



Photolytic degradation of decabromodiphenyl ethane (DBDPE)

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HIGHLIGHTS

- ▶ Photolytic degradation rates of DBDPE vary in different matrices.
- ▶ Photolytic degradation kinetics of DBDPE are investigated.
- ▶ Nona-, octa-, and hepta-BDPEs are formed in DBDPE degradation.

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ABSTRACT

The photolytic degradation of decabromodiphenyl ethane (DBDPE), an alternative flame retardant to decabromodiphenyl ether, was investigated in a variety of matrixes (*n*-hexane, tetrahydrofuran, methanol/water, humic acid/water, and silica gel) by irradiation under ultraviolet light and in *n*-hexane under natural light. Photolytic degradation of DBDPE occurs in all the matrixes investigated within the irradiation period (<320 min). The degradation experiments showed varied reaction rates, dependent on the matrixes, with increasing half-lives ($t_{1/2}$) in the order of tetrahydrofuran ($t_{1/2} = 6.0$ min) > *n*-hexane ($t_{1/2} = 16.6$ min) > humic acid/water ($30 < t_{1/2} < 60$) > silica gel ($t_{1/2} = 75.9$ min) > methanol/water ($t_{1/2} > 240$ min). The reaction in tetrahydrofuran, *n*-hexane, and silica gel matrixes can be described by the pseudo first order kinetics. Nevertheless, the matrixes have little effect on the degradation product distributions of DBDPE. A numbers of debrominated intermediates were identified. The degradation involves the initial formation of nona-BDPEs and the subsequent decomposition of these congeners to lower brominated congeners (octa- and hepta-BDPEs) within the irradiation time. To our knowledge, the present work is the first attempt to investigate the photolytic degradation kinetics and the identification of intermediates, as well as the degradation mechanism, during the degradation of DBDPE. Further research is needed to understand the photolytic degradation pattern of DBDPE in the natural environment.

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1. Introduction

Decabromodiphenyl ethane (DBDPE) is an additive in brominated flame retardants (BFRs) that was introduced by the Albemarle Corporation (Richmond, USA) in the early 1990s as an alternative to the commercial decabromodiphenyl ether (deca-BDE) mixture, one of the most commonly used BFRs worldwide (Kierkegaard et al., 2004). One reason for the commercialization of DBDPE was that it meets the demands of the German dioxin ordinance, producing no polybrominated dibenzo-*p*-dioxins under pyrolysis conditions. Similar to deca-BDE, DBDPE is added in a vari-

ety of polymeric materials that are widely used in electronic equipment. Due to the ban or restriction on deca-BDE, increasing demands for DBDPE are expected. For example, the production volume of commercial DBDPE in China was estimated to be 12 000 tons in 2006 and to increase with a rate of up to 85% per year (Hu et al., 2008). In Japan, the annual consumption of DBDPE had already exceeded that of deca-BDE by the late 1990s (Kajiwara et al., 2008). DBDPE attracted growing attention in recent years as a result of its worldwide occurrence in sewage sludge, sediment, air, and house dust (Wang et al., 2010; Covaci et al., 2011). Although recent findings have indicated that DBDPE was bioavailable to biota (Hu et al., 2008; Zhang et al., 2009), the environmental behaviors and fate of DBDPE have not been adequately investigated.

Photochemical degradation is an important transformation pathway in the consideration of the fate of organic brominated compounds (Lenoir et al., 1991; Eriksson et al., 2004) because these

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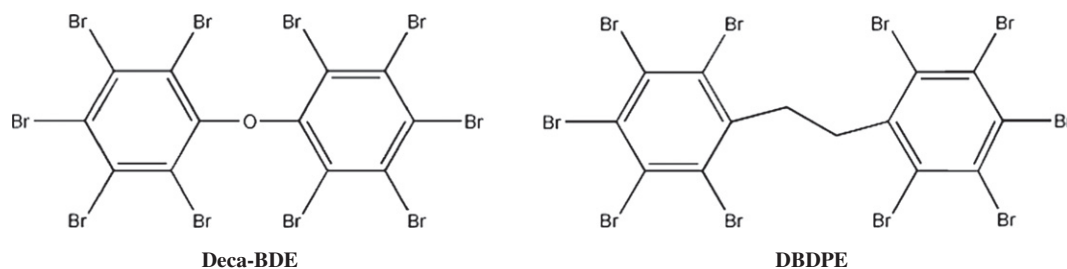


Fig. 1. Chemical structures of deca-BDE and DBDPE.

compounds are susceptible to ultraviolet (UV) light, resulting in the loss of bromine and the possibility of rearrangements (Söderström et al., 2004). Special emphasis has been paid to the importance of the photodegradation of highly brominated diphenyl ether (in particular deca-BDE) (Shih and Wang, 2009). It has been shown that approximately 50% of the hepta- and hexa-BDE homologs, 13% of the penta-BDE homolog, and about 2% of the tetra-BDE homolog found in the environment arises from the degradation of deca-BDE (Schenker et al., 2008). This degradation process increases the toxicity of deca-BDE. DBDPE is structurally similar to deca-BDE. The difference is that the phenyl-ether linkage in deca-BDE is replaced by a phenyl-ethane linkage in DBDPE (Fig. 1). Nevertheless, the degradation of DBDPE and the effect on its environmental fate have only been studied to a limited extent. In a recent study, Kajiwara et al. (2008) observed no appreciable debromination of DBDPE that was incorporated into high-impact polystyrenes (HIPS) and TV casings during 224 d of exposure to natural sunlight, while debromination of deca-BDE occurred with a half-life of 51 d. Jakab et al. (2003) investigated the thermal decomposition of deca-BDE and DBDPE in HIPS and found that the two BFRs decompose by different pathways in HIPS containing antimony trioxide. DBDPE decomposes mainly by the cleavage of the aliphatic C–C bonds resulting in the formation of bromotoluenes, whereas deca-BDE decomposes by an intermolecular ring closure pathway producing brominated dibenzofuran derivatives. Despite the poor bioavailability of DBDPE due to its large molecular weight (Betts, 2009), its potential degradation to lower brominated congeners, which may be more bioavailable and toxic as observed for deca-BDE degradation products, should be of concern.

The purpose of the present study is to preliminarily evaluate the photolytic degradation of DBDPE under UV irradiation. The degradation was performed in different solvent matrixes, i.e. *n*-hexane, tetrahydrofuran, methanol/water, and humic acid/water as well as on silica gel. As a comparison, the photodegradation of DBDPE in *n*-hexane under natural sunlight and the photodegradation of deca-BDE in *n*-hexane were also investigated. The degradation kinetics of DBDPE were described, and the degradation intermediates formed were identified. This study may have some

implications to understanding the behavior and fate of DBDPE in the environment.

2. Materials and methods

The irradiation systems and exposure times selected are shown in Table 1. The inherent reactivity of DBDPE was investigated in the organic solvent systems. Silica gel, which is an important substrate of organic pollutants in environment, was also selected as an artificial matrix aimed at simulating the soil and sediment system. The methanol/water and humic acid/water systems were selected to simulate the aquatic environment found in nature. Unfortunately, due to the extremely low aqueous solubility of DBDPE, the photolytic studies in pure water are difficult to conduct.

2.1. Materials and preparations

Technical DBDPE and deca-BDE products were purchased from the Chemical Market of Guangzhou, China. DBDPE standard in toluene was obtained from Wellington Laboratories (Guelph, Canada). Commercially available humic substances were obtained from Sigma–Aldrich (Buchs, Switzerland), containing $46.1 \pm 0.2\%$ carbon, $4.4 \pm 0.2\%$ hydrogen, and $0.62 \pm 0.03\%$ nitrogen. The solvents used in the experiments were all high-performance liquid chromatography (HPLC) grade. Silica gel (70–230 mesh, Merck, USA) was Soxhlet extracted by dichloromethane to remove any organic matter prior to use.

Solutions of DBDPE were prepared by dissolving 2 mg of solid DBDPE in 10 mL of an acetone, tetrahydrofuran, and toluene mixture (20:30:50) using ultrasonic treatment (Kierkegaard et al., 2004). The samples were evaporated to 1 mL using a gentle stream of nitrogen and then mixed with four different 100 mL solvent matrixes: *n*-hexane, tetrahydrofuran, methanol/water, and humic acid/water. The effects of the mixture solvent were examined by comparing degradation of DBDPE standard in pure solvent (toluene, as received) and in toluene with 1% of the mixture solvent, no significant difference on degradation rate (less than 0.5%) or degradation products can be found after 80% of origin DBDPE

Table 1

The initial concentration, exposure time, rate constants and half-lives ($t_{1/2}$) of DBDPE and deca-BDE during the photolytic degradation in different matrixes.

	Exposure time (min)	Initial concentration (mg L ⁻¹)	Half-life (min)	Rate constant (min ⁻¹)
<i>n</i> -Hexane (UV) ^a	0/1/2/4/8/12/20/30/45/70	4.05	16.6	4.18×10^{-2}
Tetrahydrofuran (UV)	0/1/2/4/8/14/20/30	4.51	6.0	1.15×10^{-1}
Methanol/water (4:1)(UV)	0/4/8/16/30/50/80/120/150/180/240	0.41	>240	NC ^b
Humic acid/water (UV)	0/5/15/30/60/90/120/180	0.12	$30 < t_{1/2} < 60$	NC
Silica gel (UV)	0/2/4/10/18/30/50/80/120/180/250/320	0.47 ^c	75.9	9.13×10^{-3}
<i>n</i> -Hexane (natural sunlight)	0/10/20/40/60/90/120	2.70	$20 < t_{1/2} < 40$	NC
<i>n</i> -Hexane (deca-BDE)	0/4/8/15/25/50	6.33	18.1	3.83×10^{-2}

^a Ultraviolet.

^b Not calculated because of the degradation does not follow the first-order kinetics.

^c Concentration in extracts (0.200 g silica gel extracted by 1 mL of *n*-hexane).

was degraded. After mixing, the humic acid/water matrix was shaken for 48 h in the dark. For the silica gel matrix, 100 mL of the DBDPE solution was added directly onto 20 g of silica gel and kept in the dark for 12 h to volatilize the solvent. The dissolved organic carbon of the humic acid/water system was quantified as 4.61 mg L^{-1} . Technical deca-BDE dissolved in *n*-hexane was also prepared.

2.2. Experimental setup

Solutions of DBDPE, which were dissolved in or adhered to different matrixes, were exposed to artificial UV-light in reaction vessels. For the silica gel matrix, the irradiation samples were homogenized in the reaction vessels using a stir bar on a magnetic stirrer. An additional DBDPE in the *n*-hexane matrix was exposed to natural outdoor sunlight. Each group consisted of exposed samples, matrix blanks, and control samples kept in the dark. Each sample was performed in triplicate. The indoor experiments were performed with a GGZ-125 125 W high-pressure mercury lamp (Yaming Lighting, Shanghai, China), housed on the top of the reactor to serve as an irradiation source and a quartz immersion well with circulating water. The quartz photoreactor was positioned in a water bath with constant water circulation to keep the temperature at a constant 20°C . Sample aliquots were removed from the photoreactor to glass vials at specified time points (Table 1) and were subsequently kept in the dark. The time intervals were chosen based on some preliminary tests. The silica gel samples were ultrasonically extracted using 1 mL of *n*-hexane for 30 min, with an average recovery of $87.2 \pm 6.0\%$. The sunlight irradiation experiments were performed on June 20, 2009 on the roof of the lab building at the Guangzhou Institute of Geochemistry, Chinese Academy of Sciences, ($23^\circ15'\text{N}$, $113^\circ36'\text{E}$) in Guangzhou, China.

2.3. Chemical analysis

Samples taken from the *n*-hexane, tetrahydrofuran, and silica gel matrixes were analyzed with a Shimadzu 2010 gas chromatograph-mass spectrometer (GC-MS) in both electron-capture negative-ionization (ECNI) and electron impact (EI) modes. A DB-5HT ($15 \text{ m} \times 0.25 \text{ mm}$ inner diameter (i.d.), 0.1 mm film thickness, Agilent Technologies, USA) capillary column was used to separate the analytes. The initial oven temperature was maintained at 110°C for 5 min, then increased at a rate of $30^\circ\text{C min}^{-1}$ up to 310°C and held for 8 min. The injection was set to the splitless mode with an injection temperature of 290°C . In the ECNI mode, methane was used as a chemical ionization moderating gas at an ion source pressure of $2.4 \times 10^3 \text{ Pa}$. Helium was used as the carrier gas at a flow rate of 1 mL min^{-1} in both modes. The ion source temperature was set to 260°C . The m/z of 79 and 81 were selected to monitor the DBDPE and lower-brominated congeners in selected ion monitoring (SIM) under ECNI mode. Full scan data acquisition under EI mode was performed with m/z from 75 to 1000.

For the analyses of the samples in the methanol/water and humic acid/water matrixes, an Agilent 1200 HPLC equipped with a kromasil C_{18} reversed-phase column ($25 \text{ cm} \times 4.6 \text{ mm} \times 5 \mu\text{m}$, AKZO Nobel, Sweden) and a UV detector (Agilent Technologies, USA) were used for the separation and quantification. The detection wavelength was set at 230 nm , and the mobile phase was an optimized mixture of methanol with tetrahydrofuran (70:30), pumped with the flow rate of 1.0 mL min^{-1} . After quantification, the samples from the methanol/water and humic acid/water matrixes were extracted with *n*-hexane by liquid-liquid extraction to remove the degradation products for GC-MS-EI full-scan analysis, while the other quantifications were performed using GC-MS with ECNI mode.

3. Results and discussion

3.1. Photolytic degradation: kinetics and half-lives

Absorption spectra for DBDPE were measured in tetrahydrofuran using a PerkinElmer Lambda 850 UV spectrophotometer (USA). The maximum absorption wavelength λ_{max} was at 238 nm (Fig. S1), which is lower than the λ_{max} of BDE 209 (306 nm) according to Eriksson et al. (2004). No degradation of DBDPE was observed in the dark control samples over the same time periods; in contrast, photolytic degradation of DBDPE occurred in all the matrixes investigated. The degradation kinetics of DBDPE during the UV irradiation processes in the different matrixes are shown in Fig. 2. It was found that within the experiment period, 33.7–99.6% of the DBDPE was lost for all the experiments. The degradation kinetics in *n*-hexane, tetrahydrofuran, and on silica gel matrixes could be described by the pseudo first order kinetic model ($r^2 = 0.997$ for *n*-hexane, 0.993 for tetrahydrofuran, and 0.978 for silica gel). The calculated rate constants (k) and half-lives ($t_{1/2}$) are shown in Table 1.

The degradation rates were dependent on the matrixes. The photolytic half-life of DBDPE in tetrahydrofuran (6.0 min) was the shortest followed by that in *n*-hexane (16.6 min) indicating a rapid degradation in these matrixes (Table 1). The difference in the rate constant between the tetrahydrofuran and *n*-hexane matrixes may be attributed to the difference in the reactive species, intermediate products such as free-radical like $\cdot\text{OH}$ and $\cdot\text{O}_2$ produced by the photooxidation of tetrahydrofuran in the air (Stenberg et al., 1970).

The photolytic half-lives of DBDPE in the humic acid/water (30–60 min) and on silica gel (75.9 min) matrixes were much longer compared with those in the pure organic solvent matrixes. It has been suggested that humic materials may have a significant influence on the performance of photodegradation of halogenated compounds (Chu et al., 2005). Bezares-Cruz et al. (2004a) suggested that in the presence of humic acid the transformation of deca-BDE by solar irradiation is appreciably slowed. Chu et al. (2005) found that low doses of humic substances acting as a supplementary hydrogen source can accelerate the photodegradation rate of polychlorobiphenyls (PCBs), while they can retard the reaction at a higher dose because of the photochemical quencher effect. A likely quenching effect of humic acid on the DBDPE photodegradation at 90 min was observed as shown in Fig. 2. This quenching effect is presumably due to the elevated concentrations of humic

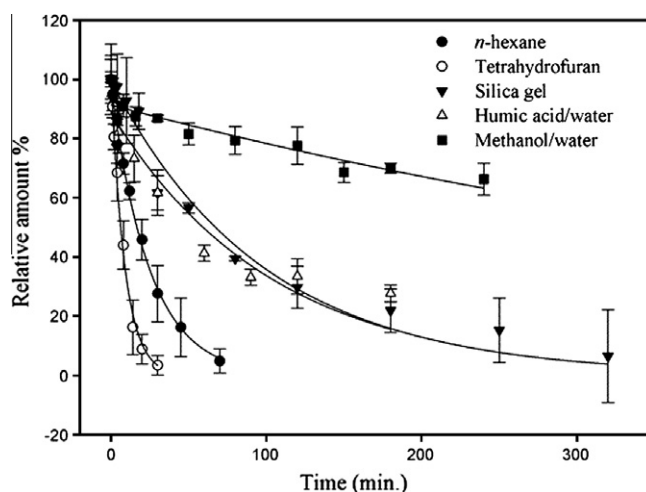


Fig. 2. Kinetic curves of the photolytic degradation of DBDPE in different matrixes under UV irradiation.

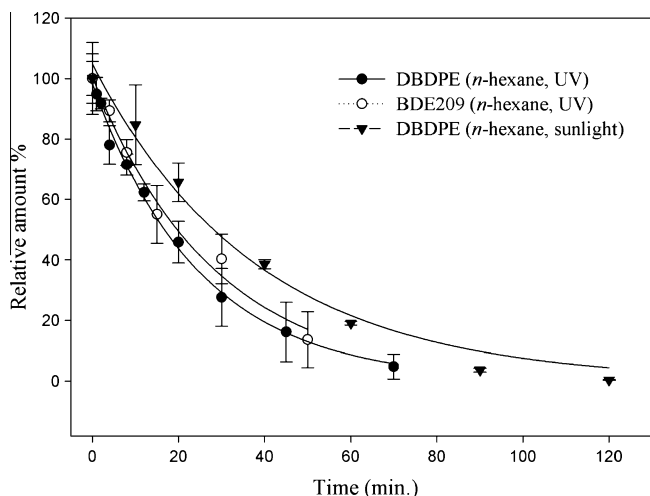


Fig. 3. Comparison of UV and natural light irradiation on the photolytic degradation kinetics of DBDPE and the difference of deca-BDE and DBDPE under UV irradiation.

substances relative to the decreased DBDPE concentration. This may also explain the non-first-order kinetic of this degradation.

Although the silica gel has a smooth surface on which the target compound adsorbs (rather than migrates into), the degradation rate on this matrix was significantly reduced compared to the organic solvents. A previous study (Söderström et al., 2004) indicated that the photolytic half-life for deca-BDE on a silica gel matrix was short (<15 min) and was comparable to that in toluene.

DBDPE exhibited the lowest degradation rate in the methanol/water solution with a half-life >240 min, but the degradation intermediates can clearly be found. The experimental data in this matrix did not fit the first-order reaction well due to the low solubility of DBDPE in methanol/water. We speculated that the low water solubility of DBDPE in this matrix results in its adsorption to the glass wall of the reaction vessel, which may reduce the reaction rate. A relatively low reaction rate in the methanol/water

solution for deca-BDE compared to that in tetrahydrofuran has also been observed in the experiment by Eriksson et al. (2004).

The degradation rate of DBDPE in *n*-hexane under outdoor sunlight increased with the increasing irradiation time (Fig. 3), differing with the behavior under UV irradiation. This finding is due to the irradiation experiment starting at 9 AM. The light intensity of sunlight and the temperature increased during the experiment period. The light intensity has been reported as an important parameter influencing the degradation of organic chemicals by photoactivity (Shih and Wang, 2009). The photolytic degradation behavior of DBDPE was compared with deca-BDE (Fig. 3). The two compounds exhibit similar degradation behaviors in *n*-hexane. DBDPE decomposed a little faster than deca-BDE with a half-life of 16.6 min (the half-life for deca-BDE is 18.1 min), but the rate constant was on the same order of magnitude (4.18×10^{-2} for DBDPE and 3.83×10^{-2} for deca-BDE). Kajiwara et al. (2008) recently found that DBDPE incorporated into HIPS was more resistant to UV irradiation than deca-BDE during sunlight exposure for 224 d. The authors attributed this to the differences in the molecular structure of the two compounds (i.e. the ether bond in deca-BDE and the aliphatic C–C bridge in DBDPE). However, our result suggests that the matrixes (e.g. HIPS) that DBDPE and deca-BDE are incorporated into may play a more important role in their photolysis behaviors.

3.2. Identification of degradation products

Despite the differing photolytic degradation rates of DBDPE in the matrixes, no obvious differences in the debromination products formed during the irradiation processes (under both UV and sunlight conditions) were found (Table S1). The GC–MS chromatograms for the photolytic degradation of DBDPE in *n*-hexane obtained at 0, 20, 45, and 60 min are shown in Fig. 4. To identify these debromination intermediates, full-scan mass spectra with EI mode were obtained. Since the standards of these compounds were not available commercially, the homolog groups of BDPEs can be identified only within structural isomer groups according to the GC–MS retention times and EI full-scan spectra.

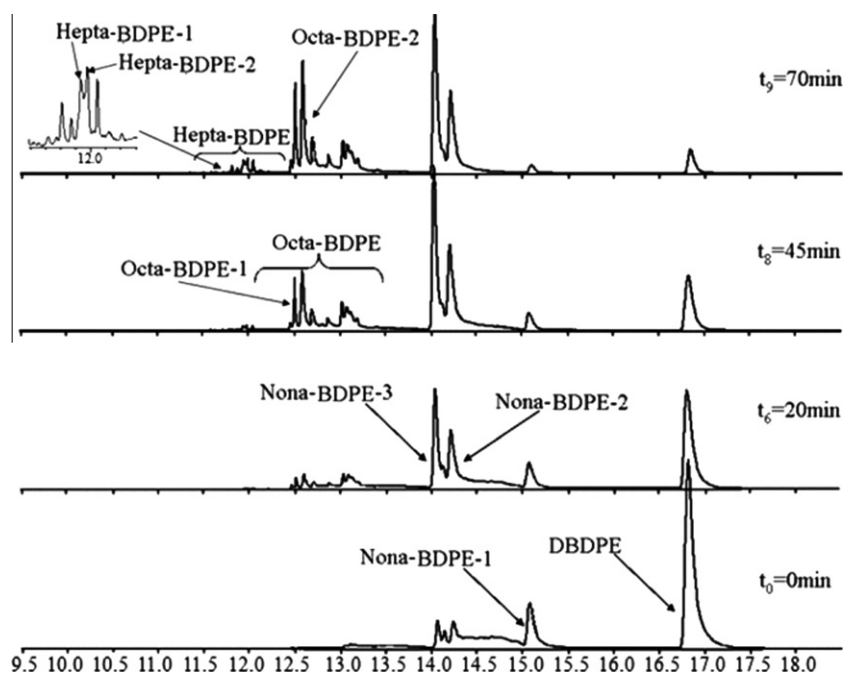


Fig. 4. GC–MS chromatograms (ECNI) of DBDPE and the degradation intermediates (nona-, octa-, and hepta-BDPEs) in *n*-hexane at 0, 20, 45, and 70 min degradation under UV irradiation.

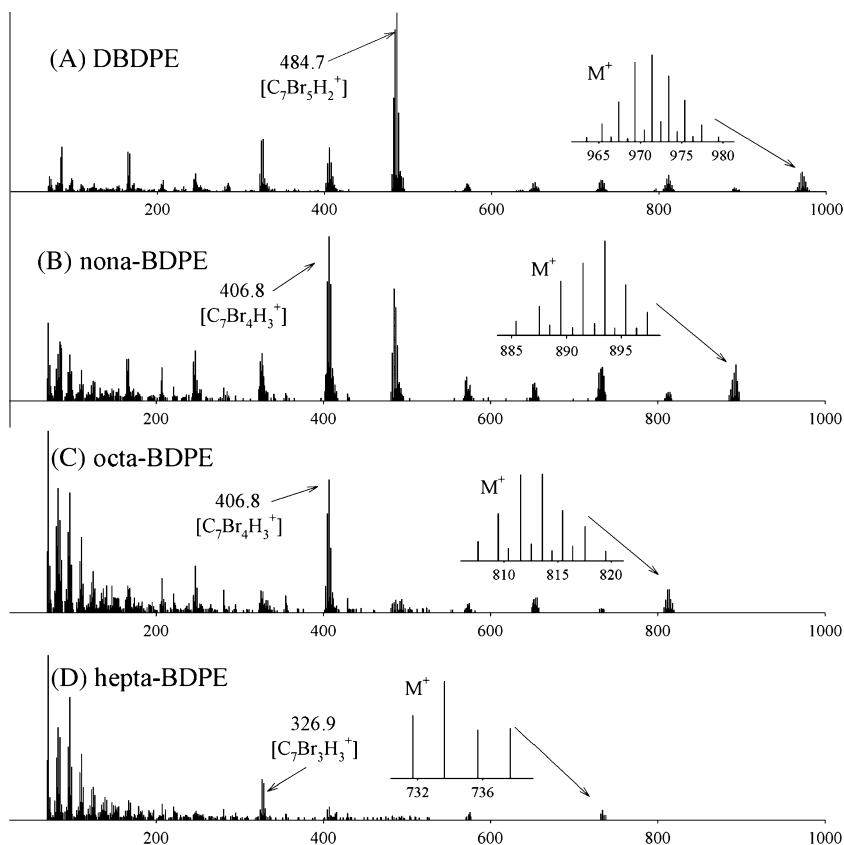


Fig. 5. Electron impact (EI) full scan mass spectra of DBDPE, nona-BDPEs, octa-BDPEs, and hepta-BDPEs.

The EI full-scan mass spectrum for DBDPE and the degradation intermediates in *n*-hexane observed during the experiment process are given in Fig. 5. The molecular ions for these peaks were obtained as m/z 893.5, 813.6, and 733.5, suggesting the formation of nona-, octa-, and hepta-BDPE homologs. The most abundant fragment ions for DBDPE, nona-BDPE, octa-BDPE, and hepta-BDPE were at m/z 484.7, 406.8, 406.8, and 326.9, respectively, corresponding to the ion fragment of $C_7Br_5H_2^+$ (pentabromotoluene), $C_7Br_4H_3^+$ (tetrabromotoluene), and $C_7Br_3H_3^+$ (tribromotoluene). Though the molecular formula can be deduced from the mass spectra, the substitution pattern of the bromines on the aromatic rings cannot be determined at this time. Thus, the major lower brominated BDPE congeners found in the irradiated samples were numbered in Fig. 4.

Although nona-BDPEs were found in the original solutions, the findings could still indicate that the degradation of DBDPE started from the loss of one bromine atom to form nona-BDPE congeners as shown in Fig. 6. The presence of nona-BDPEs in the original solutions may be a result of impurities of the technical products and/or degradation during sample injection as observed for polybrominated diphenyl ethers (Björklund et al., 2004). The concentrations of nona-BDPE-2 and -3 (defined in Fig. 4) increased continuously from 0 to 45 min, after which their concentrations began to decline. In contrast, the continuously declining concentration of nona-BDPE-1 (defined in Fig. 4) during the experiment period (0–70 min) may suggest that no generation of this congener occurs or that the formation rate of this compound is slower than its degradation (to less brominated BDPEs) or transformation (to nona-BDPE-2 or -3 via rearrangement) rate. This debromination process is different from that of deca-BDEs in the present study in which all three nona-BDEs concentrations increased before 25 min of irradiation (Fig. S2). Our observation for deca-BDE is also in agreement

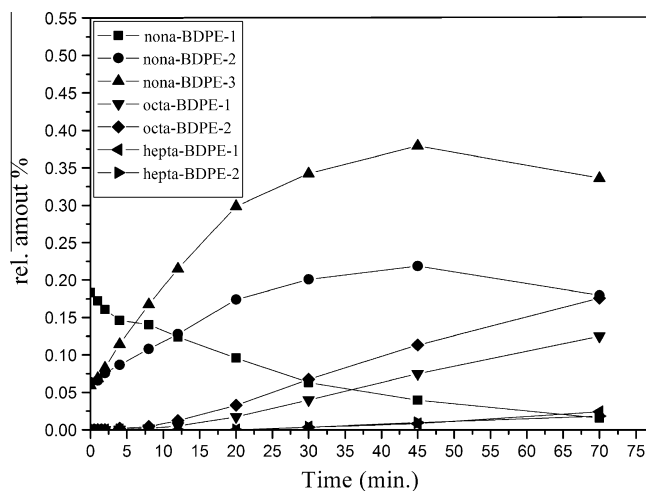


Fig. 6. Relative distribution of photolytic degradation intermediates over the 70 min irradiation period in *n*-hexane. The fraction of a degradation intermediates was calculated by its peak area normalized to that of DBDPE at t_0 .

with previous studies (Shih and Wang, 2009). The consistently increasing concentrations of octa-BDPEs (which appeared at 4 min) during the degradation processes demonstrates the continuous formation of lower brominated BDPE congeners following the loss of the first bromine atom. Formation of hepta-BDPE congeners occurred at approximately 30 min and exhibited increasing amounts as the irradiation time increased. Though tetra- to hexa-BDPEs were not observed in our experiments, their occurrence from the degradation of higher brominated congeners is expected

at longer exposure times. Previous studies (Bezares-Cruz et al., 2004b; Lagalante et al., 2011) have also found that even lower brominated PBDE congeners (tetra- to hexa-BDEs) were formed after longer irradiation period.

The current photolytic degradation experiments were performed on DBDPE in solvents and on silica gel. Large differences in the photolytic degradation behaviors of DBDPE may exist between lab matrixes and the natural environmental media such as atmospheric particles, soil, and water as suggested previously for deca-BDEs (Raff and Hites, 2007). Additional evidence is therefore needed to understand the potential photolytic degradation kinetics and to examine the occurrence of degradation intermediates of DBDPE in the real environment.

4. Conclusions

Photolytic degradation of DBDPE occurs in various solvents and on silica gel under UV irradiation within the degradation processes of 320 min. The degradation rates were strongly dependent on the matrixes, with the fastest rate in tetrahydrofuran ($t_{1/2} = 6.0$ min) and lowest rate in methanol/water ($t_{1/2} > 240$ min). The experimental data in tetrahydrofuran, *n*-hexane, and on silica gel matrixes follow the first-order reaction. Nevertheless, the matrixes have a minor influence on the degradation intermediates of DBDPE. During the degradation, varied amounts of nona-, octa-, and hepta-BDPE congeners were observed. Further research is needed to determine the occurrence of photolytic degradation of DBDPE in the natural environment.

Disclosure statement

All authors declare they have no actual or potential competing financial interests.

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Appendix A. Supplementary material

Supplementary data associated with this article can be found, in the online version, at <http://dx.doi.org/10.1016/j.chemosphere.2012.05.006>.

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