

Dechlorination of PCBs in Water Under UV Irradiation and the Relationship Between the Electric Charge Distribution on the Carbon Atom and the Site of Dechlorination Occurrence

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Photodegradation is a process in which chemical bonds are broken by the energy from UV light. Photodegradation of polychlorinated biphenyls (PCBs) involves the loss of chlorine atoms from the benzene ring, the order for ease of loss is *ortho* > *para* > *meta*. Because of the low solubility of PCBs in water, some organic solvents such as *n*-hexane (Miao et al. 1996; 1999; Chang et al. 2003), 2-propanol (Yao et al. 1997; 2000), and alcohols (Hawari et al. 1991; Grittini et al. 1995) have been used in PCB photochemical studies in recent years. The present research was designed to investigate the photolytic characteristics of seven PCB congeners in water under UV irradiation, and to study their major photodecomposition pathway. In addition, the electric charge distribution on carbon atoms of the PCBs, as computed by the Modified Neglect of Differential Overlap (MNDO) method, was utilized to establish the relationship between the electric charge distribution on carbon atoms and the site of photodechlorination occurrence for PCB congeners.

MATERIALS AND METHODS

Standard PCB congeners (99% purity) including five *ortho* substituted congeners, 2-MonoCB (2-monochlorinated biphenyls) which is IUPAC number 1 of PCB congeners (PCB-1), 2,6-DiCB (PCB-10), 2,3,4-TriCB (PCB-21), 2,4,5-TriCB (PCB-29), and 2,4,6-TriCB (PCB-30) and two non-*ortho* substituted congeners, 3,4-DiCB (PCB-12) and 3,5-DiCB (PCB-14), were obtained from AccuStandard Co. (New Haven, CT., USA). The stock solutions (1 mg/mL) were prepared in acetone and stored at -20°C. LC grade *n*-hexane and acetone were purchased from E. Merck, Germany.

The experimental methods from a previous study on UV irradiation in *n*-hexane were followed (Chang et al. 2003). Each test solution (100 mL) containing an individual PCB congener (concentration 1 µg/mL in pure water) was irradiated under a 15W UV lamp at a wavelength of 254 nm in a separate glass beaker with upper surface area of 38.5 cm². The distance between the UV lamp and the upper surface of the solution was 50 cm. Experiments were performed at room temperature (25°C) and were conducted in triplicate. Eighteen beakers for each PCB congener were prepared for sampling in triplicate at 0, 0.5, 1, 2, 3 and 6 hrs

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(but sampling at 0, 10, 30, 60, 90 and 120 min for the PCB-10 sample). Before sampling each test solution was quantified to original volume (100 mL) by adding water. The irradiated sample (10 mL) was extracted by *n*-hexane (2 mL) twice. The *n*-hexane was combined and concentrated to 2 mL. The extracts (2 μ L) were applied directly to the gas chromatograph for analysis. The half-lives ($t_{1/2}$) of individual PCB congeners were calculated by the equation for a pseudo first-order reaction (Yen et al. 2000).

The photoproducts were identified by matching their retention times and mass spectra with those authentic standards. Photodecomposed products were analyzed by GC (HP 6890 series GC system, Hewlett Packard Co., USA) / MS (HP 5973 Mass selective detector, Hewlett Packard Co., USA) equipped with a HP-5MS capillary column (30 m \times 0.25 mm i.d., 0.25 μ m film thickness, Hewlett Packard Co., USA).

The concentrations of the PCB congeners and photoproducts were quantified by GC-ECD. The gas chromatograph (Varian star 3600CX, Walnut Creek, CA) was equipped with an electron capture detector (ECD) and a DB-5 fused silica capillary column (30 m \times 0.53 mm i.d. film thickness 1.5 μ m, J&W Scientific, Folsom, CA). Temperatures of the injection port and electron capture detector were set at 280 and 300°C, respectively. The column was held at 170°C for 2 min, then increased to 260°C at 3°C min⁻¹, and finally held at 260°C for 30 min. Nitrogen was used as the carrier gas, with a linear velocity of 27.3 cm/s and split ratio of 15:1.

The electric charge distribution on carbon atoms of the PCB congeners were computed by the MNDO method provided by CS MOPAC Pro (Version MOPAC 93) and included as part of the desktop modeling software CS Chem3D Pro (Cambridge Soft Co., Cambridge, MA).

RESULTS AND DISCUSSION

The half-lives of the seven PCB congeners in this investigation ranged from 0.15 to 2.13 hours (Table 1). PCB congeners with a coplanar configuration (PCB-12 and PCB-14) were found to have a longer half-life, 2.01 and 2.13 hours,

Table 1. Half-life of PCB congeners upon exposure to UV (254 nm) in water

PCB congeners	Half-life (hours)
PCB-1 (2-)	0.38
PCB-10 (2,6-)	0.15
PCB-12 (3,4-)	2.01
PCB-14 (3,5-)	2.13
PCB-21 (2,3,4-)	0.38
PCB-29 (2,4,5-)	0.73
PCB-30 (2,4,6-)	0.47

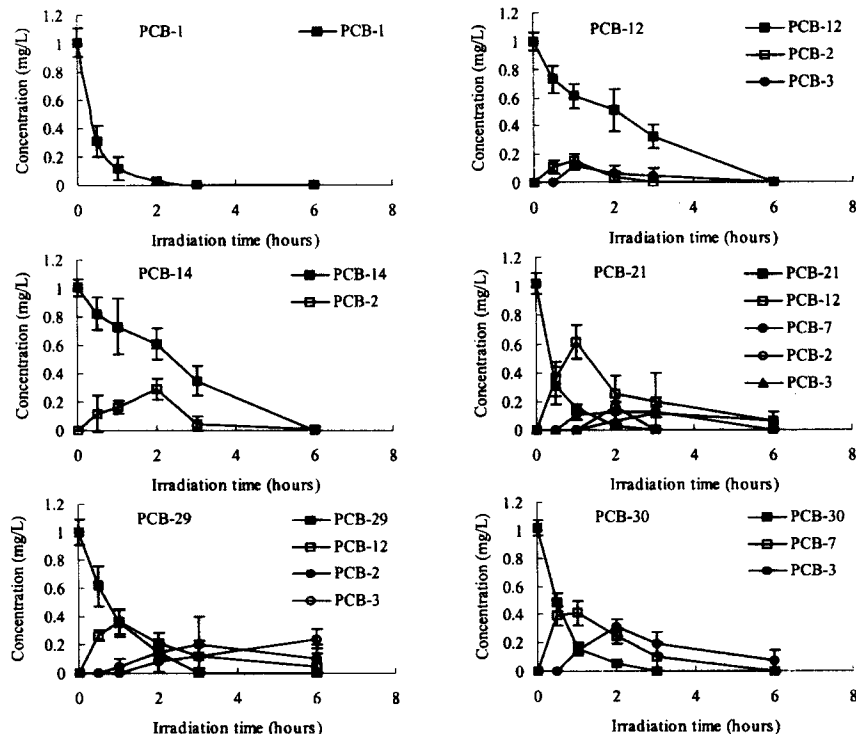


Figure 1. Products and amounts for photodechlorination of PCB-1, 12, 14, 21, 29 and 30.

respectively, under 254 nm UV irradiation in water. The longer half-life in a planar configuration is attributed to the presence of extended conjugation between two phenyl rings (Miao et al. 1999). Whether in water (this study) or in *n*-hexane (previous study, Chang et al. 2003), coplanar PCB congeners were difficult to photodechlorinate. Although the half-lives of photodecomposition of the two coplanar PCB congeners under UV light are longer, they were much shorter than that under anaerobic dechlorination in sediment by microbial degradation (Chang et al. 2000; Chen et al. 1997; 1999; 2000; 2001a, b).

The original PCB congeners remained in culture and the yield of their photoproducts at different times after UV irradiation were determined (Figures 1 and 2). Figure 1 shows the PCB dechlorination products and how their amounts under UV irradiation changed as time elapsed. For PCB-1, 10, 21, 29 and 30 which are substituted with one to three chlorines on the benzene ring, the degradation was found to occur on *ortho*-chlorine. The major product of PCB-21 and 29 was PCB-12, and the major product of PCB-30 was PCB-7. The sole product for PCB-10 was PCB-1 (Figure 2). Dissipation of PCB-10 is accompanied with the appearance of PCB-1 at an early stage, however, most of these PCBs were dissipated within 2 hours after irradiation. The amounts of dechlorination

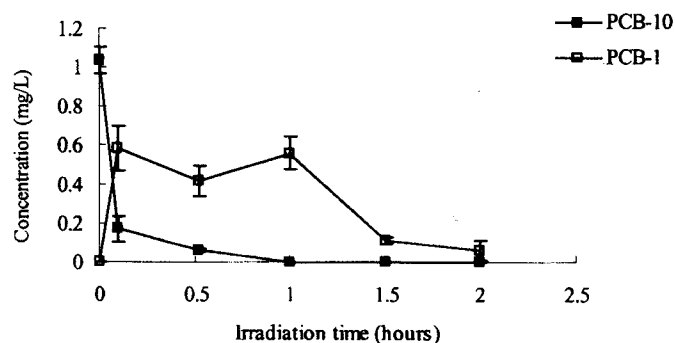


Figure 2. Products and amounts for photodechlorination of PCB-10.

products and of original PCB remaining are listed in Table 2. The results showed that major photodechlorination occurred at the *o*-substituted chlorine of the benzene ring (Figure 3). This result is counter to those for previous studies which

Table 2. Dechlorination products and mass percentage of PCB congeners after exposure to UV in water for 1 hr

PCB congeners	Dechlorination products		
	-1 Cl	-2 Cl	-3 Cl
PCB-1 (11.88**)	BP*		
PCB-10 (0.98)	PCB-1 (41.18)	BP	
PCB-12 (61.31)	PCB-2 (16.08)	BP	
	PCB-3 (12.06)		
	PCB-2 (15.92)	BP	
PCB-14 (72.64)	PCB-5 (0.00)	PCB-1 (0.00)	BP
PCB-21 (12.32)	PCB-7 (10.84)	PCB-2 (1.97)	
	PCB-12 (60.49)	PCB-3 (0.00)	
	PCB-7 (0.00)	PCB-1 (0.00)	BP
PCB-29 (35.68)	PCB-9 (0.00)	PCB-2 (5.03)	
	PCB-12 (36.18)	PCB-3 (0.00)	
	PCB-7 (40.39)	PCB-1 (0.00)	BP
PCB-30 (15.76)	PCB-10 (0.00)	PCB-3 (14.78)	

*BP: Biphenyl, identified with GC-MS.

**Percentage of PCB amounts relative to the original compound in parenthesis.

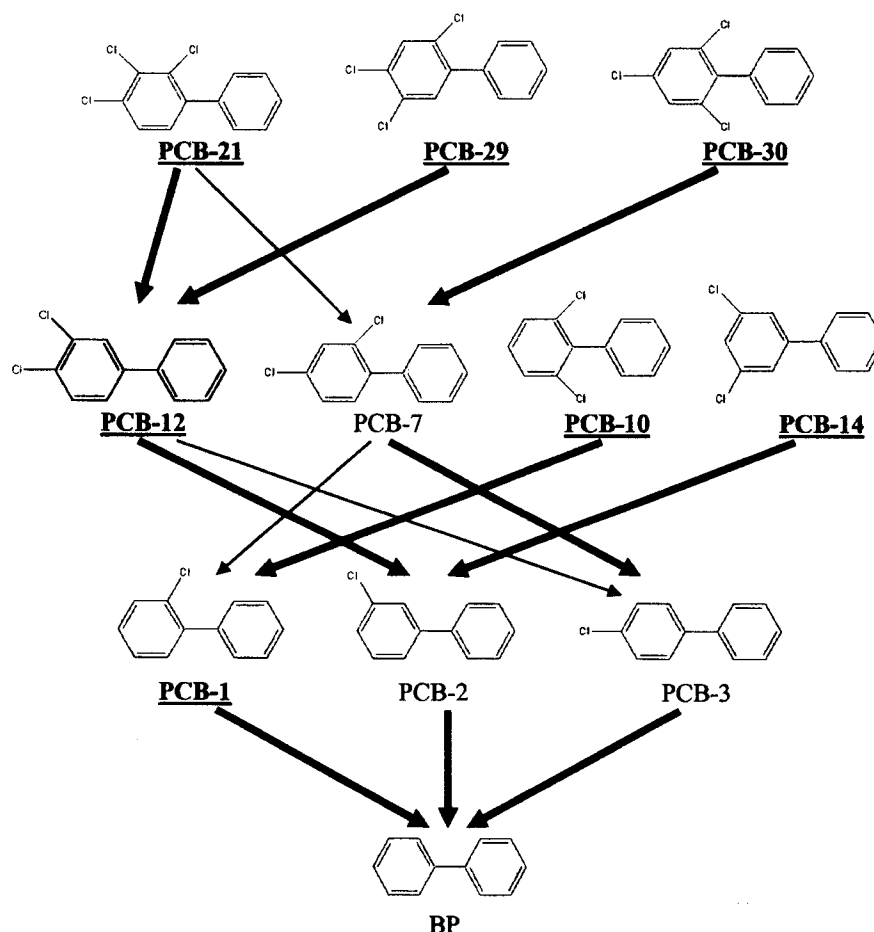


Figure 3. Possible photodechlorination pathways of seven PCB congeners (written in boldface) in this study. **→** major pathway, **→** minor pathway

incubation in 1, 2, 3-TCB-acclimated mixed cultures before reductive dechlorination by anaerobic microorganisms (Holliger et al. 1992; Chang et al. 1997). Generally, reductive dechlorination by anaerobic microorganisms was found to exclude the middle chlorine of three adjacent chlorines; i.e., *o*-position dechlorination was not found. The results in this study suggest that microbial dechlorination may be related to enzyme systems in organisms and the molecular configuration of the PCB, but photodechlorination is affected by the physical-chemical properties of PCB molecular and irradiation energy. Possible routes of photodechlorination for the seven PCB congeners in this study are shown in

Figure 3.

In this study, we proposed that photodechlorination of PCBs was related to the charge distribution on the carbon with an attached chlorine atom. The electric charge distributions on carbon atoms for the PCB congeners were computed by the MNDO method and are shown in Table 3. The results suggested that the photodechlorination may be related to the charge distribution on the chlorinated carbon as the higher the charge distribution for a chlorine attached carbon, the easier photodechlorination occurred. For example, the charge distributions on PCB-21 are 0.028073, 0.019440 and 0.014847 at carbon-2, -3 and -4, respectively. The chlorine at the carbon-2 is eliminated prior to that on the carbon-3 and the carbon-4. Among three photodechlorination products (PCB-12, -7 and -5), PCB-12 is the major product (Tables 2 and 3).

Electric charge distributions on a carbon atom combined with the monitoring information of photodechlorination products from the experiments were utilized to deduce the possible pathways of PCB dechlorination. The attached chlorine with the smallest charge distribution (Carbon-4 for PCB-21) was the most difficult one to eliminate.

From the experiment on photodechlorination of PCBs in water solution, several conclusions were made. PCB congeners with coplanar structure (such as PCB-12 and PCB-14) showed lower photosensitivity and longer half-life.

Table 3. Reaction occurrences and the electric charge distribution of carbon atoms at PCB from photodechlorination reactions

Reactant	The position of carbon atom	The charge of carbon atom (by MNDO)	Product	Reaction Pathway
PCB-1	2	0.019448	BP	M
PCB-10	2	0.015675	PCB-1	M
	6	0.015684	PCB-1	M
PCB-12	3	0.007749	PCB-3	M
	4	0.016348	PCB-2	M
PCB-14	3	0.005077	PCB-2	M
	5	0.005072	PCB-2	M
PCB-21	2	0.028073	PCB-12	M
	3	0.019440	PCB-7	M
	4	0.014847	PCB-5	ND
PCB-29	2	0.021408	PCB-12	M
	4	0.014783	PCB-9	ND
	5	0.013108	PCB-7	ND
PCB-30	2	0.014083	PCB-7	M
	4	0.001616	PCB-10	ND
	6	0.014106	PCB-7	M

MNDO: Modified Neglect of Differential Overlap method; BP: biphenyl; m: minor pathway; M: Major pathway; ND: not detected.

Photodechlorination occurred on elimination of *o*-substituted chlorine, predominantly. Elimination of an attached chlorine is related to the electric charge distribution for a chlorine attached carbon.

Dechlorination of PCBs by UV irradiation in water is similar to that in *n*-hexane. Photodechlorination occurred on the benzene ring which attached more chlorine atom and at higher electric charge distribution for a chlorine attached carbon.

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REFERENCES

- Chang BV, Chen IM, Yuan SY, Wang YS (1997) Reductive dechlorination of hexachlorobenzene by an anaerobic mixed culture. *Water Air Soil Pollut* 100: 25-32
- Chang FC, Yen JH, Wang YS (2000) Study on the biodegradation of polychlorinated biphenyls by indigenous aerobic microorganisms in Taiwan. In: *Proceedings of the 20th International Symposium on Halogenated Environmental Organic Pollutants & POPS 45*, Monterey, California USA pp 392-395
- Chang FC, Chiu TC, Yen JH, Wang YS (2003) Dechlorination pathways of *ortho*-substituted PCBs by UV irradiation in *n*-hexane and their correlation to the charge distribution on carbon atom. *Chemosphere* 51: 775-784
- Chen IM, Chang FC, Wang YS (1997) Reductive dechlorination of hexachlorobenzene and polychlorinated biphenyls in anaerobic sediments from tropical rivers with enrichment. In: *Proceedings of the 17th Symposium on Chlorinated Dioxins and Related Compounds 33*, Indianapolis, Indiana USA pp 189-192
- Chen IM, Chang FC, Wang YS (1999) Chromatographic and thermodynamic data of dechlorination reaction of polychlorinated biphenyls. In: *Proceedings of the 19th Symposium on Chlorinated Dioxins and Related Compounds 41*, Venice, Italy pp 463-466
- Chen IM, Chang FC, Chang BV, Wang YS (2000) Specificity of microbial activities in the reductive dechlorination of chlorinated benzenes. *Water Environ Res* 72: 675-679
- Chen IM, Chang FC, Wang YS (2001a) Comparisons of PCBs dechlorination occurrences in various contaminated sediments. *Chemosphere* 43: 649-654
- Chen IM, Chang FC, Wang YS (2001b) Correlation of gas chromatographic properties of chlorobenzenes and polychlorinated biphenyls with the occurrence of reductive dechlorination by untamed microorganisms. *Chemosphere* 45: 223-229
- Grittini C, Malcomson M, Fernando Q, Korte N (1995) Rapid dechlorination of polychlorinated biphenyls on the surface of a Pd/Fe bimetallic system. *Environ Sci Technol* 29: 2898-2900
- Hawari J, Demeter A, Greer C, Samson R (1991) Acetone-induced photodechlorination of Aroclor 1254 in alkaline 2-propanol: probing the

- mechanism by thermolysis in the presence of di-*t*-butyl peroxide. *Chemosphere* 22: 1161-1174
- Holliger C, Schraa G, Stams ADM, Zehnder AJB (1992) Environment and properties of an anaerobic mixture reductively dechlorinating 1,2,3-trichlorobenzene to 1,3-dichlorobenzene. *Appl Environ Microbiol* 58: 1636-1644
- Miao XS, Chu SG, Xu XB (1996) Photodegradation of 2,2',5,5'-tetrachlorobiphenyl in hexane. *Bull Environ Contam Toxicol* 56: 571-574
- Miao XS, Chu SG, Xu XB (1999) Degradation pathways of PCBs upon UV irradiation in hexane. *Chemosphere* 39: 1639-1650
- Yao Y, Kakimoto K, Ogawa HI, Kato Y, Baba K, Hanada Y, Shinohara R, Yoshino E (1997) Study on photolysis pathways of PCBs by UV irradiation in alkaline 2-propanol. *J Environ Chem* 7: 39-46
- Yao Y, Kakimoto K, Ogawa HI, Kato Y, Kadokami K, Shinohara R (2000) Further study on the photochemistry of non-*ortho* substituted PCBs by UV irradiation in alkaline 2-propanol. *Chemosphere* 40: 951-956
- Yen JH, Lin KH, Wang YS (2000) Potential of the insecticides acephate and methamidophos to contaminate groundwater. *Ecotoxicol Environ Saf* 45: 79-86