Formation kinetics and hydrolysis properties of organic peroxides from monoterpene-derived Criegee intermediates with various organic acids

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It is well recognised that secondary organic aerosols (SOA) represent a major fraction of tropospheric fine particles that can contribute to serious air pollution, damage human health and affect Earth's climate. SOA are typically originated from complex atmospheric (photo)chemical oxidation processes of volatile organic compounds (VOCs), which are emitted from natural and man-made sources. It has been suggested that organic peroxides (ROOR, where R denotes H or an organic group), as a major class of SOA components, can significantly contribute to aerosol toxicity and related health effects. This is mainly due to their oxidising properties, which is also regarded as so-called reactive oxygen species (ROS). Despite their atmospheric and health importance, the analytical identification of compound-specific organic peroxides in atmospheric aerosols is highly challenging, due to their labile properties, complex composition and limited availability of standards. This represents a significant knowledge gap that limiting our understanding of atmospheric processes of organic peroxides and further assessment of their health effects.

In this study, we synthesize a number of atmospheric relevant organic peroxides through liquid phase ozonolysis. Specifically, large excess of ten selected individual carboxylic acid (i.e., cis-pinonic acid, cis-pinic acid) was added into acetonitrile solvent containing either α-pinene or 3-carene. High concentrations of O_3 were bubbled through these solutions resulting in the formation of stabilized Criegee intermediates (SCIs), which can subsequently react with the added carboxylic acid to form target α-acyloxyalkyl hydroperoxide (AAHP), as shown in Fig. 1. The synthesized AAHP standards (ca. 20) were identified individually by means of liquid chromatography coupled to a high-resolution mass spectrometer. The AAHP formation kinetics were also obtained by tracking the temporal profiles of individual carboxylic acids in the same liquid phase ozonolysis process, and the relative rate constant for SCI with various carboxylic acids generally varied small within a factor of 2-3. The synthesized AAHP solution was further used for hydrolysis purpose, and the difference among their hydrolysis rate can be up to two orders of magnitude. As a final proof-of-concept, four AAHPs were unambiguously identified and semi-quantified in the laboratory generated α-pinene SOA and 3-carene SOA samples, and their mass contribution to total SOA was semi-quantified as 0.28% and 0.21% respectively. Our results improve the molecular-level understanding of organic peroxides in SOA and useful for more accurate assessment of their environment fate and health impact.



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