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Temperature dependent kinetic measurements of isoprene oxidation products exposed to OH, NO3 and SO4- in aqueous solution.

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The troposphere contains a complex mixture of numerous gases, liquid water and diverse solid particles which undergo intricate processes. Volatile organic compound (VOC) emissions from anthropogenic and biogenic sources are very important for the tropospheric chemistry and other processes such as secondary organic particle mass formation. Emissions of biogenic volatile organic compounds (BVOCs) exceed those VOCs coming from human activity by a factor of 10 [1]. Isoprene (2-methyl-1,3-butadiene, C5H8) emissions represent approximately 40% of the emitted BVOCs, leading to an estimated source strength of 500-750Tgyr-1 [2]. As isoprene has a small Henry coefficient, its oxidation occurs solely in the gas phase. The formed first oxidation products methacrolein (MACR), methyl vinyl ketone (MVK), methacrylic acid (MAA) and acrylic acid (ACA) are therefore firstly located in that phase. Even if the Henry coefficients of the main isoprene oxidation products MACR and MVK are already higher than those of isoprene partitioning of theses compounds into the aqueous phase of rain, fog and cloud droplets and particles was 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 their Henry coefficients. To evaluate the importance of liquid phase reactions of early isoprene oxidation products for the organic particle mass production, kinetic studies are necessary.

Therefore, this work investigated the temperature dependence of methacrolein, methyl vinyl ketone, methacrylic acid and acrylic acid exposed to NO3, SO4- and OH radicals in the range of 278K to 318K in the aqueous phase. Furthermore, the effect of the acid–base equilibrium on the reactivity of the two acids was studied by measuring the kinetics of the dissociated and undissociated acids. The measurements were performed using a laser-photolysis laser long path absorption (LP-LLPA) technique.

The measurements' analysis confirmed in all cases the much higher reactivity of the hydroxyl radical (k∼10ˆ9M-1s-1) in comparison to the sulfate (k∼10ˆ8 M-1s-1) and the nitrate (k∼10ˆ7M-1s-1) radical, with methacrylic acid showing steadily the highest reactivity among the investigated substances. The temperature dependence of the measured rate constants is most distinct for nitrate radical reactions and weakest for those with sulfate radicals. Referred to the two different considered pH-values of the acids, the protonated form reacts slightly faster than the unprotonated form and shows a less distinct temperature dependence.

[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.