PHOTOLYSIS OF PENTABROMO DIPHENYLETHERS FROM THE TECHNICAL MIXTURE DE-71™: BDE 85, BDE 99 AND BDE 100 IN THF/HEXANE

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Introduction

Polybrominated diphenyl ethers (PBDEs) are used in large quantities as flame retardants. Despite their societal benefits, PBDEs have migrated from the products in which they were used and are found in the environment and in humans. PBDEs are commercially available as three products: decabromo-, octabromo- and pentabromo diphenylethers. Penta and octa are mixtures of several congeners.[1] Typical compositions of the technical penta product (pentaBDE), given in weight percent of BDE congeners present (WHO/ICPS, 1994), are: 24-38 tetraBDEs, 50-60 pentaBDEs and 4-8 hexaBDEs.[2] The estimated world market demand for pentaBDE in 2001 was 7500 metric tons, distributed by > 95 % to North America, 2 % to Europe, 2 % to Asia and 1% to the rest of the world.[3] In Europe the production and application of the technical penta and octa-product was banned by Directive 2003/11/EEC.[4]

Sjödin et al.[5] investigated the unknown congeners in the technical mixture Bromkal 70-5DE by gas chromatography on various columns, and Konstantinov et al.[6] identified the minor components in the technical mixtures DE-71™, using ^{1}H-NMR and GC/MS. A fairly complete identification of the components in the mixture is desirable because the congener profiles observed in the environment can be reconciled with those of the commercial formulations. Some lower-brominated BDEs are persistent and can bio-accumulate, and there is concern about their potential health hazard. The major BDEs of environmental concern are BDE 47, 85, 99, 100, 153, 154 and 183[1], where the lower brominated congeners in environmental samples may -at least partly- result from the reductive debromination of BDE 209 and other highly brominated diphenyl ether congeners, through photochemical transformation[7-9], anaerobic microbial degradation[10] and/or metabolism by fish[11,12].

The present study investigates the products formed from photolysis of BDE 85, 99 and 100 in THF, isolated from the technical mixture DE-71™ via preparative chromatography, and attempts to assign the degree of bromination and the substitution pattern of individual congeners.

Materials and Methods

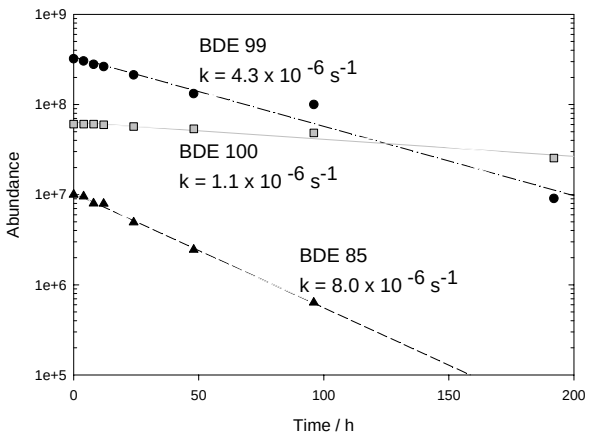
Chemicals: The technical pentaBDE mixture DE-71™ was obtained from Great Lakes Chemical Corp. (ref. 95500F05A), 2,4,4'tribromdiphenylether BDE 28 from Albemarle Corp. (ref. 8996-3), 4,4'dibromdiphenylether BDE 15 (99,9%) from Aldrich, tetrahydrofuran (99.9%, stabilised) from Riedel de Haen and was distilled using a 75 cm Vigreux column. Acetonitrile (HPLC grade, 99.8%) was from VWR/Prolabo. n-Hexane (for organic trace analysis) from Merck, and sodium sulfate - Na_2SO_4 (+ 99%, anhydrous) from Aldrich. The water was purified with a Seralpur Pro 90 CN system (Veolia Water Systems, Austria).

Instruments and Quantification: The technical pentaBDE mixture DE-71™ (0.2588 g) was dissolved in 25 mL of THF and 60 µl of the solution was injected into an Agilent 1100 system

with quaternary pump, autosampler and DAD detector with following parameters: detection wavelength 230 nm, width 8 nm, flow 8ml/min, preparative column Zorbax Eclipse XDB-C8 RP (21.2 × 150 mm, 5 µm - Agilent) at room temperature. The preparative chromatography was used to isolate the principal compounds from the technical pentaBDE mixture DE-71™, especially to obtain BDE 85, BDE 99 and BDE 100 for the photolysis experiments. The fractions were manually collected from the outlet of the HPLC. The polybrominated diphenyl ethers were eluted by a mixture of acetonitrile and water (80:20). On this account the collected fractions were submitted to liquid-liquid extraction using, 2 × 3 mL of n- hexane. The two hexane fractions were passed trough a column (10 cm long and 0.9 cm inner diameter) containing approx. 8 g of anhydrous sodium sulphate in order to remove humidity traces. The samples for the photolysis experiment were prepared mixing 1 ml of the hexane extracts of BDE 99, BDE 85 and BDE 100 with 2 mL of THF. The photolysis was performed by 6 lamps (Philips TL29D16, 16 W each) at a distance of 20 cm between light source and cuvette for time periods up to 192 h. The irradiated samples (3 mL) were concentrated to 0.5 mL by a flow of N_2 The samples were analysed by a quadrupole GC-MS instrument (5890 Series II and MSD 5970, Hewlett Packard) using electron impact ionisation (70eV) and an autosampler (7673A, Hewlett Packard) with the following parameters: a 15 m column (DB-5HT, Chrompack), 0.25 mm inner diameter, 0.1 µm film thickness, 1µl injection volume, 300°C injector temperature, 340°C transfer line temperature, 1ml/min He as carrier gas, and a temperature program described by Rayne and Ikonomou[13]: hold at 100°C for 1 min, 2°C/min to 140°C, 4°C/min to 220°C, 8°C/min to 330°C and hold for 1.2min.

Results and Discussion

The congeners formed during the irradiation of the BDE 85, 99 and 100 in THF were identified by GC/MS (total ion chromatogram - m/z > 100), discussing retention times and mass spectra. Table 1 shows the transformation pathways of the compounds and Fig. 1 (left) shows the time dependent concentration profiles with the observed rate constants of BDE 99, 100 and 85 with initial concentrations of about 180 mg/L, 40 mg/L and 8 mg/L, respectively. Concentrations were estimated from the weight percentage of the individual BDEs determined in DE-71™ using the ^{1}H-NMR spectroscopic data of Konstantinov et al.[6] (BDE 99: 42.5 %, BDE 85: 3.18 %, BDE 100: 10.90 %). Debromination rate constants of BDEs 99 and 85 were found to be much higher than for BDE 100. There are two Br atoms in *ortho* position in BDE 100, whereas the BDEs 99 and 85 have Br atoms in *ortho*, *meta* and *para* position in the higher substituted phenyl ring. The UV spectrum (fig.1 right) of BDE 100 shows a lower absorption than BDE 85 and 99, leading to a smaller overlap with the emission spectrum of the lamps. This may explain the higher photostability of BDE 100. The overlap of the lamp intensity with the absorption is too low for a precise determination of the quantum yield.



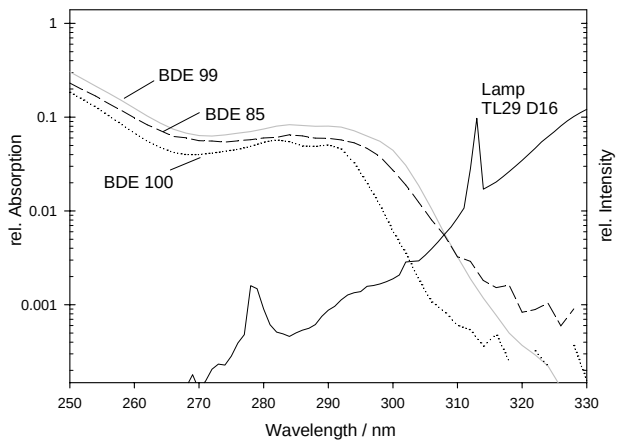


Figure 1: Photodecomposition of BDE 85, BDE 99 and BDE 100 in THF on a semi-logarithmic scale (left figure) and overlap of the UV spectra of the BDE 85, 99 and 100, separated by HPLC and taken at a concentration of the technical mixture (751 mg/L) with the light intensities from the TL29D16 lamp (semi-logarithmic scale, right figure).

Table 1: Products observed from photolysis of BDE 99, 100 and 85 in THF/hexane (2:1 volume ratio).

No. of Br atoms	congener	ret. time (min)	abundance* after 8 days	position of Br atoms ring 1			ring 2		
5	**2,2',4,4',5-BDE 99**	41.1	95 % loss	o	p	m	o	-	p
4	2,3',4,4'-BDE 66	36.7	main product	-	p	m	o	-	p
	2,4,4'5-BDE 74	36.3**	minor product	o	p	m	-	-	p
	2,2',4,4'-BDE 47	35.9	main product	o	p	-	o	-	p
	2,2',4,5-BDE 48	35.2	minor product	o	p	m	o	-	-
	2,2',4,5'-BDE 49	35.1	main product	o	-	m	o	-	p
3	3,4,4'-BDE 37	31.3**	minor product	-	p	m	-	-	p
	2,4,4'-BDE 28	30.1	main product	o	p	-	-	-	p
	2',3,4-BDE 33			-	p	m	o	-	-
	2,4',5-BDE 31	29.4	minor product	o	-	m	-	-	p
	2,3',4-BDE 25	29.3	minor product	-	-	m	o	-	p
	2,2',4-BDE 17	29.2	minor product	o	p	-	o	-	-
	2,4,5-BDE 29	29.0	minor product	o	p	m	-	-	-
	2,2',5-BDE 18	28.4	minor product	o	-	m	o	-	-
2	4,4'-BDE 15	22.8	minor product	-	p	-	-	-	p
5	**2,2',4,4',6-BDE 100**	39.9	53 % loss	o	p	o	o	-	p
4	2,2',4,4'-BDE 47	35.9	main product	o	p	-	o	-	p
	2,4,4',6-BDE 75	34.8	minor product	o	p	o	-	-	p
	2,2',4,6'-BDE 51	34.6	main product	o	-	o	o	-	p
	2,2',4,6-BDE 50	33.9**	minor product	o	p	o	o	-	-
3	2,4,4'-BDE 28	30.2	minor product	o	p	-	-	-	p
	2,2',4-BDE 17	29.3	minor product	o	p	-	o	-	-
5	**2,2',3,4,4'-BDE 85**	42.7	> 99 % loss	o	m	p	o	-	p
4	2,3',4,4'-BDE 66	36.7	main product	-	m	p	o	-	p
	2,2'3,4'-BDE 42			o	m	-	o	-	p
	2,2',4,4'-BDE 47	35.9	main product	o	-	p	o	-	p
3	3,4,4'-BDE 37	31.3**	main product	-	m	p	-	-	p
	2,4,4'-BDE 28	30.1	main product	o	-	p	-	-	p
	2',3,4-BDE 33			-	m	p	o	-	-
	2,2',3-BDE 16			o	m	-	o	-	-

* Main products are > 10% of the loss of the pentaBDEs on the basis of total ion signal m/z > 100.

** Not a component of DE-71[6]; assigned on the basis of mass spectrum and retention time[13,15,16].

TetraBDE 47 is the most prominent congener derived from photolysis from all three pentaBDEs of the present study (85, 99 and 100). Photodebromination leads mainly via triBDE 28 and diBDE 15 to monoBDE 3 (Palm et al.[14]). Further debromination of tetraBDE 47 leads to triBDE 28 (95 %) and triBDE 17 (5 %) and from triBDE 28 to diBDE 15 (95 %) and diBDE 8 (5 %); the products formed from diBDE 15 were monoBDE 3 and monoBDE 1 (99 and 1 %) respectively (Palm, 2005, unpublished). TetraBDE 66 was the second most abundant tetraBDE formed from pentaBDE 99 and pentaBDE 85. Although tetraBDE 66 and tetraBDE 42 would co-elute[15,16], the identification as BDE 66 is certain because tetraBDE 42 (2,2',3,4') can not be formed from pentaBDE 99. It is difficult to differentiate among tetraBDE 66 and tetraBDE 42 from pentaBDE 85, but we are expecting a

preference of tetraBDE 66, where the debromination occurs via an *ortho* Br atom. The congeners tetraBDE 51 and 75, formed from pentaBDE 100, almost co-elute[15] However, a larger yield of tetraBDE 51 is expected, since debromination of the phenyl ring with more Br atoms should be favoured. Rayne and Ikonomou[13] and Korytar et al.[15] reported the co-elution of BDE 28, 33 and 16. BDE 16 cannot be formed from BDE 99, so the triBDE product at 30.1 min from BDE 99 can only be BDE 28 or 33, and BDE 28 is the most probable assignment. Furthermore, the potential precursor of BDE 33 would be BDE 48, present at 8 days only with estimated from time profile monitored up to 4 days.

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