Laser-based studies of reactions of important atmospheric radicals with organic compounds in the aqueous phase

T. Schaefer, D. Hoffmann, C. Weller, K. Parajuli, P. Barzaghi and H. Herrmann
Leibniz-Institut für Troposphärenforschung, Permoserstr. 15, 04318 Leipzig

Degradation and conversion of organic compounds in the atmosphere is often initiated by radical reactions. These reactions take place in the gas, particle and liquid phase (cloud droplets, fog, rain and aqueous particles) of the atmosphere. Important and very reactive atmospheric free radicals within the atmospheric multiphase system are OH, NO_3, sulfur- oxy- and halogen radicals. Radical reactions can contribute significantly to the formation of ozone, other secondary pollutants, particle mass and acidity production.

The modeling of atmospheric chemical processes requires still much kinetic as well as mechanistic information of radical reactions. However, the multiphase chemistry of many important reactions is not yet investigated. Therefore, different thermostated laser-photolysis-long-path-absorption (LP-LPA) set-ups were used, to study OH, NO_3 and halogen radical reactions towards different organics (alcohols, acids, carbonyls) in the aqueous phase. OH radicals were generated by the photolysis of hydrogen peroxide (H_2O_2) at λ = 248 nm in aqueous solution. Kinetic measurements of OH reactions have been carried out by competition kinetics technique using the thiocyanate reference system. In contrast to this, the rate constants for NO_3 and halogen radical reactions were determined by direct measurements following the decay of the radical concentration as a function of the time and the reactant concentration. NO_3 radicals were produced by laser flash photolysis of $NaNO_3$ (λ = 248 nm, pH = 0.5). To study halogene radical reactions, Br and Cl were generated by the photolyses of bromoacetone and chloroacetone, respectively. Furthermore, the effect of the ionic strength and the temperature on many investigated reactions was studied.

Recent kinetic results obtained will be presented and discussed. The results of this study will be used for further development of CAPRAM, i.e. the Chemical Aqueous Phase Radical Mechanism. This mechanism incorporates an explicit description of the inorganic aqueous phase chemistry and an explicit oxidation scheme of organic compounds containing up to four carbon atoms.