

Laser-based Kinetic and Spectroscopic Investigations of X_2^- -radical anions ($X = \text{Cl}, \text{Br}$) with Aromatics in Aqueous Solution

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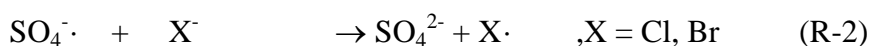
1. Introduction

In the chemistry of the aqueous tropospheric particles free radicals like the dihalogenide radical anions Cl_2^- and Br_2^- may play an important role in marine, continental and remote area [1].

Therefore in this study rate constants and the activation energies of reactions of X_2^- radical anions with some aromatic compounds have been investigated. Also the absorption spectrum of the Cl_2^- radical anion has been measured in the range from 260 to 720 nm. The transition from ground state to first excited state has been observed. The aromatic compounds for which the rate coefficients with the X_2^- radical anions have been measured include benzene as well as much better water-soluble aromatic acids, phenols, nitrophenols and anilines. Nitrogen containing phenols and derivatives which are very toxic as well as anilines have been identified at significant concentration levels within cloud- and rain-water [2]. They are formed by reactions of NO_3 or OH/NO_2 with benzene, toluene etc. [3]. Aromatic acids, phenols and their derivatives also have been found in significant concentration levels within cloud- and rainwater [11]. They are typical oxidation products from reactions of benzene or toluene with $\text{OH}\cdot$ radicals.

2. Experimental set-up

For the kinetic and spectroscopic investigations a laser-photolysis-longpath-absorption(LP-LPA) apparatus as shown in Figure 1 was used. X_2^- radicals were generated by excimer-laser photolysis of aqueous solutions containing peroxodisulfate and halogenide according to:



The X_2^- radicals have been monitored by long path absorption applying the output of a 400 W halogen lamp and a 150 W deuterium lamp at 340 nm for Cl_2^- and 360 nm for Br_2^- recorded with a monochromator/photomultiplier combination. Since some of the aromatic compounds

used for kinetic investigations do absorb at 340 nm $\text{Cl}_2^- \cdot$ has been monitored at 632 nm using a slightly different apparatus with a He/Ne-Laser as light source in these cases. Details of the experimental method applied in the present work can be found elsewhere [10].

3. Results

3.1 Absorption spectra of the $\text{Cl}_2^- \cdot$ radical anion

The absorption spectra of the $\text{Cl}_2^- \cdot$ radical anion has been measured in the wavelength region from 260 nm to 720 nm. The transition from ground state to first excited state $A \ ^2\Pi_{g1/2} \leftarrow X \ ^2\Sigma_{u1/2}^+$ has been experimentally proved for the first time. The observed spectra as shown in Figure 2 is in good agreement with former experimental results [4], as well as with theoretical predictions [5].

3.2 Reactions of $\text{X}_2^- \cdot$ radical anions with aromatic compounds

For reactions of $\text{X}_2^- \cdot$ radical anions with aromatic compounds there are principal three different reaction pathways may occur:

- **H-atom abstraction**

- **Addition** to the aromatic system where a π -complex is formed

- **Electron-transfer** from aromatic ring to $\text{X}_2^- \cdot$ -radical-anion

Using the assumption that the different reaction pathways do not affect each other the observed rate coefficients should be the sum of the single processes according to:

$$\frac{d[\text{X}_2^-]}{dt} = k_{\text{obs}} \cdot [\text{X}_2^-] \cdot [\text{Ar}] = (k_{\text{H}} + k_{\text{Add}} + k_{\text{ETR}}) \cdot [\text{R}] \cdot [\text{X}_2^-]$$
$$\Rightarrow k_{\text{obs}} = k_{\text{H}} + k_{\text{Add}} + k_{\text{ETR}}$$

Ar = aromatic compound

k_{obs} = experimentally observed rate coefficient

k_{H} = rate coefficient of H-atom abstraction

k_{Add} = rate coefficient of addition

k_{ETR} = rate coefficient of electron transfer

3.2.1 Reactions of $\text{Br}_2^- \cdot$ radical anions with aromatic compounds

To determine whether the reactions of the $\text{Br}_2^- \cdot$ radical anion with aromatic compounds follow a H-atom abstraction mechanism a correlation from our laboratory [6] between C-H and approximated O-H bond dissociation energy (BDE) and the rate coefficient for H-atom abstraction reactions of $\text{Br}_2^- \cdot$ can be used according to:

$$\log k_{\text{H}} = (27 \pm 8) - (0.06 \pm 0.02) \cdot \text{BDE} / \text{kJ} \cdot \text{mol}^{-1} \quad n = 15, r = 0.85$$

In Table 1 the ratios of the rate constants calculated for H-atom abstraction and experimentally observed are listed as well as the bond dissociation energy of the weakest C-H or O-H bond are listed.

Tab. 1: Observed and for H-atom abstraction calculated rate constants

Compound	BDE /kJ·mol ⁻¹	k _{obs} / l·mol ⁻¹ ·s ⁻¹	(n·k _H) / k _{obs}
C ₆ H ₅ N(CH ₃) ₂	411 [7]	(9.4 ± 1.2)·10 ⁸	1·10 ⁻⁶
p-HOC ₆ H ₄ OH	336 [8]	(5.3 ± 1.0)·10 ⁷	0.26
p-CH ₃ OC ₆ H ₄ OCH ₃	412 [7]	(10 ± 2.0)·10 ⁷	1·10 ⁻⁵
p-HOC ₆ H ₄ COOH	381*	(6.7 ± 1.0)·10 ⁶	2·10 ⁻³
p-CH ₃ OC ₆ H ₄ COOH	410*	(1.6 ± 0.3)·10 ⁶	5·10 ⁻⁴
C ₆ H ₆	461 [7]	(1.4 ± 0.2)·10 ⁵	0

From Table 1 it can be seen that for hydroquinone there probably is a significant contribution of the H-atom abstraction channel in its reaction with the Br₂⁻ radical anion. For all aromatics that do not carry OH substituents H-atom abstraction seems to be almost negligible as an important reaction pathway. Hence these compounds will react via single electron transfer which may proceed by concerted outer-sphere electron transfer from the aromatic rings or by inner-sphere addition / elimination.

3.2.2 Reactions of Cl₂⁻ radical anions with aromatic compounds

To determine whether the reactions of the Cl₂⁻ radical anion with aromatic compounds follow a H-atom abstraction mechanism a correlation from our laboratory [10] between C-H and approximated O-H bond dissociation energy (BDE) and the rate coefficient for H-atom abstraction reactions of Cl₂⁻ can be used according to:

$$\log k_H = (29.8 \pm 6.5) - (0.065 \pm 0.016) \cdot \text{BDE} / \text{kJ} \cdot \text{mol}^{-1}, n = 14, r = 0.92$$

In Table 2 the ratios of the rate constants calculated for H-atom abstraction and experimentally observed are listed.

Tab 2: Bond dissociation energy of the weakest C-H or O-H bond and calculated rate constants for H-atom abstraction reactions

Compound	BDE/kJ·mol ⁻¹	k _{obs} / l·mol ⁻¹ ·s ⁻¹	(n·k _H) / k _{obs}
2,4-(NO ₂) ₂ C ₆ H ₃ OH	365* [7]	(6 ± 1)·10 ⁶	0.2
C ₆ H ₅ COOH	443 [7]	(5.0 ± 0.9)·10 ⁴	2·10 ⁻⁴
6-NO ₂ -3-CH ₃ C ₆ H ₃ OH	365* [7]	(1.5 ± 0.1)·10 ⁸	8·10 ⁻³

* BDE for phenol

From Table 2 it can be seen that only for 2,4-dinitrophenol there is a contribution of the H-atom abstraction channel in its reaction with the Cl₂⁻ radical anion.

4. Conclusion

For reactions of X_2^- radical anions with aromatics in aqueous solution only few data are available in the literature. All reactions in this study have been investigated for the first time. The found rate coefficients are quite high and hence reactions with X_2^- radical anions may be a significant loss for aromatics in the aqueous tropospheric droplets.

In the course the reactions of X_2^- with aromatic compounds via electron transfer HO_2 radicals will be formed. These radicals may after dissociation react with ozone to form OH radicals. Similarly to the X_2^- radicals, OH radicals may react with aromatic compounds and again $HO_2\cdot / O_2^-$ radicals could be formed. Hence, X_2^- radical anions may initiate a chain reaction that may reduce the concentrations of aromatic compounds as well as ozone in aqueous droplets and hence in its surrounding gas phase.

5. Acknowledgements

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6. Literature

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