Photolytic degradation of polybromodiphenyl ethers under UV-lamp and solar irradiations

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ABSTRACT

Polybromodiphenyl ethers (PBDEs) are widely used flame retardant additives and have been mainly used in polymers for many plastic and electronic products. PBDEs have been found to bioaccumulate in both aquatic and terrestrial ecosystems and even human bodies. The technical product with the highest use is decabrominated diphenyl ether (BDE-209). Therefore, we chose to examine the solar and UV-lamp degradation of BDE-209. A linear increase of the photodegradation rate constant for BDE-209 was observed with the solar light intensity. The degradation reactions follow the pseudo-first-order kinetics. The photodegradation of BDE-209 produced other less brominated diphenyl ethers under ultraviolet light exposure, suggesting that the photodegradation of BDE-209 is a sequential dehalogenation mechanism. BDE-209 underwent rapid reductive debromination in these photodecomposition experiments. The formation rate constants of three nonabromodiphenyl ethers increase with the order of BDE-206, BDE-207 and BDE-208, indicating debromination mainly occurred at *para > meta > ortho* positions. These findings of the process properties and reductive debromination mechanism of the photolytic degradation of PBDEs can facilitate the design of remediation processes and also aid in predicting their fate in the environment.

1. Introduction

There have been serious concerns about polybromodiphenyl ethers (PBDEs) in the environment because they show a high potential for bioaccumulation in mammals, fish, and human bodies worldwide [1]. PBDEs were the most commonly used additive brominated flame retardants and have been used in many industrial and domestic applications such as building materials, vehicles, furniture, carpets, electronic circuit boards, etc. [2]. They are resistant towards acids and bases as well as heat and also to reducing or oxidizing chemicals [3]. Waste disposal is one of the ways that PBDEs are released to the environment. Leachate, ash, and air emission from landfills and incineration where products containing PBDEs have been disposed can become possible sources of emission of these brominated flame retardant compounds to the environment.

PBDEs cause neurodevelopmental toxic effects and have been identified as endocrine disruptors [4]. PBDEs are biomagnified in the environment. Comparatively high levels of PBDEs are constantly found in aquatic biotopes from different parts of the world. They have been detected frequently in sediments, sludge, fish and mammals [5–9]. In China, the country's birds of prey have

some of the highest levels of PBDEs ever recorded in animals [10]. Meng et al. [11] reported that human in China exposure to PBDEs via inhalation was relatively high compared with similar studies in other countries. The major PBDEs found in environment samples are 2,2′,4,4′-tetrabromodiphenyl ether (BDE-47), 2,2′,4,4′,5-pentabromodiphenyl ether (BDE-99), and 2,2′,4,4′,6-pentabromodiphenyl ether (BDE-100) [12]. However, Meng et al. [11] found BDE-209 was the dominant congener of total intake for humans (excluding nursing infants) in China.

Approximately 75% of the PBDE congeners used as flame retardants are 2,2′,3,3′,4,4′,5,5′,6,6′-decabromodiphenyl ether (BDE-209) making it important to understand its degradation processes and fate in the environment. However, few published studies are available regarding biotic and abiotic transformation of BDE-209. BDE-209 was reported to debrominate to nonaBDE and octaBDE by anaerobic sewage sludge after incubation for 238 days [13]. Debromination of BDE-209 and an octaBDE mixture was also observed with anaerobic bacteria including *Sulfurospirillum multivorans* and *Dehaloccoides* species [14]. In sediments, BDE-209 can be biotransformed into lower mass PBDE congeners that are of great concern to environmental health and its debromination half-life in sediments was over a decade [15]. Slow biodegradation and few microorganisms are found to degrade BDE-209. Chemical reduction degradation of PBDEs with zerovalent iron was proposed [16]. However, the photolytic decomposition and the effect of photolytic

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factors on photodegradation reaction of PBDEs are not well documented.

Compared to PCBs, PBDEs are likely to be more susceptible to environmental degradation due to the C–Br bond being weaker than the C–Cl bond [17]. Photolysis is a potential abiotic transformation mechanism of PBDEs in the environment and has been reported to occur under a variety of conditions [18–21]. Due to the extremely low aqueous solubility of PBDEs and the adsorption of them to container walls from aqueous solutions, the detailed studies about the photodegradation behaviors and kinetics in water are hardly performed. Hexane can provide good transparency of light, solvency and hydrogen donor ability for PBDEs [22]. The objective of this study was to perform the photolytic degradation experiments of BDE-209 to understand the photodegradation kinetics and mechanism under UV and solar lights in Taiwan. This also included determining the time course of degradation and the evaluation of photodegradation efficiency of PBDEs in hexane under different light intensity and initial concentration. The photodecomposition of BDE-209 to three nonaBDEs was evaluated. The resulting photodegradation products were identified to elucidate the fate of PBDEs in the environment.

2. Materials and methods

2.1. Chemicals

Decabromodiphenyl ether (BDE-209; 98% purity) and hexachlorobenzene, used as an internal standard, were obtained from Fluka. A mixture of 39 PBDEs congeners (EO-5113) having from one to seven bromine atoms was obtained from Cambridge Isotope Lab Inc. A PBDE mixture (TBDE-79X) containing three penta congeners, seven hexacongeners, eight heptacongeners, six octacongeners and three nonacongeners was purchased from Wellington Laboratories. Three individual congeners (2,2′,3,3′,4,4′,5,5′,6-nonabromodiphenyl ether (BDE-206), 2,2′,3,3′,4,4′,5,6,6′-nonabromodiphenyl ether (BDE-207) and 2,2′,3,3′,4,5,5′,6,6′-nonabromodiphenyl ether (BDE-208)) were purchased from Cambridge Isotope Lab Inc. 4-Monobromodiphenyl ether (BDE-3) was obtained from Sigma–Aldrich.

2.2. Irradiation experiments

The UV-lamp irradiation experiments were performed in the laboratory with artificial ultraviolet light. A photochemical reactor was equipped with two 15 W UV lamps. Three different irradiation ranges of wavelength, 300–330 nm, 350–400 nm, and 300–400 nm, were performed to study the effect of UV wavelength on degradation. In addition, solar irradiation experiments were performed on 4th May and 27th May 2006 on the roof of the Agricultural Environment Building at National Chung Hsing University, Taichung, Taiwan (24°07′14.9″N 120°40′29.0″E), and the intensity of solar radiation during the experimental period was measured by a light meter. Each series consisted of solvent blanks, control samples kept in the dark, and the samples to be exposed. All samples were measured at the same time. All experiments were performed in triplicate. The initial concentrations of BDE-209 and BDE-3 were around 12.5 mg/L and 18.0 mg/L in hexane, respectively. At the appropriate sampling time, the photodegradation was terminated by removing the vials from the light exposure and immediately initiating analysis.

2.3. Chemical analysis

The concentration of BDE-209 in samples was quantified with a gas chromatograph (GC) (Agilent 6890) equipped with a
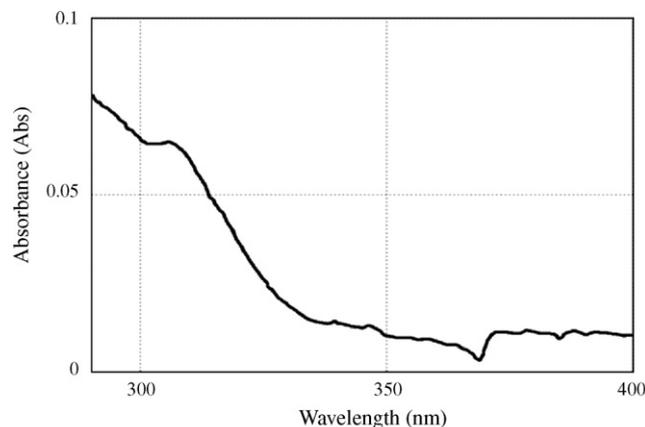

Fig. 1. Absorption spectrum of BDE-209 in hexane (290–400 nm).

micro-electron capture detector (μECD), a programmable pressure on-column injection port, and a DB5-HT capillary column (length = 15 m, i.d. = 0.25 mm, film thickness =0.1 μm). Nitrogen gas was used as the carrier gas and makeup gas. The injector temperature was 320 °C, the initial oven temperature was 150 °C, maintained there for 0.5 min, temperature programmed to 330 °C at 25 °C min^{-1}, and held for 5 min. The detector temperature was 340 °C. The molecular masses and bromine content of compounds produced during photolysis were determined with a GC–MS (Agilent 5975 inert MSD), using a column and chromatographic conditions which were identical to that of the GC-μECD system

3. Results and discussion

3.1. Absorption spectrum and reaction kinetics

Absorption spectrum of BDE-209 dissolved in hexane is shown in Fig. 1. The molar absorptivity generally decreased with the increase of wavelength between 300 and 350 nm and the local maximum wavelength was 306 nm. These data are useful for the interpretation of the following photodegradation results. Fig. 2 shows the disappearance of BDE-209 under different range of UV light. The concentrations of BDE-209 from dark control samples were analyzed over the same period of time. The concentration of BDE-209 did not change significantly in vials which were not exposed to UV light. Upon UV irradiation, photodegradation occurs for BDE-209 during all the experiments. The decay kinetics for BDE-
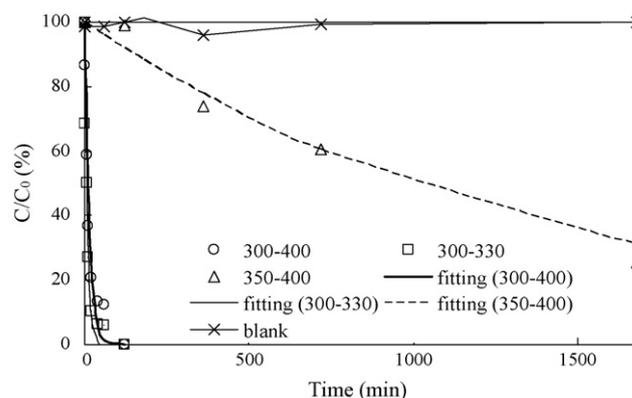

Fig. 2. UV-lamp photodegradation of BDE-209 in hexane (initial concentration: 40.0 mg/L).

209 depends on the irradiation wavelength. Under the lower range of UV light (300–330 nm, UV-B), the photodegradation reaction of BDE-209 was the fastest. After 2 h of exposure to the UV-B light, the remaining BDE-209 was not detectable. For the higher range of UV light (350–400 nm, UV-A), the BDE-209 concentration was reduced to approximately 40% of the original concentration after exposing 720 min. The photochemical reaction under UV-A light seems the slowest. Using the UV light between 300 and 400 nm, the decay rate of BDE-209 was not significantly different from that with UV-B light.

The experimental data were analyzed for their fitness of the first-order and second-order reaction models. The pseudo-first-order kinetic model can describe the degradation kinetics well (Fig. 2). The degradation rate constants (k) were determined by assuming a pseudo-first-rate kinetics: $C = C_0 e^{-kt}$, where C is the concentration of BDE-209, C_0 is the initial concentration of BDE-209 and t is the reaction time. The reaction rate constants were $0.051 \pm 0.0026\,h^{-1}$ for the UV light at 350–400 nm, $0.11 \pm 0.0075\,min^{-1}$ at 300–330 nm, and $0.050 \pm 0.0081\,min^{-1}$ at 300–400 nm. This result was consistent with the absorption spectrum analysis (Fig. 1). The strong light absorption capacity of BDE-209 and its maximum absorption wavelength are in the UV-B range, indicating the photons within this wavelength range can break most aryl carbon–bromine bonds easily.

3.2. Effect of initial concentration of BDE-209

Since the pollutant concentration could be an important parameter controlling the degradation process, the effect of the initial concentration of BDE-209 on the UV-lamp photodegradation rate was investigated over the concentration range of 16–53 mg/L (Fig. 3). Apparently, the photodegradation reactions can be fitted with the pseudo-first-order kinetic model well. The reaction rate constants were $0.11 \pm 0.011\,min^{-1}$ for 53 mg/L, $0.12 \pm 0.015\,min^{-1}$ for 42 mg/L, $0.12 \pm 0.017\,min^{-1}$ for 37 mg/L, and $0.12 \pm 0.0076\,min^{-1}$ for 16 mg/L. Although the degradation rate constants slightly decrease with the increase in initial BDE-209 concentrations, the degradation rate constant values with the corresponding confidence intervals show that the differences between these reaction rates are not significant. This result was consistent with the assumption of the pseudo-first-order rate kinetic law. The initial concentration does not have a significant effect on the photodegradation rates.
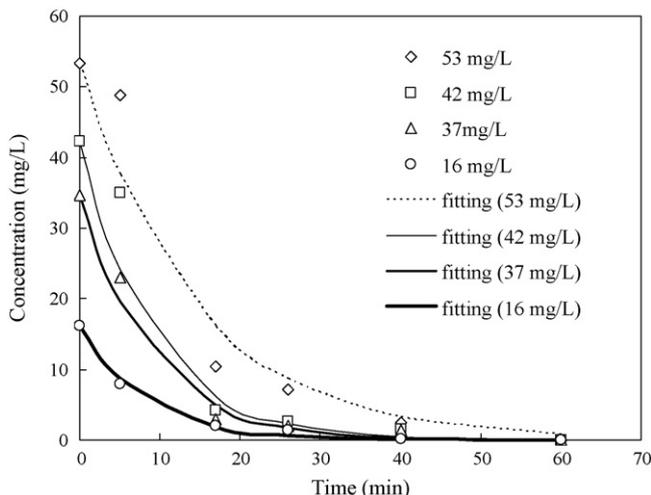

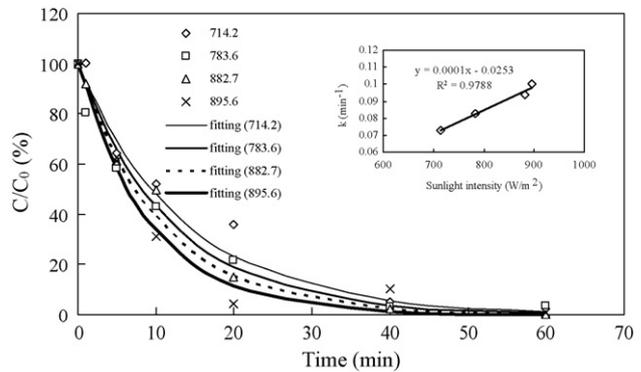**Fig. 3.** Effect of initial concentration on the degradation of BDE-209 under UV irradiation.

Fig. 4. Effect of sunlight intensity (W/m^2) on the degradation of BDE-209 (initial concentration: 12.5 mg/L).

3.3. Effect of solar light intensity

Intensity of the irradiation has been reported to be an important parameter influencing the degradation of organic chemicals by photoactivity [22–25]. Results reported in Fig. 4 show that the photolytic degradation rates follow first-order kinetics and that these rates also vary with respect to the light intensity. After 60 min of exposure to sunlight on different dates, the BDE-209 concentrations decreased to less than 5% of the original concentrations. The reaction rate constants were $0.073 \pm 0.0062\,min^{-1}$ for 714.2 W/m^2, $0.083 \pm 0.0032\,min^{-1}$ for 783.6 W/m^2, $0.094 \pm 0.0032\,min^{-1}$ for 882.7 W/m^2, and $0.10 \pm 0.0076\,min^{-1}$ for 895.6 W/m^2. The inset in Fig. 4 shows the relationship between the reaction rates and the absorbed light intensity. The linear increase of the reaction rate constants for decabromodiphenyl ether over a sunlight intensity range of 714.2–895.6 W/m^2 was observed. It indicated that an increased photodegradation rate was caused by more photons at a higher light intensity. This is consistent with the experimental results reported for dichloroacetic acid and 2,4-dichlorophenol photodegraded by solar irradiation [23]. Their photodegradation efficiency increases linearly with the solar intensity up to the value around 15 W/m^2. Lee et al. [24] also found that the photodegradation rates of bisphenol-A increased with the increase in light intensity of UV lamps.

The reaction rate constants of BDE-209 were in the range of 0.06–0.08 min^{-1} for the solar irradiation in Taichung, Taiwan (24°07′N 120°40′E). Bezares-Cruz et al. [22] observed the solar degradation rate constants at the different exposure times in mid-latitude (40°29′N 86°59.5′W) were $1.12 \times 10^{-1}\,min^{-1}$ (July) and $6.66 \times 10^{-2}\,min^{-1}$ (October). The values of the solar degradation rate constants in our study are similar to theirs. Our observations are slightly lower than theirs and might be due to the lower solar intensity at the time of this study.

3.4. Effect of different brominated PBDE congeners

The changes of concentration of three selected PBDE congeners under UV-lamp irradiation are shown in Fig. 5. BDE-209 and BDE-207 are almost completely decomposed after 60 min whereas BDE-3 was decomposed only about 60% in the same time. The calculated photodegradation rate constants for three PBDEs were $0.12 \pm 0.0049\,min^{-1}$ for BDE-209, $0.057 \pm 0.0080\,min^{-1}$ for BDE-207, and $0.018 \pm 0.0011\,min^{-1}$ for BDE-3, respectively. The photodegradation rates of the highly bromo-substituted PBDE congeners, BDE-209 and BDE-207, were much faster than the low brominated PBDE congener, BDE-3. This is consistent with the previous observation of a faster dechlorination for high-chlorinated aliphatic compounds indicated by Scherer et al. [26]. Trojanowicz et al. [27] found that higher chloro-substituted phenols can per-
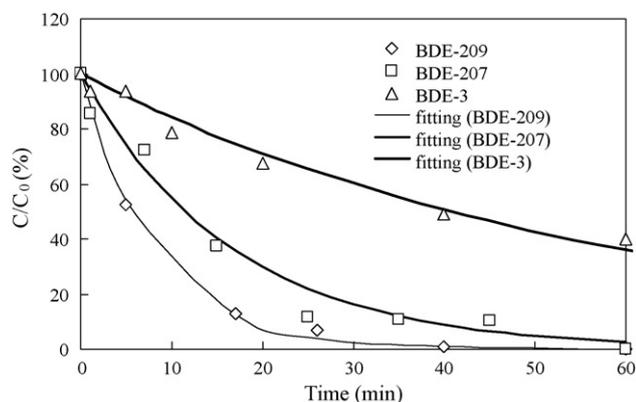
Fig. 5. The degradation of PBDE congeners with UV-light in hexane (initial concentrations of BDE-3, BDE-207 and BDE-209 are 2.99, 1.56 and 2.34 mg/L, respectively).

form faster reductive reactions. It is known that highly chlorinated compounds are generally more sensitive to reductive dechlorination than their lower chlorinated analogues [16,26,28]. A similar positive trend between the photochemical debromination rate and the degree of bromination was observed [19]. Our results are consistent with the findings that lower brominated diphenyl ethers degrade slower than highly brominated congeners by UV light.

3.5. Degradation products

The solar degradation of decaBDE was repeated three times with the irradiation times of 0, 1, 5, 10, 20, 40, 60 min and good reproducibility was obtained. The total estimated concentration of reaction intermediates for each congener group for the photodegradation experiments are shown in Fig. 6. The mass balance over time varies by less than 13% in these solar irradiation experiments. In comparison to mass balances of around 45% in the study of chemical reduction of BDE-209 with zero valent iron [16] and around 130% in the solar photodecomposition of BDE-209 [22], the mass balances
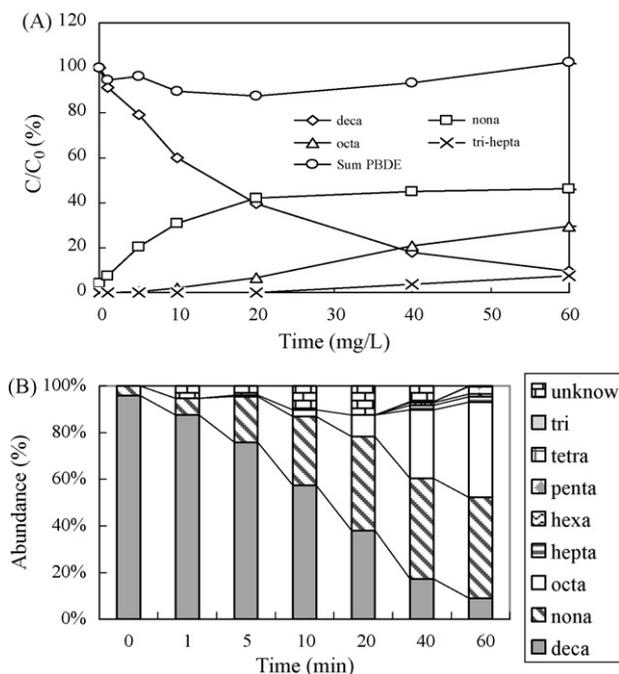

Fig. 6. Solar degradation kinetic (A) and product distribution of BDE-209 with time (B) in hexane (initial concentration: 12.5 mg/L).
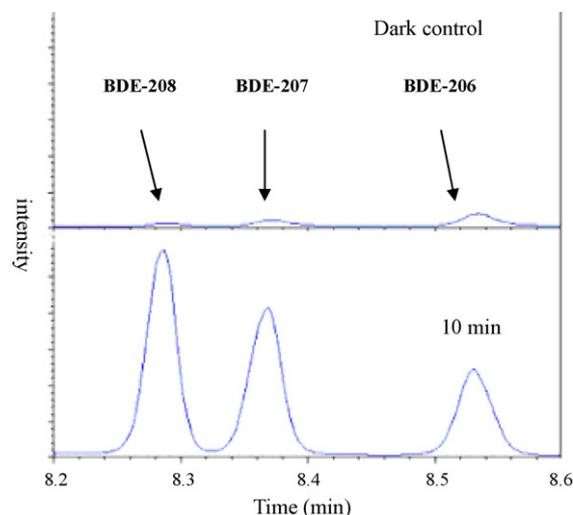

Fig. 7. GC chromatograms of nonabromodiphenyl ethers. The chromatograms illustrate the formation of BDE-208, BDE-207 and BDE-206 overtime under solar degradation conditions.

in this study do not vary a lot. However, the quantitative data clearly indicated that decaBDE decreased rapidly as a result of 90% decomposition yield for about 60 min. When decaBDE disappears, there is formation of lower brominated congeners (triBDEs through nonaBDEs). Nonabrominated DEs were the most abundant congeners at the initial stage of the reaction, where this fraction accounted for around 40% of total BDEs. The other congeners (octaBDEs, hepta to triBDEs) gradually increased over the 60 min exposure time, as nonaBDEs are transformed to octaBDEs that are then sequentially transformed to hepta–triBDEs.

These results indicate that the first step of degradation of BDE-209 is the loss of one bromine atom to form all three nonaBDE congeners and then these congeners subsequently are reduced to form the octaBDEs. Overtime, the extent of debromination became significant as indicated by the increasing concentration and number of triBDE–heptaBDE congeners appearing on product distribution data in these samples. Sequential debromination was observed, suggesting these organobromine compounds adsorb ultraviolet light and then undergo stepwise bromine losses. Upon solar irradiation, the photodegradation of decabromodiphenyl ether in environmental media such as soil, metal oxides, and sediment, mainly undergoes a reductive debromination to other polybrominated diphenyl ethers [18,29]. The photodegradation of decabromodiphenyl ether mainly seems to be a sequential debromination process [22].

Fig. 7 shows the chromatograms of three nonabromodiphenyl ethers BDE-206, BDE-207 and BDE-208 of UV-exposed samples in the beginning and after 10 min, respectively. Peaks for BDE-207 and BDE-208 do increase rapidly relative to the peak of BDE-206 with increasing UV-exposure time. The first-order rate constants of formation of BDE-206, BDE-207 and BDE-208 are 0.387, 0.615 and 0.815 min^{-1}, respectively. This indicates that the photodebromination of BDE-209 chiefly occurred at *para* position > *meta* position > *ortho* position. A similar effect has been reported in the dechlorination of PCB by microscale and nanoscale zerovalent irons in a water/methanol solution [30]. Chlorines in the *para* and the *meta* position were predominantly removed over chlorines in the *ortho* position. For PBDEs, Gerecke et al. [31] presented that anaerobic biodebromination of PBDE at the *ortho* positions has been less frequently observed than reduction of the *para* and the *meta* positions.

4. Conclusion

This study elucidated that photodegradation of BDE-209 was a sequential debromination reaction. The results showed that (1) the photodegradation reaction of BDE-209 was the fastest in the UV-B range, (2) photodegradation conversion of BDE-209 was not affected by the initial concentrations of BDE-209, (3) the photodegradation rate constant increases with increasing solar light intensity, (4) the photodegradation of highly bromo-substituted PBDE congeners was faster than low brominated PBDE congeners, and (5) photodebromination of BDE-209 occurred mostly at *para* position > *meta* position > *ortho* position. The photolytic chemical reduction of PBDEs under solar light can rapidly degrade PBDEs to lower bromine substituted diphenyl ethers. In the environment, biodegradation by microorganisms or chemical reduction–oxidation can continuously degrade these less brominated BDEs. These findings indicate that photoreactions of PBDEs are an important process in polybrominated diphenyl degradation and these results could facilitate improved waste treatment designs as well as lead to better fate predictions of PBDEs in the environment.

Acknowledgments

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