Kinetic measurements on radical reactions of isoprene oxidation products in the tropospheric multiphase system

Luisa Schöne, Dirk Hoffmann, and Hartmut Herrmann

Institute for Tropospheric Research, Chemistry, Leipzig, Germany (schoene@tropos.de)

The chemistry of volatile organic compound (VOC) from anthropogenic and biogenic sources is important for the understanding of tropospheric processes such as the organic particle mass formation. Emissions of biogenic volatile organic compounds (BVOCs) can exceed those of VOCs coming from anthropogenic sources by a factor of 10 [1]. Isoprene (2-methyl-1,3-butadiene, C_5H_8) emissions represent approximately 40 % of the BVOCs due to the source strength of 500-750 Tg yr^{-1} [2]. The isoprene chemistry takes place in the gas phase. The main oxidation products are methacrolein (MACR), methyl vinyl ketone (MVK), methacrylic acid (MAA) and acrylic acid (ACA). Although the Henry coefficients of the main isoprene oxidation products MACR and MVK are already higher than those of isoprene, partitioning of these compounds into the aqueous phase of rain, fog and cloud droplets and particles was mostly neglected. Correspondingly, aqueous phase oxidation processes of MACR and MVK were sparsely investigated in the past. A recent study [3], however, reports much higher aqueous phase concentrations of MACR and MVK than expected from simply consideration of their Henry coefficients. To evaluate the importance of aqueous phase reactions of isoprene oxidation products for the organic particle mass production, kinetic studies are necessary.

This work investigated the temperature dependent reactivities of the following isoprene oxidation products methacrolein, methyl vinyl ketone, methacrylic acid and acrylic acid towards NO_3, SO_4^- and OH radicals between 278 K and 318 K in the aqueous phase. Furthermore, pH effects on the reactivity of the two acids were studied by measuring the kinetics of both the dissociated and undissociated forms. The measurements were performed using a laser-photolysis laser long path absorption (LP-LLPA) technique.

The measurements' analysis confirmed in all cases a much higher reactivity of the hydroxyl radical (k $\sim$ $10^9 M^{-1}s^{-1}$) compared to the sulfate (k $\sim$ $10^8 M^{-1}s^{-1}$) and the nitrate (k $\sim$ $10^7 M^{-1}s^{-1}$) radical. Among the investigated substances, methacrylic acid showed the highest reactivity towards all three radicals. The temperature dependence of the measured rate constants is most distinct for nitrate radical reactions and weakest for those with sulfate radicals. The experimental data obtained will be presented and discussed within this contribution.

[1] Guenther et al., 1995: Global-model of natural volatile organic-compound emissions. *Journal of Geophysical Research – Atmosphere*, 100(D5), 8873–8892.

[2] Guenther et al. 2006: Estimates of global terrestrial isoprene emissions using MEGAN (Model of Emissions of Gases and Aerosols from Nature). *Atmospheric Chemical Physics*, 6, 3181–3210.

[3] van Pinxteren et al., 2005: Schmücke hill cap cloud and valley stations aerosol chemical composition during FEBUKO (II): Organic compounds. *Atmospheric Environment*, 39, 4305-4320.