Laboratory Aqueous-Phase Oxidation of IEPOX

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Isoprene is the most abundant biogenic volatile organic compounds (BVOCS) apart from methane with a global source strength of 594 ± 34 Tg y^{-1}.[1] The gas-phase oxidation of isoprene is well studied as recently reviewed by Wennberg, et al. [2] Under pristine conditions one of the major oxidation products are the isomeric isoprene epoxydiols (IEPOX). Following products of IEPOX are often linked to the hydrolysis of the epoxide ring. However, the hydrolysis rate constant is determined to be k_{hyd} (H^+) = 0.036 L mol^{-1} s^{-1} [3] leading to a lifetime of more than one hour at a typical pH of 2 and even longer in more neutral solutions. Therefore, we investigated the oxidation of IEPOX by hydroxyl radicals in aqueous solution concerning their kinetics as well as the formed products and its distribution, which will be presented here.

For the investigation of the OH radical driven oxidation kinetics a laser flash photolysis – laser long path absorption technique (LFP-LLPA) is used. The determination of the products and product distribution is performed using a temperature-controlled aqueous-phase photoreactor. 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. A second order rate constant of (1.3 ± 0.1) × 10^9 L mol^{-1} 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. [4] Smaller carbonyl compounds, such as methylglyoxal (maximum molar fraction of 10.3%), glyoxal (6.6%), hydroxyacetone (7.4%) and glycolaldehyde (6.9%) are detected as main oxidation products. However, there are still unassigned compounds formed. Alltogether, the products identified in the OH oxidation pathway are able to explain 21% to 30% of the atmospheric processing of IEPOX depending on the conditions.

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