

Photochemical Oxidation of Organic Hydroperoxides and Epoxides (ISOPOOH and IEPOX) in the Atmospheric Simulation Chamber SAPHIR

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Volatile organic compounds (VOCs), predominantly emitted from vegetation, influence atmospheric photochemistry by undergoing oxidation reactions with the hydroxyl radical OH that is part of the catalytic cycles of hydrogen oxides (OH, HO_2) and nitrogen oxides (NO, NO_2).

The major first-generation oxidation products of isoprene under pristine conditions (low NO case) are isomers of isoprene hydroxyl hydroperoxides (ISOPOOHs), which are further oxidized by the OH radical to isomers of epoxydiols (IEPOX). Due to its reactive functional groups and solubility, IEPOX exhibits a strong SOA (Secondary Organic Aerosol) forming potential and its reactive uptake onto particles has been observed globally in rural environments. [1]

By employing synthetic standards of 1,2-ISOPOOH [2], 4,3-ISOPOOH [3], cis-IEPOX [3] and trans-IEPOX [3], their photo-oxidation was investigated in the atmospheric simulation chamber SAPHIR utilizing mass spectrometry techniques for detection. Various experiments under different conditions were performed. Measured trace gas and radical concentrations were compared to a state-of-the-art model (MCM 3.3.1).

While the current knowledge of IEPOX oxidation can be confirmed by our experimental results, at least for the 1,2-ISOPOOH isomer a significant additional loss process is needed to bring experimental results and model calculations into agreement. A photo-induced process independent of the OH radical concentration accounts for this unknown loss.

This process potentially is of atmospheric relevance as less IEPOX is formed out of isoprene and consequently the SOA forming potential is lower than previously expected.

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