



Products of BVOC oxidation: ozone and organic aerosols

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Biogenic Volatile Organic Compounds (BVOC) are important precursors in photochemical O₃ and secondary organic aerosol (SOA) formation. We conducted a series of laboratory experiments with OH-induced oxidation of monoterpenes to elucidate pathways and efficiencies of O₃ and SOA formation.

At high NO_x conditions ([BVOC] / [NO_x] < 7 ppbC / ppb) photochemical ozone formation was observed. For [U+P061]-pinene as individual BVOC as well as for the monoterpene mixes emitted from different plant species we observed increasing ozone formation with increasing [NOX]. Between 2 and 3 O₃-molecules were formed from 1 monoterpene when ozone formation was BVOC limited. Under such high NOX conditions, new particle formation was suppressed. Increasing [BVOC] / [NOX] ratios caused increasing efficiency of new particle formation indicating that peroxy radicals are the key intermediates in both, photochemical ozone- and new particle formation.

The classical chemistry of peroxy radicals is well established (e.g. Master Chemical Mechanism). Peroxy radicals are produced by addition of molecular oxygen to the alkyl radical formed after OH attack at the BVOC. They either react with NO which leads to ozone formation or they react with other peroxy radicals and form chemically stable products (hydroperoxides, alcohols and ketones).

Much less knowledge exists on such reactions for Highly Oxidized Peroxy Radicals, (HOPR). Such HOPR were observed during ozonolysis of several volatiles and, in case of monoterpenes as precursors, they can contain more than 12 Oxygen atoms (Mentel et al., 2015). Although the OH-initiated formation of HOPR is yet not fully understood, their basic gas phase reactions seem to follow classical photochemical rules. In reactions with NO they can act as precursor for O₃ and in reactions with other HOPR or with classical less oxidized peroxy radicals they can form highly oxidized stable products and alkoxy radicals. In addition, HOPR-HOPR reactions lead to the formation of dimers that, in case of monoterpenes as reactants, consist of a skeleton with 20 carbon atoms. These dimers seem to play a major role in new particle formation and their existence may explain the observations of Wildt et al. (2014) who found power law dependence with an exponent approaching -2 between new particle formation and ozone formation.

The monomer products of HOPR-HOPR reactions play a dominant role in SOA mass formation because their vapour pressures are low enough to allow condensation on pre-existing particulate matter (Ehn et al., 2014). Furthermore, the minor impacts of NOX on particle mass formation (Wildt et al., 2014) are explainable by similar yields of alkoxy radicals in HOPR-HOPR and HOPR-NO reactions, respectively.