

DECHLORINATION OF PCBs BY UV IRRADIATION IN WATER AND THEIR CORRELATIVE OF THE CHARGE DISTRIBUTION ON CARBON ATOM

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Introduction

Contamination of the global environment by PCBs was first reported by Jensen in 1966, and their persistence and presence has been a serious problem of concern ever since. For environmental decomposition of PCBs, photodegradation induced by the ultraviolet content of sunlight is thought to be a significant route^{1,2} and the photoreaction has been proved to be enhanced by the presence of various sensitizers as well as semiconductors. Moreover, PCBs have been shown to be effectively decomposed upon UV irradiation in alkaline 2-propanol. In 1971, Safe and Hutzinger irradiated 2, 2', 4, 4', 6, 6'-hexaCB in hexane and methanol separately at 310 nm and found that 2, 2', 4, 4', 6, 6'-HexaCB was photodegraded to form products though dechlorination and other photochemical reaction¹. The impact of solar degradation of PCBs in the aquatic environment had been investigated and been concluded that photodegradation of PCBs exhibits an environmental significance².

Photodegradation is a process in which chemical bonds are broken under the UV irradiation. The chain reactions of photodegradation involve the loss of a chlorine atom in the order: *ortho* > *para* > *meta*. The photodegradation of PCBs has been conducted with UV, Co60 gamma irradiation, quartz, mercury lamp or other lamp simulating sunlight.

Because of the low solubility of PCBs in water, some organic solvents such as *n*-hexane^{3, 4, 5, 6}, cyclohexane^{7, 8}, iso-octane⁹, benzene³, 2-propanol^{10, 11, 12, 13, 14}, and alcohols^{7, 15, 16, 17, 18, 19, 20} have been used in PCBs photochemical studies.

In this study, we investigated the photolytic characteristics of the twenty-two PCB congeners in *n*-hexane under the UV irradiations, and tried to suggest the major photodecomposition pathway of the irradiated PCB congeners. On the other hand, the MNDO method was utilized to establish the electronic charge values of carbon atoms on PCB congeners. Basis on the computed information, we try to establish the relationship between the electronic charge distribution of carbon atoms on PCB congeners and the photodecomposition occurrence site of PCB congeners.

Materials and methods

Standard PCB congeners (99 % purity) including five *ortho* substituted congeners 2-monoCB (PCB-1), 2,6-DiCB (PCB-10), 2,3,4-TriCB (PCB-21), 2,4,5-TriCB (PCB-29), 2,4,6-TriCB (PCB-30) and one non-*ortho* substituted congener 3,4-DiCB (PCB-12), 3,5-DiCB (PCB-14) for contrast were obtained from AccuStandard Co. (New Haven, CT., USA). The stock solution (1 mg/mL) were prepared in *n*-hexane and stored at -20°. HPLC grade *n*-hexane was purchased from E. Merck, Germany.

Each test solution (100 mL) containing an individual PCB congener (2 mg/mL in water) was irradiated under a 15W UV lamp at wavelength of 254 nm in the separate glass beaker with upper surface area 38.5 cm². The distances between the UV lamp and upper surface of solution were 50 cm.

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Experiments were performed at room temperature (25°) and were conducted in triplicate. Each test solution was quantified to original 100 mL by adding water before sampling. The sample was extracted by *n*-hexane. The extract solution (2 mL) were applied directly to the gas chromatograph for analysis. The half-lives of individual PCB congeners were calculated by the pseudo first order reaction.

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 x 0.25 mm i.d., 0.25 mm film thickness, Hewlett Packard Co., USA).

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

The electronic charge distribution of carbon atoms on the PCB congeners were computed by MNDO (Modified Neglect of Differential Overlap) 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

Irradiation under UV lamp in water, the photodegradation of all individual PCB congeners are fitted the pseudo first order reactions, which is in agreement with the former researches. The PCB-adducts and polychlorinated terphenyls were not observed after UV irradiation. The half-life of the seven PCB congeners in this investigation was shown in Table 1.

The half-life of these seven PCBs was ranged from 0.15 to 2.13 hours. Half-lives of PCB congeners with coplanar (PCB-12 and PCB-14) were found to be much longer. Their half-lives are 2.01 and 2.13 hours, respectively, under 254 nm UV irradiation. In a planar configuration, because the extended conjugation was presented between two phenyl rings to lead to the longer half-life of photodegradation have reported. Although the half-lives of above two PCB congeners showed the longer under UV light, they were much shorter than that under anaerobic dechlorination in sediment by microbials degradation^{21, 22, 23, 24, 25, 26}

In this study, we proposed that photodechlorination of PCBs was related to the charge distribution on the chlorine atom attached carbon. The electronic charge distribution on carbon atoms for the PCB

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

PCB congeners	Half-life (hours)
PCB-1	0.38
PCB-10	0.15
PCB-12	2.01
PCB-14	2.13
PCB-21	0.38
PCB-29	0.73
PCB-30	0.47

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Table 2. Reaction occurrences and the electronic charge distribution of carbon atoms at PCB from photodechlorination reactions

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

congeners were computed by MNDO method. The charge values of the carbon atoms for the PCB congeners were calculated and shown in Table 2. From the results, photodechlorination was related to the charge distribution of the chlorinated carbon. The higher the charge distribution for chlorine attached carbon, the easier the photodechlorination occurrence was found on this carbon.

From the experiment of photodechlorination on PCBs in *n*-hexane solution, several conclusions were induced. PCB congeners with coplanar (such as PCB-12 and PCB-14) structure showed the lower photosensitivity and longer half-life. Photodecomposition of PCB congeners is dechlorination. Photodechlorination was occurred prior to *o*-substitute chlorine. Different chlorine numbers attach on the benzene ring, photodechlorination occurred on the more chlorine attached benzene ring. Position to eliminate the attached chlorine is related to the electronic charge distribution on the chlorine attached carbon. In other words, Photodechlorination of PCB was occurred first on the more chlorine attached benzene ring and at higher electronic charge distribution carbon.

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