

Rapid formation of aerosol precursors from *o/m/p*-Xylene and their contribution to secondary organic aerosol formation

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Aromatic compounds contribute significantly to the formation of tropospheric secondary organic aerosol (SOA) that have strong implications on health and on climate. While combustion generated small hydrocarbons are in decline, several single-ring aromatics persist or even exhibit upwards trends in certain urban environments due to their extensive usage in solvents, paints, adhesives, self-care products, and so on [1, 2]. Thus, the sources of aromatics are primarily anthropogenic, yet occasionally biogenic sources can be significant too.

Xylenes (C₈H₁₀) are a group of three dimethylbenzenes that differ by the position of their methyl substituents, and thus provide an ideal testbed for molecular oxidation mechanism generation. To form SOA, the volatile xylenes need to oxidize to low volatility aerosol precursors with multiple oxygen containing polar functional groups, ultimately up to highly oxygenated organic molecules (HOMs) [3,4]. They do this through the autoxidation mechanism, which is a sequential process involving repeated peroxy radical isomerization processes and oxygen additions, and often rapidly terminates to products with carbon to oxygen ratio above one. Recently, we showed that the crucial aromatic oxidation intermediate, the bicyclic peroxy radical (BPR), associated with toluene oxidation is unstable and its decomposition is pivotal to the following autoxidation and subsequent HOM formation. Here we establish the general importance of this aromatic derived BPR decomposition to the formation of SOA.

We have performed a joint theoretical-experimental characterization of *ortho*-, *meta*- and *para*-xylene oxidation pathways towards multifunctional aerosol precursors. The experimental work was conducted in a glass flow reactor (5 cm o.d. and 100 cm length) under ambient conditions with variable reaction time controlled by a moveable injector or by changing the flow rate through the reactor. Nitrate chemical ionization mass spectrometry was used for reaction product detection. Detailed quantum chemical computations on the reaction mechanism supported by master equation modelling of the corresponding reaction rates were conducted to validate the importance of the newly found BPR rearrangement pathway and to verify the timescales required for the highly oxygenated reaction product detection. Finally, the isomeric xylenes were oxidised in an environmental chamber and the resulting SOA yields were quantified by Aerosol Mass Spectrometry.

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