New insights in isoprene photooxidation: from chamber studies to global model

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Introduction

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**Chemical mechanism**:

- High NO$_x$: problems with organic nitrates, small carboxylic acid formation ...
- Low NO$_x$: very poor understanding due to experimental challenges
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Unfortunately, everything is intermingled: isoprene still accounts for a very large fraction of the uncertainty in atmospheric chemistry (past-present-future)
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Outline

1. Chamber studies

2. GEOS-Chem
Chamber studies GEOS-Chem Framework

**Isoprene** 100 ppb

NO 500 ppb

$\text{H}_2\text{O}_2$ 2.2 ppm

RH $< 5\%$

\[ \text{VOC}_1(t) \ldots \text{VOC}_n(t) \]

\[ \text{CF}_3\text{O}^- \]

\[ \text{VOC}.\text{CF}_3\text{O}^- \]

\[ \text{VOC}.\text{H}.\text{HF} + \text{CF}_2\text{O} \]

Cluster $m/z + 85$

Transfer $m/z + 19$

$H\psi$

Dipole Polarizability

**Su's Model**

**Near-explicit Kinetic Model**

From the comparison model/data derivation of branching ratios rate constants, ...

**Calibrated Profile**

Experimental calibration for nitric acid

[VOCl]

$\text{t}$

Crounse et al. 2006, Paulot et al. 2009

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Advantages

- Fast and direct measurements of a wide range of VOC (organic nitrates, small carboxylic acids, organic peroxides)
- Measurement of inorganic species: HONO, HO$_2$NO$_2$, H$_2$O$_2$, HNO$_3$, N$_2$O$_5$ (indirect) → strong constraints to derive a mechanism

![Isoprene nitrate](image.png)

**Figure**: Isoprene nitrate
Major conclusions

- δ hydroxy channel
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  - Constraints on $\sim 30\%$ of the carbon
  - Formation of large acids
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- Isoprene nitrates
  - Overall yield: $12 \pm 3\%$
  - Large discrepancy between the $\beta$ ($\sim 6.7\%$) and $\delta$ hydroxychannels ($\sim 24\%$)
  - Short-lived ($\delta$-hydroxy isoprene nitrates) with substantial recycling of NO$_x$: need to be included in the mechanism
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  - Other nitrates may have a significant role
    - MVK and MACR nitrates are formed with yields exceeding 10%
    - MVK nitrate and propanone nitrate ($\sim 1\%$) are very long-lived

Glycolaldehyde and hydroxyacetone (Butkovskaya 2006)
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- Large formation of small carboxylic acid
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Summer NH Isoprene nitrate

Chamber studies

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Formic acid Northern Hemisphere summer

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Work in progress and acknowledgements

- Low NO\textsubscript{x} chemistry: isoprene (Paulot et al. in review) and atmospheric relevant products: MVK, MACR, MBO, ... (Crounse et al. in preparation)
  - Fate of the peroxides
  - OH recycling

  **Current chemical schemes are very wrong over tropical regions (not specific to GEOS-Chem).**

- Compare model with CIMS measurements collected during INTEX-B, TC4 and ARCTAS.
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