Kinetic and Spectroscopic Investigations of the Br_2^- Radical in Aqueous Solution

A contribution to subproject CMD

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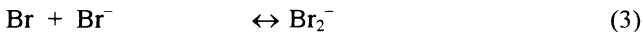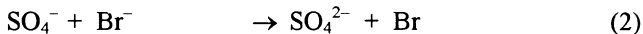[2]Institut für Troposphärenforschung, Permoserstr. 15, D-04303 Leipzig, Germany

Introduction

In the aqueous phase of the troposphere Br atoms are formed through the very fast reactions of the Br^- ions with radicals like NO_3, OH or SO_4^-. At high bromide concentrations, Br_2^- radical anions will be formed in diffusion-controlled reactions. Because of the high aqueous phase abundance of Br^- in marine areas it is necessary to investigate the reactivity of the dibromide radical anion for a better understanding of its impact upon tropospheric chemical processes.

Experimental

The experiments described in the present study were performed with a laser photolysis long-path absorption apparatus (LP-LPA) designed for direct spectroscopic and kinetic studies of radicals in liquid phase which absorbs in the UV-visible range. This experiment has been optimised over the last couple of years and descriptions of former versions may be found elsewhere (*e.g.* Herrmann *et al.*, 1995).

Br_2^- was generated by laser photolysis of peroxodisulfate according to:

$$S_2O_8^{2-} + h\nu(\lambda=248nm) \rightarrow 2\ SO_4^- \tag{1}$$

$$SO_4^- + Br^- \rightarrow SO_4^{2-} + Br \tag{2}$$

$$Br + Br^- \leftrightarrow Br_2^- \tag{3}$$

Bromide is present in large excess (0.1 M) to shift the equilibrium between Br and Br_2^- towards the dibromide radical anion.

Spectroscopic results

To guarantee that the conversion of the sulfate radical anions to dibromide radical anions is complete, the absorption spectrum has been detected 50 μs after the laser flash. The spectrum obtained is shown in Fig. 1 in comparison to the literature spectrum published by Zehavi and Rabani (1972). Two absorption bands have been found at $\lambda_{1,max}$ = 360 nm and $\lambda_{2,max}$ = 684 nm, with an intensity ratio of I_1/I_2 = 15.
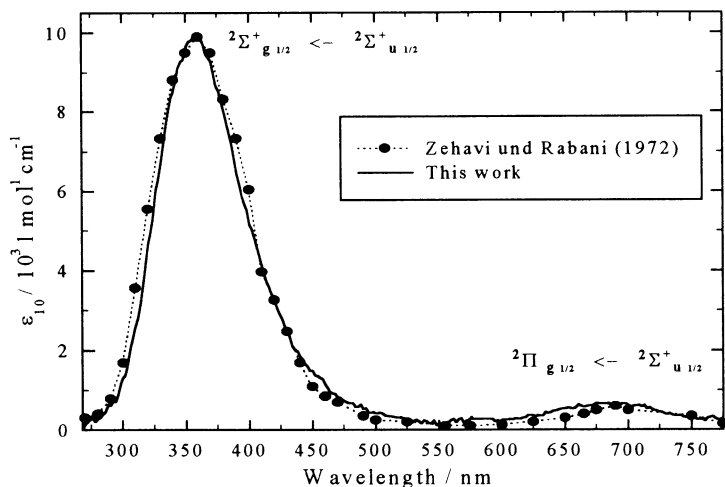

Fig. 1: Absorption spectrum of the dibromde radical anion, T = 298 K, pH 5.6, t = 50 μs, $[S_2O_8^{2-}]$ and $[Br^-]$ = 5 × 10^{-4} M. Normalised (Zehavi and Rabani, 1972) with ε_{max} (360 nm) = (9900 ± 600) L mol^{-1} cm^{-1}.

The absorption bands determined experimentally are in good agreement with theoretical calculations of the absorption spectrum of the Br_2^- radical (Fornier de Violet, 1981), in which for the two different electronic transition absorption maxima at λ = 372 nm and λ = 697 nm have been determined. These spectral proportions are typical for dihalogenide radical anions.

Kinetic results

The self reaction of Br_2^- proceeds under disproportion of two Br_2^- radicals in a Br_3^- complex and a Br atom via the reactions (4a) and (4b):

$$Br_2^- + Br_2^- \quad \rightarrow \quad Br_3^- + Br \qquad (4a)$$

$$Br_3^- \qquad \leftrightarrow \quad Br_2 + Br^- \qquad (4b)$$
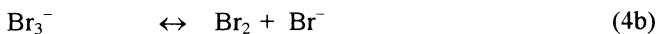
For the determination of the rate constant, the reciprocal concentration is plotted versus time. Form the slope of the straight line the second order rate coefficient has been determined for 8 experiments in which 32 single experiments have been avaraged. The avarage rate coefficient for reaction 4 is $k_4 = (5.2 \pm 0.2) \times 10^9$ M^{-1} s^{-1} at $T = 298$ K, pH 5.8 and I = 0.1 mol L^{-1}. Extrapolation to an ionic strength of I = 0 M (Davies equation) leads to: k_4 (I→0) = $(1.7 \pm 0.1) \times 10^9$ M^{-1} s^{-1}. This value is in good agreement to available literature data, where rate coefficients between 1.6×10^9 M s^{-1} and 2.8×10^9 M s^{-1} have been published (D'Angelantonio et al., 1988; Buxton and Dainton, 1968; Wong et al., 1975; Thornton and Laurence, 1973).

Table 1: Data compilation for H-atom abstraction reactions of Br$_2^-$ with different organic compounds in aqueous solution, rate coefficients per equivalent abstractable H atom k_H and bond dissociation energy BDE of the weakest C–H bond ($T = 298$ K, pH = 5.5, I = 0,1 M)

Reactant	k_{2nd} /M^{-1} s^1	n$_H$	k_H /M^{-1} s^1	log k_H	BDE /kJ·mol^{-1}
methanol	$(1.0 \pm 0.2) \times 10^3$	2	$(3.3 \pm 0.7) \times 10^2$	2.52 ± 0.09	401 ± 1 [2]
ethanol	$(3.8 \pm 1.0) \times 10^3$	2	$(1.9 \pm 0.5) \times 10^3$	3.3 ± 0.1	389 ± 4 [3]
1-propanol	$(7.7 \pm 0.8) \times 10^3$	2	$(3.9 \pm 0.4) \times 10^3$	3.59 ± 0.04	385 [4]
2-propanol	$(1.8 \pm 0.6) \times 10^4$	1	$(1.8 \pm 0.6) \times 10^4$	4.3 ± 0.1	381 ± 4 [3]
2-butanol	$(4.4 \pm 0.9) \times 10^4$	1	$(4.4 \pm 0.9) \times 10^4$	4.64 ± 0.09	381 [4]
formic acid [1]	$(4.0 \pm 0.5) \times 10^3$	1	$(4.0 \pm 0.5) \times 10^3$	3.60 ± 0.05	387 [4]
acetic acid [1]	< 1000	3	< 350	< 2.6	410 ± 8 [5]
diethylether	$(8.2 \pm 1.7) \times 10^3$	4	$(2.1 \pm 0.4) \times 10^3$	3.32 ± 0.08	383.7 ± 1.7 [3]
methyl-*tert.*-butylether	< 2700	12	< 250	< 2.4	410 [4]
tetrahydro-furan	$(8.8 \pm 1.6) \times 10^3$	4	$(1.1 \pm 0.2) \times 10^3$	3.04 ± 0.08	385 ± 4 [3]
acetone	< 60	6	< 10	< 1.0	411.3 ± 7.5 [3]
dichloro-methane	$(1.3 \pm 0.2) \times 10^3$	2	$(6.5 \pm 1.0) \times 10^2$	2.81 ± 0.07	411.7 ± 5.0 [3]
trichloro-methane	$(1.1 \pm 0.5) \times 10^3$	1	$(1.1 \pm 0.5) \times 10^3$	3.0 ± 0.2	392.5 ± 2.5 [3]
2-butanone	< 1200	5	< 250	< 2.4	410 [4]

[1] The investigations with organic acids were performed at pH = 1 and I = 0.2
[2] Average of the literature data (Dóbé et al., 1996) and (Johnson and Hudgens, 1996)
[3] (Handbook of Chemistry and Physics, 1994), [4] (Benson, 1989), [5] (Singleton et al., 1989).

With saturated aliphatic organic compounds the Br_2^- radical anion reacts via H-atom abstraction according to:

$$Br_2^- + RH \quad \rightarrow \quad R + 2Br^- + H^+ \quad\quad\quad (5)$$

The results of the investigations concerning the H-atom abstraction reactions of the Br_2^- radical anion are listed in Table 1.

Based on the kinetic data provided in Table 1 the logarithms of the rate constants of the reactions of the Br_2^- radical anion per equivalent abstractable H-atom as a function of the C–H bond dissociation energy (BDE) are plotted in Fig. 2. From the slope of the line shown in Fig. 2 the following equation is obtained:

$$\log k_H = (26 \pm 10) - (0.06 \pm 0.02) \ BDE \ /kJ \ mol^{-1} \quad\quad (I)$$

This equation can be used to calculate rate coefficients of H-atom abstraction reactions of Br_2^- radical anions that are experimentally not easily available even if the C–H bond energy is known.
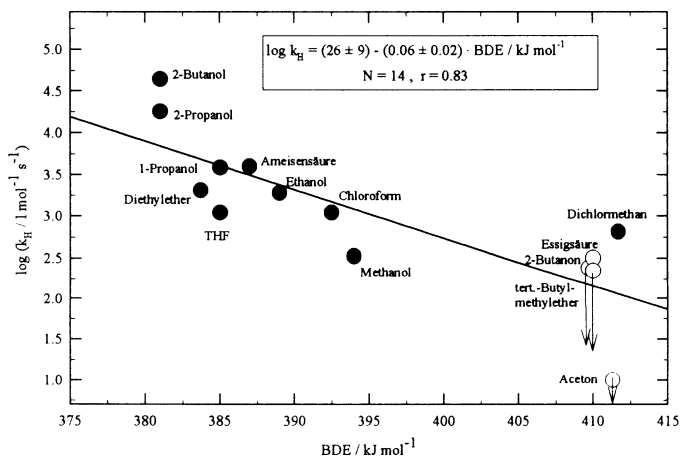

Fig. 2:   Logarithms of the rate constants per equivalent H-atom of H-atom abstraction reactions of the Br_2^- radical anion as a function of the C–H bond energy (BDE).

Conclusions

The absorption spectrum of the dibromide radical anion has been determined in the wavelength range between 250 nm and 770 nm. H-atom abstraction reactions of Br_2^- with several organic constitutents of the tropospheric aqueous phase have been determined for the first time. The recombination reaction of Br_2^- may lead to the formation of Br_2 which, under certain conditions may be

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released from aqueous phase particles and hence lead to a formation of gas phase bromine atoms. The data presented can be used in modelling studies to investigate the possible impact of the Br_2^- radical on the chemistry of free radicals in the tropospheric aqueous phase.

Acknowledgements

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