

Photochemistry of Non-ortho Substituted PCBs by UV Irradiation in Alkaline 2-Propanol

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Introduction

Safe and Hutzinger first reported a laboratory study on photolysis of polychlorinated biphenyls (PCBs) in 1971¹⁾. Since that time, many publications dealing with the photochemical behaviors of these compounds have been published and have noted that the principal photoreaction mechanism is reductive dechlorination. The objective of our research has been to elucidate the respective photolysis pathways, especially the dechlorination pathways of non-ortho substituted PCBs in terms of their dioxin-like toxicity and the fact that ortho chlorines are generally released more readily than meta and para substituents during PCB photodecomposition²⁻⁴⁾ resulting in the formation of such congeners from ortho substituted congeners. We have previously reported the photodechlorination pathways of fourteen non-ortho substituted PCBs including the most toxic 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) by ultraviolet (UV) irradiation in alkaline 2-propanol⁵⁻⁷⁾. In this study, we investigated the photolytic characteristics of the rest six non-ortho substituted congeners, namely 3,4-DiCB, 3,5-DiCB, 3,3',5-TriCB, 3,4,5-TriCB, 3,3',4,5-TetraCB, and 3,4,4',5-TetraCB, under the same experimental conditions.

Materials and Methods

The experiments were performed as described previously⁵⁻⁷⁾. Each solution (2 L) containing an individual PCB congener (0.2 mg/L) in NaOH (0.4 % w/v) 2-propanol was separately irradiated in a photochemical reactor with a low pressure mercury lamp ($\lambda_{max} = 254$ nm). The aliquots (20 mL) for different irradiation times (0, 10, 20, 30, 60, 90, 120, 150, 180, and 240 min) were extracted with hexane and concentrated with a Kuderna-Danish concentrator. The concentrates (1 mL) were analyzed by GC/MS after addition of internal standards. The photoproducts were identified by comparing their retention times and mass spectra with those of authentic standards. The quantitation was performed by using the internal standard method in which n-hexadecane-d₃₄ was used for biphenyl (BP) and MonoCBs whereas n-eicosane-d₄₂ was used for DiCBs, TriCBs, and TetraCBs.

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Results and Discussion

Summarized in Table 1 are the results of the successive dechlorination obtained from the photolytic reactions of target congeners and related congeners, in which the data of 3-CB, 4-CB, 3,3'-DiCB, 3,4'-DiCB, 4,4'-DiCB, 3,3',4-TriCB, 3,4,4'-TriCB, and 3,4',5-TriCB have been reported⁵⁻⁷). The average recovery was 104 %.

During the photolysis of 3,3',4,5-TetraCB, eight dechlorination products, i.e., 3,3',5-TriCB, 3,3',4-TriCB, 3,3'-DiCB, 3,4'-DiCB, 3,5-DiCB, 3-CB, 4-CB, and BP, were detected, among them the main monodechlorinated product was confirmed to be 3,3',5-TriCB. For 3,4,4',5-TetraCB, the dechlorination also proceeded only on its more substituted ring and almost exclusively at the 4-position to form 3,4',5-TriCB. The preferential para dechlorination was further observed in the case of 3,4,5-TriCB. These results are in agreement with our previous observation that 3,3',4,4',5-PentaCB, 3,3',4,5,5'-PentaCB, and 3,3',4,4',5,5'-HexaCB are dechlorinated mostly at the para positions of their 3,4,5-substituted rings^{6, 7}). It is considered that the steric congestion of the 3,4,5-arrangement enhances the reactivities of 4- and 3- / 5-chlorines and makes the reactions to occur only on the more substituted ring. Moreover, the steric compression by the two vicinal chlorines, viz. 3- and 5-chlorines, brings about the preferential dechlorination of the 4-chlorine. The three congeners mentioned above were found to be photolyzed very rapidly. For instance, the complete decomposition was observed after 10-min irradiation in the case of 3,4,5-TriCB. The similar photolysis rates obtained for 3,3',4,5-TetraCB and 3,4,4',5-TetraCB are attributable to their similar molecular structures.

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		
3,3',4,5- (2.3)*	3,3',5- (26.7)	3,3'- (3.3)	3- (0.5)	BP (0.0)	(37.4)	
	3,3',4- (1.6)	3,4'- (2.8)	4- (0.0)			
3,4,4',5- (0.8)	3,4',5- (45.0)	3,4'- (8.3)	4- (0.9)	BP (0.2)	(67.3)	
		3,4,4'- (2.6)	4,4'- (7.8)			3- (0.8)
		3,5- (0.9)				
3,3',5- (74.2)	3,3'- (5.7)	3- (0.4)	BP (0.0)		(80.7)	
	3,5- (0.4)					
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)				
3,4,5- (0.0)	3,5- (46.6)	4- (30.4)	BP (3.2)		(95.8)	
	3,4- (7.2)	3- (8.4)				
3,5- (37.3)	3- (16.8)	BP (1.1)			(55.2)	
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)	
3,4- (1.2)	4- (24.3)	BP (12.5)			(46.0)	
	3- (8.0)					
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.

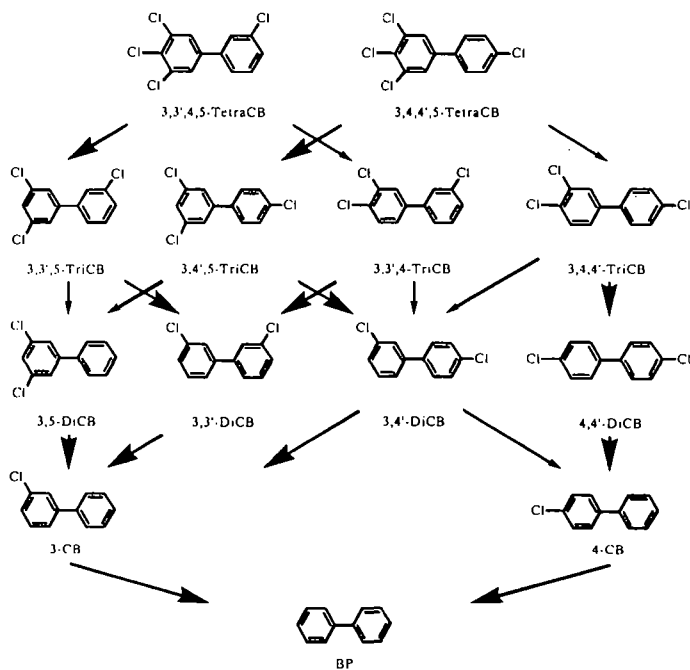


Figure 1. Photolysis pathways of 3,3',4,5-TetraCB and 3,4,4',5-TetraCB by UV irradiation in alkaline 2-propanol. Broad and thin full line arrows show the major and minor dechlorination pathways, respectively.

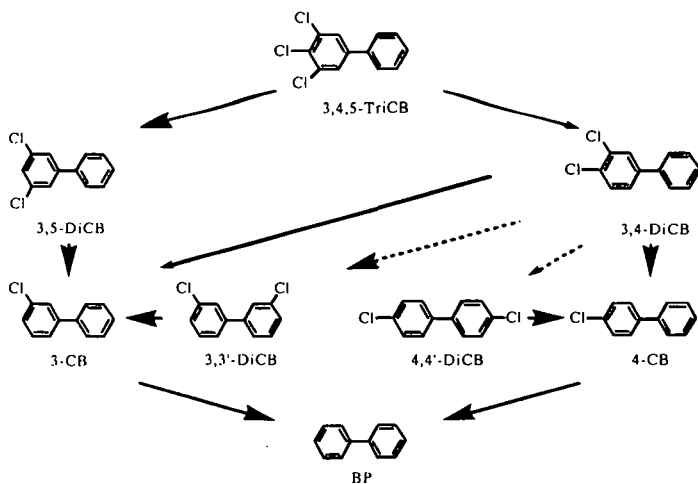


Figure 2. Photolysis pathways of 3,4,5-TriCB by UV irradiation in alkaline 2-propanol. Broad and thin full line arrows show the major and minor dechlorination pathways, respectively, while broad and thin dotted line arrows show the major and minor rearrangement pathways, respectively.

For 3,3',5-TriCB, we previously inferred that the dechlorination proceeds mostly on the more substituted ring from the result of the photolysis of 3,3',5,5'-TetraCB^{6, 7)} and this has been proved to be true in the present study. The steric effect of starting material and the stabilities of products account for the dechlorination pattern. That is to say, the steric congestion of the 3,5-arrangement makes the reactivities of 3- and 5-chlorines greater than that of 3'-chlorine. Meanwhile, 3,3'-DiCB is more stable than 3,5-DiCB due to its symmetrical structure, thus enhancing the dechlorination of 3,5-substituted ring. The observed slow photolysis rate of 3,3',5-TriCB supported the quantitative data of 3,3',5-TriCB obtained from the photolyses of 3,3',4,5-TetraCB and 3,3',5,5'-TetraCB^{6, 7)}, indicating that the compound is a relatively stable intermediate.

3,5-DiCB, as expected, was dechlorinated to give 3-CB. However, the results of 3,4-DiCB photolysis indicated that the disappearance of the compound was not solely due to its dechlorination. Besides the two dechlorination products 3-CB and 4-CB, two rearrangement products 3,3'-DiCB and 4,4'-DiCB were also detected during the photolysis of 3,4-DiCB. This is a new finding disclosing the unique photorearrangement for the non-ortho substituted PCBs up till present, although the existence of such a reaction has been reported for several ortho substituted PCBs^{1, 3)}. The main rearrangement product was found to be 3,3'-DiCB and this could be due to the fact that 3,3'-DiCB is more stable than 4,4'-DiCB⁵⁾. Since the concentration of the test solution used was low, the rearrangement is thought to be an intramolecular reaction³⁾. The quantitative results indicated that dechlorination was the principal photochemical process during which 3,4-DiCB lost meta chlorine mainly to generate 4-CB. Based on these determinations, the photolysis pathways of the above congeners are summarized in Figures 1 and 2.

Through the hitherto studies⁵⁻⁷⁾, we have elucidated the overall photodechlorination pathways of all the non-ortho substituted PCB congeners in alkaline 2-propanol. Furthermore, the occurrence of photorearrangement has been first reported in the case of 3,4-DiCB with its products being identified. Our results reveal, clearly, that dechlorination is much more important than rearrangement during PCB photolysis. These informations might be of significance for treating PCBs by applying photolytic techniques as well as the study of the environmental fate of PCBs.

References

1. Safe, S. and Hutzinger, O. *Nature*, **1971**, 232, 641-642.
2. Bunce, N. J. *Chemosphere*, **1982**, 11, 701-714.
3. Yao, Y.; Tanaka, H.; Kakimoto, K.; Ogawa, H.I.; Kato, Y.; Hanada, Y. and Shinohara, R. *Abstracts of the '96 Annual Meeting of the Society of Environmental Sciences, Japan*, **1996**, 58-59.
4. Yao, Y.; Kakimoto, K.; Ogawa, H.I.; Kato, Y.; Baba, K.; Hanada, Y.; Shinohara, R. and Yoshino, E. *J. Environ. Chem.* **1997**, 7, 39-46.
5. Yao, Y.; Kakimoto, K.; Ogawa, H.I.; Kato, Y.; Hanada, Y.; Shinohara, R. and Yoshino, E. *Bull. Environ. Contam. Toxicol.* **1997**, 59, 238-245.
6. Yao, Y.; Kakimoto, K.; Ogawa, H.I.; Kato, Y.; Hanada, Y.; Shinohara, R. and Yoshino, E. *Chemosphere*, **1997**, 35, 2891-2897.
7. Yao, Y.; Kato, Y.; Hanada, Y. and Shinohara, R. *Abstracts of the 17th International Symposium on Chlorinated Dioxins and Related Compounds (Dioxin '97), Organohalogen Compounds*, **1997**, 33, 246-249.