Study on the Photodechlorination Pathways of Non-ortho Substituted PCBs by UV Irradiation in Alkaline 2-Propanol

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Abstract

The photodechlorination pathways of the very toxic non-ortho substituted PCBs including 3,3',4,4',5,5'-HexaCB, 3,3',4,4',5-PentaCB, 3,3'4,4'-TetraCB and the related congeners irradiated at 254 nm in alkaline 2-propanol were elucidated. The results indicated that the reactivities of para and meta chlorines of PCBs are controlled by their electronic effect and steric effect, as well as the stabilities of dechlorination products.

Introduction

Polychlorinated biphenyls (PCBs) are of continuing concern due to their ubiquitous persistence and presence in large amounts. These compounds are toxic, especially the congeners with no chlorine substituents at the ortho-positions showing dioxin-like toxicity such as 3,3',4,4',5-PentaCB (PCB 126), 3,3',4,4',5,5'-HexaCB (PCB 169), and 3,3'4,4'-TetraCB (PCB 77). Recently Järnberg and co-workers investigated the levels of PCBs in Swedish sediments and biological samples and reported that 3,3',4,4',5-PentaCB may pose a greater threat to the environment than the well-known 2,3,7,8-chlorinated dioxins[1].

For the environmental breakdown of PCBs, photodegradation is thought to be a very important route. Moreover, commercial PCB mixtures have been shown to effectively undergo photo-decomposition in organic solvents by ultraviolet (UV) light. Although many studies have demonstrated that reductive dechlorination is the main mechanism for these photoreactions, little is known about the respective photolytic characteristics of non-ortho substituted PCB congeners. The objective of our research was to elucidate their photodechlorination pathways for providing useful information for the establishment of effective and safe photolytic treatment process of PCBs. We have previously investigated the photodechlorination pathways of several ortho substituted PCBs including 2,4,4'-TriCB, 2,2',5-TriCB, 2,2',5,5'-TetraCB[2] by UV irradiation in alkaline 2-propanol. In this paper, we wish to report the photolytic fate of some non-ortho substituted PCBs including the most toxic 3,3',4,4',5-PentaCB under the same conditions.

Experimental Methods

The irradiation experiments were carried out in a photochemical reactor (Model HLV-A, Taika Kogyo Co., Ltd., Japan) using a low pressure mercury lamp (Model L-15W, λ max =254 nm, Taika Kogyo Co., Ltd.). Each PCB congener in alkaline (NaOH 0.4 % w / v) 2-propanol was separately photolyzed with the irradiation times of 0, 10, 20, 30, 60, 90, 120, 150, 180 and 240 min. The concentration of the congeners was set at 0.1 or 0.2 mg/L. The 20 mL aliquots for different irradiation times were extracted with hexane, concentrated and analyzed by GC (HP 5890 SERIES II, Hewlett-Packard Co., USA) / MS (Automass 20, JEOL, Japan) after addition of n-hexadecane-d34, n-eicosane-d42 and n-tetracosane-d50 as internal standards. A DB-5MS capillary column (30 m × 0.25 mm i.d., 0.25 μm film thickness, J&W Scientific, USA) was used for separating photo-

products. The carrier gas was helium. The column was maintained at 60 °C initially for 2 min, and then raised to 280 °C at 10 °C / min with a final holding time of 2 min. The temperatures of the injector, interface and ion source were 240 °C, 250 °C and 200 °C, respectively. The ionization energy was 70 eV and the scanning mass range was from 35 to 500 amu.

The identification of the dechlorination products was performed by comparing their GC retention times and mass spectra with those of authentic standards, and the quantitation was performed by the internal standard method in which n-hexadecane-d34 was used for biphenyl (BP), MonoCBs, n-eicosane-d42 was used for DiCBs, TriCBs, TetraCBs, and n-tetracosane-d50 was used for PentaCBs and HexaCB.

Results and Discussion

The congeners chosen for this study cover the bulk of non-ortho substituted PCBs, with the chlorine substituents varying from one to six. The results of these experiments are presented in Table 1. The data clearly revealed the presence of successive dechlorination of PCBs and all the congeners used were observed to be photolyzed effectively under our experimental conditions.

Table 1. Dechlorination products of the PCB congeners in alkaline 2-propanol.

Starting material	Dechlorination products						Σ
	- 1 Cl	- 2 Cl	- 3 Cl	- 4 Cl	- 5 Cl	- 6 Cl	
3,3',4,4',5,5'- (2.5)*	3,3',4,5,5'- (10.3)	3,3',5,5'- (64.2)	3,3',5- (9.3)	3,3'- (0.5)	3- (0.0)	BP (0.6)	(92.8)
	3,3',4,4',5- (0.6)	3,3',4,5'- (3.9)	3,4',5- (0.3)	3,5- (0.1)	4- (0.0)		
		3,3',4,4'- (0.1)	3,3',4- (0.2)	3,4'- (0.1)			
			3,4,4'- (0.1)	4,4'- (0.0)			
3,3',4,5,5'- (23.3)	3,3',5,5'- (65.2)	3,3',5- (5.4)	3,3'- (0.1)	3- (0.0)	BP (0.0)		(97.3)
	3,3',4,5'- (3.2)	3,3',4- (0.1)	3,5- (0.0)	4- (0.0)			
		3,4',5- (0.0)	3,4'- (0.0)				
3,3',4,4',5- (6.3)	3,3',4,5'- (43.2)	3,3',5- (21.0)	3,3'- (2.4)	3- (0.4)	BP (0.1)		(85.9)
	3,3',4,4'- (3.4)	3,4',5- (2.7)	3,4'- (2.1)	4- (0.1)			
		3,3',4- (2.7)	4,4'- (0.7)				
		3,4,4'- (0.7)	3,5- (0.1)				
3,3',5,5'- (72.6)	3,3',5- (14.7)	3,3'- (0.6)	3- (0.0)	BP (0.0)			(88.0)
		3,5- (0.1)					
3,3',4,5'- (30.9)	3,3',5- (40.6)	3,3'- (3.5)	3- (0.5)	BP (0.0)			(82.0)
	3,4',5- (5.0)	3,5- (0.3)	4- (0.0)				
	3,3',4- (1.2)	3,4'- (0.0)					
3,3',4,4'- (22.8)	3,3',4- (20.5)	3,4'- (19.8)	3- (3.2)	BP (0.2)			(98.1)
	3,4,4'- (6.9)	3,3'- (14.0)	4- (1.5)				
		4,4'- (9.2)					
3,4',5- (71.7)	3,4'- (13.4)	3- (4.1)	BP (0.3)				(93.2)
	3,5- (3.1)	4- (0.6)					
3,3',4- (5.1)	3,3'- (31.4)	3- (11.5)	BP (1.2)				(78.7)
	3,4'- (28.1)	4- (1.4)					
3,4,4'- (4.6)	4,4'- (35.5)	4- (7.3)	BP (1.6)				(70.2)
	3,4'- (16.7)	3- (4.5)					
3,3'- (80.0)	3- (7.8)	BP (5.4)					(93.2)
3,4'- (41.0)	3- (28.9)	BP (5.4)					(78.7)
	4- (3.4)						
4,4'- (51.2)	4- (12.4)	BP (18.8)					(82.4)
3- (42.6)	BP (10.9)						(53.5)
4- (40.6)	BP (38.2)						(78.8)

* Data in parentheses represent the respective molar percentages of the congeners relative to the initial amount of corresponding starting materials and the total amounts of starting material and related dechlorination products after 10-min irradiation.

3-CB and 4-CB were found to be dechlorinated to BP with no photochemical rearrangement observed in the photolysis of 2-CB[3]. The comparison of the photolysis rates between 3-CB and 4-CB demonstrated that para chlorine is more readily to be released than meta chlorine, in agreement with the finding of Hawari et al. that in the dechlorination of polychloro aromatics, e.g., hexachlorobenzene, para elimination is more preferential than that of meta[4].

3,3'-DiCB and 4,4'-DiCB, like 3-CB and 4-CB, were dechlorinated through meta and para eliminations, respectively. The obtained half-life of 3,3'-DiCB was about 1/4 that of 4,4'-DiCB, thus supporting the observation mentioned above. For 3,4'-DiCB, the dechlorination proceeded also mainly at the para position. All of these results are probably attributed to the difference in total π electron density between para and meta chlorines of PCB radical anion formed in photochemical chain reaction. Previous study has shown that the electronic effect of para position is greater than that of meta position for 3,4-DiCB in alkaline 2-propanol[5].

Likewise, 3,3',4-TriCB was proved to be dechlorinated a little more at the para position of its more substituted ring. In contrast with 3,3',4-TriCB, it was observed that 3,4,4'-TriCB lost the meta chlorine mostly in the same 3,4-substituted ring. The steric effect of starting material and the stabilities of dechlorination products are though to be the decisive factors for controlling dechlorination pattern in the cases of 3,3',4-TriCB and 3,4,4'-TriCB, because the steric congestion of the 3,4-arrangement enhances the reactivities of 3- and 4-chlorines and enables the dechlorination to occur only in the more substituted ring without the production of 3,4-DiCB. In the meanwhile, the para dechlorination product of 3,3',4-TriCB and the meta dechlorination product of 3,4,4'-TriCB, namely 3,3'-DiCB and 4,4'-DiCB, are more stable than 3,4-DiCB due to their symmetrical structures, thus the dechlorinations proceed preferentially at para and meta positions, respectively. For 3,4',5-TriCB, the slow dechlorination was confirmed to proceed mostly at the meta position of its more substituted ring while the para dechlorination product, 3,5-DiCB was also detected. In this case, although the steric factor enables the main dechlorination to occur on the 3,5-substituted ring, the steric repulsion by the meta chlorines is smaller than that caused by 3- and 4-chlorines of the 3,4-substituted ring described above, hence the increased relative reactivity of the 4'-chlorine results in the para dechlorination.

3,3',4,4'-TetraCB was observed to be dechlorinated mostly at the para position to produce 3,3',4-TriCB. This is in accord with our expectation basing on the report of Kannan et al. that the π electron densities of para chlorines are nearly ten times those of meta chlorines in 3,3',4,4'-TetraCB molecule[6]. For 3,3',4,5'-TetraCB, the dechlorination proceeded at all substituted positions and the relative reactivities of the chlorine substituents varied in the order of 4- > 3- > 3'- or 5'-position being in agreement with the discussion mentioned above. The data obtained from the photolysis of 3,3',5,5'-TetraCB suggested that the dechlorination occurs mostly in the more substituted ring in the case of 3,3',5-TriCB.

During the photolysis of 3,3',4,4',5-PentaCB, most of its monodechlorinated products arised from the para dechlorination of its more substituted ring. The same is true in the photolysis of 3,3',4,5,5'-PentaCB. In these cases, no dechlorination of their less substituted rings was observed.

For 3,3',4,4',5,5'-HexaCB, as expected, the dechlorination proceeded very rapid and almost exclusively at the para position to form 3,3',4,5,5'-PentaCB, and the further dechlorination patterns of its dechlorination products were consistent with the observed behaviors of the corresponding congeners described above.

The overall investigation on the mass balance between the starting material and the dechlorination products in each photochemical process demonstrated that the reductive dechlorination is the main photoreaction especially in the initial step. Other reactions such as the decomposition of BP, the formation of polymeric products, etc. are thought to occour with the proceeding of the photochemical process according to the previous reports[3,7]. Based on these observations, the respective photodechlorination pathways of these congeners are defined and summarized in Figure 1.

This study elucidated the complete photodechlorination pathways of 3,3',4,4',5,5'-HexaCB and the related lower chlorinated congeners in alkaline 2-propanol for the first time and the results showed that 1. the more chlorinated PCB congeners are generally more reactive toward photodechlorination, 2. dechlorination occurs mostly on the more substituted ring, 3. antisymmetrical congeners are more readily to be dechlorinated than relatively stable symmetrical ones,
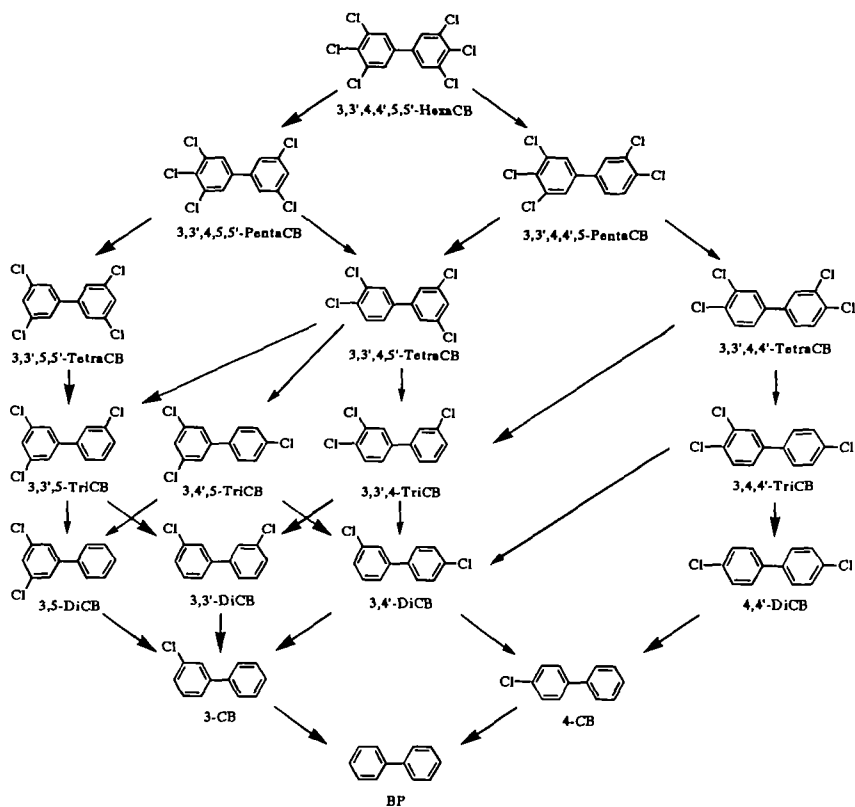
Figure 1.   Photodechlorination pathways of 3,3',4,4',5,5'-HexaCB by UV irradiation in alkaline 2-propanol. Broad arrows show the major pathways and thin arrows show the minor pathways.

4. dechlorination occurs preferentially at the position to produce symmetrical product, 5. the π electronic densities of para and meta chlorines affect their relative reactivities.

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