Photodegradation of decabromodiphenyl ether in solvents under simulated solar irradiation

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Introduction

The polybrominated diphenyl ethers (PBDEs) have been identified as being of particular concern due to their global distribution and bioaccumulating properties, observed in animals including humans. However, yet information regarding its environmental transformation rates and pathways are largely unknown.

The aim of this study was to perform a more detailed study of the photolytic debromination of BDE 209 (deca-BDE) to evaluate if this was a potential source for BDE 47 and others lower brominated BDEs in the environment, and if it is also responsible for the formation of polybrominated dibenzofurans (PBDFs). In addition, photodegradation experiments have been carried out under different temperatures and with different solvents to evaluate the importance of these factors in the rate and pathways of the BDE 209 degradation.

Materials and Methods

1- Deca-BDE for degradation studies

The deca-BDE (>98%) used into the degradation studies was purchased from Fluka Chemie AG. The solutions tested were prepared dissolving the deca-BDE in toluene (12,5 $ng.\mu L^{-1}$, and 12000 $ng.\mu L^{-1}$) and in methanol/water (15,0 $ng.\mu L^{-1}$); both solvents were analytical grade from Riedel de-Häen (Germany).

2- UV irradiation experiments

Irradiation experiments were performed in a QUV accelerated weathering tester (Q-Panel Lab Products, Cleveland, USA) equipped with four UVA-340 lamps as the radiation source. The lamps give spectra as close as possible to sunlight in the critical, short wavelength UV region between 365 nm and the solar cut-off of 295 nm.

The photochemical process takes place when the 1,5 mL of stock solutions of deca-BDE are exposed in a Duran glass vials placed 5 cm to the irradiation of the lamps. The samples were removed initial at various time points between 0 and 48 h (0 min, 15 min, 30 min, 1 h, 2 h, 4h, 8 h, 24 h and 48 h). After the first evaluation of the experiments, the experiments were carried out just between 0 and 4 h.

3- Standard Solutions

The PBDEs standards solutions used for quantification were: EO 5099 (containing 39 PBDEs: BDE 1, BDE 2, BDE 3, BDE 7, BDE 8, BDE 10, BDE 11, BDE 12, BDE 13, BDE 15, BDE 17, BDE 25, BDE 28, BDE 30, BDE 32, BDE 33, BDE 35, BDE 37, BDE 47, BDE 49, BDE 66, BDE 71, BDE 75, BDE 77, BDE 85, BDE 99, BDE 100, BDE 105, BDE 116, BDE 119, BDE 126, BDE 138, BDE 153, BDE 154, BDE 155, BDE 166, BDE 181, BDE 183 and BDE 190) and Deca-BDE both from Cambridge Isotope Laboratories (Andover, MA, USA). The technical Octa-BDE mixture (DE-79) from Great Lakes Chemical Corporation (Indiana, USA) was used for the quantification of octa-BDEs.

For the quantification of PBDFs and PBDDs was used the EDF-4152 solution (containing 2,3,7,8 TBDD, 1,2,3,4,7,8 HxBDD, 1,2,3,6,7,8 HxBDD, OBDD, 2,3,7,8 TBDF, 1,2,3,7,8 PeBDF, 2,3,4,7,8 PeBDF, 1,2,3,4,7,8 HxBDF, 1,2,3,4,6,7,8 HpBDF, ^{13}C-2,3,7,8 TeBDD, ^{13}C-1,2,3,7,8 PeBDD, ^{13}C-1,2,3,4,7,8 HxBDD, ^{13}C-1,2,3,6,7,8 HxBDD, ^{13}C-1,2,3,7,8,9 HxBDD, ^{13}C-2,3,7,8 TBDF, ^{13}C-1,2,3,7,8 PeBDF, ^{13}C-2,3,4,7,8 PeBDF, from Cambridge Isotope Laboratories (Andover, MA, USA).

The internal standards of PBDEs and PBDFs were: the EO 5100 containing ^{13}C labelled BDE 3, ^{13}C-BDE 15, ^{13}C-BDE 28, ^{13}C-BDE 47, ^{13}C-DE 99, ^{13}C-BDE 100, ^{13}C-BDE 118, ^{13}C-BDE 153 and ^{13}C-BDE 183, the ^{13}C-BDE 209 and the EDF 4154 containing ^{13}C-2,3,4,7,8 PeBDF and ^{13}C-1,2,3,4,7,8 HxBDD from Cambridge Isotope Laboratories (Andover, MA, USA).

The recovery standards were the EO 5101 containing ^{13}C-BDE 126 and ^{13}C-BDE 77 and the EDF 4153 containing ^{13}C-2,3,7,8 TBDF, ^{13}C-2,3,7,8 TBDD, ^{13}C-1,2,3,7,8 PeBDF, ^{13}C-1,2,3,7,8 PeBDD, ^{13}C-1,2,3,6,7,8 HxBDD and ^{13}C-1,2,3,7,8,9 HxBDD, also from Cambridge Isotope Laboratories (Andover, MA, USA).

4 -Instrumental analysis

Quantitative analyses were performed by HRGC-HRMS using a Micromass Ultima mass spectrometer, equipped with an Agilant 6890 gas chromatograph. For all the analyses, HRGC was operated in the splitless injection mode, and the spliteless injector purge valve was activated 2 min after sample injection. The HRMS was operated at 10,000 resolution under positive EI conditions with the filament in the trap stabilization mode at 600 µA of air, an electron energy of 35 eV and perfluorokerosene used as the calibrant. All measurements were performed in the selected ion monitoring (SIM) mode, monitoring the two most abundant isotopic peaks for each ion cluster.

Full scan analysis were conducted using Trace GC (ThermoFinnigan, USA) with low resolution quadrupole MS Voyager, (ThermoFinnigan, USA) equipped with a CP-SIL 8 CB Low bleed/MS (15 m x

0.25 mm i.d., 0.25 µm film thickness) capillary column. 2µL of sample was injected using an autosampler with the injector operated in the splitless mode at 250 ºC with an injection time of 1 min. The Interface temperature was set to 270 ºC and the source temperature were 250ºC, respectively. The oven temperature was initially held at 140ºC for 1 min and then ramped to 325ºC (5 min) at a rate of 10ºC/min.

High-performance liquid chromatography (HPLC) was performed on a Beckman System Gold equipped with a UV detector Module 166 (Beckman) and a C_{12} column (Synergi 4µ Max-RP 8OA) from Phenomenex. The detection wavelength was set to 254 nm, and the mobile phase was 5% or 0% water in acetronitrile.

Results and Discussion

The results obtained (Figure 1) clearly show that photolytic degradation of deca-BDE (70 to 90%) occurs under simulated solar irradiation.

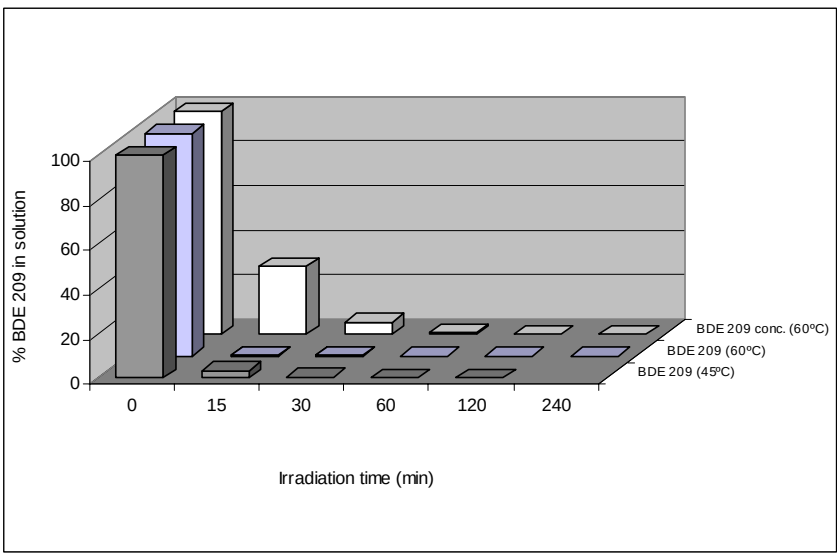

Figure 1 – The percentage of BDE 209 present in solution during irradiation experiments.

The BDE 209 was rapidly transformed to lower bromo congeners in the first minutes of irradiation. The first step of degradation is the loss of one bromine atom to form two nona-BDEs congeners (BDE 206 and BDE 207) followed by the formation of at least five octa-BDEs. Many hepta-BDEs were also formed as well as small amounts of hexa-BDEs, the same was verified by other groups (Söderström G. 2004; Ahn M. 2006).

As reported in other works (Eriksson J. 2004) the area under HPLC peaks that corresponds to deca-BDE decreased after irradiation (Figure 2), this indicates that most of the compound had decomposed to lower brominated PBDEs. However, the decrease in the total area might be due to the formation of PBDFs or uncharacterized compounds. In this work we will try to characterize all the compounds formed in the degradation of deca-BDE.

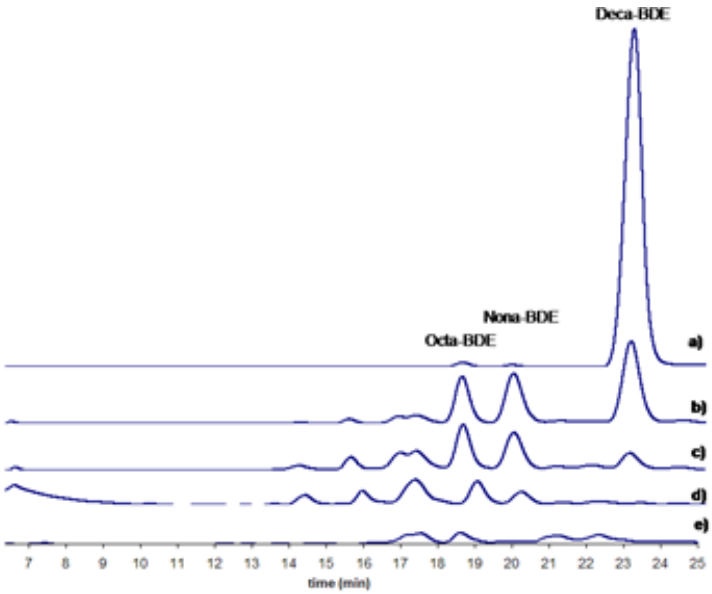

Figure 2- HPLC chromatograms showing disappearance of deca-BDE after irradiation a) 0 H, b) 15 min, c) 30 min, d) 1H, e) 2H.

From this work it can be concluded that formation of lower brominated diphenyl ethers can occur from the photolysis of decabromodiphenyl ether in the environment. However, from the results obtained it is unlikely that photolysis reactions of decabromodiphenyl ether explain the widespread occurrence of tetra- penta- and hexabromodiphenyl ether congeners in the environment, it is much more likely that the levels of these congeners found are a result mainly of the emissions of the commercial mixture pentabromodiphenyl ether and octabromodiphenyl ether flame retardants. Although, any photolysis of decabromodiphenyl ether that does occur in the environment could make a contribution to the levels of the lower brominated congeners present in the environment, which are more accumulative and toxic.

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