Photocatalytic Decomposition of Decabromodiphenyl Ether (BDE-209) over BiOBr Driven by Visible Light: Kinetics and Intermediates

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Introduction

Polybrominated diphenyl ethers (PBDEs) have recently aroused global concern due to their increasing levels in the environment and biota, and potential adverse effects on wildlife and human (de Wit 2002; Norén & Meironyté 2000). Photolytic and biotic degradation of PBDEs have been reported previously (Ahn et al. 2006; Fang et al. 2008; Gerecke et al. 2006; Söderström et al. 2004). However, most studies have been focused on PBDE environmental transformation, and information on the potential method for eliminating PBDE contamination in the environment was limited (Li et al. 2007; Nose et al. 2007; Sun et al. 2009; Zhou et al. 2007). Bismuth oxyhalides (BiOX (X = Cl, Br, I)), a novel series of photocatalysts, have demonstrated excellent photocatalytic activities (An et al. 2008) and been successfully applied for sodium pentachlorophenate (PCP-Na) decomposition (Chang et al. 2010). Thus, the aim of the present study was to investigate the photocatalytic degradation of decabromodiphenyl ether (BDE-209), the major constituent in the commercial deca-PBDE product, over BrOBi driven by visible light in surfactant solution, in order to further our studies on the photodestruction of PBDEs in surfactant solutions (Li et al. 2008; Li et al. 2009).

Materials and Methods

BDE-209 (purity > 98%) was purchased from Tokyo Chemical Industry Co., Ltd. (Tokyo, Japan). Standard mixture solutions of 39 PBDE congeners (BDE-AAP-A-15X) and hexachlorobenzene (HCB) were obtained from AccuStandard Inc. (New Haven, CT, USA). Polybrominated dibenzofuran (PBDF) standard solutions were supplied by Cambridge Isotope Laboratories, Inc. (Andover, MA, USA). Hexane and methanol were of HPLC grade and obtained from J.T. Baker Inc. (USA) and Fisher Scientific Inc. (USA), respectively. Nonionic surfactant of Brij 35 (TM) was purchased from Amresco (USA). The catalyst of BiOBr was prepared according to the reference (Chang et al. 2010). The crystal structure of as-prepared catalyst was examined by XRD (Bruker D8 ADVANCE) with 2θ scope of 10-70° using Cu-Kα X-ray source (l = 0.15418 nm). UV-Vis DRS was measured at room temperature on a Hitachi U-3010 spectrophotometer by using $BaSO_4$ as reference. The absorption spectra were obtained by the reflectance spectra conversion based on the Kubelka-Munk method. The photocatalysis experiment was carried out in an XPA-Ⅱ photochemical reactor, using a 500 W Xe lamp or a 400 W metal halide lamp as the light source (Xujiang Electromechanical Plant, Nanjing, China). As for a typical photocatalytic process, 0.10 g as-prepared BiOBr powders were added into 250 mL 0.4 mM Brij 35 solution. The initial concentration of BDE-209 in Brij 35 solution was around 400 nM. Then, the suspensions were irradiated with continuous magnetically stirring. The slurries of

reaction mixture was taken out and centrifuged at 8000 r min^{-1} for 15 min. The supernatant was treated based on the method reported (Li et al. 2010). The precipitated BiOBr was extracted with 3.5 mL hexane and the extract was analyzed directly after the mixture was centrifuged. BDE-209 were quantified by GC-ECD (Agilent 6890 plus) using a DB-5 column (15 m × 0.25 mm × 0.25 μm). The temperature program was: 60℃, hold for 2 min, rate 15℃ min^{-1} to 140℃, hold for 1 min, and rate 8℃ min^{-1} to a final temperature of 300℃, hold for 15 min. 1 μL of sample was auto-injected in the high-pressure splitless mode (289 kPa for 2 min) at 280℃. The temperature of detector was 300℃. PBDEs and PBDFs as the possible photoproducts of BDE-209 were qualified by GC-MS (Shimadzu GCMS-QP 2010 Plus, Kyoto, Japan) equipped with a DB-5MS column (15 m × 0.25 mm × 0.10 μm). The injector parameters and oven program were the same as above. The temperatures of ion source and transfer line were 250 and 280℃, respectively. The EI mass spectra were recorded in SIM mode by measuring molecular fragment ions.

Results and Discussion

In the X-ray diffraction (XRD) pattern shown in Figure 1(a), all the diffraction peaks match well with the crystal structure of the tetragonal BiOBr phase (space group: P4/nmm (129), JCPDS No.: 78-0348), demonstrating the high purity of the as-prepared sample. Based on Tuac's approach (Guo et al. 2010), the bandgap of visible-light-response BiOBr photocatalyst was determined at 2.7 eV through its UV-Vis diffuse reflectance spectrum (UV-Vis DRS, as shown in Figure 1(b)).

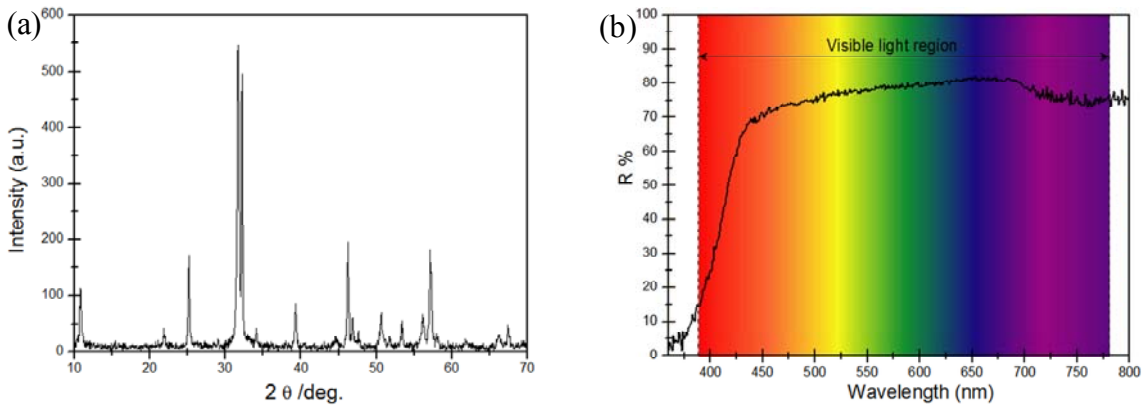

Figure 1. XRD pattern (a) and UV-Vis DRS spectrum (b) of as-prepared BiOBr photocatalyst.

Photodegradation of BDE-209 in 0.4 mM Brij 35 solution under different conditions was shown in Figure 2. About 30% of BDE-209 was photodecomposed in Brij 35 solution under Xe lamp irradiation (Figure 2(a)) after 30 min of irradiation. In contrast, significant degradation of BDE-209 was observed in the reaction system containing both Xe lamp and BiOBr, and almost no BDE-209 was detected in solution or on catalyst samples after 2 min of irradiation (Figure 2(b)). This suggested that the degradation of BDE-209 can be efficiently enhanced by BiOBr photocatalyst. A comparable degradation process also occurred with the presence of BiOBr while a metal halide lamp was used

(Figure 2(c)). According to the information provided by the manufacturer, the energy distributions of the Xe lamp and metal halide lamp were from 200 to 1200 nm and from 380 to 800 nm, respectively. As a result, the photocatalytic degradation of BDE-209 was actually achieved under visible light irradiation in the presence of BiOBr. Photoproducts of BDE-209 were tentatively studied. In solution samples, only three nona-BDEs (BDE-206, BDE-207 and BDE-208) were detected (Figure 3(a)). Nona-BDEs appeared in 0-min solution sample was probably the impurities in BDE-209 used for this study or the degradation products formed during analysis. Two PBDFs were found and identified as 2-monoBDF and 2,8-diBDF (Figure 3(b)). This indicated that the photocatalytic decomposition of BDE-209 in present systems may cause the formation of lower brominated PBDEs and PBDFs. On the other hand, no PBDE or PBDF photoproducts were found on catalyst samples.

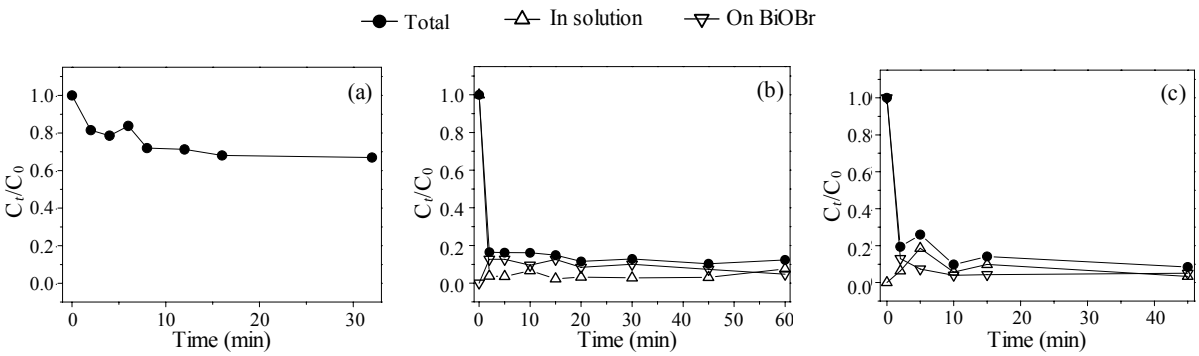

Figure 2. Photodegradation of BDE-209 in 0.4 mM Brij 35 solution under different conditions: (a) Xe lamp; (b) Xe lamp, 0.10 g BiOBr; (c) Metal halide lamp, 0.10 g BiOBr.

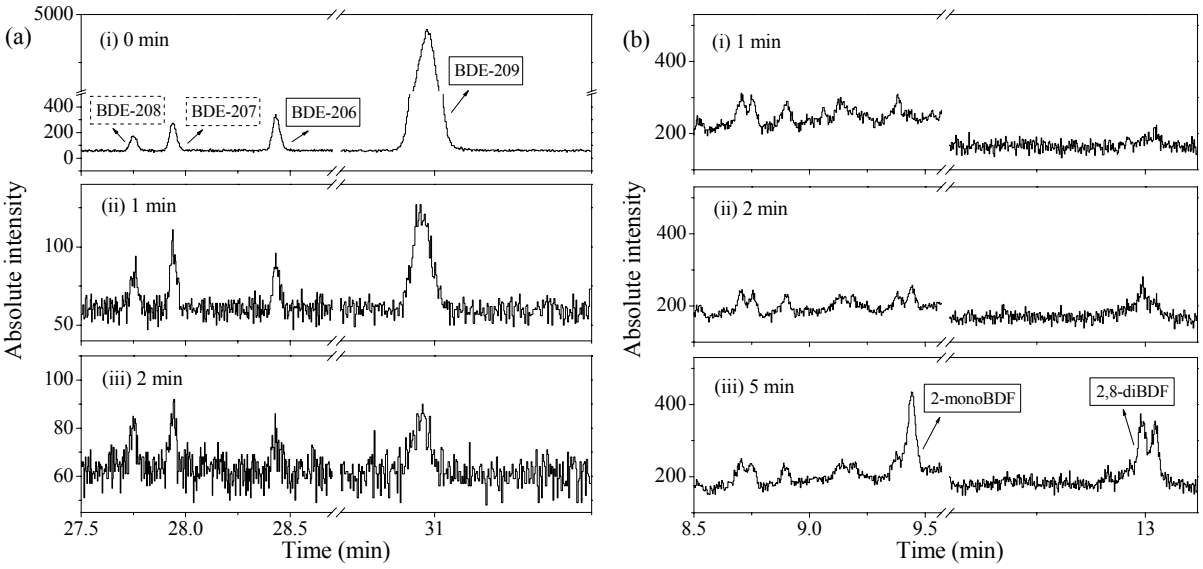

Figure 3. The extracted ion chromatograms of PBDEs (a) and PBDFs (b) as photoproducts of BDE-209 in solution samples irradiated for 0 min (i), 1 min (ii) and 2 min (iii), respectively

(Congeners in solid closed square were confirmed by analytical standards while in dash closed square were identified by mass spectra obtained by GC-MS).

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