

Some recent tropospheric multiphase chemistry developments

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In the first part, results on the multiphase oxidation of isoprene and its oxidation products are presented. The experimental work includes a number of absolute rate constant measurements of free radical reactions (OH, NO₃ and SO₄⁻) with unsaturated compounds derived from the isoprene degradation such as methyl vinyl ketone, methacrolein, methacrylic acid and acrylic acid. Kinetic measurements were carried out as a function of the temperature and the pH of the aqueous measurement solution applying the laser-photolysis technique. The OH radical addition to the double bond in the molecules is fast with second order rate constants at T = 298K of $k_{2nd, \text{methacrolein}} = (1.0 \pm 0.1) \cdot 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, $k_{2nd, \text{methyl vinyl ketone}} = (7.4 \pm 0.7) \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$, $k_{2nd, \text{methacrylate}} = (1.2 \pm 0.1) \cdot 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, $k_{2nd, \text{methacrylic acid}} = (1.2 \pm 0.1) \cdot 10^{10} \text{ M}^{-1} \text{ s}^{-1}$, $k_{2nd, \text{acrylate}} = (6.5 \pm 1.0) \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$ and $k_{2nd, \text{acrylic acid}} = (5.4 \pm 0.8) \cdot 10^9 \text{ M}^{-1} \text{ s}^{-1}$. Reactions of NO₃ and SO₄⁻ with the reactants are one or sometimes even two orders of magnitude slower. In parallel to the kinetic measurement, product studies have been performed by HPLC-MS. First results of these studies are presented. Reaction products of the methacrolein oxidation by OH radicals were analyzed offline as a function of the number of laser pulses. Identified reaction products are functionalized carbonyl compounds and carboxylic acids such as glycolaldehyde, methylglyoxal, pyruvic acid, hydroxyacetone and glyoxal.

In the second part, we report the reactive uptake of α -pinene oxide, β -pinene oxide, campholenic aldehyde and carveol on acidic sulfate aerosol. Organosulfates were analyzed using UPLC/ESI-QTOFMS (ultra performance liquid chromatography coupled to electrospray ionization quadrupole time-of-flight mass spectrometry). Organosulfates were only found in the samples from the reactive uptake of α -pinene oxide, β -pinene oxide and campholenic aldehyde in the presence of acidic sulfate seed particles. Significant amounts of organosulfates were detected in the β -pinene oxide sample than other precursor VOCs. Campholenic aldehyde and carveol showed a very little or no organosulfate, indicating that epoxides most likely serve as precursors for the formation of organosulfates in the atmosphere. This study provides evidence for the importance of the reactive uptake of epoxides in the formation of atmospherically relevant organosulfates.