SUNLIGHT PHOTOLYSIS OF 39 MONO-HEPTA PBDE CONGENERS IN LIPID

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Introduction

Recent studies indicate that levels of certain polybrominated diphenyl ether (PBDE) congeners, comprising brominated flame retardants, are increasing rapidly in the environment[1,2]. Certain PBDEs (and metabolites) are of toxicological concern because of interference with the thyroid hormone system. Like PCBs, 209 PBDE congeners are theoretically possible and numbered similarly, but few, synthetically-preferred congeners, comprise the major constituents of the three commercial PBDE mixtures ("Deca" or DE-85®, "Octa" or DE-79®, and "Penta" or DE-71®). For example, tetra-hexa-PBDEs (47, 99, 100, 154, 153) plus low levels of 28 and 183 comprise "Penta", "Octa" contains mostly hepta and hexa-PBDEs, and "Deca" is about 98% pure.

Sources, fate, and distribution of PBDE congeners in the environment are still being evaluated. PBDE congeners reported in most biotic environmental samples generally match those in the "Penta" mixture and PBDE 47 is almost always the most persistent congener. In some sediment samples, deca-PBDE (209) has also been found. Concerning photolysis, deca-PBDE 209 photodegrades relatively rapidly in UV or sunlight[3-5], however, few photolysis studies of other PBDE congeners have been reported[6]. When a new standard mixture of 39 PBDEs (mono- through hepta) became commercially available (Cambridge Isotope Labs), we investigated their ***relative*** photolysis on a congener-specific basis in a biologically relevant concentration (ng/g) and lipid matrix exposed to sunlight. Our study objectives were to investigate the extent of PBDE photodegradation and potential formation of lower-brominated PBDEs, that are potentially more bioavailable and of greater toxicity through thyroid hormone disruption processes.

Materials and Methods

Triolein, a triacylglycerol lipid (99% pure, Sigma Chemical), was thinly dispersed (0.5 g in a 48 cm x 2.5 cm x 0.1 mm thick layflat polyethylene tube; Brentwood Plastics Co, made for semipermeable membrane devices to contain no slip additives, plasticizers or antioxidants). The 39 PBDEs (Table 1) were added to the lipid with 50 µL nonane carrier, dispersed throughout the lipid with kneading action, and the tube was flattened to eliminate air pockets and create a thin lipid film sandwiched in a UV transparent membrane. The tube ends were then heat-sealed. One tube was kept at room temperature in darkness; two were exposed outdoors to late-summer, early afternoon sunlight for either 2 min or 120 min. Also included was a blank to monitor background levels of PBDEs. After exposure, a surrogate mixture of nine ^{13}C-PBDEs (3, 15, 28, 47, 99, 100, 118, 153, and 183) from 5 to 12.5 ng each (Cambridge Isotope Labs) was added. PBDEs were recovered from each lipid bag via dialysis (twice with 200 mL hexane for 16 hrs then 4 hrs). Gel permeation chromatography (Biobeads S-X3), high pressure size exclusion chromatography

(Phenogel), and low pressure (< 70 kPa) flash (40-63 μm, 3-g) silica gel column chromatography were used for cleanup. After an initial 4-mL cyclopentane dump fraction, all PBDEs were collected in one eluate (15% MTBE in cyclopentane). Although PBDEs 33 and 28 co-elute, all other PBDEs were resolved using a 50 m x 0.20 mm x 0.11μm Ultra-2 column (Agilent Corp) set at 350 kPa (50 psi). Two-μL injections (nonane) were made through a septumless Merlin Micro-seal into a heated (285 ºC) Siltek-treated (Restek Corp) Spiral Uniliner that was connected to a 2.5 m x 0.32 mm Siltek-treated retention gap to the capillary column. The temperature program was 130 ºC (1 min hold) to 155 ºC at 12 ºC/min to 215 ºC at 2 ºC/min and to 350 ºC at 3 ºC/min (5 min final hold). For GC/High Resolution (>8000 R.P.) MS, an Agilent 5890A GC/Micromass 70-AS MS, calibrated to > 1000 Da with tris(pentadecafluoroheptyl)-s-triazine, acquired a total of seven groups of selected ions. Both molecular and $(M\text{-}Br_2)^+$ fragment ions for PBDEs and ^{13}C-PBDEs were measured. The PBDE $(M\text{-}Br_2)^+$ ions are also exact molecular ions for brominated dibenzofurans (PBDFs), therefore possible PBDF photolysis products eluting within an ion group might be differentiated from higher brominated PBDEs by the absence of PBDE molecular ions.

Results and Discussion

Photolyzed PBDEs were quantitatively measured by our GC/HRMS isotope dilution method and background corrected from our blank. The thin-film capillary column resolved all 39 PBDEs except for tri-PBDEs 33/28 (Figure 1). PBDEs with the etheral oxygen are not planar like certain PCBs; thus their GC elution is generally in distinct homolog groups. All 39 PBDEs in Table 1 are listed in correct retention order. One notable exception is the latest known eluting penta-PBDE (105) (not included in the mix of 39 PBDEs) elutes soon after the earliest hexa-PBDE (155).

Several distinctive results emerged from this sunlight photolysis experiment (Table 1). PBDEs 116, 166, 181, and 190 were the most photolytic. All four PBDEs are structurally similar--all are ***fully***-brominated on one aromatic ring. Hepta-PBDE 183, all other hexa-PBDEs, and two penta-PBDEs (85 and 126) degraded to about half of initial nominal amount. Third and perhaps most importantly, several PBDEs (47, 66, 77, 99, and 100) were formed in significant amounts. These tetra-penta-PBDEs are evidently more photolytically stable debromination products. Fourth, no net significant photolysis of mono-tri-PBDEs occurred within the two hours of sunlight exposure. No PBDFs were detected, but we lacked PBDF standards to ensure correct elution.

Our photolytic results match some of the tendencies and mechanisms demonstrated in recent photolysis research with 22 individual PCB congeners[7]. Although none of the studied PCBs were fully chlorinated on one aromatic ring, researchers noted the preference to dechlorinate on the most substituted ring. Also, the importance of relative charge distribution on carbon atoms was shown. Those carbons (bonded to chlorine) with the highest relative partial charge became the most stable by dechlorination and eventual radical reaction with hydrogen to further stabilize the resulting compound[7]. A similar stability mechanism should occur by our analogy to debromination. Perhaps most significantly, our tetra-PBDE 47 photolysis product results match Chang et al.[7] finding that tetra-PCB 47 had the longest photolytic half-life of all 22 PCBs studied[7]!

Several implications are apparent. The highest brominated PBDEs (deca-, the three nona-, and some octa-PBDEs) are fully brominated on at least one aromatic ring and should rapidly photolyze to hexa-octa-PBDEs, then further to the most photolytically stable tetra-penta-PBDEs, which also are major constituents of the “Penta” commercial flame retardant. Thus, it is plausible that PBDE 47 is typically the predominant PBDE in the environment (along with PBDEs 99 and 100) and that

Table 1. Results of Sunlight Exposure of 39 PBDE Congeners in Lipid

	Congener	Ambient Indoor Light % of Total	2 min Sun % of Total	120 min Sun % of Total	Bkg Amt subtracted from Blank
	Nominal: 5 ng				(ng)
2-Mono-PBDE	1	98	98	92	
3-Mono-PBDE	2	96	96	96	
4-Mono-PBDE	3	90	88	94	0.1
	Nominal: 5 ng				
2,6-Di-PBDE	10	96	102	96	
2,4-Di-PBDE	7	98	100	98	
3,3-Di-PBDE	11	104	108	104	
2,4'-Di-PBDE	8	106	106	106	
3,4-Di-PBDE	12	100	96	98	
3,4'-Di-PBDE	13	96	102	100	0.04
4,4-Di-PBDE	15	100	98	100	0.03
	Nominal: 5 ng				
2,4,6-Tri-PBDE	30	104	96	100	
2,4',6-Tri-PBDE	32	102	100	98	
2,2',4-Tri-PBDE	17	106	102	102	0.03
2,3',4-Tri-PBDE	25	100	100	94	0.04
2',3,4-PBDE/2,4,4'-PBDE	33/28	103	100	99	0.08
3,3',4-Tri-PBDE	35	106	100	104	
3,4,4'-Tri-PBDE	37	106	102	106	
	Nominal: 5 ng				
2,4,4',6-Tetra-PBDE	75	102	100	108	
2,2',4,5'-Tetra-PBDE	49	102	100	106	0.06
2,3',4',6-Tetra-PBDE	71	102	98	96	
2,2',4,4'-Tetra-PBDE	47	94	96	136 ▲	1.3
2,3,4,4'-Tetra-PBDE	66	100	94	134 ▲	
3,3',4,4'-Tetra-PBDE	77	94	86	114 ▲	
	Nominal: 7.5 ng				
2,2',4,4',6-PentaPBDE	100	101	97	115 ▲	0.2
2,3',4,4',6-PentaPBDE	119	96	88	100	
2,2',4,4',5-PentaPBDE	99	95	95	116 ▲	1.1
2,3,4,5,6-PentaPBDE	116	88	64 ▼	11 ▼	
2,3,4,4',6-PentaPBDE	118	93	96	87	
2,2',3,4,4'-PentaPBDE	85	87	83	71 ▼	
3,3',4,4',5-PentaPBDE	126	93	96	68 ▼	
	Nominal: 10 ng				
2,2',4,4',6,6'-Hexa-PBDE	155	91	94	68 ▼	
2,2',4,4',5,6'-Hexa-PBDE	154	87	84	63 ▼	0.13
2,2',4,4',5,5'-Hexa-PBDE	153	89	88	56 ▼	0.09
2,2',3,4,4',5'-Hexa-PBDE	138	90	77	49 ▼	
2,3,4,4',5,6-Hexa-PBDE	166	67 ▼	41 ▼	14 ▼	
	Nominal: 12.5 ng				
2,2',3,4,4',5',6-Hepta-PBDE	183	83	78	46 ▼	0.06
2,2',3,4,4',5,6-Hepta-PBDE	181	54 ▼	26 ▼	11 ▼	
2,3,3',4,4',5,6-Hepta-PBDE	190	50 ▼	24 ▼	10 ▼	

▲ Major Debromination Photolysis Product (> 125% of Initial Amount)
▲ Minor Debromination Photolysis Product (>110% but < 125% of Initial Amount)
▼ Moderate Photolytic Breakdown (<75% but > 40% Remaining)
▼ Major Photolytic Breakdown (< 40% Remaining)

some of their source could be from debromination of the higher PBDE mixtures. Significantly rapid PBDE photolysis within a neutral lipid matrix implies the need to further research the fate of PBDEs in thin surface microlayers in the aquatic environment and in pertinent organisms. By becoming more bioavailable and more structurally similar to the thyroid hormones, the lesser brominated PBDEs could result in photo-induced toxicity.

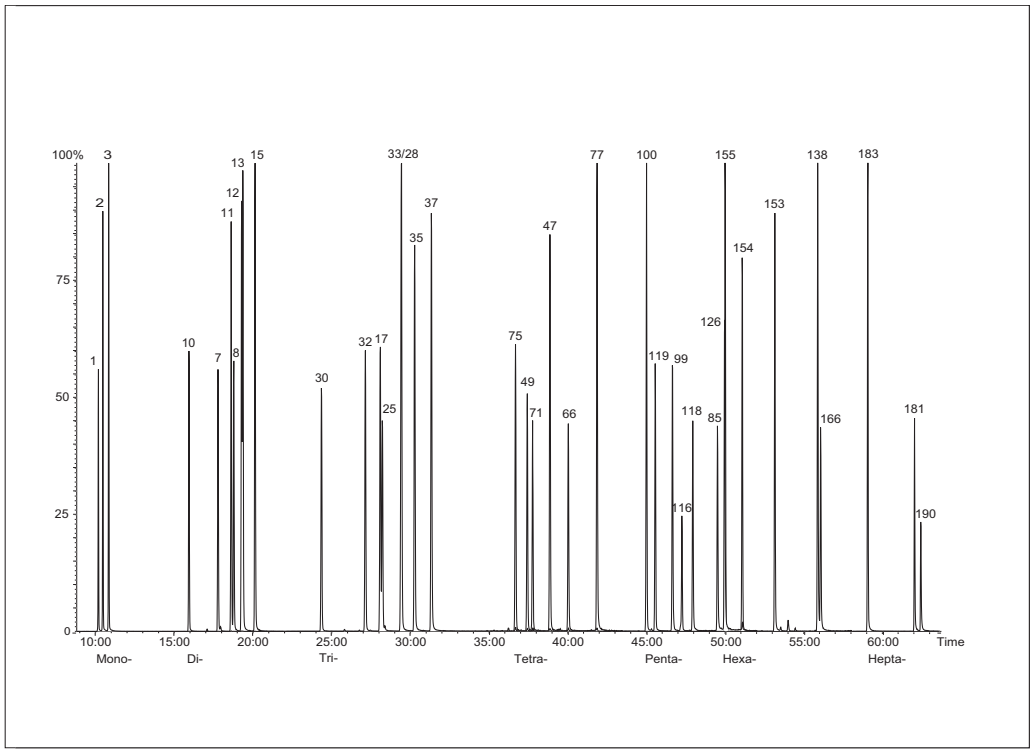

Figure 1. GC/HRMS Chromatogram (Composite of M^+ ions) of 39 Mono-Hepta-PBDE Congeners in Table 1.

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