CRI-HOM: Modelling HOMS for UKCA and the effect on new particle formation

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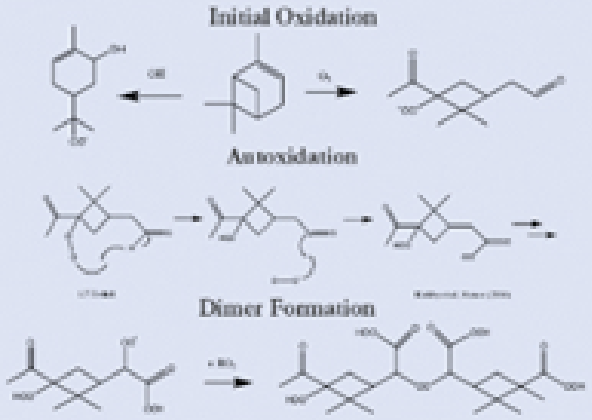
[1]Kirkby et al (2016)
[2]Jenkin et al (2019)
[3]Berndt et al (2018)
[4]McFiggans et al (2019)
[5]Ehn et al (2012)
[6]Jokinen et al (2014)
[7]Quéléver et al (2019)
[8]Roldin et al (2019)

Highly oxygenated organic molecules (HOMs), formed from species such as α-pinene, add to existing aerosol and can nucleate new particles without sulphuric acid. Thus, HOMs can affect the radiative balance of the atmosphere and modelling them accurately is vital for studies of climate change.

Autoxidation of α-pinene oxidation productions – addition of O_2 via intramolecular H-shifts – leads to HOM production by reducing volatility and also increasing the ability of the resultant species to nucleate new particles. HOM dimers can also form and their size and multiple heteroatoms makes the very involatile.[1]

Our new mechanism describes HOM formation via autoxidation and dimerisation as an addition to the tropospheric chemistry scheme Common Representative Intermediates v2.2 (CRI)[2] and is the first HOM mechanism suitable for use in global climate models like UKCA-UKESM.

Our mechanism also reproduces experimentally determined HOM yield and variation with NO, and temperature as well as observed [HOM] over the boreal forest.



To established chemical mechanism (CRIv2.2[2]), add new RO_2 and HOM species, autoxidation and dimerisation reactions with initial rate coefficients.

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Simulate flow cell experiments[3].

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Compare model output to experimental data and adjust rate coefficients.

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Final mechanism

Iterative process

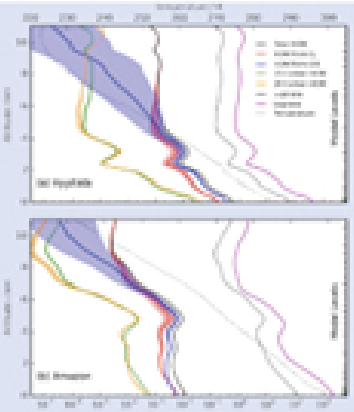
Mechanism Development & Testing

The mechanism adds autoxidation and dimer formation to CRI v2.2, without perturbing the underlying chemistry, and is the first mechanism to constrain these rates by fitting model data to experimental observations.[3]

We also reproduce the experimentally observed suppression of 20-carbon dimer concentrations with increasing isoprene[4], attributing this to scavenging of both OH and the RO_2 produced from α-pinene oxidation. This suppression will have consequences for the resultant SOA burden – temperature-driven increases in future isoprene emissions may not increase SOA. **Thus, we present a tool to investigate the proposed feedback between temperature and SOA and climate sensitivity to BVOCS.**

HOM yield (4-6%) agrees with numerous observations[5,6] and is modelled to increase with temperature due to the strongly temperature dependent autoxidation rate coefficients, in agreement with experimental observations[7]. Yield also decreases for NO_x > 1 ppb with RO_2+NO outcompeting autoxidation, also in agreement with observation.

HOMs with altitude

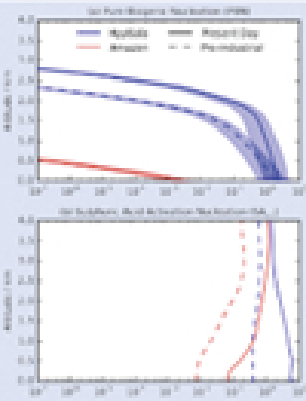


HOM vertical profile – higher isoprene in Amazon suppresses 20-carbon dimer (shading shows different autoxidation temperature dependencies).

HOM profiles calculated using UKCA model output in the pre-industrial (PI) and present day (PD) in the rainforest and boreal forest. Higher isoprene concentrations in the Amazon suppress 20-carbon dimer formation (left) and the higher condensation sink (CS) results in lower [HOM] in the Amazon. The mechanism also reproduces observed [HOM], including 20-carbon dimers in the boreal forest of Hyytiälä.[3]

Uncertainty in autoxidation temperature dependence was predicted to have negligible effect below ~4 km (shading left shows results from different autoxidation temperature dependences (6000-12077 K)).

In Hyytiälä, new particle formation (NPF) from HOM (PBN) is particularly important, contributing ~60% of all NPF in the PI and ~20% in the PD in the lowest 500m while lower [HOM] in the Amazon renders HOMs less important. The heightened importance of PBN in the PI is attributed to lower [H_2SO_4] and a lower ion CS with ion -induced PBN[8] more important than the neutral pathway.



Nucleation rates = PBN in Hyytiälä predicted to be important, particularly in PI (shading shows variation in ion-production rate).

Conclusions

- **The first HOM mechanism suitable for GCMs - reproduces observed [HOM], HOM yield and dependence on NO, and temperature as well as isoprene-driven suppression of HOMs.**
- **We predict a 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 with studies planned to investigate climate sensitivity to BVOCs and the feedback between temperature, BVOC emissions and aerosol.**

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