

## Highly-oxidized multifunctional compounds (HOM) from oxidation of aromatics

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Oxidation of volatile organic compounds (VOCs) is an important source of atmospheric secondary organic aerosol (SOA). Aromatics are among the most abundant VOCs produced by anthropogenic activities (e.g. combustion and petroleum industry), with also significant natural emissions, and are a known source of SOA especially at urban atmospheres (Ziemann and Atkinson 2012).

Recently, a process called autoxidation (Crouse et al. 2013, Rissanen et al. 2014) has received considerable attention as a potential gas-phase pathway to very low-volatile condensable material (Ehn et al. 2014), which is needed in the first-steps of ambient SOA formation. This process requires only a single-oxidant attack and leads to highly-oxidized product species in second time-scales with a high-efficiency. This process is autocatalytic and after the initiation relies only on the specific molecular structures which facilitate internal isomerization reactions, progressing the pseudo-unimolecular oxidation sequence. Preliminary experiments have shown that highly-oxidized species form also during aromatic oxidation. However, aromatics are exceptionally stable VOCs and thereby the autoxidation mechanisms generated for simpler cyclic alkenes (Mentel, et al. 2015, Rissanen, et al. 2015) are not directly applicable to the aromatic oxidation system.

Flow reactor investigations were performed in University of Helsinki and environmental chamber experiments were conducted in *Forschungszentrum Jülich*. In Helsinki, a suite of aromatic oxidation experiments (toluene, anthracene, naphthalene) were done in order to characterize the autocatalytic oxidation pathways, which potentially involve bicyclic peroxy radicals (Birdsall, et al. 2010) as radical chain carriers. In Jülich, benzene (and deuterated benzene) oxidation experiments were performed in closer to atmospheric conditions in order to inspect the yield of highly-oxidized species from OH initiated autoxidation, but also to investigate the oxidation mechanism. In both places, Chemical ionization mass spectrometry (CIMS) with nitrate (NO<sub>3</sub><sup>-</sup>) ionization was used to detect the highly-oxidized product species. In addition, a suite of other gas-phase analysis methods was applied to monitor the experimental conditions and the evolution of the reacting gas-mixture.

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