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Photodebromination behaviors of polybrominated diphenyl ethers in methanol/water systems: Mechanisms and predicting descriptors

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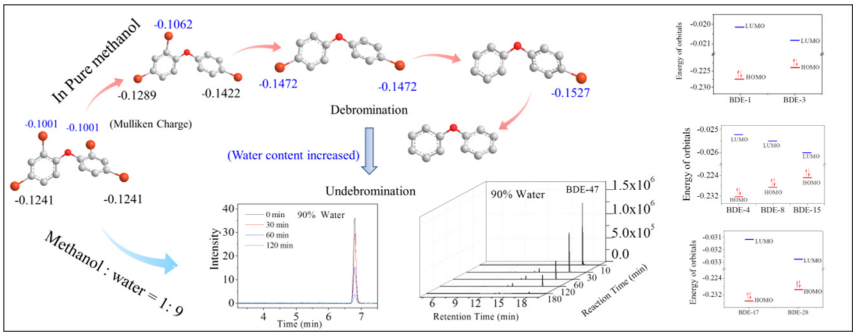
HIGHLIGHTS

- PBDEs with a narrower HOMO-LUMO gap tend to degrade faster than other BDE isomers.
- Mulliken charge is a good descriptor to predict the debromination pathways of PBDEs.
- The higher water content changed the degradation manner of PBDEs in methanol/water system.
- The debromination pathways of BDE-47 are consistent in various solvent.

GRAPHICAL ABSTRACT



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ABSTRACT

This study investigated the photodebromination behaviors of polybrominated diphenyl ethers (PBDEs) in methanol or methanol/water systems. The kinetics of three sets of bromated diphenyl ether (BDE) isomers were compared in the same reactors, and the results showed that the PBDE isomers with lower energy of lowest unoccupied molecular orbital and higher energy of highest occupied molecular orbital will be degraded faster by ultraviolet (UV) light than other BDE isomers. The overall debromination pathways of 2,2′,4,4′-tetrabromodiphenyl ether (BDE-47) were elucidated, and we found that the bromine substituents with higher Mulliken charges were preferentially removed. This demonstrated that Mulliken charges can be used to predict the photodebromination pathways of PBDEs. In methanol/water systems, when the ratio of methanol and water decreased, the degradation rate of BDE-47 decreased, whereas that of diphenyl ether increased. This phenomenon can be attributed to the mechanism of photodegradation of PBDEs gradually shifting from the reductive debromination to the undebromination process as the ratio of methanol and water decreases. The chromatogram of high-performance liquid chromatography and gas chromatography–mass spectrometry during this process also verified this explanation. The debromination pathways of BDE-47 are consistent in methanol/water systems with different methanol to water ratios and in different organic solvents.

1. Introduction

Polybrominated diphenyl ethers (PBDEs) are a class of brominated flame retardants (BFRs), which have been widely used in electronics,

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textiles and other products due to their popularity for fire prevention (Alaee et al., 2003; Rahman et al., 2001; de Wit, 2002). PBDE belong to category of additive BFR that easily leaches from electronic products and thus is more readily released into the environment. It has been reported that PBDEs are present in numerous matrices, such as water, air, soil, sediment, birds, fish and human blood (Pan et al., 2016; Klosterhaus et al., 2012; Moon et al., 2012; Kim et al., 2013; Wang et al., 2013; Yang et al., 2013; Fromme et al., 2014). PBDEs can cause endocrine disruption, and neurotoxic effects in various species, such as fish and human beings (ManchesterNeesvig et al., 2001; Stapleton et al., 2011). Due to their existence in various environmental matrices and their potential toxicity to humans and wildlife, numerous studies have investigated the environmental fate and treatment technologies for PBDEs, such as adsorption (Liu et al., 2012; Olshansky et al., 2011), photodegradation (Eriksson et al., 2004), advanced oxidation process (Shi et al., 2015), and zero-valent iron degradation (Zhuang et al., 2011).

Among these environmental processes, photodegradation has received a great deal of attention due to the potential generation of brominated congeners and other derivatives, some of which, like polybrominated dibenzo-*p*-dioxins and dibenzofurans (PBDD/Fs), are even more toxic than PBDEs themselves (Eriksson et al., 2004; Birnbaum et al., 2003; Rayne et al., 2006; Altarawneh and Dlugogorski, 2013). PBDEs are highly hydrophobic and show a strong affinity for organic matter, with log K_{ow} of PBDEs ranging from 5.55 to 12.11 (Usenko et al., 2011). Therefore, organic solvents are used for simulating a lipophilic environment. Numerous studies have focused on the photodegradation of PBDEs in such solvents, including methanol, acetonitrile, hexane and tetrahydrofuran (THF), etc. (Eriksson et al., 2004; Rayne et al., 2006; Rayne et al., 2003; Soderstrom et al., 2004; Fang et al., 2008; Christiansson et al., 2009; Davis and Stapleton, 2009; Xie et al., 2009). However, some aspects are not fully understood as yet, and these are summarized as follows: 1) differences between the kinetics of BDE isomers are not fully understood and explained; 2) the overall debromination pathways of one common BDE congener (i.e. 2,2′,4,4′-tetrabromodiphenyl ether (BDE-47)) was not established, and a useful descriptor to predict the debromination pathway of PBDEs by UV light is needed; 3) the effect of water on the photodecomposition kinetics and mechanism is still unclear; and 4) the effect of solvent on the debromination pathway of PBDEs has not been well demonstrated.

In this study, all these questions were investigated through the case study of the photodecomposition of PBDEs in methanol/water systems or in other organic solvents. The objectives were 1) to compare the kinetics of several pairs of isomer BDEs in methanol and use quantum insight to explain the differences; 2) to obtain the comprehensive debromination pathway of BDE-47 and develop a quantum descriptor to predict the debromination pathway of PBDEs by UV light; 3) to elucidate the effect of water on the degradation kinetics and mechanisms of BDEs by UV light; and 4) to verify whether the debromination behaviors of PBDEs change in different organic solvents.

2. Material and methods

2.1. Materials

PBDEs standards (i.e. BDE-47, BDE-28, BDE-17, BDE-15, BDE-8, BDE-7, BDE-4, BDE-3, BDE-1, DE) were purchased from AccuStandard, Inc., USA. HPLC grade methanol, hexane, acetonitrile, isooctane, acetone and tetrahydrofuran were obtained from Anpel Laboratory technologies, Inc. (Shanghai, China).

2.2. UV irradiation experiments

The photodegradation experiments were performed in 22 mL quartz glass vessels. The vessels were placed around a 100 W mercury lamp in a photoreactor (Fig. S1). The lamp was set in a cold well to keep the temperature around 25 °C.

To help improve our understanding of the difference between the kinetics of BDE isomers, three sets of BDE isomers (i.e. BDE-28 and BDE-17; BDE-15, BDE-8 and BDE-4; BDE-3 and BDE-1) were selected to conduct the photodegradation experiments. Experiments comparing of different isomers as in previous studies (such as BDE-99 and BDE-100; BDE-47 and BDE-75) were all conducted separately in different reactors. Considering the short photoreaction time in methanol and the similar chemical properties of the isomers involved, the results could be influenced greatly by small differences in conditions among separate reactors. Therefore, we spiked the isomers into the same reactor to avoid any such differences that might affect the result, thereby, generating more precise information to elucidate this phenomenon.

For the photodegradation experiment of BDE-47 and its debromination products (i.e. BDE-28, BDE-17, BDE-15, BDE-8, BDE-7, BDE-4, BDE-3, BDE-1, DE), all of the BDE standards were prepared in pure methanol, which were presented at 5 ppm. At selected times, 0.5 mL solution was sampled for gas chromatography–mass spectrometry (GC–MS) analysis.

To determine the effect of water content on the photodegradation of BDE-47 and DE, the methanol contents were 10%, 30%, 50%, 70% and 100%. The vessels were then placed in the photoreactor. At selected times, 0.5 mL solution was sampled directly for HPLC analysis; another 0.5 mL of solution was taken out and extracted by 1 mL hexane three times. The extracts were blended and evaporated using a gentle nitrogen gas, and then, 1 mL isooctane was added to re-dissolve the pollutants. GC–MS was used to analyze the target pollutants. The recovery for the extraction of BDE-47 by hexane was between 82.2% and 97.3%.

For the degradation of BDE-47 in different organic solvents, 2 mL 50 ppm BDE-47 acetone solution was added in 22 mL quartz reactor, and then the solvent was evaporated by gentle nitrogen gas, 20 mL organic solvent (i.e. tetrahydrofuran, hexane, isooctane, acetonitrile) were separately added in the reactor to re-dissolve BDE-47. The reaction procedures were the same as described above.

2.3. Instruments

The concentration changes in the parents BDEs were analyzed on an Agilent 1260 HPLC equipped with a UV detector and a C_{18} reversed-phase column. The detection wavelength was set at 226 nm, and the mobile phase was acetonitrile and water (90:10). The flow rate was 1 mL min^{-1} and the injection volume is 20 μL.

Products analyses were performed on a GC–MS, which coupled a Thermo-Trace GC Ultra instrument to a Thermo-DSQ II mass spectrometer (Thermo-Electron Corporation, Waltham, USA). The electron impact ionization mode was set at an electron energy of 70 eV. A 30-m DB-5MS capillary column (0.25 mm i.d., 0.25 μm film thickness) was used for the separation. Helium gas (1.0 mL min^{-1}) was used as the carrier gas. A 1 μL sample was injected into the GC–MS in a splitless mode. The temperature of the injection inlet was set to 280 °C. The temperature of the oven was maintained at 100 °C for 1 min, increased by 20 °C/min to 210 °C, and then by 4 °C/min to 260 °C for 10 min. The quantification of identified degradation products was acquired in a selected ion monitoring (SIM) mode. The quadrupole temperature and ion source temperature were set at 250 °C and 280 °C, respectively. Data processing was performed by Xcalibur software (Thermo Fisher, US).

2.4. Computational methods

The initial BDE structures were obtained by drawing certain PBDEs on a Chemdraw package then preliminarily optimized with MOPAC with AM1 theory on Chem3D package. The initiating structure was then optimized using the Gaussian 09 program (Frisch et al., 2003) with the density functional theory (DFT), Becke, three-parameter, Lee-Yang-Parr (B3LYP) method, in conjunction with 6-31G (d), a split-valence basis set with polarization function (Becke, 1993; Hehre et al., 1972). Previous studies have demonstrated that the values of the