

## Characteristics of peroxides in secondary organic aerosols

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Although it is clear from a mechanistic point of view that organic peroxides must be formed during atmospheric oxidation of hydrocarbons, measurements of organic (hydro)peroxides in secondary organic aerosol (SOA) are scarce. Estimates of peroxide content in secondary organic aerosol (SOA) from biogenic precursors span a large range from 6-120 wt.-% (Mertes et al. 2012; Docherty et al., 2005). Recently it was discovered that ozonolysis and OH-reaction of  $\alpha$ -pinene and of other terpenes produce highly oxygenated multifunctional (HOM) compounds, which can contain several hydroperoxy groups (Ehn et al., 2014). Due to their low volatility these compounds are expected to partition into the particle phase. It is also believed that organic peroxides are susceptible to photolysis and may thus be lost from the particle phase leading to a shrinkage of aerosols with important consequences for SOA lifetime (Henry and Donahue, 2012; Hodzic et al., 2015).

We investigated the content and fate of particulate organic peroxides in  $\alpha$ -pinene SOA under the following conditions: ozonolysis in the dark (i) with and (ii) without OH scavenger and (iii) exposure of SOA to UV-light. The experiments were performed in the PSI smog chamber at 50% relative humidity. During each experiment several filter samples were collected and the peroxide content was determined with a long path absorption photometer using iodometry. Organic species in the gas phase were monitored with a proton-transfer-reaction mass spectrometer and the chemical composition of SOA was continuously measured with an aerosol mass spectrometer (AMS). We developed a box-model, referred to as a "hybrid 3D-volatility basis set" (hybrid 3D-VBS), to describe the evolution of SOA and HOM yields, peroxide (OOH) content and oxidation state in the context of a thermodynamic framework.

We observed peroxide molalities in freshly formed SOA from 1.1 to 1.9 nmol  $\mu\text{g}^{-1}$ . However, a large fraction of this is labile and rapidly decays. This is reflected in the evolution of mass spectral features by the AMS and the SOA mass. We established initial OOH yields and confirmed independently previously determined molar HOM yields (Ehn et al., 2014) using other techniques. Furthermore, irradiation of SOA did lead to evaporative losses as observed by others (Henry and Donahue, 2012). However, due to our longer observation time we could show that this occurs to a lesser extent. Our measurements also indicate that photolysis of peroxides is not the main reason for aerosol evaporation.

The hybrid 3D-VBS model was constrained by HOM measurements, their volatility, peroxide content

and O:C ratios from AMS measurements. It reproduces the experimentally observed organic mass loadings and yields, the molar OOH yield and, in addition, provides organic molar yields and the time-resolved mass contribution of all ROOH compounds.

We will discuss the implications of these findings which will improve our understanding of various aspects of SOA.

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