Aqueous Phase Reactions of Isoprene-derived Hydroxy Hydroperoxides (ISOPOOH)

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Introduction

Secondary organic aerosol (SOA) makes up a large part of the total atmospheric aerosol, having a strong influence on Earth's radiation budget and acting as cloud condensation nuclei. Especially fine particulate matter (i.e., $PM_{2.5}$), which affects local air quality and can have adverse effects on human health, show a high fraction of OA[1]. In recent years, progress has been made to understand the SOA formation potential of gas-phase precursors. The formation of SOA in cloud and aerosol water, however, has not been studied as comprehensively.
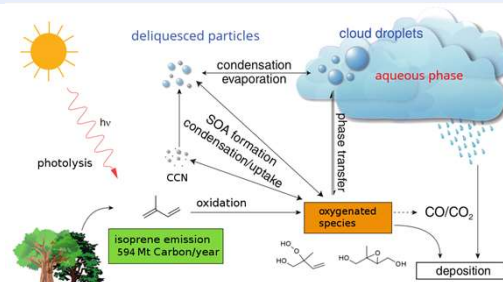

Fig. 1: Overview of atmospheric processes involving isoprene oxidation.

Isoprene is the most abundant non-methane biogenic volatile organic compound in the atmosphere. Deciduous plants, such as trees and shrubs emit estimated 600 Tg yr^{-1} on a global scale[2], which is about 5 times the sum of all other terpene emissions combined. 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 gas-phase isoprene oxidation especially in rural areas leads to products that significantly contribute to the formation of SOA[3]. In the present work, aqueous-phase reactions of an synthetic standard of isoprene-derived hydroxy hydroperoxide has been investigated.

Aqueous phase Bulk reactor experiments
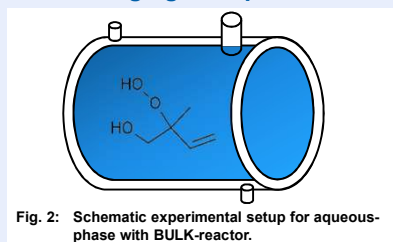
OH scavenging and quantification

- V = 250 mL
- Temperature-controlled
- Continuously stirred

- Reaction times up to 100 h
- Solution of 1,2-ISOPOOH in MilliQ Water (~0.01 mmol L^{-1})

Fig. 2: Schematic experimental setup for aqueous-phase with BULK-reactor.

During the course of the investigated reaction, OH radicals transform deuterated isopropanol to deuterated acetone, which was derivatized with o-(2,3,4,5,6)-pentaflourobenzyl)-hydroxylamine hydrochloride (PFPHA). The resulting imine can be quantified via GC-MS. To avoid further reaction during derivatization, ethyleneglycol is added in excess during sampling **(Fig.3)**.
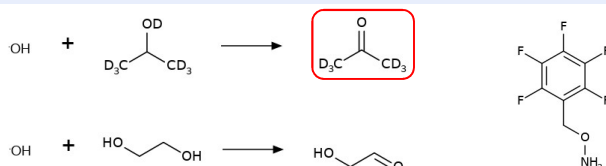

Fig. 3: OH scavenging reactions during the course of the experiment (above) and after sampling (below) and derivatization agent o-(2,3,4,5,6)-pentaflourobenzyl)-hydroxylamine hydrochloride (right).

Thermic decay of 1,2-ISOPOOH

The quantification of acetone-d6 via GC-MS was utilized to monitor the thermic decay of 1,2-ISOPOOH under variation of temperature.
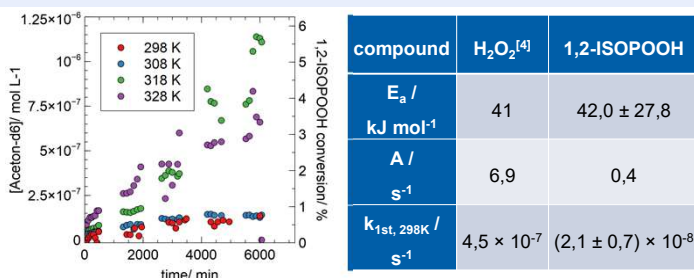

compound	H_2O_2[4]	1,2-ISOPOOH
E_a / kJ mol^{-1}	41	42,0 ± 27,8
A / s^{-1}	6,9	0,4
$k_{1st, 298K}$ / s^{-1}	$4,5 \times 10^{-7}$	$(2,1 \pm 0,7) \times 10^{-8}$

Fig. 4: Acetone-d6 formation via OH radicals during the thermic decay experiments (left) and corresponding Arrhenius parameters of the homolytic bond cleavage (right).

The thermic decay of 1,2-ISOPOOH was found to be a comparatively slow process. Although experiments were performed over the course of up to 100 h, the maximum conversion rate did not surpass 6% of the total ISOPOOH concentration. Consequently, the Arrhenius parameters were determined for the homolytic bond cleavage of 1,2-ISOPOOH. As the thermic decay yields a small fraction of OH radicals, other reaction pathways might be more important for atmospheric oxidation, such as Fenton-type reactions, photolysis or the reaction with sulfur (IV).

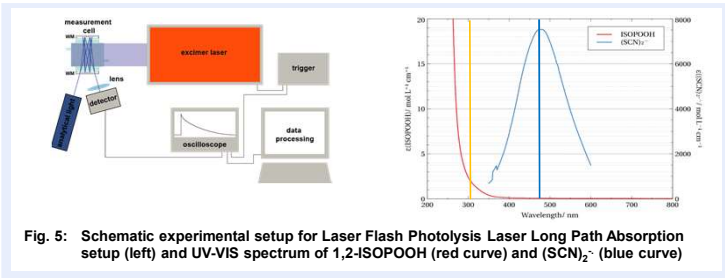## Quantum yield and UV-VIS spectrum

Fig. 5: Schematic experimental setup for Laser Flash Photolysis Laser Long Path Absorption setup (left) and UV-VIS spectrum of 1,2-ISOPOOH (red curve) and $(SCN)_2^-$ (blue curve)

- Photolysis by Excimer laser $\lambda = 308$ nm
- CW- Analysis laser $\lambda = 473$ nm
- System characterized by photolysis of equimolar H_2O_2 solution
  $E_{MK} = 70.6 \pm 2.2$ mJ

$$^{\bullet}OH + SCN^- \rightleftharpoons SCNOH^{\bullet -}$$
$$SCNOH^{\bullet -} \rightleftharpoons SCN^{\bullet} + OH^-$$
$$SCN^{\bullet} + SCN^- \rightleftharpoons (SCN)_2^{\bullet -}$$
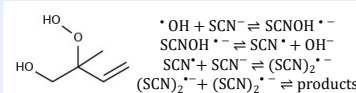$$(SCN)_2^{\bullet -} + (SCN)_2^{\bullet -} \rightleftharpoons products$$

Fig. 6: Structure of 1,2-ISOPOOH and reactions of SCN^- with OH radicals.

The formation of $SCNOH^{\bullet -}$ was used to scavenge the OH radicals from 1,2-ISOPOOH photolysis. The absorbance of $(SCN)_2^{\bullet -}$ was monitored over the course of 2 μs after the pulsed photolysis. The maximum absorbance was used to calculate the quantum yield with H_2O_2 as a reference system.

$$\Phi_{1,2\text{-ISOPOOH}} = 0.31 \pm 0.01$$

Aqueous S(IV) oxidation with 1,2-ISOPOOH

- Reaction of 1,2-ISOPOOH with Na_2SO_3 in aqueous solution investigated
- Acidity controlled pH = 4
- Fixation of HSO_3^- with HCHO under formation of hydoxymethylsulfonate (HMSA) upon sampling
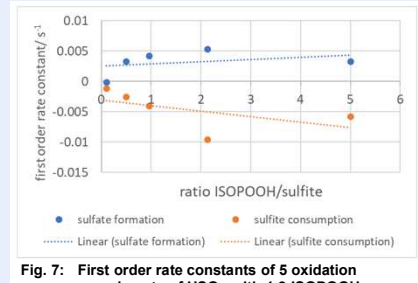- Analysis of both HSO_3^- and SO_4^{2-} via ion chromatography (IC)

Fig. 7: First order rate constants of 5 oxidation experiments of HSO_3^- with 1,2-ISOPOOH.

- Preliminary second order rate constant of $k_{2nd} = 483$ L mol^{-1} s^{-1}
- Previously reported value: 1000 ± 300 mol L^{-1} s^{-1} [5]
  -> Further investigations needed to improve reproducibility.

References

[1]**Volkamer, R.;** Jimenez, J.L.; San Martini, F.; Dzepina, K.; Zhang, Q.; Salcedo, D.; Molina, L.T.; Worsnop, D.R.; Molina, M.J. Geophys. Res. Lett. (2019) 33, L17811. [2]**Sindelarova, K.**; Granier, C.; Bouarar, I.; Guenther, A.; Tilmes, S.; Stavrakou, T.; Müller, J.-F.; Kuhn, U.; Stefani, P.; Knorr., W. Atmos. Chem. Phys. (2014) 14, 9317–9341. [3]**Claeys, M.**, B. Graham, G. Vas, W. Wang, R. Vermaylen, V. Pashynska, J. Cafmeyer, P. Guyon, M. O. Andreae, P. Artaxo, W. Meanhaut Science (2004) 303 1173. [4]**Hiroki, A.**, LaVerne, J. A., J. Phys. Chem. B 2005, 109 (8), 3364-3370. [5]**Dovrou, E.**, Rivera-Rios, J.S., Bates, K.H., Keutsch, F.N. (2019) Environ. Sci. Technol., 53, 12476-12484.