



Ionic Strength Dependencies of Electron Transfer Reactions of Nitrate Radicals in Aqueous Solution

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The degradation of many organic compounds in the atmosphere can be initiated by oxidation reactions with atmospheric radicals such as NO_3 . Beside the H-abstraction, also the electron transfer reaction can be of importance as possible reaction pathway in aqueous solution.

Especially for some phenolic compounds (e.g. nitrophenols, halogenated phenols, cresol, ...) is the electron transfer reaction the dominating reaction pathway. This work investigated the reactivity of NO_3 -radicals towards phenolic compounds in aqueous solution. Salt effects can influence rate constants of reactions, therefore ionic strength dependencies were located in the centre of this work. Using a laser-photolysis-long-path-laser-absorption (LP-LPA) set-up, rate constants for the reactions of nitrate radicals with different substituted phenols in aqueous solution have been measured as a function of the ionic strength. Thereby, considerable salt effects have been observed for some of the reactions investigated.

In the context of this work different correlations between the measured rate constants and properties of the target compounds were found. These correlations enlarge the understanding of NO_3 -reactions on the one hand and allow on the other hand a prediction of unknown rate constants. Further, new correlations were found between parameters like the dipole moment of the reactants and/or the Gibbs free reaction enthalpy and the kinetic salting coefficient. These correlations represent, for the first time, a possibility of predicting ionic strength effects for the reactions between two neutral compounds.

The kinetic data and correlations obtained will be used as input parameters for existing tropospheric chemistry models like CAPRAM (Chemical Aqueous Phase Radical Mechanism)