

**Recent IfT Multiphase Chemistry Studies:  
Isoprene and Terpene-derived Systems**  
H. Herrmann, D. Hoffmann, Y. Iinuma, O. Böge and A. Kahnt  
Leibniz-Institut für Troposphärenforschung  
Abteilung Chemie  
Permoserstraße 15  
04318 Leipzig  
herrmann@tropos.de

In the first part of this contribution results on the multiphase oxidation of isoprene are presented which include a number of absolute rate constant measurements of reactions of the radicals OH, NO<sub>3</sub> and SO<sub>4</sub><sup>-</sup> with unsaturated compounds derived from the isoprene degradation such as methyl vinyl ketone, methacrolein and methacrylic 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 of  $k_{2nd, \text{methacrolein}} = (1.0 \pm 0.1) \cdot 10^{10}$ ,  $k_{2nd, \text{methyl vinyl ketone}} = (7.4 \pm 0.7) \cdot 10^9$ ,  $k_{2nd, \text{methacrylate}} = (1.2 \pm 0.1) \cdot 10^{10}$  and  $k_{2nd, \text{methacrylic acid}} = (1.2 \pm 0.1) \cdot 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ . The corresponding NO<sub>3</sub> and SO<sub>4</sub><sup>-</sup> reactions with the unsaturated carbonyl compounds are one or sometimes two orders of magnitude slower. In parallel to the kinetic measurement, product studies have been performed by HPLC-MS following pulsed photolysis and first results of these studies are presented. Oxidation products of the methacrolein and methyl vinyl ketone 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 chamber investigations on the formation of organosulfates from reactive uptake of  $\alpha$ -pinene oxide,  $\beta$ -pinene oxide, campholenic aldehyde and carveol is described. 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  $\alpha$ -pinene oxide,  $\beta$ -pinene oxide and campholenic aldehyde in the presence of acidic sulfate seed particles. In particular, significantly higher concentrations of organosulfates were found in the sample from  $\beta$ -pinene oxide reactive uptake 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.