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Investigation of photodegradation products generated after UV-irradiation of five polybrominated diphenyl ethers using photo solid-phase microextraction

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Abstract

In this study, the photoinduced degradation of five polybrominated diphenyl ethers (PBDEs), BDE-47, BDE-100, BDE-99, BDE-154 and BDE-153, is studied using solid-phase microextraction polydimethylsiloxane fibers as photolytic support. PBDEs are extracted from aqueous solutions using SPME fibers that are subsequently exposed to UV irradiation for different times (from 2 to 60 min). Photodegradation kinetics of the five PBDEs, tentative identification and photochemical behavior of the generated photoproducts, as well as photodegradation pathways, have been studied employing this on-fiber approach technique (photo-SPME) followed by gas chromatography–mass spectrometry analysis. Aqueous photodegradation studies have also been performed and compared with photo-SPME. All the photoproducts detected in the aqueous experiments were previously found in the photo-SPME experiments. In this study, reductive debromination by successive losses of bromine atoms is confirmed as the main photodegradation pathway of PBDEs. A large number of PBDEs were obtained as photoproducts of the five target analytes. Other mechanism of photodegradation observed was intramolecular cyclization from the homolytic dissociation of the C—Br bond; thus, polybromo-dibenzofurans were generated. This work contributes to the study of the photodegradation of PBDEs and shows the potential of photo-SPME to evaluate the photo-transformation of organic pollutants.

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1. Introduction

Polybrominated diphenyl ethers (PBDEs) are a class of compounds widely used as flame retardant additives. The environmental concerns about these substances have risen in the last years and they are now considered as emerging environmental pollutants [1–3]. Three major commercial formulations of PBDEs are produced: deca-BDE, octa-BDE and penta-BDE. In general the lower brominated mixtures are more toxic than the higher brominated ones. The toxicological concerns about exposure to low environmental concentrations of PBDEs focus on their potential to act as hormone disruptors, neurodevelopmental toxics, and, in some cases, carcinogenic agents. In addition, the combustion of these compounds could generate highly toxic products, such as polybrominated dibenzofurans and polybrominated dibenzo-*p*-dioxins [3–6].

Therefore, it is of great concern to understand the degradation of PBDEs in the environment. Deca-BDE and other highly brominated PBDEs are rapidly debrominated in the environment to less brominated PBDEs as recent studies indicate [7,8]. Biodegradation might not be significant while

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photodegradation appears to be one of the main causes of degradation.

Several authors have investigated the photolytic lability of individual congeners, mainly of decabromo-diphenyl ether, and found that when PBDEs are dissolved in organic solvents, debromination occurs in the presence of UV light [9–12]. Ohta et al. [9] studied the photochemical behavior of deca-BDE in organic and water-like solvent (a mixture of toluene–ethanol–water, 1:3:6) under UV light and sunlight. They observed a rapid photodecomposition of deca-BDE in toluene under UV-light and they confirmed the debromination as the photochemical pattern of the studied compound. Söderström et al. [10] also studied the photodegradation of deca-BDE in different matrices (toluene, silica gel, sand, soil and sediment) under UV-light and outdoor sunlight, showing the same conclusions that Ohta et al. [9], but they identified the presence of polybrominated dibenzofurans (PBDFs) in some of the analyzed samples. Photodegradation studies have rarely been performed on other PBDE congeners than BDE-209. Recently, however, Peterman et al. [13] briefly reported on sunlight photolysis of a mixture of 39 PBDEs in triolein. Also, in a very recent study Eriksson et al. [12] examined the UV-light degradation rate of individual PBDE congeners in methanol, tetrahydrofuran and methanol–water mixtures. They observed that the rate of photodecomposition of PBDEs seems to be dependent on the degree of bromination; the lower brominated congeners degrade slowly, whereas the octa- and deca-BDE congeners decompose rapidly. In addition, they studied the decomposition products of BDE-209. Several nona-, octa-, hepta- and hexa-BDEs were identified, whereas, the generated compounds with less than six bromine atoms were tentatively identified as PBDFs.

The aim of this work is to contribute to the study of the photodegradation of PBDEs, employing a new, simple and fast methodology called photo solid-phase microextraction (photo-SPME). In this study, the compounds included—BDE-47, BDE-99, BDE-100, BDE-153 and BDE-154—are the most abundant congeners in penta-BDE commercial formulations which are considered as the most toxic ones [14]. In addition, three of these compounds—BDE-47, BDE-99 and BDE-100—are the PBDE congeners most commonly found in environmental samples. SPME is a suitable technique for the extraction of persistent organic pollutants that has been recently applied to the determination of PBDEs [15]. The possibility of performing photochemical studies in SPME fibers has been demonstrated [16–21]. In this technique, after the extraction of the target compounds, the fiber is exposed to light for a selected period of time. Finally analyses are performed by gas chromatography–mass spectrometry (GC–MS).

Photo-SPME presents the well-known advantages of SPME and permits to simplify the classical way to carry out photochemical studies. Moreover, as the photoproducts are generated “in situ” in the fiber coating, they are directly analyzed, so sample manipulation and possible losses of photoproducts are minimized. Thus, photodegradation kinetics of the five studied PBDEs, photodegradation pathways, identity and photochemical behavior of generated photoproducts have been determined by photo-SPME. Among the generated photoproducts, various polybromo-dibenzofurans have been found.

In this work, SPME was also used to extract photoproducts in direct photodegradation of aqueous solutions containing PBDEs, through experiments conducted in the classical way (extraction after irradiation), in order to compare photo-SPME and aqueous photodegradation. Close photodegradation behavior was observed in both cases and the generation of the same photoproducts was confirmed.

2. Experimental

2.1. Reagents and materials

2,2′,4,4′-Tetrabromo-diphenyl ether (BDE-47); 2,2′,4,-4′,5-pentabromo-diphenyl ether (BDE-99), 2,2′,4,4′,6-pentabromo-diphenyl ether (BDE-100), 2,2′,4,4′,5,5′-hexabromo-diphenyl ether (BDE-153) and 2,2′,4,4′,5,6′-hexabromo-diphenyl ether (BDE-154) at 50 μg/mL in nonane were supplied by Wellington Labs. (Techno Spec, Barcelona, Spain). Water solutions of each PBDE (2 ng/mL) were prepared by the addition of an intermediate acetone solution of 2 μg/mL. All solvents used (analytical grade) were purchased from Merck (Mollet del Vallés, Barcelona, Spain).

2.2. GC–MS analysis

Analysis were performed using a Varian 3800 gas chromatograph (Varian Chromatography Systems, Walnut Creek, CA, USA) equipped with a 1079 split/splitless injector and a Saturn 2000 ion trap mass spectrometer (Varian Chromatography Systems). The system was operated by Saturn GC–MS WorkStation v5.4 software. Experimental parameters were as follows: column HP-5MS, 30 m × 0.25 mm i.d., 0.25 μm film; temperature program: 60 °C, hold 2 min, rate 15 °C/min to 250 °C, rate 5 °C/min to a final temperature of 280 °C, hold for 8 min. Helium was employed as carrier gas, with a constant flow of 1.2 mL/min. Injector was programmed to return to the split mode after 2 min from the beginning of a run. Injector, trap, manifold and transfer line temperatures were 280, 250, 120 and 280 °C, respectively. The mass spectrometer was used in the positive electron ionization mode at 70 eV with automatic gain control. A range of *m*/*z* 100–650 was scanned at a scan rate of 1 s/scan. Multiplier was set at a nominal value of 1850 V.

2.3. Solid-phase microextraction and photodegradation procedures

A headspace solid-phase microextraction (HS-SPME) sampling procedure for PBDEs was taken from that

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