

## Aqueous-Phase Chemistry of Isoprene-derived Dihydroxycarbonyl Compounds

Tobias Otto\*, Bastian Stieger, Andreas Tilgner and Hartmut Herrmann  
*Leibniz Institute for Tropospheric Research (TROPOS), Atmospheric Chemistry  
Department (ACD), Permoserstraße 15, 04318 Leipzig, Germany*

Isoprene is the most abundant non-methane volatile organic compound with an annual biogenic emission of  $594 \pm 34 \text{ Tg yr}^{-1}$ .<sup>1</sup> It is undergoing rapid gas-phase oxidation under NO-dominated as well as HO<sub>x</sub>-mediated regimes. Globally, isoprene emission often coincides with low NO and high HO<sub>x</sub>-conditions leading to its first generation oxidation products, the isoprene hydroxy hydroperoxides or ISOPOOH. Further oxidation by OH yields isoprene epoxydiols or IEPOX and, upon further OH attack DHMP (2,3-Dihydroxy-2-methylpropanal) with an annual global production of  $54 \text{ Tg yr}^{-1}$ .<sup>2-4</sup> These compounds most likely partition to the tropospheric aqueous phase as suggested by their predicted Henry's law constants.

The present study investigates the kinetics and product formation to derive the radical-driven oxidation mechanism of DHBO and DHMP in aqueous solution. It is investigated how product yields might change under aerosol proxy conditions compared to dilute aqueous systems. Besides the influence of changing ionic strength, radical switching from hydroxyl radicals as the primary oxidant towards the sulphate radical anion (SO<sub>4</sub><sup>-</sup>) and the nitrate radical (NO<sub>3</sub>) is expected to occur. Kinetic measurements were conducted applying laser flash photolysis – long path absorption technique (LFP-LPA) to determine temperature dependent reaction rate constants for the reactions of DHBO and DHMP with the three radicals mentioned. The determined OH radical reaction rate constants of both compounds are in the range of  $10^8$  to  $10^9 \text{ mol L}^{-1} \text{ s}^{-1}$ . Besides the kinetics, product analysis was applied by means of different GC/MS methods as well as CE/UV to elucidate the oxidation mechanism. The product study revealed hydroxyacetone, glycolaldehyde, methylglyoxal and a variety of further hydroxydicarbonyl species as aqueous-phase oxidation products.

Overall, the obtained results might explain a fraction of Isoprene-derived SOA which is not yet accounted in literature (cf. Riedel et al.<sup>5</sup>). A generational oxidation scheme will be presented mapping products at each generation completed with their O/C ratio, their C/C\* for more organic particles and their solubility for more aqueous particles. Finally, the kinetic and mechanistic experimental findings will be implemented into the chemical mechanism CAPRAM and the resulting model simulation results for aerosol and cloud as well for gas phase chemistry will be discussed.

<sup>1</sup> K. Sindelarova, C. Granier, I. Bouarar, A. Guenther, S. Tilmes, T. Stavrakou, J.-F. Müller, U. Kuhn, P. Stefani, and W. Knorr, *Atmos. Chem. Phys.*, 2014, 14, 9341.

<sup>2</sup> K. H. Bates, T. B. Nguyen, A. P. Teng, J. D. Crouse, H. G. Kjaergaard, B. M. Stoltz, J. H. Seinfeld, and P. O. Wennberg, *J. Phys. Chem. A*, 2016, 120, 106.

<sup>3</sup> J. M. St. Clair, J. C. Rivera-Rios, J. D. Crouse, H. C. Knap, K. H. Bates, A. P. Teng, S. Jørgensen, H. G. Kjaergaard, F. N. Keutsch, and P. O. Wennberg, *J. Phys. Chem. A*, 2016, 120, 1441.

<sup>4</sup> K. H. Bates, J. D. Crouse, J. M. St. Clair, N. B. Bennett, T. B. Nguyen, J. H. Seinfeld, B. M. Stoltz, and P. O. Wennberg, *J. Phys. Chem. A*, 2014, 118, 1237

<sup>5</sup> T. P. Riedel, Y.-H. Lin, Z. Zhang, K. Chu, J. A. Thornton, W. Vizuete, A. Gold, and J. D. Surratt, *Atmos. Chem. Phys.*, 2016, 16, 1245.