THE EFFECT OF LIGHT ON HEXABROMOCYCLODODECANEs (HBCDs) IN INDOOR DUST

Abou-Elwafa Abdallah Mohamed[1], Harrad Stuart[1], Covaci Adrian[2]

[1]Division of Environmental Health and Risk Management, University of Birmingham, Birmingham, B15 2TT, United Kingdom
[2]Toxicological Center, University of Antwerp, Universiteitsplein 1, 2610 Wilrijk, Belgium.

Introduction

Hexabromocyclododecane (HBCD) is a brominated flame retardant used widely as an additive to expanded and extruded polystyrene foams for thermal insulation of buildings, back-coating of fabrics for furniture and to a lesser extent in HIPS. In 2001, the world market demand for HBCD was 16,700 tons of which about 9,500 tons were consumed in Europe[1]. The commercial mixtures consist mainly of α-, β-, and γ-diastereomers with the latter predominant. HBCD is characterised by having a low vapour pressure, very low water solubility and a log K_{OW} value of 5.6. The oral exposure to HBCD induces hepatic cytochrome P450 enzymes in rats and can alter the normal uptake of neurotransmitters in rat brain. There are other indications that it can disrupt the thyroid hormone system and induce cancer through a non-mutagenic mechanism in humans[2].

In our recent report on HBCDs in indoor dust[3] we highlighted the marked shift from the predominance of γ-HBCD in the commercial formulations towards the α-diastereomer (ranging from 14-67%, average 32%) observed in many of the analyzed dust samples. Furthermore, we have also observed that this shift in diastereomer pattern does not occur in air samples taken at the same time and from the same location as the dust samples – i.e. indicating some post-depositional processes affecting the pattern in dust[4]. There have also been recent reports on the thermally-induced isomerisation of HBCD stereoisomers[5,6]. However, there have been no studies – to the authors' knowledge - of the factors affecting the isomer distribution of HBCDs in indoor dust under normal environmental conditions.

Given the above, the aim of the current work is to study the effect of light on HBCDs isomer distribution and degradation in indoor dust.

Materials and Methods

Domestic dust from a vacuum cleaner bag was collected in October 2007. Dust was sieved through a 500 µm mesh size sieve, well homogenized, weighed and stored in a dark clean glass container at -20°C. Approximately 1.5 g aliquots of dust were placed on clean watch glasses with a transparent quartz cover and exposed to light under normal room usage conditions. Similar aliquots of dust were placed in a dark closed box in the same room to act as "controls". At the end of the specified exposure period, dust samples were transferred to the lab where they were weighed accurately prior to extraction.

Dust samples were spiked with 25 ng of each of ^{13}C-labelled α-, β, and γ-HBCD as internal standards and extracted with hexane:dichloromethane (1:1,*v/v*) using pressurized liquid extraction (Dionex, ASE 300 system). Crude extracts were cleaned up through washing with 98% sulphuric acid and Florisil chromatography. The α-, β- and γ- HBCD isomers and together with pentabromocyclododecenes (PBCDs) recently identified as HBCD degradation products in indoor dust[7], were separated on a Varian Pursuit XRS3 C_{18} reversed phase analytical column (150 mm × 2 mm i.d., 3 µm particle size), while mass spectrometric analysis was performed using a Sciex API 2000 triple quadrupole mass spectrometer operated in electrospray negative ionization mode. Further details can be found elsewhere[7].

Results and Discussion

Table 1 summarizes the results obtained from exposure of dust samples to light for 5 weeks compared to control dust samples that were protected from light at the same place for the same exposure period. While the % contribution of the β-HBCD diastereomer to ΣHBCDs appears to be unaffected by exposure to light, there is a marked increase in the % contribution of α-HBCD to ΣHBCDs (from 25 to 40%) accompanied by a decrease in that of γ-HBCD (from 62 to 45%) observed during the first week of dust exposure to light compared to the control samples (Table 1). This rapid photolytically-mediated shift in HBCDs isomer profile towards the α-

HBCD diastereomer appears to take place mainly during the first week of light exposure as no marked change in the HBCDs isomer distribution is observed afterwards (Table 1). We also studied the effect of light exposure for a week using SRM2585 organics in indoor dust reference material. A similar increase in the % contribution of α-HBCD (from 13 to 26%) was observed accompanied by a decrease in the % of γ-HBCD (from 83 to 70%).

Table 1: Effect of light exposure on the concentrations (ng g^{-1}) of HBCDs and PBCDs

Exposure time	α- HBCD		β- HBCD		γ- HBCD		Σ HBCDs	Σ PBCDs
	Average* ± SD	average % ΣHBCDs	Average* ± SD	average % ΣHBCDs	Average* ± SD	average % ΣHBCDs		
0 weeks	112 ± 7	25	60 ± 5	13	277 ± 9	62	448	6
1 week	166 ± 9	40	64 ± 8	15	185 ± 8	45	415	11
Control[#]	121 ± 5	28	54 ± 3	12	260 ± 6	60	434	8
2 weeks	162 ± 6	41	62 ± 3	16	171 ± 4	43	395	18
Control[#]	121 ± 6	28	53 ± 4	13	251 ± 6	59	424	11
3 weeks	168 ± 4	43	53 ± 2	14	171 ± 6	43	392	28
Control[#]	117 ± 8	28	50 ± 3	12	256 ± 12	60	423	16
4 weeks	158 ± 8	43	43 ± 4	12	161 ± 14	44	362	49
Control[#]	109 ± 9	27	56 ± 7	14	240 ± 11	60	405	28
5 weeks	142 ± 9	43	46 ± 6	14	141 ± 14	43	330	68
Control[#]	109 ± 8	28	48 ± 10	12	227 ± 14	60	384	37

* n=5; [#] dust samples at the same place for the same exposure time, but protected from light.

This marked shift might be the result of direct isomerisation of γ- to α- HBCD or there could be a series of isomeric interconversions that give rise to all stereoisomers from any given one similar to the thermally-induced isomerisation of HBCDs described by Koppen *et al.*[5].

Table 2: Effect of light exposure on pure standards of HBCD diastereomers (2 ng μL^{-1} in methanol).

Time (days)	α-HBCD			β-HBCD			γ-HBCD		
	% α-HBCD	% β-HBCD	% γ-HBCD	% α-HBCD	% β-HBCD	% γ-HBCD	% α-HBCD	% β-HBCD	% γ-HBCD
0	100.0	0.0	0.0	0.0	100.0	0.0	0.0	0.0	100.0
1	98.4	0.7	0.9	1.2	98.2	0.6	3.5	0.7	95.8
2	97.8	0.8	1.4	3.6	95.5	0.9	7.5	0.8	91.7
3	97.0	1.0	2.0	6.2	92.5	1.3	10.6	1.4	88.0
4	96.5	1.2	2.3	11.7	85.8	2.5	15.6	2.9	81.5
5	94.9	2.0	3.1	16.0	80.4	3.7	22.2	3.8	74.0
6	92.9	3.1	4.0	20.1	75.5	4.5	26.9	4.7	68.4
7	90.5	4.0	5.5	23.9	71.3	4.8	32.4	5.5	62.2

For further understanding of the observed photolytically induced isomerisation of HBCDs in dust, standard solutions (2 ng μL^{-1} in methanol) of pure α-, β- and γ- HBCDs were exposed to light for a week with the % of each diastereomer monitored in each of the 3 standard solutions on a daily basis. The results (Table 2) revealed that each of the studied HBCD diastereomers can isomerise to produce different proportions of the other 2 stereoisomers upon exposure to light. However, the isomerisation from γ- to α- HBCD is predominant resulting in the observed shift in the studied dust samples exposed to light.

Not only was photolytically-induced isomerisation evident in the studied dust samples, but also a faster rate of HBCD degradation was observed in the exposed samples compared to the control group. This is indicated by the decline in ΣHBCDs concentrations and increase in ΣPBCDs with time (Table 1). Although this might not be the only pathway for HBCD degradation in dust, the results indicate that HBCDs undergo degradation via the loss of HBr resulting in the formation of PBCDs. This is in agreement with our previous findings suggesting that elimination of HBr is the major degradation pathway of HBCDs in dust[7]. The fact that such loss occurs in the control samples – albeit at a markedly slower rate – suggests that loss of HBr is not solely photolytic.

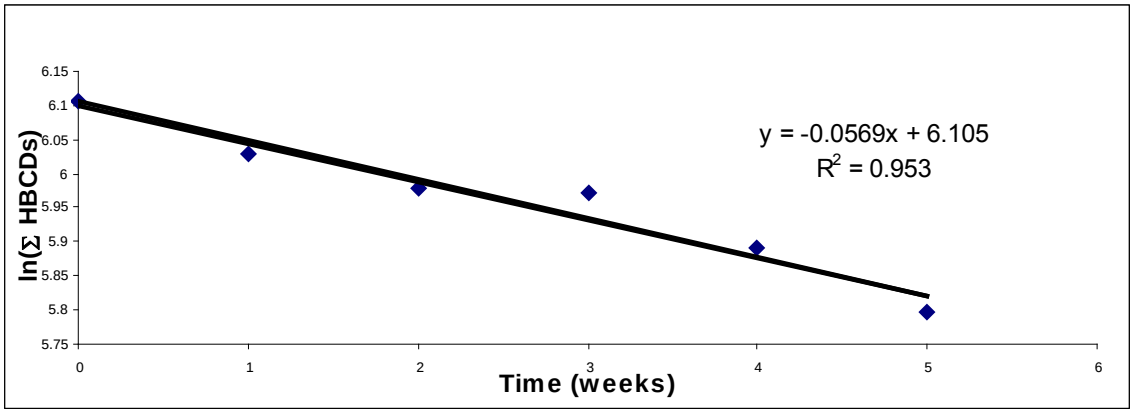

Figure 1: Determination of first order rate constant for degradation of HBCDs in indoor dust.

Assuming HBCDs degradation in indoor dust follows first order kinetics, the concentrations of ΣHBCDs in the analysed dust samples (table 1) were used to calculate the half-life of the flame retardant in indoor dust. A plot of ln (ΣHBCDs) against time (weeks) yielded a straight line (R^2 = 0.95) with a negative slope of 0.0569 $weeks^{-1}$ (Fig.1) which is equal to the first order rate constant for the degradation process. The half-life of HBCDs in indoor dust is thus an estimated 12.2 weeks.

Acknowledgements
The authors acknowledge gratefully the Egyptian government and Egyptian ministry of higher education for funding the studentship of Mohamed A. Abdallah and the Research Scientific Foundation of Flanders (FWO) for a postdoctoral fellowship to Adrian Covaci.

References
1. Bromine Science Environmental Forum, http://www.bsef.com (accessed 21/2/2008).
2. Covaci A., Gerecke A.C., Law R.J., Voorspoels S., Kohler M., Heeb N.V., Leslie H., Allchin C. and de Boer J. *Environ. Sci. Technol*. 2006; 40: 3679.
3. Abdallah M.A., Harrad S., Ibarra C., Diamond M., Melymuk L., Robson M. and Covaci A. *Environ. Sci. Technol.* 2008; 42: 459.
4. Abdallah M.A., Harrad S. and Covaci A. (*in preparation*).
5. Köppen R., Becker R., Jung C. and Nehls I. *Chemosphere* 2008; 71:656.
6. Heeb N.V., Schweizer W.B., Mattrel P., Haag R., Kohler M., Schmid P., Zennegg M. and Wolfensberger M. *Chemosphere* 2008; 71:1547.
7. Abdallah M.A., Ibarra C., Neels H., Harrad S. and Covaci A. *J. Chromatogr. A* 2008; 1190; 333.