**Isoprene Oxidation Mechanisms: Modelling OH and HO₂**

Daniel Stone,* Pete Edwards, Roisin Commane, Trevor Ingham, Andrew Rickard, Mathew Evans, Dwayne Heard

Daniel Brookes, James Hopkins, Roland Leigh, Alastair Lewis, Paul Monks, Claire Reeves, David Stewart
d.stone@leeds.ac.uk, *School of Chemistry, University of Leeds, Leeds, UK

---

**Introduction**

Tropical forests emit significant amounts of volatile organic compounds (VOCs). Isoprene is the dominant reactive VOC emitted into the atmosphere. Isoprene and other VOCs are removed from the atmosphere by oxidation processes, including OH and HO₂ radicals. OH and HO₂ radicals act by OH and HO₂ reactions with various VOCs, RO₃, CO, NO, NO₂, VOCs, OH, HO₂, RO₂, (NO₃), (O²D) and (O²D). Isoprene is oxidised rapidly with OH, but low OH concentrations predicted in regions with high isoprene emissions. Isoprene oxidation mechanisms are tested against observations of OH and HO₂ during the OP3 Field Campaign. Experimental and theoretical studies suggest potential additional OH sources in isoprene oxidation.

**OP3 Field Campaign**

- **Objectives**
  - Oxidant and Particle Photochemical Processes, Borneo 2008
  - Ground, tower and aircraft measurements
  - OH and HO₂ measured by low pressure Laser Induced Fluorescence (LIF)
  - Fluorescence Assay by Gas Expansion (FAGE)
  - On-resonance detection of OH at ~308 nm
  - HO₂ converted by chemical titration to OH

**Model Approach**

- **Dynamically Simple Model of Atmospheric Chemical Complexity (DSMACC)**
  - Flexible zero-dimensional box model constrained to observations
  - Photolysis rates from TUV with cloud correction factors from observed (NO₃)
  - Model run forwards to steady state to calculate concentrations of OH and HO₂
  - Chemistry described by the Master Chemical Mechanism (MCM) v3.1

**Model Performance**

- **MCM chemistry significantly underpredicts OH**
  - Probability distribution functions of observed to modelled ratios of OH show significant differences for data points with isoprene above and below 15 ppt
  - Model failure for OH is worse for data points with high isoprene concentrations
  - No dependence of observed to modelled ratio for HO₂ on isoprene

**Conclusions**

- Isoprene oxidation is poorly understood and misrepresented in models
  - Leads to poor replication of observations in high isoprene low NO₃ environments
  - Could have important consequences for global modelling of radiatively active gases such as O₃ and CH₄
  - MCM chemistry significantly underpredicts OH observations during OP3
  - Standard chemistry scheme in GEOS-Chem does not provide an accurate description of HO₂ concentrations in high isoprene and low NO₃ regions
  - Epoxide scheme currently available for use in GEOS-Chem has little impact on modelled OH concentrations but does improve HO₂

**Acknowledgements**

This project was funded by the UK Natural Environment Research Council (NE/D002192/1).

Further laboratory studies of isoprene oxidation chemistry are required

---

**References**

1. Guenther et al., ACP, 6, 3181-3210, 2006
2. Luther et al., ACP, 8, 2737-2749, 2008
5. Luther et al., ACP, 10, 3097-3112, 2010
6. Luther et al., ACP, 10, 9319-9349, 2010
8. Peeters et al., PCCP, 11, 28, 5305-5309, 2009
9. da Silva et al., EST, 44, 250-256, 2010