CRI-HOM: A novel chemical mechanism for simulating Highly Oxygenated Organic Molecules (HOMs) in global chemistry-aerosol-climate models

J Weber, S Archer-Nicholls, P Griffiths, T Berndt, M Jenkin, H Gordon, C Knote & A T Archibald

Weber et al (2020) *Atmospheric Chemistry & Physics*
Common Representative Intermediates (CRI)

- Tropospheric chemistry scheme tuned against fully explicit Master Chemical Mechanism v3.3.1
- Organic species lumped into surrogates based on $O_3$-forming potential - ~200 species, ~500 reactions
- Incorporated into fully coupled global climate model UM-UKCA

Jenkin et al (2008, 2015), Watson et al (2010), Utembe et al (2010)
Highly Oxygenated Organic Molecules (HOMs)

Autoxidation

\[ \text{RO}_2 \rightarrow \text{R'O}_2\text{O}_2 \]

1,7 H-shift

Rapid reduction in volatility

Kirkby et al., *Nature* (2016)

Dimer Formation

\[ \text{RO}_2 + \text{R'O}_2 \rightarrow \text{ROOR} + \text{O}_2 \]

jmw240@cam.ac.uk
Climatic Relevance

- Low volatility → condensation or new particle formation
- “Sulphuric-acid” free nucleation → greater aerosol burden (especially in PI)
- Dimers are more involatile than monomers → key species in new particle nucleation (Simon et al., 2020)

Nucleation rate in PI

Steady state approach

$$O_3 + \alpha - \text{pinene} \rightarrow \gamma\text{HOM}$$

Gordon et al (2016)
Nucleation rate in PI

- no HOMs
- with HOMs
11 species, 68 reactions (added to CRI) (cf. explicit ~ 1700 reactions Roldin et al., 2019)

Maintain reactions with standard partners (HO$_2$, NO, NO$_3$)

Add unimolecular autoxidation for RO$_2$

Introduce “generations” of RO$_2$ (1$^{\text{st}}$, 2$^{\text{nd}}$, 3$^{\text{rd}}$…) based on number of autoxidation steps undergone.

HOM monomers formed by RO$_2$ + HO$_2$ and dimers from updated RO$_2$ + RO$_2$ reactions.
Tuning the mechanism

- Rate constants for autoxidation and dimerisation largely unknown.
- Simulate flow tube experiments with box model.
- Adjust rate constants to optimise model performance

"Initiation": \( O_3 + \alpha - \text{pinene} \rightarrow RN26BO2 + \text{other} \)

1\(^{st}\) gen: \( RN26O2 \rightarrow RN25BO2O2 : k_{1^{st}} \)

2\(^{nd}\) gen: \( RN25BO2O2 \rightarrow RN24BO4O2 : k_{2^{nd}} \)

3\(^{rd}\) gen: \( RN24BO2O2 \rightarrow RN23BO6O2 : k_{3^{rd}} \)
Isoprene Inhibition

“...we show that isoprene ... can ... suppress the instantaneous mass ... derived from monoterpenes...”

“We find that isoprene ‘scavenges’ hydroxyl radicals, preventing their reaction with monoterpenes, and the resulting isoprene peroxy radicals scavenge highly oxygenated monoterpen products.”

(McFiggans et al., 2019)

SOA = secondary organic aerosol
Temperature and NO$_x$ dependence

- HOM yield agrees with literature values, bulk temperature and NO$_x$ dependence captured
- Autoxidation highly temperature dependent – explore range $\beta=6,000 – 12,000$ K ($k = Ae^{-\beta/T}$)
- NO$_x$ observed to suppress HOM formation – $\text{RO}_2 + \text{NO} \rightarrow$ complex product distribution, currently assume 50:50 isomerisation / fragmentation

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Vertical Profiles and Nucleation

Predicted surface [HOM] within factor of 2 of observation

HOM-only nucleation competes efficiently with classic H₂SO₄ nucleation, particularly in PI.
Summary and Future Work

- First HOM mechanism suitable for GCMs - reproduces observed [HOM], HOM yield and dependence on NO\textsubscript{x} and temperature as well as isoprene-driven suppression of HOMs.

- Significant regional contribution to particle nucleation by HOM, especially in the PI, with likely impacts on aerosol burden and aerosol/cloud radiative effects.

- Currently incorporating CRI-HOM into UKCA. Studies planned to investigate climate sensitivity to BVOCs and feedback between temperature, BVOC emissions and aerosol.

- **Further mechanism optimisation against new experimental data important:**
  1. effect of NO\textsubscript{x} and radical fragmentation
  2. improved temperature dependence
  3. variable nucleation rates