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Photochemical Degradation of Polybrominated Diphenyl Ethers in Micro Photo Reactor

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1. Introduction

Polybrominated diphenyl ethers (PBDE, Figure 1) were widely used as flame retardants in plastics. There are highly persistent and bio-accumulative toxicants that came to the attention after their huge quantities had been released into the environment. Due to distinct similarity of PBDE to the polychlorinated biphenyls (PCB), the PBDE present a potential health hazard. In order to decrease the environmental impact of PBDE and to stop their spread in the food chain the different degradation methods have been investigated.

Photochemical degradation of PBDE in environment is often cited as a potentially significant path of destruction PBDE molecules. However, we know little about the mechanism and the level degradation of PBDE. Still there is a need for more data on the basic characteristics of PBDEs to better understand and describe their environmental fate. Hence, the aim of this study was to investigate the photochemical degradation of PBDEs with different degrees of bromination. Many studies focused on kinetics and mechanism of the photochemical degradation of PBDE. These studies showed that exposure to artificial UV or natural sunlight leads to gradual loss of bromine from the molecules of PBDE, already in a very short time (i.e. minutes) [1-6].

Most authors used for their studies of technical decaBDE mixture, or pure congener BDE 209 [1, 2]. Very few studies used the technical octaBDE mixtures [2] or pentaBDE, or congener BDE 47, which are most abundantly represented in the environment [7, 8].

Photodegradation of PBDE by catalysis over nanoporous TiO₂ in microwave field showed very positive results. Debromination of BDE 209 after 240 minutes was very high and reached 99% (from initial value of 14 125 ng/mL). Lower brominated congeners including the tri brominated congener BDE 28 were safely determined [9].

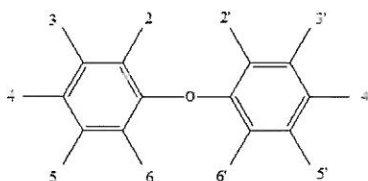


Figure 1 Structural formula of diphenyl ethers with numbered positions.

2. Method

2.1. Photochemical degradation of PBDE in the photomicroreactor

Introductory sets of continuous experiments were performed in the photomicroreactor (PMR) with a previously prepared saturated hexane solution of decaBDE. Experiments were carried out without catalyst at a constant mixture flow rate of 0.1 mL/min. The samples were taken after a single and double pass through the PMR, corresponding to residence time of 96s and 192s, respectively. Temperature during experiments was 25°C, pressure was atmospheric. Inside the microphotoreactor, a 100µm layer of liquid was irradiated with a 100W mercury lamp; light intensity was 27.9 mW/cm².

All experiments were performed with decabromodiphenyl ether, i.e. the BDE 209 congener. Since 2004, BDE 209 is the only permitted flame retardant in the EU. The choice of this congener was advantageous because it breaks down into lower brominated diphenyl ethers (pentaBDE and octaBDE) that were widely used as fire retardants in the past and now constitute the major component of BDE contamination. The initial concentration of BDE 209 was 55 460 ng/mL in hexane.

2.2. Chemicals

Decabromodiphenyl ether (BDE-209, 98%, Sigma-Aldrich s. r. o.), n-hexane (GC for analysis, Merck Chemicals).

2.3. Experimental set-up

The experiment was conducted in the apparatus combining the photochemistry with microtechnology. The light source was a high pressure Hg lamp with monochromatic filters. Light passed through a cuvette with water and toward the gap of photomicroreactor. The reaction solution continuously flowed through the photomicroreactor.

3. Results and discussion

3.1. Photochemical degradation in the photomicroreactor

Experiments in a photochemical microreactor were analyzed in an accredited laboratory. For this reason, only selected congeners were detected with the analytical standard. Figure 2 documents the results of BDE 209 degradation after one and second pass of the solution through the PMR at the light intensity 27.9 mW/cm^2 and constant liquid flow of 0.1 ml/min . Residence time in the reaction zone (irradiation time) was 96 and 192 seconds.

Debromination of BDE 209 after 96 seconds was already very high and reached 79.2%. After 192 seconds, degradation of 89.5% of the initial BDE 209 concentration was achieved.

Figure 3, Figure 4 and Figure 5 show the changes in concentration of lower BDE's during the photo degradation in PMR. The loss of bromine atoms from position 3' does not happen every time; bromine atoms in position 3' are strongly attached even in less brominated congeners, see BDE 66. Bromine atoms in positions 2, 2' and 4, 4' are held firmly, see BDE 99. Presence of BDE 47 congener shows how difficult it is to detach the bromine atoms residing in positions 2 and 4, respective 2' and 4'. It is not possible to say whether it is easier to detach bromine from ortho- or para- positions. These positions are resistant to degradations on both rings.

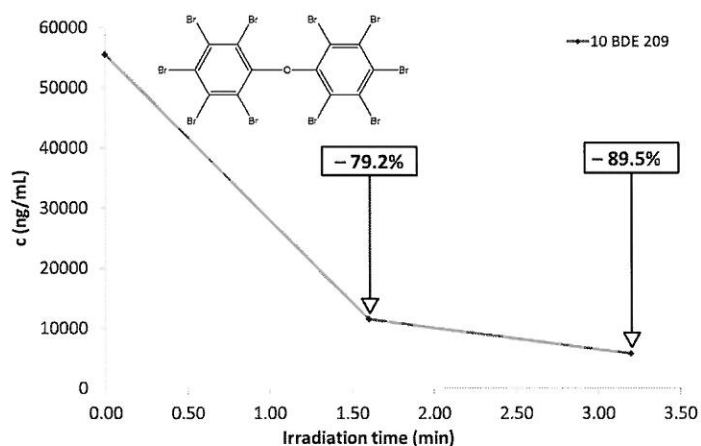


Figure 2 Photodegradation of decaBDE (BDE 209) in the photomicroreactor.

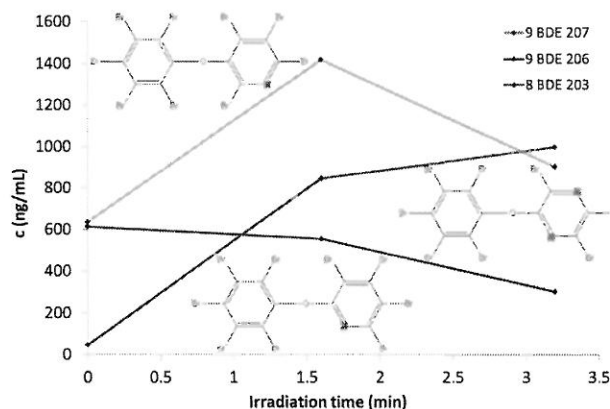


Figure 3 Photodegradation of PBDE (BDE 207, 206, 203) in the photomicroreactor.

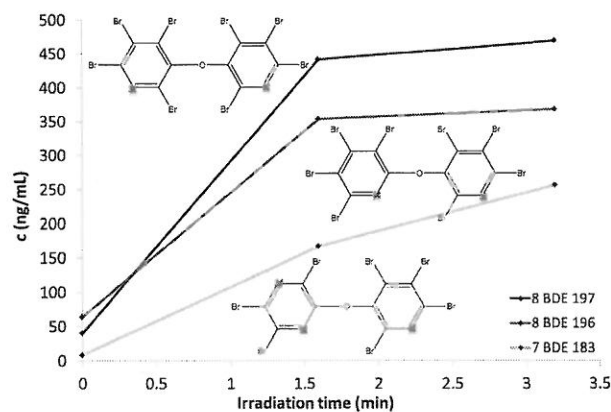


Figure 4 Photodegradation of PBDE (BDE 197, 196, 183) in the photomicroreactor.

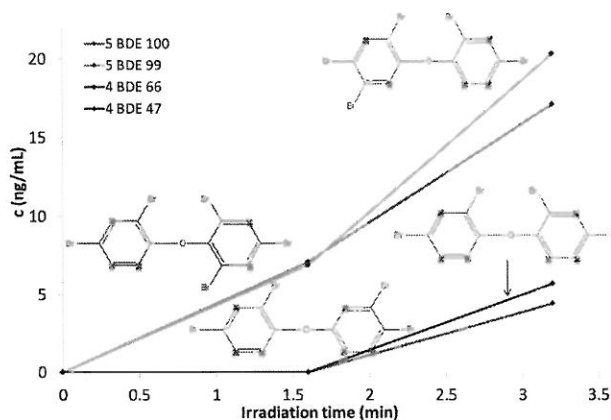


Figure 5 Photodegradation of PBDE (BDE 100, 99, 66, 47) in the photomicroreactor.

4. Conclusion

The data show that the efficiency of degradation of PBDE after one pass of the solution through the photomicroreactor was very high. The resulting spectrum of lower brominated PBDEs was similar to the spectrum obtained in the batch experiment by catalysis over nanoporous TiO_2 in microwave field after 240 min [9]. After second pass through the photomicroreactor, 89.5% BDE-209 was destroyed and the product mixture contained tetraBDE and triBDE. After very short period of UV irradiation (3.6 min), the mixture contained all tracked congeners. The congener BDE-203 proved to be the most stable, and after its build-up (achieved after the first 1.6 minutes of irradiation) degraded slowly. With time, the content of lower congeners BDE-47, BDE-66, and BDE-99 was increasing and the amount of higher congeners (octa-BDE and higher) was decreasing. The degradation does not happen in strict sequence, for example bromine atoms remain in position 3' while position 2' is vacated, see BDE-66. The results indicate that the higher concentrations of lower congeners may be obtained after another pass through the photomicroreactor.

In comparison with the experiment in microwave field, the PMR demonstrated the advantages of microtechnology consisting in our case in the higher ratio of the area of reaction surface to the volume of the reactor zone, and the continuous processing and accurate control of the reaction conditions.

Results of this introductory study serve as motivation for further research focusing especially on the methods of degradation of tetraBDE and lower brominated congeners.

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