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Photodechlorination Pathways of Non-Ortho Substituted PCBs by Ultraviolet Irradiation in Alkaline 2-Propanol

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Polychlorinated biphenyls (PCBs) are well-known environmental contaminants. Since 1966, approximately 150 PCB congeners have been detected from the total environment (Larsen et al. 1993). As the prominent examples of human exposure, PCB-contaminated cooking rice oil caused the outbreak of “Yusho” episode in western Japan in 1968 (Urabe and Asahi 1984) and a similar poisoning episode in Taiwan in 1979 (Hsu et al. 1984), respectively. Although the use of these compounds has been banned, there are still numerous transformers in existence that contain PCBs, which results in their occasional discharge into environment today. These compounds are toxic, bioaccumulative and highly stable, therefore the establishment of effective and safe treatment process of PCBs has become an increasingly important topic.

Much attention has been paid to the photolysis of PCBs to date. These studies have clearly shown that PCBs may be photolytically degraded in the presence of photosensitizers by sunlight (Hawari et al. 1992) and may effectively undergo photodecomposition in organic solvents by high energy ultraviolet (UV) light (Hawari et al. 1992). Nishiwaki (1981) reported that PCBs can be completely decomposed in alkaline alcoholic solution by UV irradiation. The high quantum yields observed are interpreted in terms of a free radical chain reaction (Hawari et al. 1991) and the reductive dechlorination is known as the main mechanism for this photochemical process. The objective of this research was to study the photolytic characteristics of non-ortho substituted PCBs which show dioxin-like toxicity for elucidating their respective photodechlorination pathways and allowing for the development of practical photolytic methods of PCBs.

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MATERIALS AND METHODS

Standard PCB congeners (99%) including 3-chlorobiphenyl (3-CB), 4-CB. 3,3'-DiCB, 3,4-DiCB, 4,4'-DiCB, 3,3',4,4'-TetraCB were purchased from GL Sciences Inc. (Japan) and 3,4'-DiCB. 3,3',4-TriCB, 3,4,4'-TriCB were purchased from Cambridge Isotope Laboratories (USA). Biphenyl (BP) (99%) was purchased from GL Sciences Inc. n-Hexadecane-d_{34} (99 atom % D) and n-eicosane-d_{42} (98.9 atom % D) were purchased from CDN Isotopes Inc. (Canada). 2-Propanol (99%, PCB quality) and hexane (pesticide quality) were purchased from Nacalai Tesque Inc. and Kanto Chemicals Inc. (Japan), respectively. All other reagents were of guaranteed grade. Stock standard solutions (100 mg/L or 200 mg/L) of these compounds were prepared separately in hexane. Mixed standard solutions for gas chromatograph / mass spectrometer (GC/MS) analysis were prepared by combining the suitable stock solutions and diluting with hexane. All of the standard solutions were stored in a refrigerator at -40°C.

The photolyses of the PCB congeners were performed in a photochemical reactor (Model HLV-A, Taika Kogyo Co., Ltd., Japan). Two L of each solution of 0.2 mg/L 3,3',4,4'-TetraCB, 3,3',4-TriCB, 3,4,4'-TriCB, 3,4'-DiCB, and 0.1 mg/L 3,3'-DiCB, 4,4'-DiCB, 3-CB, 4-CB in NaOH (0.4 % w / v) 2-propanol were separately irradiated with an immersed low pressure mercury lamp (Model L-15W, λ_{max} =254 nm, Taika Kogyo Co., Ltd.). The 20 mL aliquots for different irradiation times were withdrawn from the reactor, mixed with 80 mL saturated sodium chloride solutions and their pH were adjusted to 2 -3 with sulfuric acid (2.5 M). The samples were twice extracted with 5 mL hexane. The extracts were washed with hexane-extracted Mill-Q water, dehydrated by anhydrous sodium sulfate, and then concentrated to 1 mL with a Kuderna-Danish concentrator under reduced pressure and a gentle stream of nitrogen. One μ L of each concentrate was injected into GC (HP 5890 SERIES II, Hewlett-Packard Co., USA) / MS (Automass 20, JEOL, Japan) in the splitless mode using an autosampler (GC System Injector, Hewlett-Packard Co.) after addition of n-hexadecane-d_{34} and n-eicosane-d_{42} as internal standards. All analyses were carried out with a DB-5MS capillary column (30 m length X 0.25 mm id, 0.25 μ m film thickness, J&W Scientific, USA). Helium was used as carrier gas and the column head pressure was 50 kPa. The column was maintained at 60 °C initially for 2 min. then raised to 280 °C at 10 °C / min with a final holding time of 2 min. The injector, interface and ion source were heated at 240 °C, 250 °C and 200 °C, respectively. The ionization energy was 70 eV and the

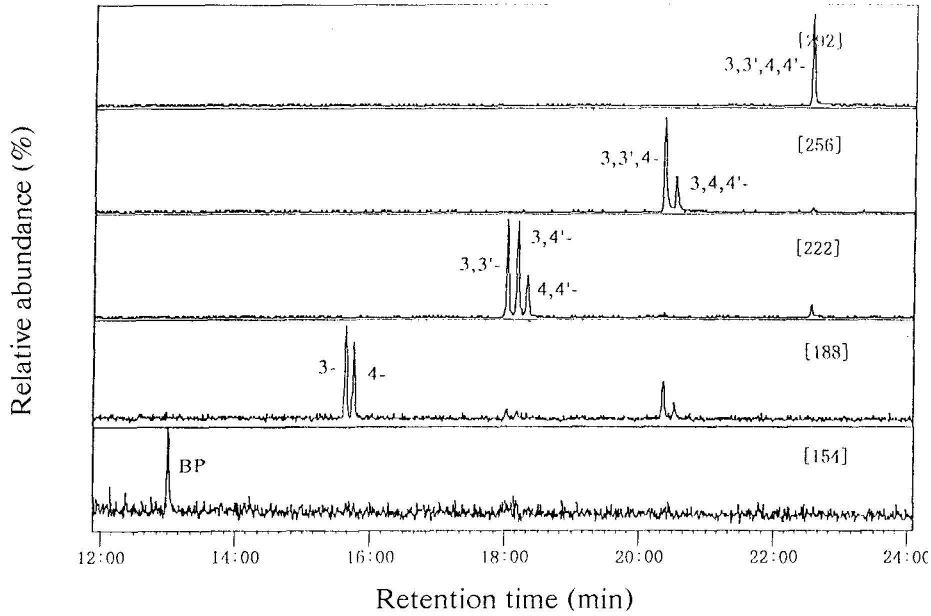

Figure 1. Mass chromatograms of 3,3',4,4'-TetraCB and its dechlorination products in alkaline 2-propanol after 10-min irradiation.

scanning mass range was from 35 to 500 amu.

The photodechlorination products were identified by matching 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-d_{34} was used for BP and MonoCBs, and n-eicosane-d_{42} was used for DiCBs, TriCBs and TetraCB.

RESULTS AND DISCUSSION

The photolysis of 3,3',4,4'-TetraCB, one of the most toxic PCB congeners, was repeated three times with the irradiation times of 0, 10, 20, 30, 60, 90, 120, 150, 180 and 240 min and good reproducibility was obtained. Figure 1 shows the mass chromatograms of 3,3',4,4'-TetraCB and its dechlorination products after 10-min irradiation. Because the retention times and the spectra were identical with those of standards, the peaks in the chromatograms were identified as the completely dechlorinated product, BP [m/z 154] , the lower chlorinated biphenyls, 3-CB, 4-CB [m/z 188] , 3,3'-DiCB, 3,4'-DiCB, 4,4'-DiCB [m/z 222] , 3,3',4-TriCB and 3,4,4'-TriCB [m/z 256] , and the starting material [m/z 292] , thus demonstrating the

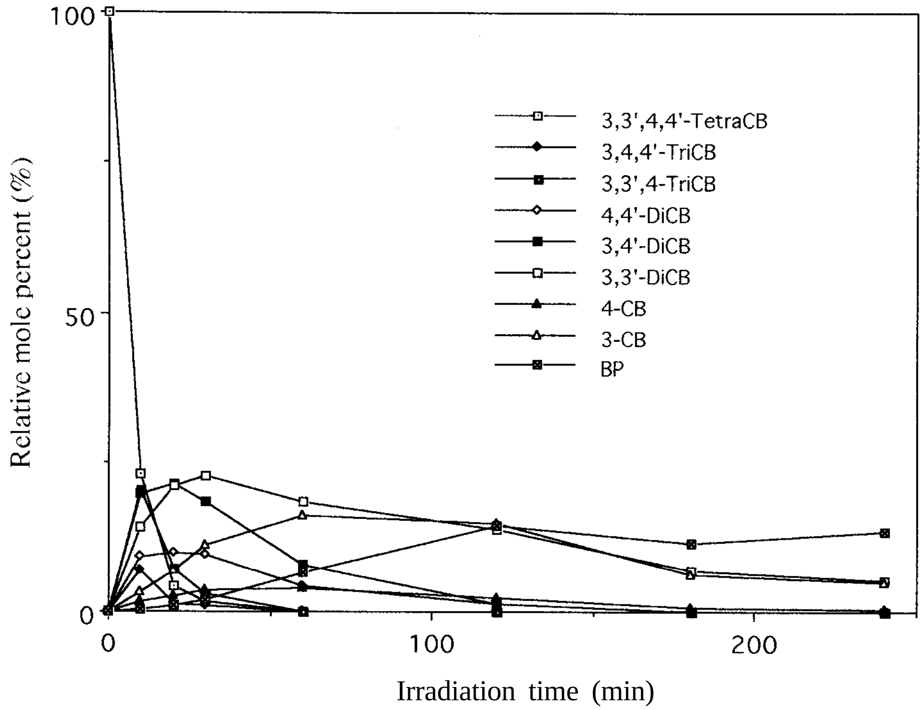

Figure 2. Relative molar distribution of 3,3',4,4'-TetraCB and its dechlorination products as a function of irradiation time in alkaline 2-propanol.

successive dechlorination of 3,3',4,4'-TetraCB and its dechlorination products. Figure 2 represents the relative molar distribution of 3,3',4,4'-TetraCB and its dechlorination products as a function of irradiation time. The quantitative data indicated that 3,3',4,4'-TetraCB decreased rapidly as a result of 99 % decomposition yield for about 30 min and the dechlorination proceeded mainly at the para position to give 3,3',4-TriCB. In addition: all of the dechlorination products were also found to be dechlorinated effectively with the result that only 5 % of 3,3'-DiCB, 5 % of 3-CB and 13 % of BP relative to the initial amount of starting material remained in the irradiated solution after 4-hr irradiation. In order to define the complete photodechlorination pathways of this TetraCB and discuss the reactivities of para and meta chlorines, the respective photolyses of the related compounds were conducted subsequently. The results of these experiments are presented in Table 1. The average recovery was 98 %. Based on these observations in which especially 3,4'-DiCB was confirmed to be generated in the photolyses of both 3,3',4-TriCB and 3,4,4'-TriCB, and to be

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

Starting material	Dechlorination products			
	- 1 Cl	- 2 Cl	- 3 Cl	- 4 Cl
3,3',4,4'-TetraCB (22.8)*	3,3',4-TriCB (20.5) 3,4,4'-TriCB (6.9)	3,3'-DiCB (14.0) 3,4'-DiCB (19.8) 4,4'-DiCB (9.2)	3-CB (3.2) 4-CB (1.5)	BP (0.2)
3,4,4'-TriCB (4.6)	4,4'-DiCB (35.5) 3,4'-DiCB (16.7)	4-CB (7.3) 3-CB (4.5)	BP (1.6)	
3,3',4-TriCB (5.1)	3,3'-DiCB (31.4) 3,4'-DiCB (28.1)	3-CB (11.5) 4-CB (1.4)	BP (1.2)	
4,4'-DiCB (51.2)	4-CB (12.4)	BP (18.8)		
3,4'-DiCB (41.0)	3-CB (28.9) 4-CB (3.4)	BP (5.4)		
3,3'-DiCB (80.0)	3-CB (7.8)	BP (5.4)		
4-CB (40.6)	BP (38.2)			
3-CB (42.6)	BP (10.9)			

* Data in parentheses are the molar percentages of the congeners relative to the initial amount of starting material after 10-min irradiation.

dechlorinated to form 3-CB and 4-CB, the respective photodechlorination pathways of these congeners are defined and summarized in Figure 3.

Hawari et al. (1991) found that in the dechlorination of polychloro aromatics, such as hexachlorobenzene, para elimination was more preferential than that of meta. In this study, 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, being in agreement with the report of Hawari et al. (1991). This was supported by the data obtained from the photolyses of 3,3'-DiCB and 4,4'-DiCB. For 3,4'-DiCB, the dechlorination proceeded also mainly at the para position. The same is true in the case of 3,3',4-TriCB which proved to be dechlorinated a little more at the para position of its more substituted ring. All of these results are consistent with the observed behavior of 3,3',4,4'-TetraCB mentioned above and they 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. Nishiwaki (1981) calculated their total 52 electron densities and reported the electronic effect as para > meta for 3,4-DiCB in alkaline 2-propanol. 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 probably the decisive factors for controlling

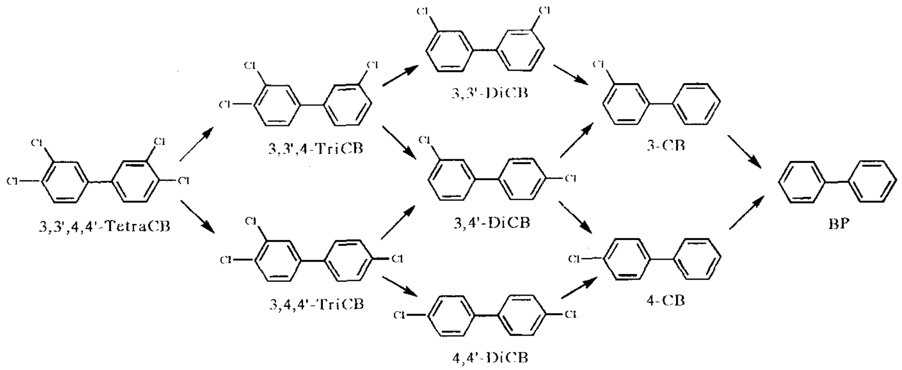

Figure 3. Photodechlorination pathways of 3,3',4,4'-TetraCB by UV irradiation in alkaline 2-propanol.

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. Considering the difference in initial molarity, we calculated the time required for 50 % decomposition yield of each congener used to compare their photolysis rates. Consequently, it was found that the photolysis rates of the congeners varied in the order of 3,4,4'-TriCB ~ 3,3',4-TriCB > 3,3',4,4'-TetraCB > 4-CB > 3-CB > 3,4'-DiCB > 4,4'-DiCB > 3,3'-DiCB. This result agrees generally with the view that the more chlorinated PCB congeners are more reactive toward photodechlorination (Lépine et al. 1991) and supports our argument described above. The similar photolysis rates obtained for 3,4,4'-TriCB and 3,3',4-TriCB can be attributed to the fact that they are dechlorinated in the same rings. Besides, it is considered that the antisymmetries of the TriCBs make them more rapidly photolyzed than the symmetrical TetraCB. For 4-CB and 3-CB, they are more rapidly to be dechlorinated than the DiCBs since BP has the relatively stable symmetrical structure while the dechlorination products of all the three DiCBs do not have.

Ruzo et al. (1972) studied the photolysis of 3,3',4,4'-TetraCB in hexane with 300 nm light and reported that 3,4,4'-TriCB and 4,4'-DiCB were produced. Lépine et al. (1991) investigated the photodegradation products of 3,3',4,4'-

TetraCB in cyclohexane with the same wavelength light and reported on a slight formation of 3,4,4'-TriCB and 3,3',4-TriCB. In this study, more dechlorination products were discovered for 3.3',4,4'-TetraCB and all of the congeners examined were confirmed to be dechlorinated effectively under the irradiation with low pressure mercury lamp in alkaline 2-propanol. The difference in wavelength of UV source is thought to be another important factor for the different results in addition to the influence of reaction solvents. It is worth noting that 90 % of the irradiation emitted by low pressure mercury lamp is at 254 nm which corresponds to those of the absorption peaks of many PCBs (Yao et al. 1997) including all the non-ortho substituted congeners in UV region. Furthermore, this wavelength is of considerably higher energy than 300 nm. Previous study has indicated that the photolysis rate of 2,4,4'-TriCB in alkaline 2-propanol increased when the UV source was changed from high pressure mercury lamp (λ_{max} =365~366 nm) to low pressure mercury lamp (Yao 1995).

The overall investigation of the mass balance between starting material and dechlorination products in each photochemical process demonstrated that the reductive dechlorination is the main photoreaction especially in the initial step. The fact that the mass balance became imbalanced with the proceeding of the photochemical process suggested the presence of other reactions. The decomposition of BP plays an important role in this imbalance according to the previous report (Yao et al. 1996) which noted that BP can also be decomposed effectively under the same experimental conditions. Moreover, the observation that all the test solutions changed from colorless to yellow during the photolyses suggested the formation of polymeric products (Hutzinger et al. 1974).

This study elucidated the complete photodechlorination pathways of 3,3',4,4'-TetraCB and the related lower chlorinated congeners in alkaline 2-propanol for the first time and the results indicated that the reactivities of para and meta chlorines of PCB congeners are controlled by their electronic effect and steric effect, as well as the stabilities of dechlorination products.

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