

POSTER

H. Herrmann · H.-W. Jacobi · G. Raabe · A. Reese
R. Zellner

Laser-spectroscopic laboratory studies of atmospheric aqueous phase free radical chemistry

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Abstract Nitrate radical (NO_3) reactions with benzene (R-1), toluene (R-2), p-xylene (R-3), p-cresol (R-4) and mesitylene (R-5) have been studied by laser photolysis/long path laser absorption (LP-LPLA) in aqueous solution. Rate constants of $k_1 = (4.0 \pm 0.6) \cdot 10^8$, $k_2 = (1.2 \pm 0.3) \cdot 10^9$, $k_3 = (1.6 \pm 0.1) \cdot 10^9$, $k_4 = (8.4 \pm 2.3) \cdot 10^8$ and $k_5 = (1.3 \pm 0.3) \cdot 10^9 \text{ l mol}^{-1} \text{ s}^{-1}$ were obtained at $T = 298 \text{ K}$. In addition, reaction rate coefficients for $\text{SO}_5^- + \text{Fe}^{2+} \rightarrow \text{prod.}$ (R-6) and $\text{SO}_5^- + \text{Mn}^{2+} \rightarrow \text{prod.}$ (R-7) of $k_6 = (4.3 \pm 2.4) \cdot 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$ and $k_7 = (4.6 \pm 1.0) \cdot 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$ ($T = 298 \text{ K}$, $I \rightarrow 0$) have been obtained by the application of laser photolysis/UV-VIS broadband diode array spectroscopy. A new laser photolysis/UV-long path laser absorption experiment has been applied to study the reaction of the Cl_2^- radical anion with dissolved sulfur(IV). For the reactions $\text{Cl}_2^- + \text{HSO}_3^- \rightarrow 2\text{Cl}^- + \text{H}^+ + \text{SO}_3^-$ (R-8) and $\text{Cl}_2^- + \text{SO}_3^{2-} \rightarrow 2\text{Cl}^- + \text{SO}_3^-$ (R-9) rate coefficients of $k_8 = (1.7 \pm 0.2) \cdot 10^8 \text{ l mol}^{-1} \text{ s}^{-1}$ ($T = 298 \text{ K}$, $I \rightarrow 0$) and of $k_9 = (6.2 \pm 0.3) \cdot 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$ ($T = 279 \text{ K}$, $I \rightarrow 0$) were obtained.

detection of short-lived transient species in solution, especially radicals and radical ions, is of interest.

Experimental

Three different laser spectroscopic experiments are applied for the study of the nitrate radical (NO_3), the peroxymonosulfate (SO_5^-) and the sulfate (SO_4^-) radical anion, and the dichloride radical anion (Cl_2^-) in aqueous solution. Each experiment utilizes excimer-laser based generation of radicals and the sensitive detection of transient species by time-resolved long path (laser or diode array) absorption measurements. The experiment for the study of NO_3 has been described elsewhere [2, 3] as well as the laser photolysis/long path diode array absorption experiment applied here for the study of the absorption spectra of SO_4^- and SO_5^- [4, 5]. A new experiment for the study of Cl_2^- radical anions has been developed, a schematic of which is shown in Fig. 1. In short, sulfate radicals are generated by excimer-laser (Lambda Physik LPX 110 iCC) photodissociation of peroxydisulfate anions. Sulfate radicals subsequently react with chloride anions added in excess to form chlorine atoms which in turn form Cl_2^- by adding chloride. Cl_2^- -concentration are monitored by the time-resolved detection of the 325 nm output of a HeCd laser the beam of which is folded through the reaction cell by means of a set of mirrors in White's configuration [6]. An optical pathlength of $d = 120 \text{ cm}$ is obtained. The laser intensity is monitored by means of a photodiode. The diode output is fed to an oscilloscope (Gould 4050) and monitored as a function of time.

Introduction

Applications of time-resolved laser spectroscopic methods are presented for the study of free radical reactions in aqueous solution. The motivation of this investigation is to study aqueous phase tropospheric chemistry [1]. The experimental methods developed here may also be applied to studies in fields with different backgrounds where the time-resolved sensitive

Results and discussion

Kinetic results of the reactions of NO_3 with some aromatics in aqueous solution are summarized in Table 1. All reactions are very fast and near the diffusion-controlled limit. Currently, there are no literature data available for comparison.

For the reactions



rate coefficients of $k_6 = (4.3 \pm 2.4) \cdot 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$ and $k_7 = (4.6 \pm 1.0) \cdot 10^6 \text{ l mol}^{-1} \text{ s}^{-1}$ have been obtained at

H. Herrmann (✉) · H.-W. Jacobi · G. Raabe · A. Reese · R. Zellner
Institut für Physik. und Theor. Chemie, FB 8, Universität GH Essen,
Universitätsstrasse. 5, D-45117 Essen, Germany

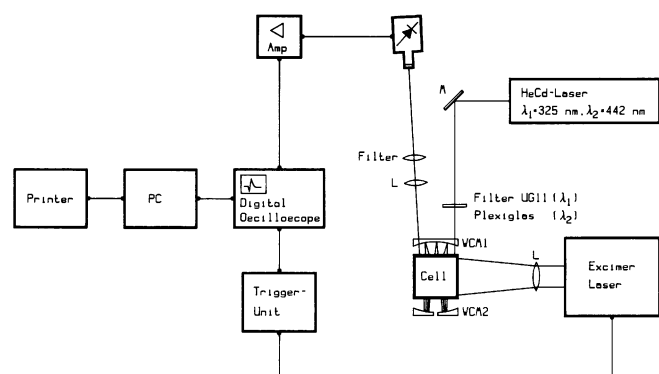


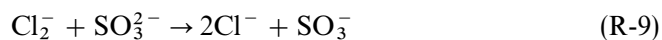
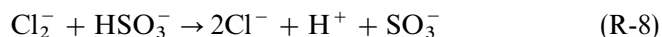
Fig. 1 Laser-photolysis-long-path UV-laser absorption (LP-LPLA)-experiment for the study of dichloride radical-anion (Cl_2^-) kinetics in aqueous solution

Table 1 Second order rate coefficients for the reactions of NO_3 with aromatic organic compounds in aqueous solution

Reactant	$k_{\text{NO}_3+\text{X}}/\text{lmol}^{-1} \text{s}^{-1}$
Benzene	$(4.0 \pm 0.6) 10^8$
Toluene	$(1.2 \pm 0.3) 10^9$
p-Xylene	$(1.6 \pm 0.1) 10^9$
p-Cresol	$(8.4 \pm 2.3) 10^8$
Mesitylene	$(1.3 \pm 0.3) 10^9$

$T = 298 \text{ K}$, $\text{pH} = 4.5$ and $I \rightarrow 0 \text{ M}$. Former determinations are only available for reaction (R-6) where experimental determinations led to $k_6 = 3.2 \cdot 10^6 \text{ lmol}^{-1} \text{s}^{-1}$ [7] and $k_6 \geq 2 \cdot 10^8 \text{ lmol}^{-1} \text{s}^{-1}$ [8], respectively. Additionally, from a modelling study a value of $k_6 \approx 1 \cdot 10^7 \text{ lmol}^{-1} \text{s}^{-1}$ [9] has been derived. In principal, the latter value is confirmed by the present study whereas the two former experimental determinations show considerable deviations from the result of the present determination.

The reaction



were investigated at $T = 298 \text{ K}$ and rate coefficients of $k_8 = (1.7 \pm 0.2) \cdot 10^8 \text{ lmol}^{-1} \text{s}^{-1}$ and $k_9 = (6.2 \pm 0.3) \cdot 10^7 \text{ lmol}^{-1} \text{s}^{-1}$ ($I \rightarrow 0$) were obtained in the present work. There are two previous determinations of k_8 . Huie et al. [10] found $k_8 = 3.4 \cdot 10^8 \text{ lmol}^{-1} \text{s}^{-1}$ ($T = 298 \text{ K}$, $\text{pH} = 3.0$, $I = 0.1 \text{ M}$) [10] in 1987. A more recent determination from the same group led to a value of $k_8 = 4.7 \cdot 10^8 \text{ lmol}^{-1} \text{s}^{-1}$ ($T = 298 \text{ K}$, $\text{pH} = 3.2$, $I = 0.1 \text{ M}$) and an addition mechanism was suggested [11]. A correction of the literature data for $I \rightarrow 0$ by the Davies approach [12] leads to $k_8 = 2.0 \cdot 10^8 \text{ lmol}^{-1} \text{s}^{-1}$ [10] and $k_8 = 2.9 \cdot 10^8$

$\text{lmol}^{-1} \text{s}^{-1}$ [11], respectively. Corresponding literature data for the rate constant of reaction (R-9) are currently not available.

From a third set of experiments, performed at low pH, it was concluded that a reaction between dissolved SO_2 ($\text{SO}_{2(\text{aq})}$) and Cl_2^- does not take place. Information about a reaction between dissolved SO_2 and the dichloride radical anion is currently not available from the literature.

Conclusion

Nitrate radical reactions with aromatic compounds have been demonstrated to be very fast in aqueous solution and may therefore significantly influence the tropospheric budget of this radical when aromatic compounds are transferred to the aqueous phase. New kinetic data could be provided for reactions of SO_5^- and Cl_2^- with the reactants Fe(II), Mn(II) and S(IV), respectively. The results from laser-based spectroscopic kinetic laboratory experiments, as described in the present study, will serve as input parameters for numerical modelling of heterogeneous tropospheric chemistry systems in order to better understand the potential oxidation capacity of this environment.

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