



Debromination of Bromobenzene Induced by Hydrated Electrons in Aqueous Solution

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The nanosecond laser flash photolysis (LFP) experiments were adopted to investigate the kinetics and mechanisms of the reaction between bromobenzene and hydrated electrons (e_{aq}) in aqueous solution. The results showed that the rate constants of first-order and second-order reaction were $6.3 \times 10^5 \text{ s}^{-1}$ and $1.7 \times 10^{10} \text{ L mol}^{-1} \text{ s}^{-1}$, respectively. The final products were biphenyl, bromobiphenyl and Br^- , which determined by gas chromatography-mass spectrometry (GC-MS) and ion chromatography (IC). The optimal structure of bromobenzene anion radicals, the bond lengths and bond angles were calculated and analyzed by time-dependent density functional theory (TD-DFT)-UB3LYP method and the primary absorption peaks of the anion radicals lied in the ranges of 250-600 nm. The main reaction pathway was speculated that bromobenzene molecules generated unstable anion radicals when attacked by hydrated electrons and then the molecules debrominated to generate benzene radicals and Br^- .

Keywords: Laser flash photolysis, Hydrated electrons, Bromobenzene, Anion radicals.

INTRODUCTION

Halogenated aromatic carbons (HACs) are important organic chemical raw materials, which are widely used for pesticides, pharmaceuticals, material synthesis, *etc.* They have been found in gases, smoke, airborne particles, surface and drinking waters, soils and sediments¹⁻⁵. The majority of these compounds are chlorinated and brominated. They are confirmed to have significant toxicological effects in liver, kidney and even the central nervous system of human^{6,7}. Hydrated electron addition to halogenated aromatic carbons is known to liberate halogen ion by dissociative electron capture process due to the high electron affinity of the halogen^{8,9}. In the literature, there were some studies concerning the reaction between hydrated electrons and halogenated aromatic compounds. Lichtscheidungl and Getoff¹⁰ demonstrated that the primary reaction pathway of halobenzene with hydrated electrons was gradual dehalogenation. Naik and Mohan⁹ confirmed that dehalogenation would be more easily when the radius of halogen substitution was larger and the electron affinity was stronger⁹. Higashino *et al.*¹¹ reported that the characteristic absorption spectra of fluorobenzene anion radicals lied in the ranges of 300-500 nm by radiolytic degradation experiments and time-dependent density functional theory (TD-DFT). However, less is known about the kinetic of hydrated electrons attachment to bromobenzene and the structure of the anion radical.

In this study, layer flask photolysis (LFP) experiments were adopted to investigate the kinetics of the reaction between bromobenzene and hydrated electrons in aqueous solution. The optimal structure of bromobenzene anion radicals, the bond lengths and bond angles were calculated and analyzed by time-dependent density functional theory (TD-DFT)-UB3LYP method. The final products were determined by gas chromatography-mass spectrometry (GC-MS) and ion chromatography (IC).

EXPERIMENTAL

Bromobenzene was of chromatographic purity (> 99 %) and purchased from J&K Technology Co., Ltd.; Pyrene-tetrasulfonate (PyTS) was of chromatographic purity (≥ 98.0 %) and purchased from Sigma-Aldrich; High-purity N_2 (99.999 %) was purchased from Shanghai Biou xi Gas Industry Co.. All experimental aqueous solutions were prepared with deionized water and pre-saturated with N_2 .

Experimental instruments and methods: The layer flask photolysis was carried out with a Quanta Ray LAB-150-10 Nd:YAG laser and the excitation wavelength was 355 nm. The details of layer flask photolysis were described previously¹². The laser pulse energy was measured by a Nova PE25BB-SH-V2 pyroelectric head (Ophir Optronics Ltd.). The sample was placed in the 1×1 cm quartz cuvette. All the experiments were performed under the temperature $25 \text{ }^\circ\text{C} \pm 1^\circ\text{C}$. To avoid secondary

photolysis of the sample by the analyzing light, suitable filters were employed.

Gas chromatography (7890A, Agilent, USA) coupled with a mass spectrometry (5975C, Agilent, USA) (GC-MS) was performed to identify the degradation products. GC-MS was equipped with a DB-5 MS column (30 m × 0.25 mm × 0.25 μm). Helium was used as the carrier gas at a constant flow rate of 1 mL min⁻¹. The GC temperature program was 60 °C (hold for 5 min) to 280 °C (hold for 10 min) at 5 °C min⁻¹. Both injection and ion source temperature were 250 °C. Before GC-MS analysis, 50 mL irradiated samples were extracted by 5 mL dichloromethane.

The concentration of Br⁻ generated from bromobenzene degradation was determined by IC, which consisted of a hydrophilic anion exchange column and an autosampler. A Dionex IonPac AS11 column (2 × 250/4 × 250 mm) and the eluent of 10 mM KOH at a flow rate of 0.33 mL min⁻¹ were employed. Injection volume was 10 mL.

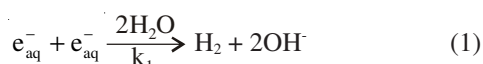
Calculation method: Density functional theory (DFT)-UB3LYP method in combination with the 6-31 + G (d,p) basis sets were used to obtain the structure and the optical properties (absorption peak and oscillator strength) of anion radical. All calculations were performed by a Gaussian 09 software package.

RESULTS AND DISCUSSION

Production of hydrated electrons: The laser flash photolysis of 9.83 × 10⁻⁵ M PyTS in N₂ saturated aqueous solution was performed and two-photon ionization process of PyTS occurred, which led to the formation of triplet PyTS (³PyTS), cation radicals (PyTS⁺) and hydrated electrons^{12,13}. The absorption bands of ³PyTS and PyTS⁺ were at < 500 nm (the absorption peak of the former was at 430 nm, the latter 510 nm). The broad and irregular absorption at 550-750 nm was attributed to the characteristic absorption of hydrated electrons (peak at around 700 nm). That is, the absorption at 690 nm was mainly caused by hydrated electrons and less interfered by other transient absorptions. Therefore, the kinetics of the reaction between hydrated electrons and bromobenzene in solution was analyzed based on the absorption changes at this particular wavelength.

Kinetics analysis of the reaction

Rate constant of first-order reaction: Based on the hydrated electrons absorbance at this wavelength (λ = 20560 mol L⁻¹ cm⁻¹)¹⁴, the concentration of hydrated electrons at the initial time of the reaction could be calculated as 3.8 × 10⁻⁶ mol L⁻¹. There were mainly three reactions where hydrated electrons were involved, as shown in eqns. (1), (2). In the solution, the concentrations of bromobenzene (4.2 × 10⁻⁵ mol L⁻¹) and pyrenetetrasulfonate (PyTS) in rate constant of first-order reaction (9.8 × 10⁻⁵ mol L⁻¹) were much greater than the concentration of hydrated electrons. Therefore, the eqns. (2) and (3) could be approximated to first-order reaction. Therefore, it could be seen that the decay of hydrated electrons was consistent with one second-order reaction and two quasi first-order reactions.



In summary, the concentration change of hydrated electrons in the solution was in agreement with eqn. (1):

$$-\frac{d[e_{aq}^-]}{dt} = k_1[e_{aq}^-]^2 + k_2[e_{aq}^-][BrB] + k_3[e_{aq}^-][PyTS] \quad (1)$$

$$-\frac{d[e_{aq}^-]}{dt} = k_1[e_{aq}^-]^2 + k_2[e_{aq}^-] + k_3[e_{aq}^-] \quad (2)$$

After integrating eqn. (2), the concentration change of hydrated electrons was obtained, as shown in eqn. (3):

$$[e_{aq}^-] = \frac{(k_2' + k_3')[e_{aq}^-]_0 e^{-(k_2' + k_3')t}}{k_1[e_{aq}^-]_0 (1 - e^{-(k_2' + k_3')t}) + (k_2' + k_3')} \quad (3)$$

Take $A_t(e_{aq}^-) = \epsilon l$ into eqn. (3) to obtain the absorbance change of hydrated electrons in the solution, as shown in eqn. (4).

$$A(e_{aq}^-) = \frac{\epsilon l (k_2' + k_3') A_0 [e_{aq}^-]_0 e^{-(k_2' + k_3')t}}{2k_1 A_0 [e_{aq}^-]_0 (1 - e^{-(k_2' + k_3')t}) + \epsilon l (k_2' + k_3')} \quad (4)$$

The study conducted by Huang *et al.*¹⁴ showed that $k_1 = (6.5 \pm 0.2) \times 10^9$ L mol⁻¹ s⁻¹ and k_1 was substituted into eqn. (4) and $k_2 = (9.7 \pm 0.3) \times 10^5$ s⁻¹ was obtained. The rate constant of the eqn (3) was $(2.7 \pm 0.1) \times 10^5$ s⁻¹, which was studied in our previous research¹². Therefore the first-order reaction constant of eqn (2) was $(7.0 \pm 0.3) \times 10^5$ s⁻¹ (Fig. 1).

Based on the rate constant of first-order reaction, it can be seen that at the initial time, the ratio of hydrated electrons consumption rate in reaction (1), (2) and (3) was:

$$k_1[e_{aq}^-] : k_2[e_{aq}^-][PyTS] : k_3[e_{aq}^-][BrB] = 1:11:25.5$$

Thus, at the initial time, the self-quenching reaction of hydrated electrons took up only a small proportion, while the reactions with bromobenzene and pyrenetetrasulfonate had contributed more greatly to the decay of hydrated electrons, where the rate of reaction with bromobenzene was about two times of that with pyrenetetrasulfonate.

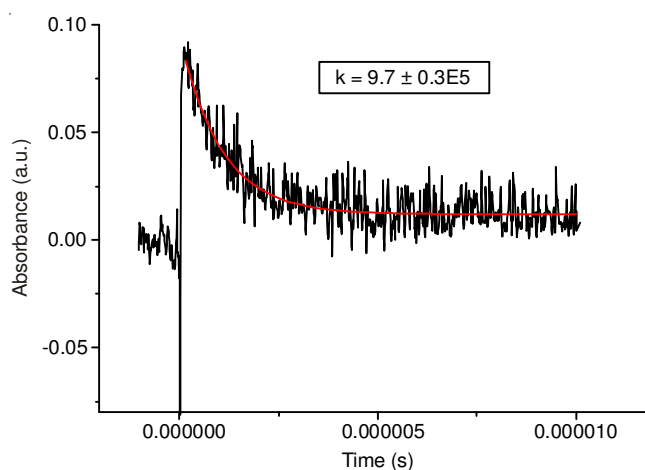


Fig. 1. Decay kinetic of hydrated electrons at 690 nm

Rate constant of second-order reaction: Using the calculation method as described, the rate constants of quasi first-order reaction between bromobenzene and hydrated electrons were obtained under different bromobenzene concentrations (19.8×10^{-5} , 15×10^{-5} , 4.2×10^{-5} , 2.9×10^{-5} and 0.8×10^{-5} mol L⁻¹) (Fig. 2). The rate constant of the second-order reaction between bromobenzene and hydrated electrons obtained as 1.7×10^{10} L mol⁻¹ s⁻¹ (shown in Fig. 3) and the findings were basically consistent with the results by Lichtscheidl and Getoff¹⁰, who employed the radiolytic degradation technology (1.0×10^{10} L mol⁻¹ s⁻¹).

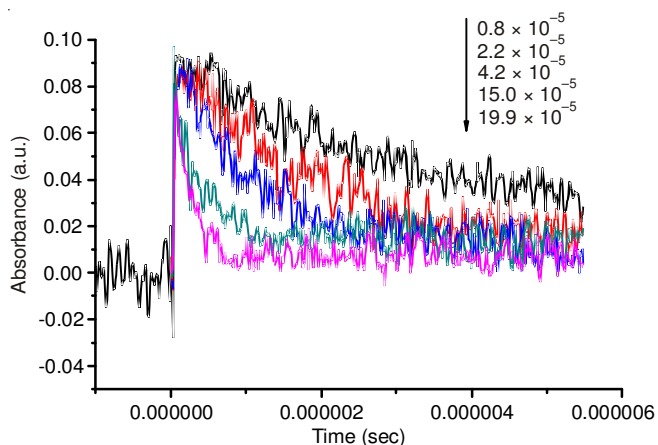


Fig. 2. Decay of hydrated electrons under different bromobenzene concentrations

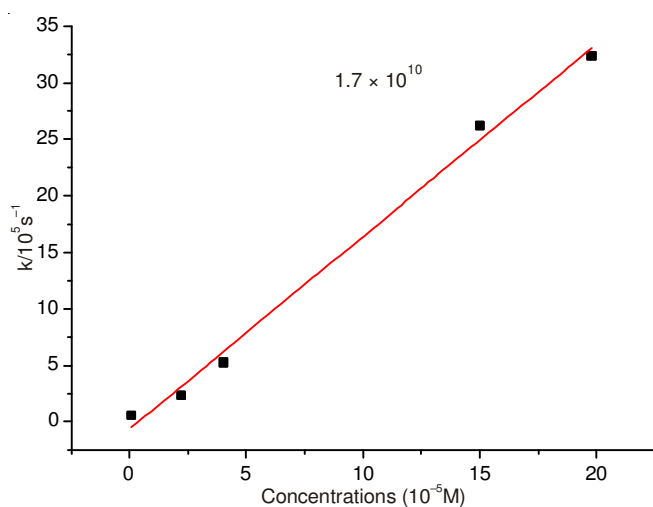


Fig. 3. Fitting of the rate constant of second-order reaction between hydrated electrons and bromobenzene

Analysis of product and reaction pathways: The pyrene-tetrasulfonate aqueous solution of bromobenzene was irradiated by 355nm laser for 10s and extracted to obtain the organic phase using dichloromethane. By using GC-MS detection, the chromatogram was obtained (Fig. 4). Apart from the bromobenzene peak at 5.75 min, unknown peaks at 12.93 min and 15.53 min were also detected. After analysis using NIST library, the substances corresponding to the two peaks were biphenyl and 2-brominated biphenyl, respectively.

In addition, bromide ions were detected by using ion chromatography after laser flash photolysis and therefore the products of the reaction between bromobenzene and hydrated

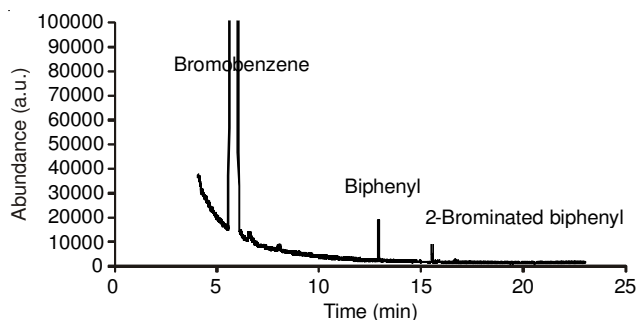


Fig. 4. GC-MS for the PyTS aqueous solution of bromobenzene after 355 nm laser flash photolysis

electrons were determined as biphenyl, 2-brominated biphenyl and bromide ions. It is probably due to the fact that bromobenzene concentration was greater and the laser energy was higher, hence resulting in a higher concentration of instantaneously generated benzyl radicals. These radicals had self-quenching reactions or reacted with bromobenzene in the solution to generate biphenyl and brominated biphenyl. Wu *et al.*¹⁵ showed that when radiolytic degradation occurred in halobenzene aqueous solution with high initial concentration, the instantaneously generated benzyl radicals could also reach a high concentration, generating biphenyl by self-quenching reaction. These were all consistent with our experimental results.

This study showed that debromination reaction occurred when bromobenzene reacting with hydrated electrons and the generated benzyl radicals could further react to generate biphenyl. The reaction pathway was inferred and shown in Fig. 5 (dotted line representing the inference result).

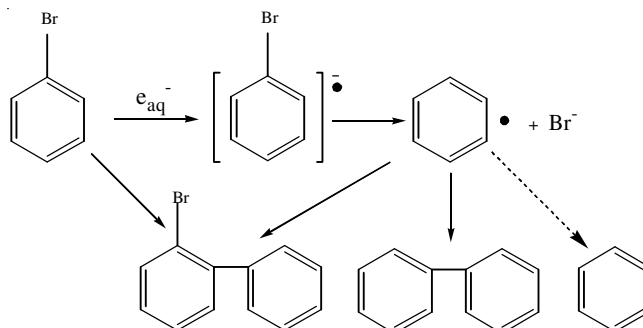


Fig. 5. Reaction pathway of bromobenzene and hydrated electrons

Bromobenzene anion radicals: The reaction mechanism of the hydrated electrons and halogenated aromatics were shown in eqn. (4) and (5): First, electron transfer occurred to hydrated electrons outside of the molecule and they entered the π^* orbital of lower energy of the halogenated aromatics. Then electron transfer occurred to the σ^* orbital of C-X and thus formed the unstable anion radicals. This reaction was the major step in the chain reaction where aromatic nucleophilic substitution occurred to free radicals^{16,17}. Although no absorption spectrum of anion radicals could be seen in the transient absorption spectrum of the laser flash photolysis experiment, we speculate that bromobenzene anion radicals were generated in the course of the reaction. UB3LYP method was used at 6-31 + G(d,p) basis set to optimize the structure of bromobenzene anion radicals (Fig. 6). The bond lengths, bond angles and absorption spectrum characteristics were calculated (Table-1).

TABLE-1
STRUCTURAL PARAMETERS OF BROMOBENZENE ANION RADICALS OPTIMIZED USING 6-31 + G(d,p) BASIS SET

	Bond lengths (Å)		Bond angles (°)	
	Anion radical	Bromobenzene ¹⁸	Anion radical	Bromobenzene ¹⁸
C1-C2	1.404	1.394	C1-C2-C3	119.9
C2-C3	1.391	1.391	C2-C3-C4	120.4
C3-C4	1.391	1.391	C3-C4-C5	119.9
C4-C5	1.404	1.394	C6-C1-C2	120.0
C5-C6	1.401	1.393	C6-C1-H7	119.8
C1-H7	1.090	1.085	C1-C2-H8	119.9
C2-H8	1.089	1.083	C3-C4-H9	120.1
C4-H9	1.089	1.085	C4-C5-H10	120.1
C5-H10	1.090	1.085	C1-C6-H11	120.2
C6-H11	1.088	1.083	C2-C3- Br12	-
C3-Br12	2.738	1.921	-	-

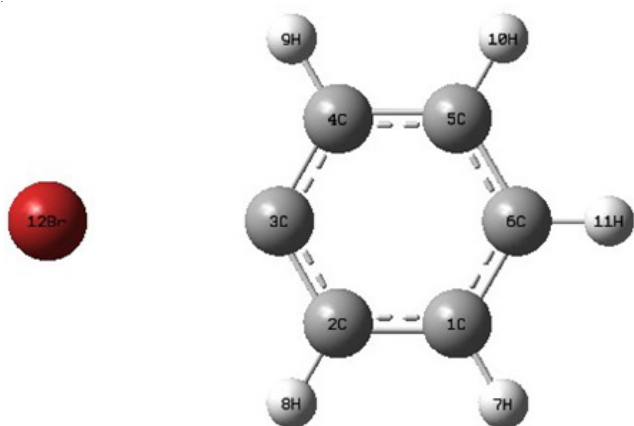


Fig. 6. Optimized structure of bromobenzene anion radicals



As seen from Table-1, the C-Br bond length of the anion radicals was 2.7381 Å, which was significantly lengthened as compared with bromobenzene. This was mainly due to the fact that when the σ^* bonds of C-Br were attacked by electrons, the electronegativity of Br was reduced, resulting in weakened covalent bonds and extended bond length. According to the bond angle data, the impact of bromine in anion radicals on benzene ring was reduced and the bromo-substituted C-C-C bond angle changed from 21.5° in bromobenzene to 20.4°.

It was also found that the absorption band of bromobenzene anion radicals was at 250-600 nm and the absorption peak appeared at 332 nm ($f = 0.2703$). Changes in absorbance at this particular wavelength was not observed during the experiment, suggesting that the C-Br bonds in anion radicals were broken within a very short period of time to form benzyl radicals and bromide ions. Beregovaya and Shchegoleva¹⁹

believed that electron transfer and dissociation of anion radical were simultaneous and previous results²⁰ showed that the electron binding energy of bromobenzene anion radicals was -0.70, with extremely fast dissociation rate and their life in gas phase was $<10^{-15}$ s. Therefore, the transient spectrum in nanosecond range was insufficient for the capture.

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