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Photodegradation of Decachlorobiphenyl

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Polychlorinated biphenyls (PCB's) are widely used in electric capacitors, heat transfer media, plasticizers, etc., because of their physico-chemical properties (Hutzinger et al. 1974). For the environmental degradation of PCB's, decomposition by sunlight may become the major pathway of degradation owing to their chemical stabilities. It is therefore important to establish the extent to which photodegradation occurs and to identify the photodegradation products for environmental safety. Under ultraviolet irradiation at 254 nm, 300 nm, or 310 nm wavelengths, PCB's were significantly decomposed and the photodegradation products were mainly less chlorinated biphenyls, caused by dechlorination reaction, in cyclohexane, hexane, or isooctane solutions (Bunce et al. 1978; Safe and Hutzinger 1971; Ruzo et al. 1974, 1975) and methoxybiphenyls, caused by replacement reaction, in methanol solution (Ruzo et al. 1974).

In the present paper, the photodegradation of decachlorobiphenyl (DCB, I) under xenon lamp irradiation in the range of 199 nm to 358 nm wavelengths and its photodegradation products were studied.

MATERIALS AND METHODS

The test compound DCB(I) was purchased from Nakarai Chemicals, Ltd. Japan. Small amounts of DCB(I) were dissolved in 100 ml of hexane to make 1 ppm, 10 ppm, and 100 ppm solutions. Small amounts of DCB(I) were also dissolved in 100 ml of methanol, acetone, and benzene, respectively, to make 10 ppm solutions. Two ml of each DCB(I) solution was taken into quartz cubic cells (1x1x5 cm). The cells were irradiated under thirty different wavelengths between 199 nm and 358 nm by using a JASCO CRM-FA xenon lamp irradiator. After 300 counts to 2000 counts irradiation (20 min to 133 min, 15 counts irradiation per min), 2 µl of the each solution was subjected to gas chromatography(GC) for the quantitative analysis of DCB(I). The irradiated solutions were also applied to GC-mass spectrometry(GC-MS) for the identification of photodegradation products.

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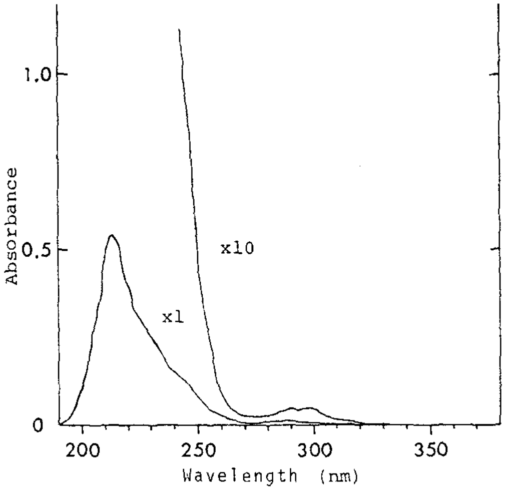


Figure 1. Ultraviolet absorption spectra of decachlorobiphenyl (DCB) in hexane solution.
x1 : 2 ppm solution, x10 : 20 ppm solution.

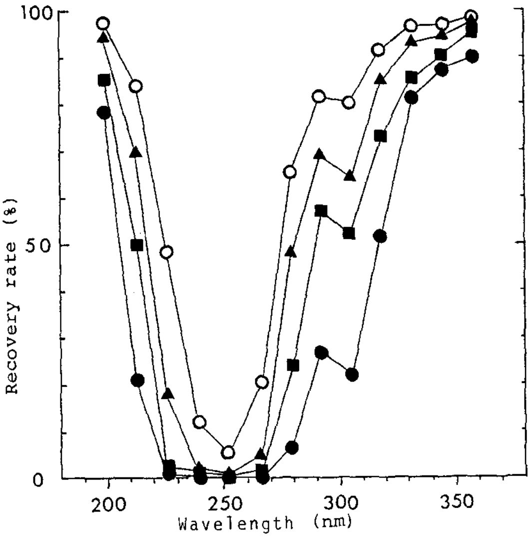


Figure 2. Recovery rates of decachlorobiphenyl(DCB) in 10 ppm hexane solution after xenon lamp irradiation.
○ : 300 counts irradiation, ▲ : 500 counts irradiation,
■ : 1000 counts irradiation, ■ : 2000 counts irradiation.

A Shimadzu 7A GC, equipped with an electron capture detector, was used with a 3 % OV-101 on Gas Chrom-Q, 60-80 mesh, 0.33 mm x 0.9 m long glass column. Carrier gas, N_2 50 ml/min. Column temp, 250 C. Injector temp, 260 C. Detector temp, 260 C.

A Hewlett Packard 5890GC and a 5970B series mass selective detector, equipped with a splitless injector, were used with a cross-linked methylsilicone capillary column, 12 m long, 0.33 µm film thickness, 0.2 mm id. Head pressure, 9 psi. EM volts, 1600. Initial time, 1 min. Initial temp, 100 C. Final temp, 240 C. Program rate, 40 C/min. Interface temp, 250 C. Carrier gas, He.

RESULTS AND DISCUSSION

The ultraviolet (UV) absorption spectra of DCB(I) shows that UV light in the range of 190 nm to 330 nm would be strongly absorbed and could produce chemical transformation (Figure 1). As shown in Figure 2, DCB(I) in 10 ppm hexane solution was easily degraded by 300 counts to 2000 counts irradiation. An exponential decrease in the concentration of DCB(I) accompanied an arithmetic increase in irradiation time until the recovery rates of DCB(I) reached lower than 1 %. The maximal degradation of DCB(I) in 10 ppm hexane solution was observed at around 250 nm wavelength, where the energy intensity was about $0.13x10^5$ erg/cm^2·sec as shown in Figure 3. At that wavelength, the recovery rates of DCB(I) were 5 % at 300 counts irradiation and lower than 1 % at over 500 counts irradiation, respectively. The recovery rates of DCB(I) in different concentrations after 500 counts irradiation are shown in Figure 4. Around 250 nm wavelength, DCB(I) in 1 ppm and 10 ppm hexane solutions was almost totally decomposed, and only 10 % of DCB(I) remained even in 100 ppm hexane solution. Photodegradation was also observed in the range of near-UV from 290 nm to 340 nm. According to Crosby et al. (1969) , a wavelength of 286.3 nm is the shortest ever recorded at the earth surface, and solar energy may probably be considered to be negligible below 295 nm wavelength. In the wavelengths over 295 nm , the minimum levels of recovery rates of DCB(I) were 62.3 % in 1 ppm solution, 66.2 % in 10 ppm solution, and 68.4 % in 100 ppm solution, respectively. Photodegradation of DCB(I) may occur under environmental conditions at wavelengths of solar energy above 295 nm. As shown in

Table 1. Recovery rate (as a percentage) of decachlorobiphenyl (DCB) in 10 ppm solution after 1000 counts xenon lamp irradiation at three different wavelengths.

Solvent	Wavelength		
	358.4 nm	305.6 nm	252.6 nm
Hexane	94.9	52.0	0.48
Methanol	96.5	16.2	0.81
Acetone	99.7	99.1	83.7
Benzene	98.4	31.9	93.0

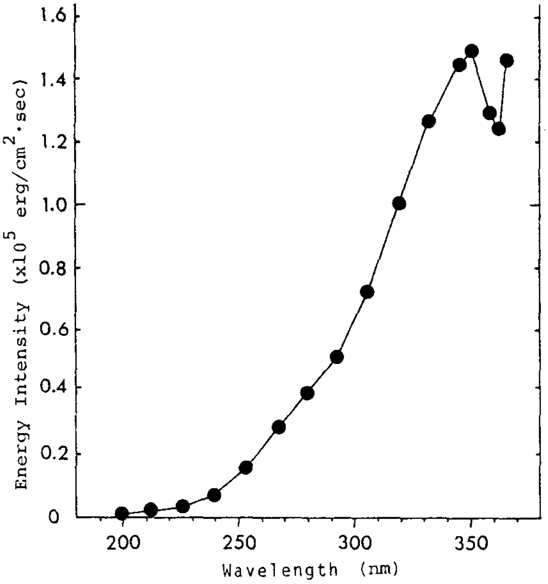


Figure 3. Energy intensity of xenon lamp used in irradiation of decachlorobiphenyl(DCB).

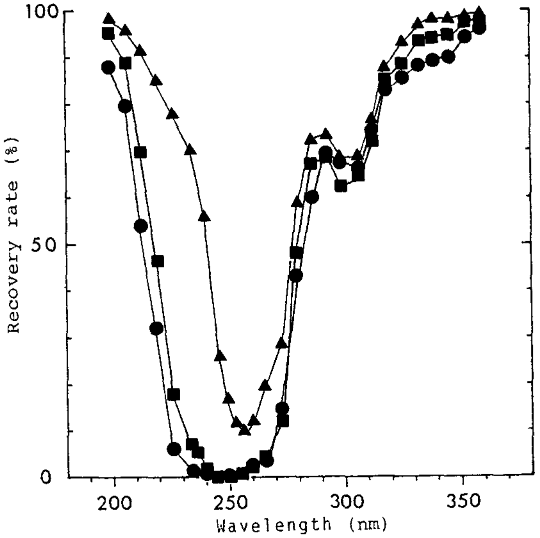


Figure 4. Recovery rates of decachlorobiphenyl(DCB) in hexane solution after 500 counts irradiation.
● : 1 ppm solution, ■ : 10 ppm solution, ▲ : 100 ppm solution.

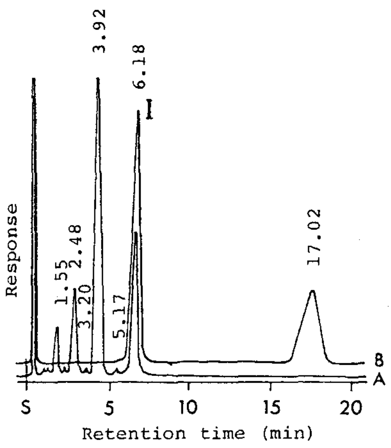
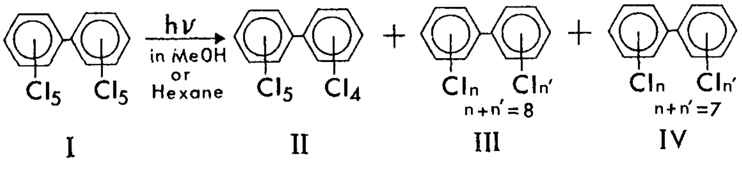


Figure 5. Gas chromatograms of photodegradation products of decachlorobiphenyl(DCB) in hexane or methanol solution (A), and in benzene solution (B). I: decachlorobiphenyl(DCB)

Table 1, methanol and benzene accelerated the photodegradation at 305.6 nm, but benzene suppressed the photodegradation at 252.6 nm, compared with hexane. In acetone solution, the photodegradation was observed somewhat only at 252.6 nm, as Arai et al. (1972) reported the photodegradation of PCB's under 254 nm wavelength was inhibited in 1.8 % acetone in 2-propanol solution.

In the photodegradation of DCB(I), two processes were observed. One was a dechlorination reaction and the other was a replacement reaction. As shown in Figure 5(A), some peaks caused by the dechlorination reaction were observed in both hexane and methanol solutions. The peak at retention time (Rt) 6.18 min was further identified as an undecomposed DCB(I), the peaks at Rt 5.17 min and Rt 3.92 min identified as nonachlorobiphenyls(II), the peaks at Rt 3.20 min and Rt 2.48 min identified as octachlorobiphenyls (III), and the peak of Rt 1.55 min identified as heptachlorobiphenyls(IV) by GC-MS (Figure 6). The photodegradation products II, III, and IV were also observed to contain 3, 5, and 2 of isomers, respectively, on GC-MS.



In benzene solution, only one photodegradation product (Rt 17.02 min on GC) caused by a replacement reaction was observed as shown in Figure 5(B). The product was further identified as a terphenyl

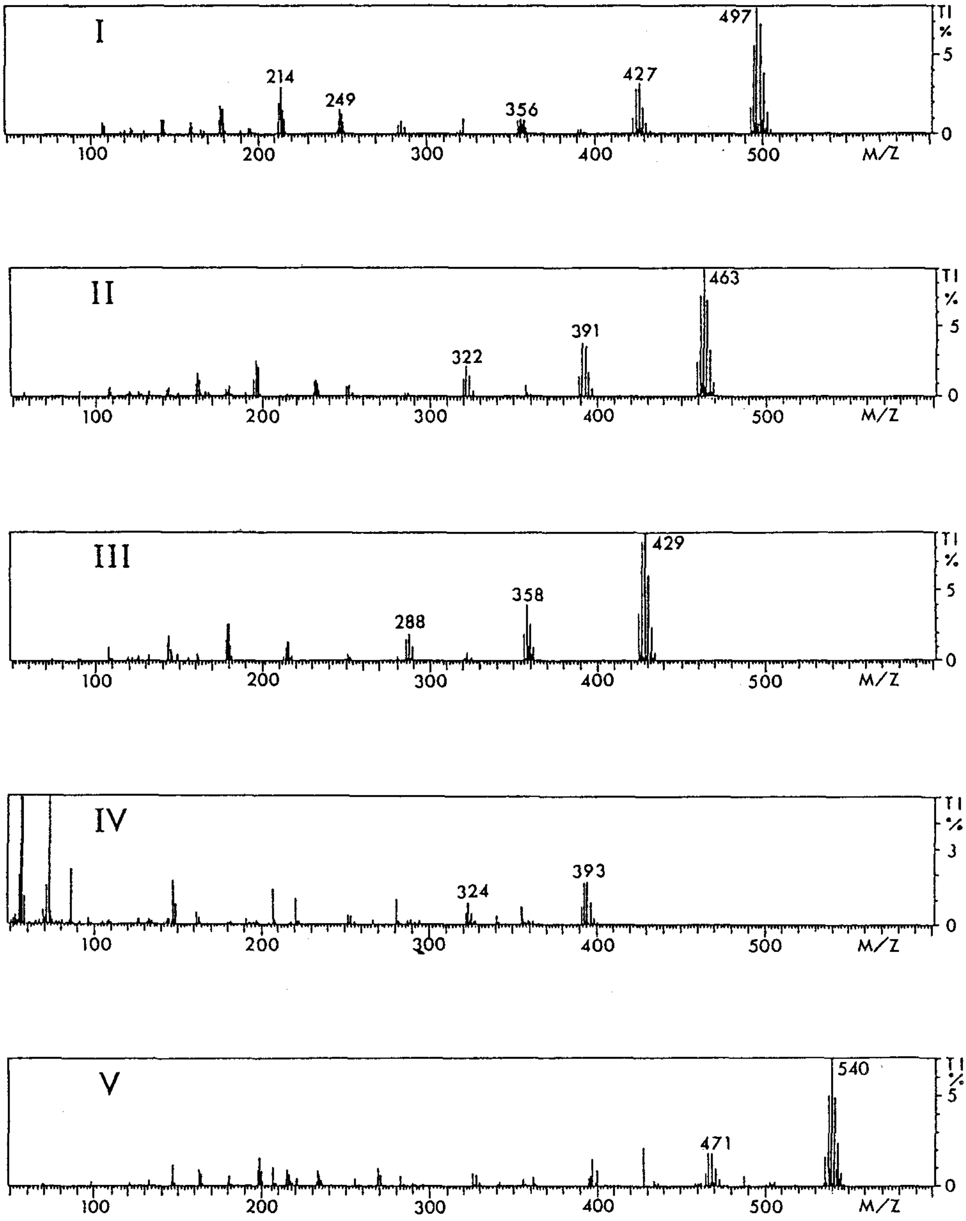
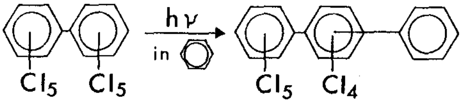


Figure 6. Mass spectra of decachlorobiphenyl(DCB) and its photodegradation products.
I: DCB, II, III and IV: products in hexane and methanol solutions, V: product in benzene solution.

derivative(V) of DCB(I), which was replaced of a chlorine atom of DCB(I) by a benzene molecule, by GC-MS (Figure 6).



I V

Though Ruzo et al. (1974) reported that methoxy groups were substituted for chlorine atoms of PCB's in methanol solution under UV irradiation. In the methanol solution of DCB(I) such a replacement reaction was not observed , but another replacement reaction was observed in the non-polar solvent benzene.

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