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Enhanced debromination of 4-bromophenol by the UV/sulfite process: Efficiency and mechanism

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ABSTRACT

Halogenated aromatic compounds have attracted increasing concerns due to their toxicity and persistency in the environment, and dehalogenation is one of the promising treatment and detoxification methods. Herein, we systematically studied the debromination efficiency and mechanism of *para*-bromophenol (4-BP) by a recently developed UV/sulfite process. 4-BP underwent rapid degradation with the kinetics accelerated with the increasing sulfite concentration, pH (6.1–10) and temperature, whereas inhibited by dissolved oxygen and organic solvents. The apparent activation energy was estimated to be 27.8 kJ/mol. The degradation mechanism and pathways of 4-BP were explored by employing N_2O and nitrate as the electron scavengers and liquid chromatography/mass spectrometry to identify the intermediates. 4-BP degradation proceeded via at least two pathways including direct photolysis and hydrated electron-induced debromination. The contributions of both pathways were distinguished by quantifying the quantum yields of 4-BP via direct photolysis and hydrated electron production in the system. 4-BP could be readily completely debrominated with all the substituted Br released as Br^-, and the degradation pathways were also proposed. This study would shed new light on the efficient dehalogenation of brominated aromatics by using the UV/sulfite process.

Introduction

Halogenated aromatic compounds (HACs) possessing C–X bonds (X = F, Cl, Br and I), are classified as an important category of synthetic organics extensively used in the synthesis of pharmaceuticals, pesticides and fine chemicals and ubiquitously occurring in the environment. They have raised serious concern for their toxicity, persistence, bioaccumulation and biomagnification (Commandeur and Parsons, 1991; Muir and Howard, 2006; Schwarzenbach et al., 2010; Van den Berg et al., 1998). As an important group of HACs, brominated aromatic compounds (BACs), such as brominated flame retardants (BFRs), tend to be bioaccumulated in human and animal tissues and pose potential risks to liver and thyroid homeostasis (Luo et al., 2010; Stubbings and Harrad, 2014; Sun et al., 2012; Weidlich et al., 2013; Zhuang et al., 2010, 2011), and thus, are under stringent control.

Recently, both oxidative and reductive debromination methods have been proposed to degrade BACs (Heeb et al., 2014; Huang et al., 2013; Keum and Li, 2005; Sun et al., 2013). However, debromination efficiency still needs further improvement, and toxic intermediates or products may be generated during both processes. For example, reduction of decabromodiphenyl ether (BDE209) by the nanoscale zerovalent iron usually leads to the formation of lower bromodiphenyl ether (Shih and Tai, 2010). Also, though brominated aromatics undergo direct photolysis, lower brominated diphenyl ether products, *e.g.*, 2,2′,4,4′-tetrabromodiphenyl ether, were generated and accumulated

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during the direct photolysis and pyruvate-assisted photolysis of BDE209 for the incomplete debromination (Jiang et al., 2014; Sun et al., 2008). Most of the recent reductive debromination methods are still challenged by the efficient and complete debromination (Lei et al., 2014; Li et al., 2007). Hydrated electron (e_{aq}^-), a powerful reducing species (E_0 = −2.9 eV), has shown great ability and promising perspective for reduction, dehalogenation, and detoxification of many refractory compounds, *e.g.*, perfluorochemical (Park et al., 2009). A recently developed method, UV/sulfite process, has a high efficiency in producing e_{aq}^- via Eq. (1) (Li et al., 2012, 2014). The process showed attractive reduction efficiency such as dechlorination (Li et al., 2014). The efficiency and feasibility of the UV/sulfite process were supported by the recent studies on the reduction of halogenated aliphatic compounds such as monochloroacetic acid, vinyl chloride, and perfluorochemicals (Li et al., 2012; Liu et al., 2013; Song et al., 2013). However, the dehalogenation efficiency for brominated aromatics by e_{aq}^- is still lacking due to the more complex mechanism of aromatics reacting with e_{aq}^- (Wentworth et al., 1967). Because of the potential risk arising from formation and accumulation of toxic intermediates of lower halogenation degree during treatment of halogenated aromatics (Jiang et al., 2014; Sun et al., 2008), efficiently complete dehalogenation is usually desirable.

$$SO_3^{2-} + h\nu \rightarrow SO_3^{\cdot-} + e_{aq}^- \quad (1)$$

Therefore, the objective of this study was to investigate the dehalogenation of brominated aromatics by the UV/sulfite process. We particularly focused on: (1) the removal efficiency and debromination kinetics, (2) the effects of the typical factors, and (3) the debromination mechanisms. 4-Bromophenol (4-BP) shows moderate direct photolysis and the mechanism has been clearly demonstrated previously (Grimshaw and De Silva, 1981; Joschek and Miller, 1966). Hence, 4-BP was selected as the model compound for its simple structure, *i.e.*, only one bromine atom substituted, which was believed to facilitate the analysis of intermediates and the insightful exploration of the dehalogenation mechanism by e_{aq}^-.

1. Materials and methods

1.1. *Materials*

All chemicals were purchased from commercial sources and used as received without further purification. 4-BP (99%) and sodium sulfite (99%) were of ACS reagent grade from Sigma-Aldrich, and methanol was of high-performance liquid chromatography (HPLC) grade from Merck. Nitrogen (N_2), oxygen (O_2), and nitrous oxide (N_2O) were of high purity (≥99.99%). All other reagents used were at least of analytical grade from Sigma-Aldrich or Sinopharm Chemical Reagent Co. Aqueous solutions were prepared with Milli-Q water (18.2 MΩ/cm).

1.2. *Experimental procedures*

Photolysis experiments were carried out in a borosilicate glass reactor with a low-pressure mercury UV lamp (10w, GPH212T5L/4, Heraeus Noblelight). For experiments requiring accurate control of temperature, another reactor equipped with a constant-temperature water circulator was used. The optical parameters of both reactors are shown in Appendix A Text S1. The photon flow (I_0, 254 nm) entering the solution was determined by the KI/KIO_3 method (Rahn, 1997) and the effective path length (*L*) was determined by the photolysis kinetics of dilute H_2O_2, as described previously (Beltran et al., 1995; Crittenden et al., 1999; Garoma and Gurol, 2005; Li et al., 2014). Oxygen-free conditions were realized by purging N_2 gas for at least 20 min prior to photolysis. Solution pH was adjusted by phosphate buffer (10 mmol/L, pH 5.0–8.0) or borate buffer (10 mmol/L, pH 8.5–10.5). Experiments were performed at 20 ± 2°C. All the experiments were repeated at least twice, and the average values along with a standard deviation are presented. More details concerning the photoreactor structure, experimental procedures, and methodology are available elsewhere (Bolton, 2000; Bolton and Linden, 2003; Li et al., 2012).

1.3. *Analytical methods*

Solution pH was determined by a pH meter (PB-10, Satorious). The concentration of H_2O_2 was determined by the I_3^- method (Klassen et al., 1994). The concentration of each BAC was measured on HPLC (Ultimate 3000, Dionex) equipped with an UV detector and a C18 column (4.6 mm × 100 mm, 3.5 μm particle size, Agilent Eclipse Plus). It was quantified at wavelength of 280 nm using the mobile phase of methanol/0.1% formic acid (80:20, *V/V*) at a flow rate of 0.5 mL/min. Bromide was detected by an ion chromatography (ICS-1100, Dionex) with 20 mmol/L KOH as the eluent and the self-regeneration suppressor (ASRS 300, Dionex) current was set at 50 mA. A Dionex AS19 column (4 × 250 mm) and a Dionex AG19 guard column (4 × 250 mm) were used for separation.

The mass spectra of degradation products were acquired using an Applied Biosystems Triple TOF 5600 (AB Sciex, USA) with an electrospray ionization (ESI) source. The degradation products were analyzed in negative and positive ESI source. AC18 column (4.6 mm × 100 mm, 3.5 μm particle size, Agilent Eclipse Plus) was used for separation. The mobile phase was methanol/water (80:20, *V/V*) at a flow rate of 0.2 mL/min, and the sample injection volume was 5 μL. The MS parameters were optimized and set as follows: source temperature, 550 °C; gas I, 55 arbitrary units; gas II, 55 arbitrary units; curtain gas, 35 arbitrary units; scan range (*m/z*), 50–800 amu. Negative ESI source: negative ion spray voltage, −4500 V; collision energy (CE), −10 V; decluttering potential (DP), −80 V; Positive ESI source: positive ion spray voltage, 5500 V; collision energy (CE), 10 V; and decluttering potential (DP), 80 V.

2. Results and discussion

2.1. *Degradation of 4-BP*

Fig. 1 shows that 4-BP underwent rapid direct photolysis, with the removal efficiency of about 83% within 20 min. The direct photolysis of 4-BP followed pseudo first-order kinetics with a rate constant of 0.0868 min^{-1}. The presence of sulfite enhanced the degradation of 4-BP markedly, and the degradation process also obeyed the pseudo first-order kinetics with a rate constant