



Photoreductive debromination of decabromodiphenyl ether by pyruvate



Zhaowu Jiang, Wensheng Linghu, Yimin Li, Chunyan Sun*

Department of Chemistry, Shaoxing University, Shaoxing 312000, Zhejiang, China

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ABSTRACT

Polybrominated diphenyl ethers (PBDEs) have aroused highly environmental concerns because of their toxicity and ubiquitousness in the biological and environmental system. Here, we report that decabromodiphenyl ether (BDE209) undergoes efficient reductive debromination reaction by pyruvate under UV irradiation (>360 nm). The photoreductive degradation kinetics of BDE209 has been further investigated under different reaction conditions. The debromination reactions occur in a stepwise process, producing a series of lower brominated congeners. The debromination shows unobvious position-selective property. The possible photoreductive mechanism has been proposed by UV–vis and kinetic isotope effect (KIE). This study not only provides a potential application of removal of PBDEs contaminations but also provides some information for the fate of PBDEs in environment.

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1. Introduction

Persistent organic pollutants (POPs) arouse significant scientific concern because they show persistent and bioaccumulative in the environment [1]. Polybrominated diphenyl ethers (PBDEs) have attracted particular attention in this field due to extensive use as flame retardants and global distribution. In recent years, PBDEs have been detected in sediments [2,3], marine organisms [4,5], food samples [6], and human mother's milk [7], even in Arctic animals [8,9]. Some researches indicated that PBDEs accumulated in the body could influence liver enzyme activity and neurological development at a key period of brain growth [10,11].

During the past few years, research on PBDEs has been greatly spread and mighty endeavors have been devoted to study the transformation of PBDEs in the environment. For example, photolytic debromination of PBDEs has been observed on the surface of clay minerals, metal oxides, silica gel, sand, soil and sediment [12,13], and in toluene, hexane or methanol/water [14–16]. The biotic reductive debromination has also been reported by anaerobic bacteria [17], juvenile rainbow trout and common carp [4,5]. Besides the studies on the environmental transformation of PBDEs, the development of potential methods for PBDEs removal in contaminated environmental system is another urgent and significant issue. Zerovalent iron reduction has been proven an effective

method for debromination of PBDEs [18–21]. Photocatalysis has also been studied for degradation of PBDEs [22–25]. For example, BDE209 could be a rapid photocatalytic debromination by TiO₂. Recently, it was found that BDE209 could be an efficient reductive debrominate under visible-light irradiation (≥420 nm) in the presence of various carboxylate anions [26]. This implies that some carbonylic species common in the environmental media may use to remediate PBDEs.

Pyruvic acid (2-oxopropanoic, PA) is widespread environmental carbonylic species, as ubiquitous components of surface water and the atmospheric aerosol. PA has been globally produced in the photochemical degradation of colored organic matter tinting rivers, lakes, and oceans and in the atmospheric oxidation of organic gas [27–29]. PA may undergo efficient photodecarboxylation via the excited triplet state, and excitation reaction by the n-π* band in aqueous PA induces its efficient photodecarboxylation. With R-cleavage of 3PA* into geminate radical pairs, the release of CO₂ follows during the subsequent reduction of PA [27,29]. These results imply that the n-π* excitation of PA might induce long-range electron transfer from the promoted carbonyl chromophore into neighboring carbonyl acceptors [29]. Considering that PBDEs can undergo reductive debromination, we realize that the long-range electron transfer from PA* might effectively reduce PBDEs to their lower bromo congeners under appropriate conditions.

In this paper, for the first time the photoreductive degradation of PBDEs by pyruvate has been investigated. BDE209 as the major product of PBDEs [1], was selected as a target PBDE. The photoreductive degradation kinetics of BDE209 has been examined. The photoreductive mechanism has been proposed on the

* Corresponding author at: No.508 Huancheng, West Road, Shaoxing, China.
Tel.: +86 575 8834 1521; fax: +86 0575 8834 1521.
E-mail address: sunchunyan@usx.edu.cn (C. Sun).

basis of experimental data. It not only provides a new method for degradation of PBDEs but also puts a new insight into the photochemistry of pyruvic acid and the fate of PBDEs in the environment due to pyruvic acid co-exist widely with the PBDEs in many environmental situations, such as the atmospheric aerosol.

2. Materials and methods

2.1. Materials

BDE209 was purchased from Aldrich Chemical Company (USA). BDE203, BDE204 and a standard solution of PBDEs (EO5103) were purchased from Cambridge Isotope Laboratories (CIL, Andover, MA). Pyruvic acid was purchased from Aldrich Chemical Company (USA). CH_3OD and CD_3OH were purchased from Cambridge Isotope Laboratories. HCl, NaOH, tetrahydrofuran, hexane, methanol were analytical reagents (Chemical Co., Shanghai). They were used without further purification. Deionized and doubly distilled water was used throughout the study.

2.2. Methods

2.2.1. Experimental setup

BDE209 stock solution (1×10^{-3} mol/L) in tetrahydrofuran was diluted with methanol to 1×10^{-5} mol/L. 0.05 mL pyruvic acid aqueous solution (1×10^{-2} mol/L) was added to 10 mL BDE209 methanol solution in a Pyrex vessel. Reaction solutions were magnetically stirred during the irradiation. The Pyrex vessel was purged with argon for 30 min to remove O_2 and protected under argon atmosphere during the irradiation. A PLS-SXE300 Xe lamp (Beijing Trusttech Co. Ltd.) was used as the light source. To eliminate the direct photolysis of BDE209, a cutoff filter was used to cut the irradiation below 360 nm. To investigate the effect of acids/bases and H_2O on the reaction kinetics, a given amount acid/base and H_2O were added under otherwise identical conditions. At given time intervals, 1 mL aliquots were used for analysis.

2.2.2. HPLC analysis

BDE209 in samples was quantified with a SHIMADZU HPLC system (LC-20AT pump and UV-vis SPD-20A detector) with a DIKMA Platisil ODS C-18 column (250×4.6 mm, 5 μm film thickness). The mobile phase was 2% water in acetonitrile at 1 mL/min and the detector wavelength was set at 240 nm. The quantification of BDE209 used a calibration curve with BDE209 standard.

2.2.3. GC- μECD analysis

Products were detected by GC- μECD analysis. The products were extracted by hexane and the internal standards pentachlorophenol (PCP) were added to all samples before the analysis with gas chromatograph (GC) (Agilent 7890A) equipped with an electron capture detector (ECD) (Agilent Technologies Co. USA) and a programmable pressure on-column injection port and a DB-5 capillary column (30 m \times 50 μm , i.d. \times 0.1 μm film thickness). Splitless 10 μL injection was performed manually at 300 $^\circ\text{C}$. The carrier gas was helium at a constant flow rate of 1.0 mL/min. The oven temperature was kept at 100 $^\circ\text{C}$ for 2 min, increased at 15 $^\circ\text{C}/\text{min}$ to 230 $^\circ\text{C}$, then increased at 5 $^\circ\text{C}/\text{min}$ to 270 $^\circ\text{C}$, and finally increased at 10 $^\circ\text{C}/\text{min}$ to 320 $^\circ\text{C}$ for 10 min. The standard samples of BDE203, BDE204 and PBDEs (EO5113) were used to identify the degradation products.

2.2.4. UV-vis absorption spectra

UV-vis absorption spectra were conducted with 10×10 mm quartz cuvettes by a Hitachi U-3010 spectrophotometer (Hitachi Co. Japan) under anoxic conditions.

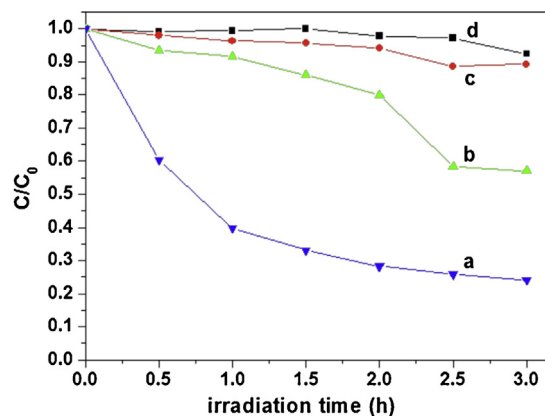


Fig. 1. Temporal curves of the photodegradation of BDE209 under different conditions. BDE209: 1.0×10^{-5} mol/L, sodium pyruvate: 5.0×10^{-5} mol/L, solvent: methanol/THF/ H_2O (V/V: 100/1/0.5); wavelength >360 nm; (a) BDE209/sodium pyruvate/Ar/UV, (b) BDE209/sodium pyruvate/air/UV, (c) BDE209/sodium pyruvate/Ar/heat (50 $^\circ\text{C}$ by water bath), (d) BDE209/Ar/UV.

3. Results and discussion

3.1. Degradation kinetics

To eliminate direct photolysis of BDE209 [15,16], the irradiation below 360 nm was filtered completely. The degradation of BDE209 was scarcely observed in methanol solution without pyruvate under the UV irradiation (Fig. 1d and Fig S1). BDE209 exhibited little degradation when the reactions were carried out in the presence of pyruvate but under the air-saturated condition (Fig. 1b). However, rapid degradation of BDE209 occurred in the anoxic BDE209/sodium pyruvate solution under UV irradiation, and more than 60% of BDE209 disappeared after 1 h of irradiation (Fig. 1a). The kinetics was fitted by pseudo-first-order process, giving a rate constant of $0.54 \pm 0.02 \text{ h}^{-1}$ ($t_{1/2} = 0.8$ h). By contrast, the reaction system containing sodium pyruvate in the dark heating in water bath under anoxic condition showed no disappearance of BDE209 (Fig. 1c). It indicated that the degradation was initiated by pyruvate-based photoreductive reaction and oxygen would decrease the degradation rate.

3.2. Product analysis

The product analysis by GC- μECD showed that the degradation of BDE209 by sodium pyruvate led to the formation of its lower brominated congeners in a stepwise way (Fig. 2). Before the irradiation, the only dominant GC peak was from BDE209, with trace nona-BDEs due to impurity. After 0.5 h, nona-BDEs appeared as main intermediates. Nona-BDEs and octa-BDEs appeared as main intermediates, concomitantly with the significant decrease of BDE209 after 1 h. After irradiation of 14 h, the octa-BDEs and hepta-BDEs were measured as the dominant intermediates. All PBDE congeners with more than octa-BDEs vanished, and transformed to hexa-BDEs penta-BDEs at further prolonged irradiation.

The degradation products were identified with chemical standards (Fig. 3). The first step was the loss of one bromine atom to form three nona-BDEs. After 0.5 h, all nona-BDEs appeared, which was identified to be BDE208, 207, and 206, respectively, according to their well-established GC elution orders [30,31]. There were five octa-BDEs observed after 2 h. BDE203 and BDE204 were identified by the chemical standards. The peak with a retention time slightly longer than that of BDE203 was BDE196, according to the relative retention times and the orders of GC elution obtained from the literatures [23,30,31]. Six hepta-BDEs were detected after 14 h of irradiation. BDE183, BDE181 and BDE190 were identified

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