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Photochemical transformation of five novel brominated flame retardants: Kinetics and photoproducts

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HIGHLIGHTS

- Photochemical behavior of five novel brominated flame retardants was investigated.
- Environmental half-lives of the target compounds were estimated.
- Debromination is a main phototransformation pathway of DPTE and BTBPE.
- Ether bond cleavage is also a main phototransformation pathway, and bromophenols were identified for BTBPE.

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ABSTRACT

Many novel brominated flame retardants (NBFRs) are used as substitutes of polybrominated diphenyl ethers (PBDEs) in recent years. However, little is known about their phototransformation behavior, which may influence the environmental fate of these chemicals. In this study, photochemical behavior of five NBFRs, allyl-2,4,6-tribromophenyl ether (ATE), 2-bromoallyl-2,4,6-tribromophenyl ether (BATE), 2,3-dibromopropyl-2,4,6-tribromophenyl ether (DPTE), 1,2-bis(2,4,6-tribromophenoxy)ethane (BTBPE), and 2,4,6-tris(2,4,6-tribromophenoxy)-1,3,5-triazine (TTBP-TAZ) was investigated. Results show all the five NBFRs can undergo photochemical transformation under simulated sunlight irradiation. Quantum yields (Φ) of the five NBFRs varied from 0.012 of TTBP-TAZ in hexane to 0.091 of BTBPE in methanol. Half-lives ($t_{1/2}$) relevant with solar irradiation of these NBFRs were estimated using the determined Φ, and the values are 1.5–12.0 d in summer and 17.1–165.0 d in winter. Debrominated and ether bond cleavage products were identified in the phototransformation of DPTE and BTBPE. Debromination on the phenyl is a main phototransformation pathway for DPTE, and both debromination and ether bond cleavage are main phototransformation pathways for BTBPE. This study is helpful to better understand the photo-transformation behavior of the NBFRs.

1. Introduction

Brominated flame retardants (BFRs) have been widely used in combustible materials to increase their fire resistance (Alaee et al., 2003; Chen et al., 2012). The most widely used BFRs, poly-brominated diphenyl ethers (PBDEs), have become ubiquitous in the environment. Because of the serious environmental and health burdens, the production and usage of some PBDEs have been banned or restricted in some countries (Altarawneh and Dlugogorski, 2014). As a result, some novel brominated flame retardants (NBFRs) have been produced and used as the substitutes of PBDEs (Covaci et al., 2011). Because of the large production and usage, NBFRs can also be released into the environment inevitably. Some NBFRs, e.g. allyl-2,4,6-tribromophenyl ether (ATE), 2-bromoallyl-2,4,6-tribromophenyl ether (BATE), 2,3-dibromo propyl-2,4,6-tribromophenyl ether (DPTE), 1,2-bis(2,4,6-tribro mophenoxy)ethane (BTBPE) and 2,4,6-tris(2,4,6-tribromophen oxy)-1,3,5-triazine (TTBP-TAZ), have been detected in indoor dust (Stapleton et al., 2008; Ballesteros-Gómez et al., 2014), sewage sludge (Zeng et al., 2014), air (Arinaitwe et al., 2014), water (Möller et al., 2011), animals (Guerra et al., 2012), and even in maternal serum and milk (Zhou et al., 2014).

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Owing to their structural similarity to PBDEs, NBFRs were assumed to be potentially persistent in the environment (Kuramochi et al., 2014). It is of significance to understand their transformation behavior that determines their environmental persistence. Photochemical transformation has been proved to be an important elimination pathway of PBDEs (Eriksson et al., 2004; Fang et al., 2008; Xie et al., 2009; Bendig and Vetter, 2013). The photolytic rate constants of PBDEs were proved to be related with the molecular structural parameters, such as bromination degree (n_{Br}), the gap of the frontier molecular orbital energies ($E_{LUMO} - E_{HOMO}$), the average formal charge on Br (q_{Br}) and the most positive formal charge on Br atoms (q^{+}_{Br}) (Chen et al., 2007; Xie et al., 2009; Wang et al., 2012). Similar to PBDEs, molecular structures of the five tribromophenoxy substituted flame retardants, ATE, BATE, DPTE, BTBPE, and TTBP-TAZ, also have bromobenzene moieties and ether bonds linked to the phenyls (Table 1). We hypothesized that these NBFRs may also undergo photochemical degradation when exposed to UV light. However, the photochemical behavior of these compounds is not yet known.

Debromination is a main photochemical reaction pathway for PBDEs (Fang et al., 2008; Sanchez-Prado et al., 2005). Besides debrominated products, more toxic polybrominated dibenzofurans and bromophenols were also detected in phototransformation of PBDEs (Eriksson et al., 2004; Bendig and Vetter, 2013). Considering the structural similarity with PBDEs, we supposed that 2,4,6-tribromophenol can be generated in the photodegradation of the five NBFRs. It is of significance to identify their photochemical products for better risk assessment (Chen et al., 2015).

In this work, photochemical transformation of the five NBFRs (ATE, BATE, DPTE, BTBPE, TTBP-TAZ) was investigated. Their photolysis rate constants (k) and quantum yields (Φ) were determined. Molecular structural descriptors were computed with the density functional theory (DFT) and employed to relate with their photochemical reactivity parameters. The photoproducts of DPTE and BTBPE were identified with GC-MS. DPTE can be highly concentrated in animals (von der Recke and Vetter, 2007), which is a representative of the NBFRs for which the molecular structures contain a phenyl. BTBPE has been broadly used and is the most widely detected in the environment among the five NBFRs (Ma et al., 2012).

2. Materials and methods

2.1. Materials

ATE (97.0% purity), BATE (98.3% purity), DPTE (99.9% purity), BTBPE (99.9% purity) and TTBP-TAZ (97.0% purity) were purchased from AccuStandard. *p*-Nitroanisole (97% purity) was from Alfa Aesar. Pyridine (99.9% purity) was from Sigma–Aldrich. All organic solvents (toluene, tetrahydrofuran, acetonitrile, hexane, and methanol) with chromatographically purity were purchased from TEDIA. Ultrapure water (18 MΩ) was obtained from a purification system of Shanghai Laike Instrument Co., Ltd.

2.2. Light irradiation experiments

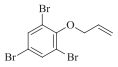
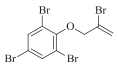
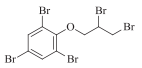
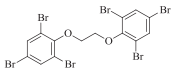
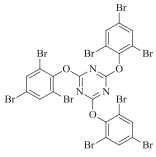
The stock solutions of ATE, BATE and TTBP-TAZ were prepared in toluene and the stock solutions of DPTE and BTBPE were prepared in tetrahydrofuran. Photolysis solutions (1 μM) were prepared by evaporating toluene or tetrahydrofuran in an aliquot of the stock solutions and subsequently re-dissolving in hexane or methanol. The experiment was performed in an XPA-1 merry-go-round photochemical reactor (Xujiang Electromechanical Plant, Nanjing, China) with a 500 W mercury lamp equipped with 290 nm filters to mimic the UV-A and UV-B portions of sunlight. Quartz tubes (outer diameter, 1.3 cm; inner diameter, 1.0 cm; $V = 15.0$ mL) containing the photolysis solutions with a stopper (including dark controls) were placed in the reactor for light irradiation. The light intensity at the surface of quartz tubes is shown in Fig. S1. A water cooling system was used to ensure a steady temperature around 28 °C in the reactor. All the photochemical experiments were conducted in triplicate.

Quantum yields were measured using *p*-nitroanisole/pyridine (PNA/pyr) as the chemical actinometer, and were calculated based on the following equation (Dulin and Mill, 1982):

$$\Phi_t = \frac{k_t}{k_a}\frac{\Sigma I_\lambda \varepsilon^a_\lambda}{\Sigma I_\lambda \varepsilon^t_\lambda}\Phi_a \quad (1)$$

where the subscript/superscript "t" and "a" refer to the target compound and the actinometer, respectively; I_λ refers to lamp irradiance at a specific wavelength, which was calculated by

Table 1
Molecular structures and values of photolysis rate constants (k), quantum yields (Φ), and relative light absorption (A_r) of the five NBFRs.

Compounds	Structures	Solvent	k (h^{-1})[a]	Φ[a]	$A_r \times 10^{-2}$
ATE		Hexane	0.262 ± 0.021	0.032 ± 0.002	2.75
		Methanol	0.189 ± 0.031	0.030 ± 0.005	2.23
BATE		Hexane	0.244 ± 0.009	0.036 ± 0.005	2.14
		Methanol	0.162 ± 0.007	0.028 ± 0.002	2.14
DPTE		Hexane	0.139 ± 0.003	0.021 ± 0.001	2.02
		Methanol	0.104 ± 0.009	0.018 ± 0.001	1.62
BTBPE		Hexane	0.344 ± 0.008	0.064 ± 0.001	3.84
		Metanol	0.214 ± 0.013	0.091 ± 0.006	2.27
TTBP-TAZ		Hexane	0.154 ± 0.013	0.012 ± 0.001	2.07
		Methanol	0.113 ± 0.011	0.022 ± 0.002	1.11

[a] The errors of k and Φ represent the 95% confidence levels.