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Chemosphere 60 (2005) 922–928

CHEMOSPHERE

www.elsevier.com/locate/chemosphere

Photochemical studies of a polybrominated diphenyl ethers (PBDES) technical mixture by solid phase microextraction (SPME)

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Received 19 May 2004; received in revised form 22 December 2004; accepted 13 January 2005
Available online 13 February 2005

Abstract

In this work the photochemical behaviour of a technical mixture of polybrominated diphenyl ethers (PBDEs) (BDE-47, BDE-99, BDE-100, BDE-153 and BDE-154) has been studied.

The mixture of BDEs was extracted from aqueous solutions using SPME fibers that were subsequently exposed to different UV irradiation times, procedure so-called *Photo-SPME*. PBDEs photochemical studies in such medium have been accomplished for the first time.

Twenty one different photoproducts, all of them generated by successive bromine atoms losses, have been identified, being their photoformation–photodegradation curves easily determined by the Photo-SPME technique.

Keywords: Polybrominated diphenyl ethers (PBDES); Photodegradation; UV irradiation; Photo-SPME; GC–MS; Brominated flame retardants (BFR)

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1. Introduction

Polybrominated diphenyl ethers (PBDEs) are brominated flame retardant chemicals (BFR) that are added to manufacture products including paints, plastics and textiles. The estimated global consumption of BFRs indicates that their usage is on the rise. PBDEs have attracted the most attention due to their high usage patterns and their persistence and hydrophobicity, two characteristics that make them amenable to bioaccumulation and biomagnification (Alaee et al., 2001; Tittlemier et al., 2002).

Since the 80s, several studies had reported the presence of PBDEs in environmental and human samples (Watanabe et al., 1987; Stanley et al., 1991; Watanabe et al., 1995; Noren and Meironyte, 1998; Hyotylainen and Hartonen, 2002; Kuosmanen et al., 2002). The European Community (EU) decided to ban

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doi:10.1016/j.chemosphere.2005.01.006

pentabromo- and octabromodiphenyl ether products starting from August 2004, based on the risk assessments (Cox and Efthymiou, 2003).

The toxicological concerns about exposure to low environmental concentrations of PBDEs focus on their potential to act as hormone disruptors, neurodevelopment toxics and, in some cases, as carcinogenic agents. In addition, the combustion of these compounds could generate highly toxic products such as polybrominated dibenzofurans (PBDFs) and polybrominated dibenzo-*p*-dioxins (PBDDs) (World Health Organization, 1994; McDonald, 2002; Palm et al., 2002).

PBDEs have similar structures to PCBs, but with an oxygen atom between the aromatic rings. The theoretical number of congeners is 209, and the numbering is analogous to the IUPAC system for numbering PCBs. In practice, not all congeners are used in commercial products. Three major commercial formulations of PBDEs are produced: decaBDE, octaBDE and pentaBDE. Although the most frequently used BFR is decaBDE, lower brominated PBDEs are more often found in environmental samples. The fully brominated deca-BDE congener is poorly absorbed, rapidly eliminated and thus not bioaccumulated; it is likely one of the least bioactive congeners of PBDEs. In contrast, the low molecular weight congeners, tri- to hexa-BDEs are almost completely absorbed, slowly eliminated and highly bioaccumulated (Pijnenburg et al., 1995). Thus, the major PBDEs found in environmental samples have been 2,2′,4,4′-tetraBDE (BDE-47), 2,2′,4,4′,5-pentaBDE (BDE-99) and 2,2′,4,4′,6-pentaBDE (BDE-100), the three most abundant compounds in the pentaBDE technical mixture studied in this work.

To evaluate the fate of PBDEs in the environment, the influence of both abiotic and biotic factors should be considered. Data on environmental fate, although limited, suggest that biodegradation is not an important degradation pathway, but the photodegradation may play a significant role and it is involved in the dissipation of these compounds in water, soils and plants. Therefore, it is very important to know the photochemical behaviour of PBDEs, their photodegradation kinetics and it is also important to identify photoproducts, which could have biological and toxicological properties completely different from those of the original compounds. Regarding to the photodegradation of these compounds, very few studies are found in literature (Watanabe and Tatsukawa, 1987; Sellstrom et al., 1998; Soderstrom et al., 2004) and mostly concerning decaBDE; showing that this highly brominated BDE undergoes rapid photolytic debromination in organic solvents (hexane, toluene) in the presence of ultraviolet light and sunlight.

Solid-phase microextraction (SPME) is a solvent-free analytical technology, which has the advantage of simplicity, lower detection limits and good reproducibility. Analytes are extracted from different types of samples with a polymer-coated fused silica fiber (Arthur and Pawliszyn, 1990). Recently, this technique has been applied to the extraction of PBDEs and PBBs in water samples (Polo et al., 2004).

In this work, photochemical behaviour and generated photoproducts of a penta-BDE technical mixture (pentamix) are studied employing *Photo-SPME*. This technique has been recently introduced and applied in the photodegradation studies of different pollutants such as PCBs, DDT and musk compounds (Lores et al., 2002a,b; Llompart et al., 2003; Sánchez-Prado et al., 2004). This is a powerful tool to carry out photodegradation studies of organic compounds. Besides, the generation of photoproducts takes place "in-situ" in the SPME fiber. Due to their higher concentration on the fibers, Photo-SPME avoids the need of any additional extraction steps for the identification of the generated degradation products. The results shown in this work confirm the potential of the new technique and contribute to the knowledge of the PBDEs photochemical behaviour. These lab studies are considered the first step to characterize their "on-fiber" photochemistry, which will give basic information to develop later studies in real environmental samples.

2. Experimental

2.1. Reagents and materials

PentaBDE technical mixture (pentamix) at 10 μg ml^{-1} in cyclohexane was supplied by Dr. Ehrenstorfer (Augsburg, Germany). The composition of the commercial pentamix was experimentally confirmed: 2,2′,4,4′-tetrabromodiphenylether (BDE-47) 4.1 μg ml^{-1}, 2,2′,4,4′,5-pentabromodiphenylether (BDE-99) 1.2 μg ml^{-1}, 2,2′,4,4′,6-pentabromodiphenylether (BDE-100) 4.1 μg ml^{-1}, 2,2′,3,4,4′-pentabromodiphenylether (BDE-85) 0.1 μg ml^{-1}, 2,2′,4,4′,5,5′-hexabromodiphenylether (BDE-153) 0.23 μg ml^{-1} and 2,2′,4,4′,5,6′-hexabromodiphenylether (BDE-154) 0.34 μg ml^{-1}. Chemical structures, retention times and quantification and identification ions selected for these compounds are depicted in Table 1.

Intermediate solutions were prepared in acetone (Merck, Mollet del Vallés, Barcelona, Spain, analytical grade). The water was deionized and further purified on a Milli-Q® water purification system from Millipore (Bedford, MA, USA). Water solutions containing the target analytes were prepared by appropriate dilution of the acetone standard solutions. The corresponding concentration of all analytes in the working water