

Kinetic Investigation of Secondary Organic Aerosol Formation of Products from Isoprene Hydroxy Hydroperoxides (ISOPOOH) Oxidation

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Despite its global significance, our understanding of sources and sinks for Secondary organic aerosol (SOA), their influence on Earth's radiation budget, local air quality and adverse effects on human health remains far from satisfactory. Major atmospheric chemistry and transport models still fail to predict the formation rate and spatial distribution of SOA. Isoprene is the most abundant non-methane biogenic volatile organic compound in the atmosphere. Mainly in rural areas, deciduous plants, such as trees and shrubs emit estimated 540 Tg yr⁻¹ (Guenther, 2006) on a global scale. Isoprene and isoprene-derived oxidation products were disregarded as SOA-precursor compounds for a long time. In the last two decades, however, it was shown that isoprene oxidation especially in rural areas leads to products that significantly contribute to the formation of SOA.

The most important sink for isoprene in rural areas is the oxidation by OH radicals leading to hydroxy-hydroperoxides (ISOPOOH), and further, to the formation of isoprene epoxydiols (IEPOX), which have been identified as important SOA precursors previously (Gaston, 2014). Moreover, recent studies indicate that an additional class of highly oxidized ISOPOOH oxidation products might contribute equally strong to SOA formation (Liu 2016). Nonetheless, kinetic investigations of the corresponding SOA formation processes are largely missing, leaving huge uncertainties in evaluating their impact on atmospheric chemistry, and thus, its implications for climatic processes.

Within the present work, the two most abundant isomers of isoprene-derived hydroxy hydroperoxides (ISOPOOH) have been synthesized using a novel synthetic procedure. The products were characterized using nuclear magnetic resonance (NMR) spectroscopy. Subsequently, the synthetic standards were investigated in the TROPOS Atmospheric Chemistry Department Chamber (ACD-C), being equipped with online MS techniques, namely PTR-ToFMS, AMS and (NO₃)-CI-API-ToFMS.

Based on these chamber experiments, ionization efficiencies, detection limits and

fragmentation pattern of the ISOPOOH isomers were determined. Moreover, to elucidate gas-particle interactions, the partitioning behaviour of 1,2-ISOPOOH was investigated in more detail for various inorganic seed particles under different conditions. For acidic seed particles a reactive uptake of 1,2-ISOPOOH with a specific uptake coefficient (according to Crowley, 2010) of $\gamma = 8.57 \cdot 10^{-3}$ was observed.

Furthermore, the OH oxidation of 1,2-ISOPOOH under low-NO_x conditions was studied. The formation of highly oxygenated organic molecules, such as dihydroxy dihydroperoxides as well as smaller isoprene-derived products from a non-IEPOX pathway (Liu 2016) were observed. Moreover, the uptake coefficients of the observed species were determined for two atmospheric conditions and two different seed particle compositions.

The results obtained will contribute to closing current knowledge gaps in isoprene gas-phase chemistry as well as gas-particle partitioning of corresponding oxidation products, thus, improving future model efforts on SOA formation rates.

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