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Experimental and theoretical investigations on debromination pathways of polybrominated biphenyls (PBBs) under ultraviolet light

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HIGHLIGHTS

- PBB-29 preferentially debrominate *para*-bromine substituent under UV light.
- Four quantum descriptors of PBBs were correlated well with their pathways.
- Debromination pathways of PBBs are based on the brominated arrangement pattern.
- Debromination prefers to occur on the benzene ring with more bromine substituents.

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ABSTRACT

Polybrominated biphenyls (PBBs) are brominated flame retardants that are widely used in textiles and electronic products. Recently, many researches have been devoted to determining their concentrations in food and in the environment. Yet, their degradation behavior has been less investigated and is not well understood. Here, we have investigated the debromination pathways of PBBs by (UV) light in the case of 2,4,5-tribrominated biphenyl (PBB-29). Our investigation indicates that *para*-bromine substituent on PBB-29 was preferentially removed. By means of density functional theory (DFT), we found that the energies of the debromination products, the C—Br bond length in the excited state (S_1), the Mulliken charge of bromine in S_1, and the lowest unoccupied molecular orbital (LUMO) in S_1 correlated well with the debromination pathways of PBBs. Further, LUMO-based prediction of PBB debromination pathways in S_1 suggests that the bromine substituent on all brominated positions (i.e. *ortho*-, *meta*- and *para*-) can be preferentially removed, as the debromination sequence is not based on the brominated position but on the specific brominated arrangement pattern. In addition, reductive debromination preferentially occurs on the benzene ring that has the highest number of bromine substituents. This study provided useful descriptors to predict the debromination pathways of PBBs, and the theoretical result greatly improve our understanding of photolytic debromination of PBBs.

1. Introduction

Polybrominated biphenyls (PBBs) are a class of brominated flame retardants that are widely used in the production of electronic products and plastics for preventing these materials from burning (de Wit, 2002). In the early 1970s, a serious industrial accident in Michigan, USA, resulted in the contamination of the local food supply with PBBs (Thomas et al., 2001), which posed a great risk to human health. Although PBBs have not been produced in most countries, they are widespread as a result of their

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environmental persistence (Chang et al., 2017; Jacobson et al., 2017; Li et al., 2018). Similar to polychlorinated biphenyls (PCBs) and polybrominated diphenyl ethers (PBDEs), PBBs are hydrophobic, bioaccumulative, and persistent. They also have various adverse effects on ecosystems and human health, including the disruption of normal hormone function and suppression of the immune system (Lauby-Secretan et al., 2013). Therefore, research is needed to understand the transformation mechanisms and environmental fate of these compounds when they were released into the environment.

Numerous studies have been carried out on the degradation kinetics and pathways of halogenated aromatic compounds (HACs). However, most of these studies focused on PBDEs (Huang et al., 2017; Wang et al., 2017d, 2018b) and PCBs (Tang et al., 2018b), PBBs received rather less attention. Photochemical reactions are important processes for the degradation of HACs(Wang et al., 2017a, 2017b, 2018a), and dehalogenation is usually the dominant mechanism in these processes (Luo et al., 2015a; Wang et al., 2017c). A previous study investigated the photodegradation of 4,4′-dibromobiphenyl (PBB-15) on titanium dioxide (TiO_2) and doped TiO_2 nanotube arrays, and found that this compound was debrominated in a step by step manner (Liu et al., 2011). However, PBB-15 only has two *para*-bromine substituents, thus, our understanding regarding the debromination sequence of bromine substituents at different positions (i.e., *ortho*-, *meta*- and *para*-) was limited. Therefore, PBB congeners with *ortho*-, *meta*- and *para*-bromine substituents should be selected to investigate their debromination kinetics and pathways under ultraviolet (UV) light.

However, most PBB congeners are not commercially available, and even if they are available, it is very costly and time-consuming to accurately determine the debromination pathways of PBBs. Therefore, other methods are needed to address this problem. The molecular properties of organic pollutants are highly related to their environmental behaviors (i.e., kinetics and reaction pathways). Fortunately, previous studies have found that the physicochemical properties of HACs are predictable by their molecular properties. Luo et al. (2015a) reviewed the structure-property relationships between dehalogenation of persistent halogenated organic compounds and their molecular properties. Keum and Li (2005) found that 2,2′,4,4′,6-pentaBDE (BDE-100) preferentially generates debromination products with lower heat of formation by n-ZVI. Lu et al. (2010) have found that the dechlorination pathways of 1,2,3,4-tetrachlorodibenzo-p-dioxin (1,2,3,4-TCDDs) by zero-valent zinc are correlated with the Mulliken charges of chlorine substituents. Luo et al. (2013) have found that the elongated bond of the BDE-21 anion correlated with their debromination pathways. In addition, our previous studies revealed that the singly occupied molecular orbitals (SOMOs) of the BDE anions can well reflect the actual debromination pathways of PBDEs in zero-valent zinc systems by comparing the size of the C–Br antibonding characterized lobes (Tang et al., 2018a). We note that there are also several pure computational studies regarding the dehalogenation of HACs (Cao et al., 2015; Fu et al., 2016; Hu et al., 2005; Luo et al., 2015b; Wang et al., 2012), but no experimental data can support these computational results, which greatly weaken the validity of the study's conclusions.

In this study, 2,4,5-tribromobiphenyl (PBB-29) was selected as target PBB congener, which has three bromine substituents separately located on the *ortho*-, *para*- and *meta*-positions. The debromination pathways of PBB-29 and its debromination products were investigated. In addition, the molecular properties (i.e. bond length, Mulliken charges, bond energies, heat of formation and molecular orbitals) of PBB molecules in ground and excited states were calculated, and a relationship between the debromination pathways of PBBs and their molecular properties was discussed.

2. Experiment

2.1. Materials

PBB-29, 2,5-dibromobiphenyl (PBB-9), 2,4-dibromobiphenyl (PBB-7), 4-monobromobiphenyl (PBB-3), 3-monobromobiphenyl (PBB-2), 2-monobromobiphenyl (PBB-1) and biphenyl in their pure form were purchased from AccuStandard, Inc., USA. The congener names, nomenclatures and structures of PBBs that were used in this study are listed in Table S1. High-performance liquid chromatography (HPLC) grade methanol was obtained from ANPEL Laboratory Technologies, Shanghai, China. All of the PBB congeners were prepared as stock solutions ($100\ mg\ L^{-1}$) in methanol.

2.2. Debromination of PBBs in methanol under UV light

Fig. S1 shows the sketch of the photoreactor instrument, which contains a 100 W UV lamp and a circulating water cooling system. In a quartz tube, a 20 mL $5\ mg\ L^{-1}$ PBB methanol solution was added. This tube was placed around the UV lamp. The distance between the lamp and tubes was 12 cm. At selected time intervals, a 0.5 mL solution was taken out for analysis.

2.3. Instrument methods

The parent PBB congener was analyzed by an Agilent 1260 HPLC system, with a Phenomenex. LunaC18 column (250 mm. × 0.4.6 mm, 5 μm film thickness). The mobile phase was acetonitrile/water (95:5), and the detector wavelength was set at 226 nm. The debromination products of the PBBs under UV light were analyzed by a Thermo Fisher Scientific gas chromatography (GC) system (GC Ultra) coupled with a dual-stage quadruple mass spectrometry (DSQ II). TG-5 MS GC column (30 m × 0.25 mm × 0.25 μm film thickness, Thermo Fisher, Inc., USA) was used for separation. The carrier gas was helium (99.999%) and a constant flow of $1.5\ mL\ min^{-1}$ was applied. The injection volume was 1 μL with a splitless mode and the injection port temperature was set at 280 °C. The over temperature was programmed from 100 °C (held for 1 min) to 189 °C (held for 3 min) at a rate of $8\ ^{\circ}C\ min^{-1}$, and then to a final temperature of 280 °C at a rate of $25\ ^{\circ}C\ min^{-1}$.

2.4. Computational methods

The structure of PBB molecules or radicals in ground states (S_0) or excited states (S_1) were optimized by the Gaussian 16 software program (Frisch et al., 2016). APFD hybrid functional and time-dependent APFD were selected as computational methods for calculating PBBs in S_0 and S_1, respectively, and 6-311 + G(d) was selected as the basis set. The vibrational frequency of each structure was also obtained to confirm the structures corresponded to minima on the potential energy surface. Since the geometries of PBBs in S_1 in gas phase and in methanol are not significantly different (Fig. S2), we mainly discussed the geometries of PBBs in gas phase. GaussView 6 was used to visualize the molecule structures, Mulliken charges, bond length and molecular orbitals.

3. Results and discussion

3.1. Debromination pathways of PBBs in methanol under UV light

PBB-29 and its potential debromination products can be completely separated by our GC method (Fig. S3). As shown in Fig. S4, when PBB-29 was exposed to UV light, its concentration decreased and its debromination products were observed in the