

Atmospheric multiphase chemistry of synthesized isoprene hydroxyhydroperoxides (ISOPOOH)

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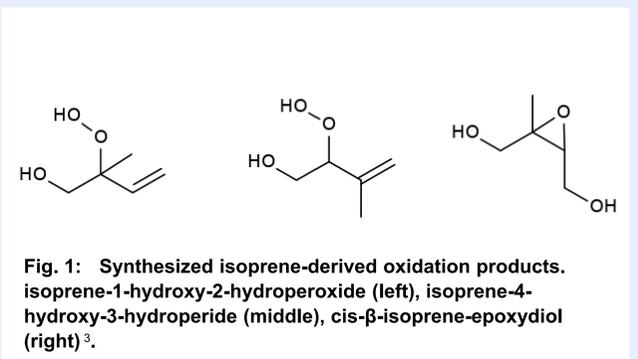
Introduction

Isoprene oxidation products

Isoprene is the most abundant non-methane biogenic volatile organic compound in the atmosphere¹. Desidious plants emit estimated 540 Tg y⁻¹ which is about 5 times as much as all terpene emissions combined.

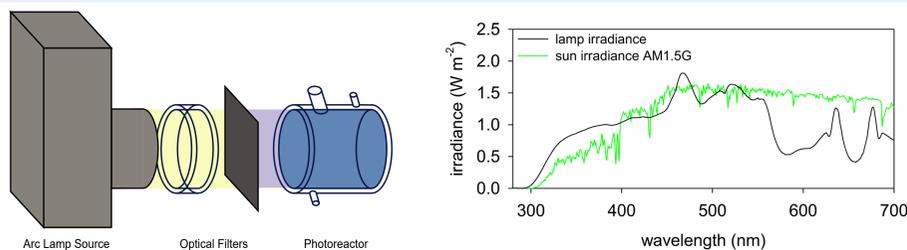
Isoprene and isoprene-derived oxidation products were disregarded as SOA-precursor compounds for a long time. In the last two decades however, it was shown that isoprene oxidation products significantly contribute to the formation of SOA². Mechanistic and kinetic understanding of the isoprene oxidation processes involved remain poor and elucidation might close one very important gap of knowledge in SOA formation chemistry.

One major limitation is the lack of synthetic standards for intermediate oxidation products of isoprene. Most of these compounds have labil functional groups additional to their relatively short carbon chain. However, three key products of atmospheric degradation of isoprene were synthesized in this work which gives access to the investigation of their chemical properties.

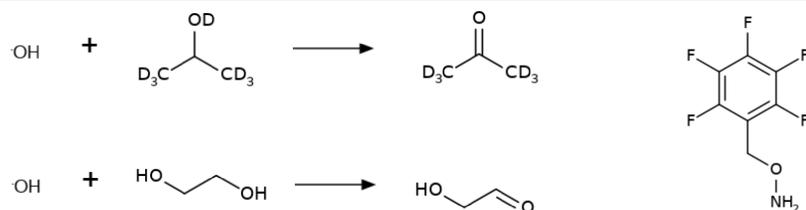


Aqueous phase Bulk reactor experiments

OH scavenging and quantification

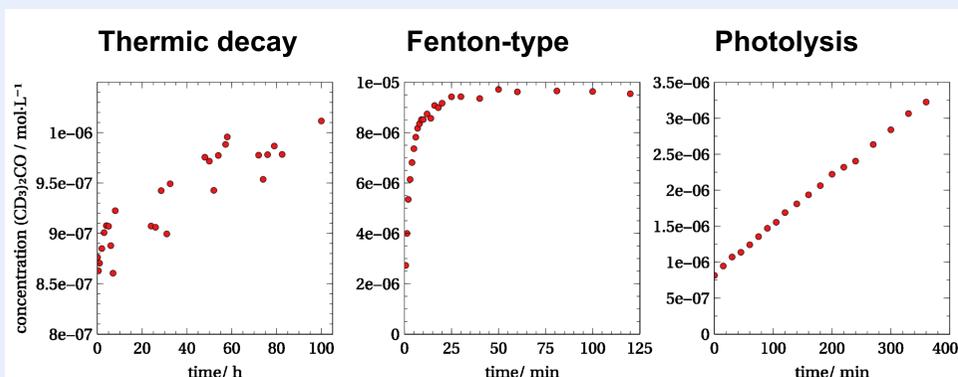


During the course of the investigated reaction, OH radicals transform deuterated isopropanol to deuterated acetone, which can be derivatized with o-(2,3,4,5,6)-pentafluorobenzyl)-hydroxylamine hydrochloride (PFPHA). The resulting imine can be quantified via GC-MS. To avoid further reaction during derivatization,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



OH formation potential of 1,2-ISOPOOH

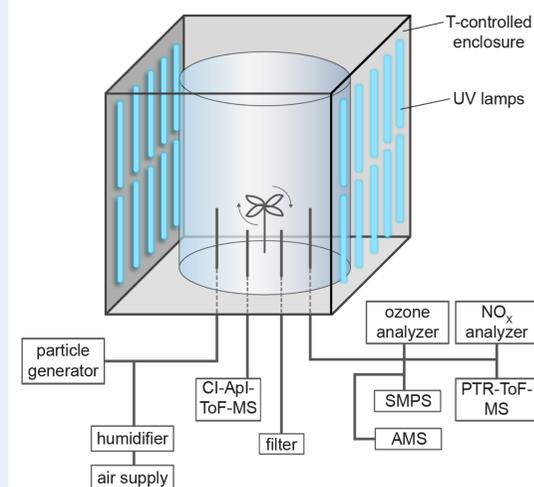
The thermic decay of 1,2-ISOPOOH was investigated as well as a Fenton-type reaction with an iron salt as well as the photolysis under actinic conditions



| | Thermic decay | Fenton-Type reaction | Photolysis |
|---------------------------------|-----------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------------------------------------------------|
| Composition of reaction mixture | $C_0(1,2\text{-ISOPOOH}) = 2.2 \cdot 10^{-5} \text{ M}$ $C_0(\text{Isopropanol-d8}) = 1.9 \cdot 10^{-2} \text{ M}$ | $C_0(1,2\text{-ISOPOOH}) = 2.1 \cdot 10^{-5} \text{ M}$ $C_0(\text{Isopropanol-d8}) = 1.9 \cdot 10^{-2} \text{ M}$ $C_0(\text{FeSO}_4) = 1.0 \cdot 10^{-4} \text{ M}$ | $C_0(1,2\text{-ISOPOOH}) = 2.2 \cdot 10^{-5} \text{ M}$ $C_0(\text{Isopropanol-d8}) = 1.9 \cdot 10^{-2} \text{ M}$ |
| k_{1st} | $1.78 \cdot 10^{-8} \text{ s}^{-1}$ | $6.30 \cdot 10^{-3} \text{ s}^{-1}$ | $5.45 \cdot 10^{-6} \text{ s}^{-1}$ |

ACD-Chamber Experiments

Experimental Setup



- Volume: 19 m³
- Material: FEP Foil
- Batch mode reactor
- T = 20°C

The reactive uptake of 1,2-ISOPOOH was investigated for two different inorganic seed particles based on (NH₄)₂SO₄. The pH was varied by additional H₂SO₄ between 0 and 4. Also experiments were carried out at relative humidities between 0% and 75%, respectively.

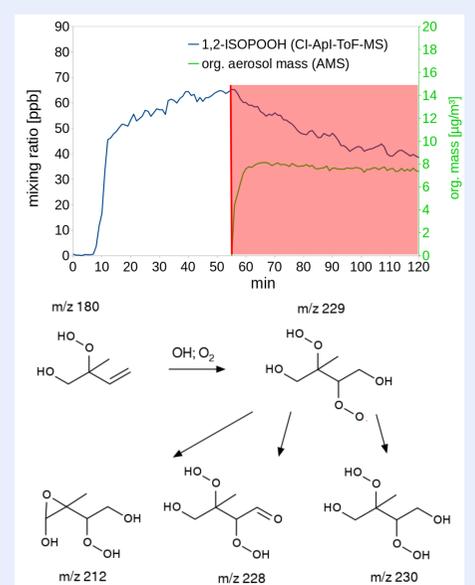
For a series of oxidation experiments, photolysis of hydrogen peroxide served as a OH radical source.

Uptake of 1,2-ISOPOOH

A series of uptake experiments under various conditions have been performed. However, only for acidic seed particles and under dry conditions a reactive uptake of 1,2-ISOPOOH was observed (Fig.6). According to⁴ the specific uptake coefficient was determined to be $\gamma = 5.33 \cdot 10^{-3}$.

Oxidation of 1,2-ISOPOOH

In experiments introducing OH radicals to the chamber the formation of ISOPOOH oxidation products from a non-IEPOX pathway⁵ were observed. The OH attack and subsequent oxygen addition lead to highly oxidized compounds, such as isoprene-dihydroxy-dihydroperoxide as well as the corresponding aldehyde. Various compounds were observed to characterize their uptake behavior on different seed particles.



References

- ¹Guenther, A.; Karl, T.; Harley, P.; Wiedinmyer, C.; Palmer, P. I.; Geron, C. Atmos. Chem. Phys.; 2006, 6, 3181–3210. ²Claeys, M., B. Graham, G. Vas, W. Wang, R. Vermaylen, V. Pashynska, J. Cafmeyer, P. Guyon, M. O. Andreae, P. Artaxo, W. Meinhardt Science (2004) 303 1173. ³Li, Y., Hao, H.-D., Wu, Y. Org. Lett. (2009) 11 2691. ⁴Crowley, J.N., Ammann, M., Cox, R.A., Hynes, R.G., Jenkin, M.E., Mellouki, A., Rossi, M.J., Troe, J., Wallington, T.J., Atmos. Chem. Phys.; 2010 10, 9059-9223. ⁵Liu, J., D'Ambro, E.L., Lee, B.H., Lopez-Hilfiker, F.D., Zaveri, R.A., Rivera-Rios, J.C., Keutsch, F.N., Iyer, S., Kurten, T., Zhang, Z., Gold, A., Surrat, J.D., Shilling, J.E., Thornton, J.A., Environ. Sci. Technol. 2016, 50, 9872-9880.