}$, $C_5H_7NO_{4,5,6}$, $C_4H_7NO_5$ (major compounds)
- **Dinitrates**: $C_4H_6N_2O_7$, $C_5H_8N_2O_8$, $C_5H_8N_2O_9$ → Probably formed by 1st gen. organonitrate + NO$_3$
- **Dimers**: $C_{10}H_{16}N_2O_{8,9,10}$ → RO$_2$ + RO$_2$

**Representative I- CIMS data.** Experiment 12th of August at dry & medium NO$_3$ conditions without seeds. CO was used as OH scavenger during the “daytime” mode.
Product time evolution – exp. Aug 12th

✓ 36 mononitrates, 20 dinitrates & 15 accretion products have been identified.
✓ Mononitrates are the dominant signal.
✓ Dinitrates increase relative to mononitrates with time.
✓ Accretion products decrease relative to mononitrates with time.

<table>
<thead>
<tr>
<th>Time</th>
<th>(M) : (D) : (A)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1st injection</td>
<td>10 : 0.72 : 0.29</td>
</tr>
<tr>
<td>2nd injection</td>
<td>10 : 0.68 : 0.17</td>
</tr>
<tr>
<td>3rd injection</td>
<td>10 : 0.72 : 0.19</td>
</tr>
<tr>
<td>Daytime</td>
<td>10 : 0.79 : 0.18</td>
</tr>
</tbody>
</table>

- Mononitrates
- Dinitrates
- Accretion products

Diagram showing the evolution of product concentrations over time.
O:C ratio time evolution – exp. Aug 12th

- O:C ratio increases from 1.06 to 1.14 with time & after a new isoprene injection.
- O:C ratio of C₄ & C₅ compounds increase with addition of NO₃ + isoprene.
- O:C ratio of C₅ compounds decreases during daytime while O:C ratio of C₄ compounds increases during daytime.
Mononitrates

- Most of the mononitrates are photolyzed rapidly during daytime.
- The major C₄H₇NO₅ products are enhanced further under the presence of both photolysis and OH chemistry.
- Less sharp reduction of compounds with chemical formula C₅H₉NO₅ under the presence of OH chemistry. Likely consumed by photolysis but formed by OH oxidation.

Potential formation pathways of C₄H₇NO₅ compounds:

\[ C_5H_9NO_4 + NO_3 \rightarrow \cdots \rightarrow C_4H_7NO_5 \]

\[ C_5H_9NO_5 + OH \rightarrow \cdots \rightarrow C_4H_7NO_5 \]
The major dinitrate (C\textsubscript{5}H\textsubscript{6}N\textsubscript{2}O\textsubscript{8}) get photolyzed.

All the major dinitrates increase under the presence of OH radicals.

## Photolysis effect

![Photolysis effect graph](image)

## Photolysis + OH radicals effect

![Photolysis + OH radicals effect graph](image)

### Dinitrates

- The major dinitrate (C\textsubscript{5}H\textsubscript{6}N\textsubscript{2}O\textsubscript{8}) get photolyzed.
- All the major dinitrates increase under the presence of OH radicals.

### Accretion products

- Sharp reduction during photolysis.
- Less pronounced reduction with both photolysis and OH chemistry.
- Possible a day-time source from OH oxidation.
Conclusions

- Mononitrates, dinitrates & accretion nitrated compounds were characterized.
- O:C ratio increases (1.06 to 1.14 at the given experiment) with time and after a new isoprene injection.
- Most of the nighttime products are photolyzed during daytime.
- Products with the chemical formula $\text{C}_4\text{H}_7\text{NO}_5$ become the dominant ones during daytime conditions and enhanced further via OH chemistry.
- $\text{C}_5\text{H}_9\text{NO}_5$ products are photolyzed during daytime but partly compensated by formation from OH chemistry.

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