

Laboratory studies of aqueous phase reactions of free radicals with organic compounds of relevance for atmospheric chemistry

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Oxygenated organic compounds are either directly emitted to the atmosphere as fuel additives or solvents or they are formed in the troposphere as intermediate products of chemical degradation of other volatile organic compounds. Their presence in the atmosphere also results in formation of other secondary pollutants and tropospheric ozone. Furthermore, more polar intermediates and products will be formed upon their gas phase oxidation which could be transferred to aqueous phase. The major degradation pathway of these organic compounds might be the reaction with OH, NO₃ and halogens radicals in the tropospheric aqueous phase.

From gas phase oxidation of aromatic hydrocarbons the following types of products can be formed via substitution reactions; e.g. benzene and toluene form nitro- and hydroxy-compounds, such as nitrobenzene, nitrotoluenes, cresols and nitrophenols. The latter, which are known to be phytotoxic and may affect human health can be rapidly formed in the gas phase as well as in aqueous phase (Barzagli and Herrmann, 2002) from the reaction of NO₃ in presence of NO₂. They represent a typical example of multiphase conversion.

The temperature dependence can be extremely important in determining the lifetimes and fates of certain species in the atmosphere, as well as their contribution to secondary pollutant formation. For certain reactions in the troposphere the effect of ionic strength can be even more important than the effect of temperature (Herrmann, 2003). Thus, in the presented studies the temperature dependent and ionic strength dependent measurements of OH, NO₃ and Br reactions with different environmental-relevant organic compounds in aqueous solution are performed.

Using a laser-photolysis-long-path-laser-absorption (LP-LPLA) set up and applying a competition kinetic method the temperature-dependent rate constants for the reactions of OH radical with acetonylacetone, isobutyraldehyde and diacetyl were measured.

Moreover, NO₃ radicals were generated by flash photolysis of nitrate anions at $\lambda = 248$ nm under acidic conditions (pH = 0.5). Rate constants for reactions with substituted phenols were investigated at room temperature and the ionic strength dependencies for the reactions of NO₃ radicals with p-cresol, p-methoxyphenol, p-nitrophenol and p-hydroxybenzoic acid were also studied.

Furthermore, a laser photolysis experiment was also applied to study the Br-kinetics of oxidation of aliphatic aldehydes and alcohols in aqueous solution. The temperature dependencies of the rate constants for the reactions of Br with propionaldehyde, butyraldehyde, methanol, ethanol and 2-propanol have been studied.

The kinetic data obtained here will be used as input parameters in forthcoming versions of our multiphase reaction mechanisms CAPRAM.

Barzagli, P. and H. Herrmann, 2002, A mechanistic study of the oxidation of phenol by OH/NO₂/NO₃ in aqueous solution, *Phys. Chem. Chem. Phys.*, **4**, 3669-3675.

Herrmann, H. 2003. Kinetics of Aqueous Phase Reactions Relevant for Atmospheric Chemistry, *Chem. Rev.*, **103**, 4691-4716.