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Formation of highly oxidized multifunctional compounds: Autoxidation of peroxy radicals formed in the oxidation of alkenes

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Recent studies show that peroxy radicals are key intermediates in particle formation. Permutation reactions involving highly oxidized peroxy radicals form stable products with extremely low volatility (ELVOC). We suggest that ELVOC are the postulated organic compounds that explain growth of small particles (Ehn et al., Nature, 2014).

To elucidate the pathways of ELVOC formation, experiments were performed in the Juelich Plant Atmosphere Chamber. We applied High Resolution Nitrate-Chemical Ionization Mass Spectrometry for detection of ELVOC including highly oxidized peroxy radicals. ELVOC were produced by ozonolysis of a-pinene and other cyclic alkenes (Rissanen et al., JACS, 2014, Mentel et al., ACPD, 2015), as well as by reactions of the target compounds with OH.

ELVOC with C10 skeletons carry a large number of oxygens, still containing 14 or 16 H-atoms. ELVOC-dimers with twice the number of C-atoms of the reactant were also observed. The formation of ELVOC can be explained by fast intramolecular H-shifts in combination with classical peroxy radical termination reactions, leading to ketones, alcohols, and hydroperoxides (including peroxy acids). The subsequent H-shifts enable the formation of an increasing number of hydroperoxide groups under reproduction of a peroxy radical (containing now two more oxygens).

Addition of NOX to the system increases the concentrations of nitrates at the expense of the corresponding peroxy radicals, confirming their identification as peroxy radicals. Furthermore, the concentrations of ELVOC dimers decrease strongly with increasing NOX suggesting that they are indeed formed by peroxy-peroxy permutation reactions.

ELVOC are involved in new particle formation, and can explain the major fraction of the early growth observed in field studies. ELVOC dimers are very likely key in new particle formation as their formation is strongly suppressed with increasing NOX in accordance with the observed NOX dependence of new particle formation (Ehn et al., Nature, 2014; Wildt et al., ACP, 2014). Formation of particle mass is less affected by NOX addition as it likely proceeds mainly via C10-ELVOC.