

# Oxidation of IEPOX in the Atmospheric Aqueous Phase

Tobias Otto, Thomas Schaefer, Hartmut Herrmann

Atmospheric Chemistry Department (ACD), Leibniz Institute for Tropospheric Research, Permoserstrasse 15,  
04318, Leipzig, Germany

Keywords: IEPOX, Oxidation, OH radical, Aqueous Phase  
Contact: tobias.otto@tropos.de

## Introduction

The majority of the emitted biogenic volatile organic compounds (BVOCs) consists of Isoprene with a global source strength of  $594 \pm 34 \text{ Tg y}^{-1}$  (Sindelarova *et al.*, 2014). The gas-phase oxidation of isoprene is well studied as recently reviewed by Wennberg *et al.* (2018). One of the major oxidation products under pristine conditions are the isoprene epoxydiols (IEPOX). Usually the secondary organic aerosol (SOA) tracers of IEPOX are described to be 2-methyltetrols, organosulfates of IEPOX, C<sub>5</sub>-alkene triols, 3-Methyltetrahydrofuran-3,4-diols, IEPOX dimers, derived organosulfates and ‘others’ (Riedel *et al.*, 2016). These products are in one way or the other linked to the hydrolysis of the epoxide ring. However, the hydrolysis rate constant is determined to be  $k_{\text{hyd}}(\text{H}^+) = 0.036 \text{ L mol}^{-1} \text{ s}^{-1}$  (Cole-Filipiak *et al.*, 2010) which results an IEPOX lifetime of more than one hour at a typical aerosol pH of 2. During this period oxidative chemistry of IEPOX is going on. Therefore, we investigated the OH radical-driven oxidation of IEPOX in aqueous solution concerning their kinetics as well as the formed products and its distribution, which will be presented here.

## Methods

For the investigation of the OH radical driven oxidation kinetics a laser flash photolysis – laser long path absorption technique (LFP-LLPA) is used. Here hydrogen peroxide ( $c = 2 \times 10^{-4} \text{ mol L}^{-1}$ ) is photolyzed to generate OH radicals. The measurement is performed applying a relative competition kinetics method using potassium thiocyanate as reference compound (Behar *et al.*, 1972; Zhu *et al.*, 2003).

The investigations concerning the products and product distribution are performed using an temperature-controlled aqueous-phase photoreactor irradiated by a filtered Xenon short arc lamp to mimic the actinic light (Otto *et al.*, 2017). The products are identified and quantified using state of the art analytical techniques, such as UPLC-HRMS for the IEPOX and possibly formed accretion products, GC-MS for smaller carbonyls and CE-UV for carboxylic acids.

## Conclusions

A second order rate constant of  $(1.3 \pm 0.1) \times 10^9 \text{ L mol}^{-1} \text{ s}^{-1}$  at 298 K for the reaction of IEPOX with OH radicals is determined in aqueous solution

using the LFP-LLPA technique. A temperature dependent study on the kinetics will be presented including their thermodynamic parameters.

The product studies of the reaction of IEPOX with OH radicals under dilute conditions gave products comparable to gas-phase studies by Bates *et al.* (2016). Smaller carbonyl compounds, such as methylglyoxal, glyoxal, hydroxyacetone and glycolaldehyde are detected as well as small amounts of C<sub>4</sub>-dihydroxy carbonyl compounds. However, there are still unassigned m/z formed.

Finally, the presented results will close the gap to earlier study (Otto *et al.*, 2017) by our laboratory on the aqueous-phase oxidation of DHBO (3,4-dihydroxy-2-butanone) and DHMP (2,3-dihydroxy-2-methylpropanal), which are 3<sup>rd</sup> generation oxidation products of IEPOX in the gas-phase.

- Bates, K. H., Nguyen, T. B., Teng, A. P., Crouse, J. D., Kjaergaard, H. G., Stoltz, B. M., Seinfeld, J. H., & Wennberg, P. O. (2016). *J. Phys. Chem. A*, *120*, 106-117.
- Behar, D., Bevan, P. L. T., & Scholes, G. (1972). *J. Phys. Chem.*, *76*, 1537-1542.
- Cole-Filipiak, N. C., O’Connor, A. E., & Elrod, M. J. (2010). *Environ. Sci. Technol.*, *44*, 6718-6723.
- Otto, T., Stieger, B., Mettke, P., & Herrmann, H. (2017). *J. Phys. Chem. A*, *121*, 6460-6470.
- Riedel, T. P., Lin, Y. H., Zhang, Z., Chu, K., Thornton, J. A., Vizuete, W., Gold, A., & Surratt, J. D. (2016). *Atmos. Chem. Phys.*, *16*, 1245-1254.
- Sindelarova, K., Granier, C., Bouarar, I., Guenther, A., Tilmes, S., Stavrou, T., Müller, J. F., Kuhn, U., Stefani, P., & Knorr, W. (2014). *Atmos. Chem. Phys.*, *14*, 9317-9341.
- Wennberg, P. O., Bates, K. H., Crouse, J. D., Dodson, L. G., McVay, R. C., Mertens, L. A., Nguyen, T. B., Praske, E., Schwantes, R. H., Smarte, M. D., St Clair, J. M., Teng, A. P., Zhang, X., & Seinfeld, J. H. (2018). *Chem. Rev.*, *118*, 3337-3390.
- Zhu, L., Nicovich, J. M., & Wine, P. H. (2003). *Aquat. Sci.*, *65*, 425-435.