

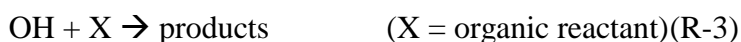
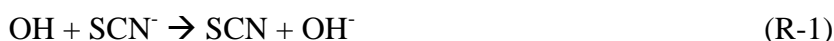
## Experimental Determination of OH-Reaction Rates with Organics ( $\geq C_2$ ) and their Importance to tropospheric Multiphase Chemistry

B. Ervens and H. Herrmann

Institut für Troposphärenforschung, Permoserstr. 15, D-04318 Leipzig, Germany

A contribution to the sub-project CMD-APP

The **C**hemical **A**queous **P**hase **R**adical **M**echanism CAPRAM2.4(MODAC mechanism) represents a very detailed mechanism for tropospheric cloud chemistry. A reduced version of CAPRAM2.4 (MODAC-mechanism), in which the concentration levels of certain marker species (OH, NO<sub>3</sub>, H<sub>2</sub>O<sub>2</sub>, S(IV), NO<sub>x</sub> and H<sup>+</sup>) are constant compared to the complete version ( $\pm 2\%$ ), led to the evidence that the organic oxidation in the aqueous phase can be described sufficiently by reactions of the OH radical. Reactions of other radicals and radical anions such as NO<sub>3</sub>, SO<sub>4</sub><sup>-</sup>, Cl<sub>2</sub><sup>-</sup>, Br<sub>2</sub><sup>-</sup> and CO<sub>3</sub><sup>-</sup> have negligible fluxes. So, the starting point for the further development of the aqueous phase mechanism used here (CAPRAM2.4 (MODAC mechanism)) are additional reactions of the OH radical with higher organics than C<sub>2</sub> compounds. For these species only some few temperature dependent kinetic data are available in literature. The experimental determination of reaction rate constants was carried out with a laser-photolysis- long-path-absorption setup. The OH radicals were formed by excimer laser photolysis of H<sub>2</sub>O<sub>2</sub> (248 nm). The values were measured relative in competition to the reference system (R-1) in the temperature interval between 283 and 328 K. The dithiocyanide radical anion (SCN)<sub>2</sub><sup>-</sup> was detected at 436 nm.



With this method the Arrhenius expressions for some reactions of C<sub>2</sub>, C<sub>3</sub> and C<sub>4</sub> organic compounds were determined. For these species investigated proper initial gas phase concentrations were used for different scenarios and their uptake processes (Henry's Law Constants, mass accommodation and gas phase diffusion coefficients) were formulated.

The results of the model calculations give evidence about the influence of higher organic compounds in the aqueous phase. The fluxes and returns of the new added reactions are compared with them of the smaller organics mainly with regards to the concentration level of the OH radical.