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Quantum Yields of Chlorinated Aromatic Compounds and Their Half-life Periods in Photodegradation

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(Received December 4, 1989)

INTRODUCTION

Chlorinated aromatic compounds, hexachlorobenzene (HCB), pentachlorophenol (PCP), decachlorobiphenyl (DCB) and octachlorodibenzofuran (OCDF), have been found to be technically impure in a number of industrial products and to be environmental contaminants resistant to biological degradation. It is unlikely that these chlorinated aromatic compounds are present in aqueous solution, because they are only slightly soluble or almost insoluble in water. However, Choudhry has reported humic substances known to be widespread in the natural water would have an ability to solubilize chlorinated aromatic compounds present in aquatic systems.^{1,2)}

Photodegradation may be an important process affecting chemicals that reside in water or surfaces. Chemicals present in the environment may undergo direct photodegradation and/or indirect photodegradation. Although a number of studies have been reported on the photodegradation of these chlorinated aromatic compounds such as HCB, PCP, DCB and OCDF,^{3–17)} photodegradation profiles in a wide range of irradiation wavelengths have not yet been made clean. We have recently reported photodegradation profiles and wavelength dependence of photodegradation of these compounds.^{18–21)} With our continuing interest in photodegradation of these compounds, further investigation was done for prediction of the environmental fates of these chlorinated aromatic compounds in the environment. In the present study, we investigated quantum yields (ϕ_i) of these chlorinated aromatic compounds along with the relative photodegradation factors in organic solutions, and estimated the sunlight photodegradation half-life times of these compounds for midday and

midseason at 40°N latitude on the surface of water bodies, aiming to get information on their behaviors in environments.

MATERIALS AND METHODS

1. Procedures

Irradiation and the quantitative analyses were done according to the methods described in the previous reports.^{18–21)} Hexachlorobenzene (HCB), pentachlorophenol (PCP), and decachlorobiphenyl (DCB) were dissolved in hexane for photodegradation experiments, and octachlorodibenzofuran (OCDF) dissolved in 1,4-dioxane. Light absorption spectra of these chlorinated aromatic compounds were recorded with a Shimadzu spectrophotometer UV-240. A 3-ml aliquot of each solution was taken into a cubic quartz cell and irradiated with a JASCO CRM-FA xenon-lamp irradiator. After irradiation, quantitative analyses were done with a Shimadzu 7A GC and a Hewlett Packard 5890 GC equipped with a 5970B mass selective detector.

2. Preparation of Actinometer Liquid

Actinometer solution was prepared according to the method of Hatchard and Parker.²²⁾ Potassium ferrioxalate was prepared by mixing 3 volumes of 1.5 M potassium oxalate and 1.5 M ferric chloride at a ratio of three to one with vigorous stirring. The precipitated potassium ferrioxalate was recrystallized from warm water and the crystals were dried in a air current at 45°C. Actinometer solution of 0.006 M was prepared by dissolving the crystals in 0.1 N sulfuric acid. The solutions were irradiated in the same manner as the above.

RESULTS AND DISCUSSION

Figure 1 shows the light absorption spectra of hexane or 1,4-dioxane solutions of HCB, PCP, DCB and OCDF. Table I records the molar extinction coefficients (ϵ_i) of the above solutions at various wavelengths (λ). Figure 1 and Table I indicate that PCP, DCB and OCDF possess absorption tails extending into the visible region contrary to the case of HCB. These spectra data were used to estimate quantum yields (ϕ_i , unit: mol·einstein⁻¹), direct sunlight photodegradation rate constants (K_{sp} , unit: sec⁻¹) and corresponding midday and midseason [light direct photodegradation half-life times $[(t_{1/2})_{sp}$, unit: min] in water.

Fig. 1 Light absorption spectra of hexane or 1,4-dioxane solutions of hexachlorobenzene (HCB), pentachlorophenol (PCP), decachlorobiphenyl (DCB) and octachlorodibenzofuran (OCDF).

HCB: 500 ppm hexane solution. PCP: 50 ppm hexane solution. DCB: 100 ppm hexane solution. OCDF: 20 ppm 1,4-dioxane solution.

Table 1 Molar extinction coefficients of chlorinated aromatic compounds.

Wave-length (nm)	Molar extinction coefficients, ϵ_{λ} , $l \cdot \text{mol}^{-1} \cdot \text{cm}^{-1}$			
	HCB	PCP	DCB	OCDF
297.5	177	2034	799	11030
300.0	169	2174	899	11491
302.5	152	2521	825	14456
305.0	113	1980	520	19284
305.6			460	
307.5	79	1235	269	20311
310.0	49	695	128	16610
312.5	21	385	58	11718
313.0	20	354	52	10952
315.0	14	226	27	7886
317.5	7	141	16	5710
318.6				5489
320.0	3	101	10	5208
323.1	1	77	8	5569
330.0	0	61	7	3404
340.0		55	5	3776
350.0		42	6	186
360.0		38	3	0
370.0		25	3	
380.0		12	2	
390.0		8	1	
400.0		6	1	

In this study, the first-order photodegradation rate constant ($K_{p\lambda}$, unit: sec^{-1}) and ϕ_{λ} , were calculated at wavelength 313 nm, because a value of quantum yield at 313 nm (ϕ_{313}) is generally used as a quantum yield of a test compound in photodegradation studies to estimate K_{sp} and $(t_{1/2})_{sp}$,²²⁾ and the use of ϕ_{313} is adopted in the chemical fate testing guidelines by Environmental Protection Agency (EPA, U.S.A.).²³⁾

In the previous report,²⁴⁾ $K_{p\lambda}$ values, ϕ_{λ} values, K_{sp} values, and $(t_{1/2})_{sp}$ values of these aromatic chlorinated compounds were estimated by Eqs. (1), (2), (3) and (4).

$$\ln(P_0/P_t) = K_{p\lambda} \cdot t \quad (1)$$

$$\phi_{\lambda} = K_{p\lambda} / (2.303 \cdot I_{\lambda} \cdot \epsilon_{\lambda} \cdot l) \quad (2)$$

$$K_{sp} = \phi_{\lambda} \cdot K_a = \phi_{\lambda} \cdot \sum K_{a\lambda} \\ = \phi_{\lambda} \cdot (2.303/j) \cdot \sum \epsilon_{\lambda} Z_{\lambda} \quad (3)$$

$$(t_{1/2})_{sp} = \ln 2 / K_{sp} \quad (4)$$

In Eq. (1), P_0 and P_t are the concentrations of a test compound at irradiation times zero and t . In Eq. (2), l is the cell path length (1.00 cm) and ϵ_{λ} is obtained from Table 1. Intensities of incident light (I_{λ} , unit: $\text{einstein} \cdot \text{mol}^{-1} \cdot \text{cm}^{-1} \cdot \text{sec}^{-1}$) were measured with the aid of simultaneous photodegradation of the actinometer solution. Optically thick solutions of potassium ferrioxalate (0.006 M) were used as chemical actinometers to determine the I_{λ} value of xenon lamp light used according to the method of Hatchard and Parker.²⁵⁾ The measured values were 2.386×10^{-6} at 313 nm, 1.880×10^{-6} at 305.6 nm, and 2.776×10^{-6} at 318.6 nm. In Eq. (3), $K_a (= \sum K_{a\lambda})$ is the sunlight absorption rate summed over all the wavelengths of sunlight which will be absorbed by a test compound. Z_{λ} is the sunlight intensity for a specific wavelength interval (N nm) centered at wavelength λ (units: $\text{photons} \cdot \text{cm}^{-2} \cdot \text{sec}^{-1} / N$ nm), and $j = 6.023 \times 10^{20}$ is a conversion constant that makes the units of Z_{λ} and ϵ_{λ} compatible. Sunlight intensity (Z_{λ}) data on the surface of water bodies as functions of time of day, season, and latitude in the range from 297.5 nm to 800 nm are available in the literature.²⁶⁾ Tables 2 and 3 list the photodegradation factors of the chlorinated aromatic compounds calculated in these manners. The ϕ_{313} values of HCB, PCP, DCB, and OCDF were thus estimated as 1.538×10^{-1} , 6.733×10^{-1} , 4.113×10^{-1} , and 2.259×10^{-2} , respectively (Table 2). As shown in Table 3, the sunlight photodegradation constants (K_{sp}) of these chlorinated aromatic compounds in summer season were the largest, and consequently, the corresponding half-life times $[(t_{1/2})_{sp}]$ were the shortest because of the high sunlight absorp-

Table 2 Photodegradation of chlorinated aromatic compounds at wavelength 313 nm.

Compound	Initial concentration (M)	Recovery rate (%) after xenon lamp irradiation							Photodegradation constant, $K_{p,313}$ (s^{-1})	Half-life time, $t_{1/2}$ (min)	Quantum yield ϕ_{313}	
		0	200	400	800	1200	2000	4000				8000
HCB	3.51×10^{-5}	100				99.5	96.6	94.2	87.6	1.709×10^{-5} ($r=0.9923$)	675.8	1.538×10^{-1}
PCP	3.75×10^{-4}	100	98.2	61.8	45.1	24.2	7.55			1.310×10^{-3} ($r=0.9404$)	8.8	6.733×10^{-1}
DCB	2.34×10^{-5}	100				87.3	75.2	63.4	38.6	1.176×10^{-4} ($r=0.9977$)	98.2	4.113×10^{-1}
OCDF	2.69×10^{-5}	100		26.1	11.4	4.74	0.78	0.12	0.001	1.361×10^{-3} ($r=0.9850$)	8.5	2.259×10^{-2}

tion rate in summer season.²⁶⁾ As mentioned in the previous report,²⁴⁾ if a test compound has a maximal photodegradation peak at above 295 nm, it will be necessary to calculate both ϕ_{313} and $\phi_{\lambda \text{ max}}$ at a wavelength of maximal photodegradation peak for the estimation of possible photodegradation in the environment. In these aromatic chlorinated compounds, DCB and OCDF had maximal photodegradation peaks at 305.6 nm and 318.6 nm, respectively, at wavelengths of above 295 nm.^{20,21)} The $\phi_{305.6}$ value of DCB was 9.352×10^{-2} , about a quarter of the ϕ_{313} value. The K_{sp} values of DCB estimated on the basis of the $\phi_{305.6}$ value were also about a quarter of the K_{sp} values on the basis of the ϕ_{313} value. On the other hand, the $\phi_{318.6}$ value of OCDF was 3.997×10^{-2} , about twice as larger as the ϕ_{313} value. The K_{sp} values of OCDF estimated on the basis of the $\phi_{318.6}$ value were also about twice as larger as the K_{sp} values on the basis of the ϕ_{313} value. As it is not necessarily expected that $\phi_{\lambda \text{ max}}$ value is always larger than ϕ_{313} value, it would be necessary to calculate both ϕ_{313} and $\phi_{\lambda \text{ max}}$ in order to estimate the environmental fate of a test compound. For accurate estimation of the environmental fates of these chlorinated aromatic compounds, water is the best solvent for photodegradation experiments. However, solubilities of these chlorinated aromatic compounds in water were so low that we had to use hexane or dioxane solvents in this study. It is supposed that ϕ_{λ} values will differ depending on the polarity of a solvent to be used, but the ϕ_{313} values of both 1,1-bis(*p*-chlorophenyl)-2,2-dichloroethylene (DDE), a photodegradation product of DDT and 1,1-bis(*p*-methoxyphenyl)-2,2-dichloroethylene, an analog of the former, were similar in water, benzene and hexane, ranging from 0.2 to 0.3.²⁷⁾ In the case of methoxychlor, the ϕ_{λ} values were similar in water, 1.1 M water in acetonitrile and hexane, ranging from 0.1 to 0.3.²⁸⁾ The ϕ_{313} value (2.798×10^{-3}) of 1,3,6,8-TCDD in 1,4-dioxane was also quite similar to the value of 2.17×10^{-3} of 1,3,6,8-TCDD in water-acetonitrile (2:3, v/v).²⁴⁾ We, therefore, supposed that the ϕ_{λ} values of these chlorinated aromatic compounds in hexane or dioxane would not be very far from those in water, and concluded that these chlorinated aromatic compounds would photodegrade in such a manner as shown in Table 3 in the environment.

ACKNOWLEDGMENTS

This research was partially supported by a grant for Environment Preservation Research from the Environment Agency of Japan.

Table 3 Specific sunlight absorption rates, photodegradation first-order rate constants and half-life times of chlorinated aromatic compounds for midday and midseason at 40°N latitude on the surface of water bodies.

Compound	Season	$\sum \epsilon_i Z_i$	Sunlight absorption rate, K_a (s^{-1})	Sunlight photodegradation constant, K_{sp} (s^{-1})	Half-life time ($t_{1/2}$) _{sp} (min)
HCB	spring	9.263×10^{15}	3.542×10^{-5}	5.404×10^{-6}	2137
	summer	1.279×10^{16}	4.890×10^{-5}	7.521×10^{-6}	1536
	fall	5.588×10^{15}	2.137×10^{-5}	3.287×10^{-6}	3514
	winter	2.279×10^{15}	8.710×10^{-6}	1.340×10^{-6}	8619
PCP	spring	4.144×10^{17}	1.585×10^{-3}	1.067×10^{-3}	10.8
	summer	4.999×10^{17}	1.911×10^{-3}	1.287×10^{-3}	9.0
	fall	2.691×10^{17}	1.029×10^{-3}	6.928×10^{-4}	16.7
	winter	1.602×10^{17}	6.216×10^{-4}	4.127×10^{-4}	27.9
DCB	spring	5.969×10^{16}	2.282×10^{-4}	9.386×10^{-5}	123.1
	summer	7.053×10^{16}	2.669×10^{-4}	1.180×10^{-4}	97.9
	fall	3.768×10^{16}	1.441×10^{-4}	5.927×10^{-5}	194.9
	winter	2.039×10^{16}	7.796×10^{-5}	3.208×10^{-5}	360.0
OCDF	spring	1.118×10^{19}	4.273×10^{-2}	9.652×10^{-4}	12.0
	summer	1.298×10^{19}	4.936×10^{-2}	1.121×10^{-3}	10.3
	fall	7.237×10^{18}	2.802×10^{-2}	6.330×10^{-4}	18.2
	winter	4.498×10^{18}	1.720×10^{-2}	3.885×10^{-4}	29.7

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要 約

芳香族塩素化合物の光分解における量子収量と半減期

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4種の芳香族塩素化合物, ヘキサクロロベンゼン, ペンタクロロフェノール, デカクロロビフェニルおよびオクタクロロダイベンゾフランのヘキサンあるいはジオキサン溶液について, キセノンランプ照射により光分解特性である量子収量(ϕ_i)を求めた。これら芳香族塩素化合物の波長 313 nm における量子収量として, それぞれ 1.538×10^{-1} , 6.733×10^{-1} , 4.113×10^{-1} および 2.259×10^{-2} モル/アインシュタインの値を得た。これら量子収量と文献記載の太陽光エネルギー強度から, 北緯 40 度の水表面における光分解速度定数と半減期を推定した。