

## Photochemistry of PCBs by UV Irradiation in Alkaline 2-Propanol

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### Introduction

Polychlorinated biphenyls (PCBs) are well-known environmental pollutants. Although the production and use of these compounds have been regulated throughout the world mostly in the 1970s, many PCB-containing units are still in use or in storage awaiting decomposition. Photochemistry of PCBs is of great interest from the viewpoint of its potential use to handle these compounds. Previous studies have shown that commercial PCB mixtures can be effectively decomposed in organic solvents by UV irradiation<sup>1</sup> and reductive dechlorination is known as the main reaction mechanism. The aim of this research was to investigate the photochemical behaviours of PCBs in alkaline 2-propanol, which is an approved efficient reaction system<sup>1, 2</sup>.

### Materials and Methods

Twenty six PCB standards (99%) were used as the photodecomposition substrates and authentic standards. All other solvents and reagents used were PCB quality or guaranteed grade. The photolysis experiments were performed in a photochemical reactor under normal atmospheric conditions. Two L of each solution containing an individual PCB congener ( $0.1 \text{ mg L}^{-1}$ ) in sodium hydroxide (0.4% w/v) 2-propanol were separately irradiated using an immersed low pressure mercury lamp ( $\lambda_{\text{max}} = 254 \text{ nm}$ ). The 20 mL aliquots for different irradiation times (0, 10, 20, 30, 60, 90, 120, 150, 180, 240 and 300 min) were extracted with *n*-hexane and the extracts were concentrated to 1 mL. Then the concentrates were analyzed by GC/MS. A scanning mass range of 35-500 amu was used and the substrates and products were identified by matching their GC retention times and mass spectra with those of authentic standards. The concentrations of these compounds were quantified by internal standard method.

### Results and Discussion

Our previous study on the photolysis pathways of ortho substituted PCBs including 2,4,4'-TriCB, 2,2',5-TriCB and 2,2',5,5'-TetraCB in alkaline 2-propanol showed that ortho chlorines are lost preferentially over para and meta substituents<sup>2</sup>. In this study, the photoproducts of 6 lower chlorinated ortho substituted PCBs including 2-CB, 2,2'-DiCB, 2,4-DiCB, 2,4'-DiCB, 2,5-DiCB and 2,6-DiCB were investigated. It was found that 2-CB was decomposed rapidly and predominantly dechlorinated to biphenyl (BP). In the meantime, trace amounts of 3-CB and 4-CB were also detected, indicating the existence of PCB rearrangement. Safe and Hutzinger previously suggested the occurrence of photorearrangement in the case of 2,2',4,4',6,6'-HexaCB irradiated at 310 nm in hexane<sup>3</sup>. As the concentration of the test solution used was low, the rearrangement is thought to be an intramolecular reaction. During the 2,2'-DiCB experiment, the formation of 2-CB, 3-CB, 4-CB, and BP was observed, in which 2-CB was confirmed to be the main product. Considering the photochemical behaviour of 2-CB mentioned above, 2,2'-DiCB is considered to be photolyzed to give 2-CB through dechlorination while 3-CB and 4-CB are the rearrangement products of 2-CB. The same is true with 2,6-DiCB. For 2,4-DiCB, 2,4'-DiCB, and 2,5-DiCB, only orthodechlorination products were found. BP was detected as the final dechlorination product in these cases. Fig. 1 shows the photolysis pathways of these compounds.

## EMV - General – Dioxins and Dioxin-Like Compounds

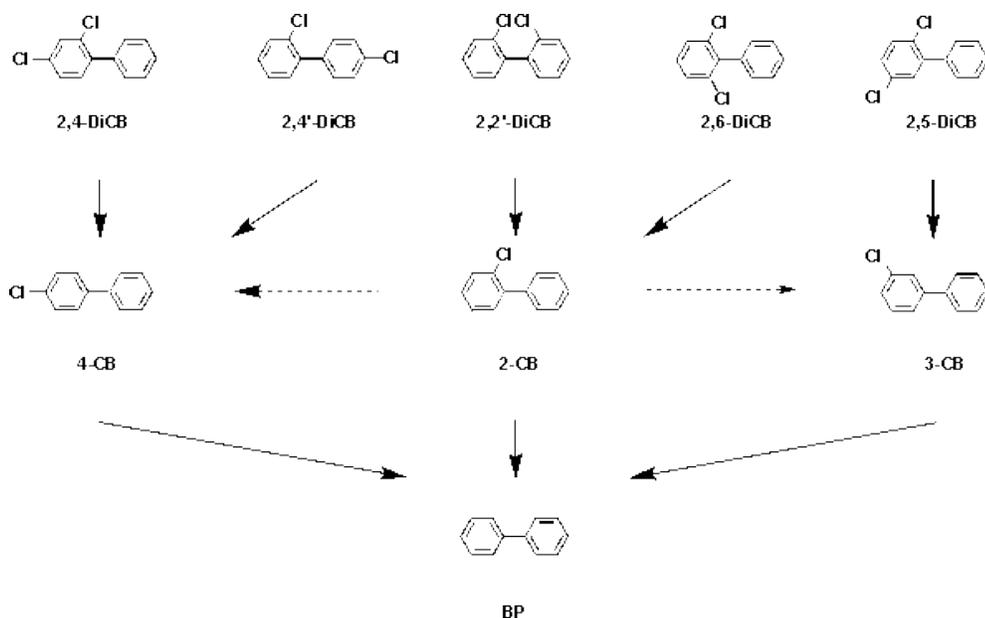


Fig. 1. Photolysis pathways of ortho substituted PCBs by UV irradiation in alkaline 2-propanol. Full and dotted line arrows show the major and minor photochemical reaction pathways, respectively, while broad and thin dotted line arrows show the major and minor rearrangement pathways, respectively.

The photodechlorination of all the non-ortho substituted PCBs including the dioxin-like 3,3',4,4',5-PentaCB (PCB 126), 3,3',4,4',5,5'-HexaCB (PCB 169), 3,3',4,4'-TetraCB (PCB 77), and 3,4,4',5-TetraCB (PCB 81) were further studied. The results revealed that para chlorine is generally released more readily than meta substituent. Dechlorination occurs chiefly on the more substituted ring and preferentially at the position to form symmetrical product. 3-CB and 4-CB were found to be dechlorinated to BP without rearrangement. 3,3'-DiCB and 3,5-DiCB were photolyzed to give 3-CB. 4,4'-DiCB was dechlorinated through para elimination. For 3,4'-DiCB, the dechlorination proceeded mostly at the para position. Likewise, 3,3',4-TriCB was dechlorinated preferentially at the para position of its more substituted ring. In contrast with 3,3',4-TriCB, 3,4,4'-TriCB mainly lost its meta chlorine. The steric effect of starting material and the stabilities of dechlorination products are thought 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 renders the dechlorination to occur only on the more substituted ring without the generation of 3,4-DiCB. In the meantime, 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 dechlorination proceeds preferentially at para and meta positions, respectively. For 3,4',5-TriCB, the dechlorination proceeded mostly at the meta position of its more substituted ring to yield 3,4'-DiCB while the para dechlorination product, 3,5-DiCB was also detected. In this instance, 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 brings about the para dechlorination. In the case of 3,3',5-TriCB, the dechlorination proceeded mostly on the more substituted ring to generate symmetrical 3,3'-DiCB. Dechlorination of 3,3',4,4'-TetraCB was observed to proceed mostly at the para position to form 3,3',4-TriCB. The electronic effect is likely to be the decisive factor in this case, as the frontier ( $\pi$ ) electron densities of para chlorines are nearly 10 times those of meta chlorines in 3,3',4,4'-TetraCB molecule<sup>4</sup>. For 3,3',4,5'-TetraCB, it was found that the dechlorination proceeded at all substituted positions and the relative reactivities of the chlorine substituents vary in the order of 4- > 3- > 3'- or 5'-position, being in agreement with the discussion described previously. For 3,3',5,5'-TetraCB, the slow dechlorination produced 3,3',5-TriCB through the loss of meta chlorine. Preferential para dechlorination was observed for 3,4,5-TriCB, 3,3',4,5-TetraCB, 3,4,4',5-TetraCB, 3,3',4,5,5'-PentaCB, 3,3',4,4',5-PentaCB, and 3,3',4,4',5,5'-HexaCB. The steric effect is considered to be the key factor for controlling dechlorination pattern in these cases. That is to say, the steric congestion of 3,4,5-arrangement increases the reactivities of 3-, 4- and 5-chlorines, notably 4-substituent, and makes the dechlorination to occur only on the more substituted ring. It is worthy to note that photorearrangement was only found for 3,4-DiCB in the whole non-ortho substituted PCB class, generating trace amounts of 3,3'-DiCB and 4,4'-DiCB. Nevertheless, reductive dechlorination was confirmed to be the major photochemical reaction. Preferential meta dechlorination was observed in this case. The complete

photodechlorination pathways of these compounds are summarized in Fig. 2. To the best of our knowledge, this is the first experimentally approved overall photodechlorination pathways of all the non-ortho substituted PCBs in organic solvent.

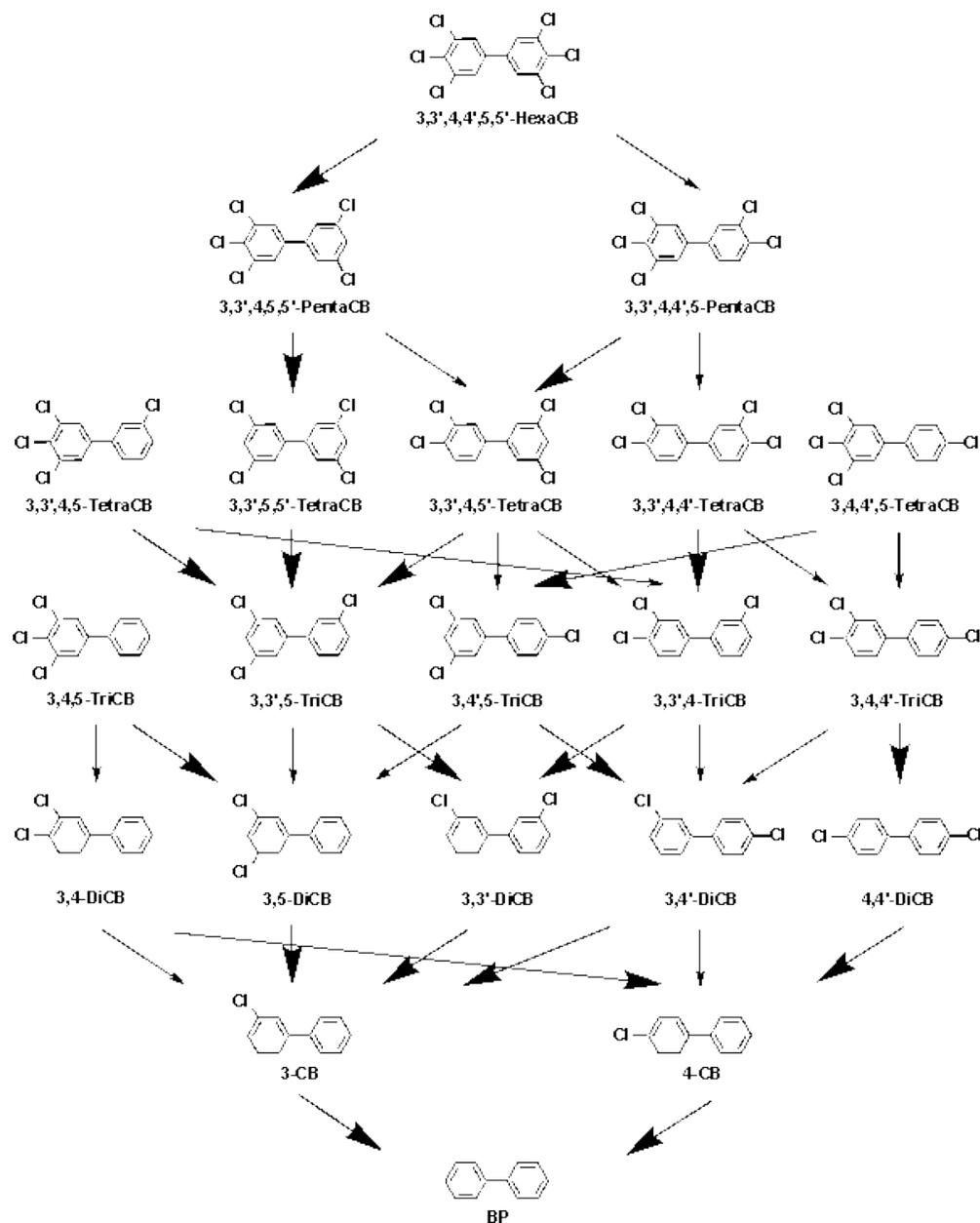


Fig. 2. The complete photodechlorination pathways of non-ortho substituted PCBs by UV irradiation in alkaline 2-propanol. Broad and thin full line arrows show the major and minor pathways, respectively.

The obtained results indicated that PCB photolytic reactions in alkaline 2-propanol are of the pseudo-first order, giving agreement with previous findings in other solvent systems<sup>5</sup>. The comparison of photolysis rates of 3 MonoCBs (2-CB, 3-CB and 4-CB) and 3 DiCBs (2,2'-DiCB, 3,3'-DiCB and 4,4'-DiCB) supported our observation that the photodechlorination of PCBs generally proceeds through the loss of the chlorine in the order of ortho>para>meta position. In addition, photoreactivity of PCB congeners is affected by the number and position of chlorine substitution. For non-ortho substituted PCBs, congeners with 3,4,5- or 3,4-arrangement generally degrade very quickly. Examples include 3,3',4,4',5,5'-HexaCB (Fig. 3), 3,3',4,4',5-PentaCB, 3,4,4',5-TetraCB, 3,3',4,5-TetraCB, 3,4,5-TriCB, 3,4,4'-TriCB, 3,3',4-TriCB, and 3,4-DiCB. 3,3',5,5'-TetraCB, 3,3',5-TriCB, 3,3'-DiCB, and 3-CB were confirmed to be the

most photostable isomers for non-ortho substituted tetra-, tri-, di-, and mono-chlorinated homologues, respectively.

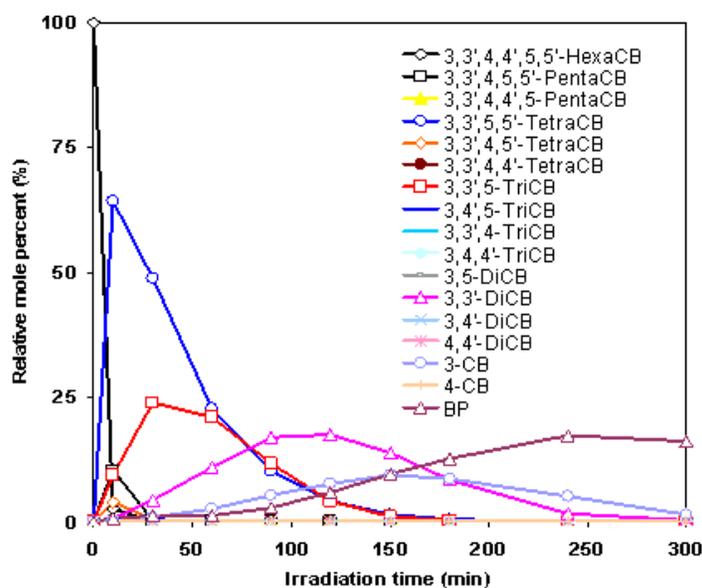


Fig. 3. Relative molar distribution of 3,3',4,4',5,5'-HexaCB and its successive dechlorination products as a function of irradiation time in alkaline 2-propanol.

The overall investigation on the mass balance between starting material and dechlorination products in each photochemical process demonstrated that reductive dechlorination is the principal photoreaction. The fact that the mass balance became imbalanced with the proceeding of PCB photodegradation suggested the presence of other reactions. The decomposition of BP may play an important role in this imbalance, because our preliminary study has indicated that BP can also be decomposed effectively under the same experimental conditions. The hydroxylation of PCB molecules is probably another factor as hydroxyproducts were detected during the photolyses, however the identification of such compounds were not performed due to the lack of corresponding standards. The observation that all the test solutions changed from colorless to yellow during the photolyses suggested the formation of polymeric products<sup>3</sup>.

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