Original Article

Photodegradation of Pentachlorophenol in Hexane by Xenon Lamp

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The photodegradation of pentachlorophenol (PCP) in hexane was investigated under xenon lamp irradiation. PCP was easily decomposed by 33.3 min (500 counts) irradiation. The maximal degradation of PCP was observed at 292.1 nm in the 100 ppm solution and in a range of 252.6 nm to 318.6 nm in the 10 ppm solution by 33.3 min irradiation. At these wavelengths, PCP was completely degraded. Reductive dechlorination and replacement reaction of a chlorine atom with a hexyl group derived from the solvent used were observed. As the photodegradation products of PCP, 2,3,4,5-tetrachlorophenol (TeCP), 2,3,4,6-TeCP, 2,3,5,6-TeCP, 2,3,4-trichlorophenol (TrCP), 2,4,5-TrCP, 3,4,5-TrCP, 2,4-dichlorophenol (DCP), 3,4-DCP, 3,5-DCP and 3-chlorophenol were identified by gas chromatography-mass spectrometry. Besides the above compounds, three isomers of monohexyltetrachlorophenol and three isomers of monohexyltrichlorophenol were also tentatively identified.

INTRODUCTION

Pentachlorophenol (PCP, **I**) is widely used as a fungicide, a bactericide or an insecticide, especially for wood preservation.¹⁾ PCP (**I**) was also used as a herbicide for paddy fields in Japan.²⁾ The occurrence of PCP (**I**) in the environment and its impact on the environment have been investigated in recent years.^{3,4)}

Some works have been done on photodegradation of PCP (**I**) under sunlight and ultraviolet (UV) light.⁴⁻¹²⁾ Kuwahara *et al.* reported that an aqueous solution of the sodium salt of PCP (**I**) exposed to sunlight suffered a great loss of parent pesticide and that the major products were several complex chlorinated benzoquinones.⁵⁻⁸⁾ Hamadmad also irradiated an aqueous solution of PCP (**I**) with sunlight and identified tetrachlorobenzoquinone and humic acid as two of its photodegradation products.⁹⁾ Crosby *et al.* proposed a photodegradation route from PCP (**I**) to dichloro-

maleic acid in an aqueous solution and suggested that the initial and rate-limiting reaction was photonucleophilic replacement of PCP (**I**) chlorine atoms by hydroxy groups.¹¹⁾ In organic solvents such as hexane and methanol, only two isomers of tetrachlorophenol (TeCP, **II**), 2,3,4,5-TeCP (**II-1**) and 2,3,5,6-TeCP (**II-3**), have been identified as the photodegradation products of PCP (**I**) under UV light irradiation.^{10,12)} Neither dimeric products nor alkylated products have been detected in organic solvents.¹⁰⁾

In the present paper, photodegradation of PCP (**I**) in hexane solution was investigated under xenon lamp irradiation to determine its photodegradation profiles at various wavelengths. Characterization of the photodegradation products was also discussed.

MATERIALS AND METHODS

1. Procedures

The test compound, pentachlorophenol

(PCP), was purchased from WAKO Purechemical Industries Co. Ltd. Authentic chlorinated phenols for gas chromatography-mass spectrometry (GC-MS) were purchased from TOKYO KASEI KOGYO Co. Ltd, WAKO Purechemical Industries Co. Ltd. and Aldrich Chemical Company Inc., except 2,3,5,6-tetrachlorophenol which was synthesized (Suzuki, unpublished data). A small amount of PCP was dissolved in 100 ml of hexane to make 10 ppm and 100 ppm solutions. Three ml of each solution was taken into a quartz cubic cell ($1 \times 1 \times 5$ cm). The cells were irradiated at 14 different wavelengths between 199.8 nm and 384.9 nm by using a JASCO CRM-FX xenon lamp irradiator. After 3.33 min (50 counts, 15 counts/min) to 33.3 min (500 counts) irradiation, $1 \mu\text{l}$ of each solution was subjected to GC-MS for quantitative analysis and identification of photodegradation products.

2. Gas Chromatography-Mass Spectrometry

A Hewlett Packard 5890 GC equipped with a splitless injector and a 5970B series mass selective detector were used with a cross-linked methyl silicone capillary column (25 m length, $0.33 \mu\text{m}$ film thickness, 0.2 mm i.d.)

Condition 1: head pressure, 15 psi; carrier gas, He; EM volts, 1800; initial time, 0 min; initial temp., 80°C ; final temp., 260°C ; program rate, $8^\circ\text{C}/\text{min}$ to 200°C , $30^\circ\text{C}/\text{min}$ to 260°C ; interface temp., 270°C ; injection temp., 270°C .

Condition 2: head pressure, 15 psi; carrier gas, He; EM volts, 2200; initial time, 2 min; initial temp., 80°C ; final temp., 250°C ; program rate, $4^\circ\text{C}/\text{min}$ to 160°C , $30^\circ\text{C}/\text{min}$ to 250°C ; interface temp., 270°C ; injection temp., 270°C .

RESULTS AND DISCUSSION

UV absorption spectra of PCP (**I**) suggest that UV light in a range of 200 nm to 350 nm wavelengths is significantly absorbed and participates in photochemical transformation (Fig. 1). As shown in Fig. 2, PCP (**I**) in 100 ppm hexane solution was easily degraded by 3.3 min (50 counts) to 33.3 min (500 counts) UV light irradiation at 292.1 nm from a xenon lamp. At this wavelength where the energy intensity was $4.171 \times 10^6 \text{ erg}/\text{cm}^2 \cdot \text{min}$ (Table 1), an exponential decrease in PCP (**I**) concentration accompanied an arithmetic increase

Fig. 1 UV absorption spectra of PCP (**I**).

—: 10 ppm hexane solution, ----: 1 ppm hexane solution.

Table 1 Energy intensity of a xenon lamp used for irradiation of PCP (**I**).

Wavelength (nm)	Energy intensity ($\text{erg}/\text{cm}^2 \cdot \text{min}$)
199.8	9.626×10^4
212.8	1.604×10^5
226.2	2.807×10^5
239.2	5.455×10^5
252.6	1.227×10^6
265.6	2.406×10^6
279.1	3.209×10^6
292.1	4.171×10^6
305.6	6.000×10^6
318.6	8.021×10^6
332.0	1.032×10^7
345.0	1.173×10^7
358.4	1.075×10^7
371.4	1.196×10^7
384.9	1.157×10^7
397.9	1.191×10^7
411.3	1.176×10^7
424.3	1.194×10^7
437.7	1.221×10^7
450.7	1.332×10^7
471.4	1.605×10^7

in irradiation time until PCP (**I**) disappeared.

In the photodegradation of PCP (**I**) hexane solution two photochemical reactions were observed. One was reductive dechlorination and the other replacement reaction of a chlorine

Fig. 2 Capillary GC chromatograms of 100 ppm hexane solution of PCP (**I**) under xenon lamp irradiation at 292.1 nm.

A: no irradiation, B: 3.33 min irradiation, C: 6.66 min irradiation, D: 13.3 min irradiation, E: 20.0 min irradiation, F: 33.3 min irradiation, **I**: PCP, **II**: TeCP, **III**: TrCP, **IV**: DCP, **V**: MCP, **VI**: unknown.

atom with a hexyl group derived from the solvent used, though Crosby *et al.* found only a reductive dechlorination reaction in hexane.¹⁰⁾ Dimeric products such as chlorinated dibenzo-*p*-dioxins, chlorinated biphenyls and chlorinated diphenyl ethers were not observed. As shown in Fig. 2, some peaks by the reductive dechlorination and the replacement reaction were observed. In the 100 ppm hexane solution, all three isomers of TeCP (**II**), 2,3,4,5-TeCP (**II**-1), 2,3,4,6-TeCP (**II**-2) and 2,3,5,6-

TeCP (**II**-3), three of six isomers of trichlorophenol (TrCP, **III**), 2,3,4-TrCP (**III**-1), 2,4,5-TrCP (**III**-2) and 3,4,5-TrCP (**III**-3), one of six isomers of dichlorophenol (DCP, **IV**), 3,4-DCP (**IV**-3), and one of three isomers of monochlorophenol (MCP, **V**), 3-MCP, were identified as reductive dechlorination products of PCP (**I**) by GC-MS based on co-chromatography with authentic compounds (Table 2 and Fig. 3). Besides the above compounds, three unknown compounds produced by replacement reaction

Table 2 Recovery rates (shown in relative intensities) of PCP (I) and its photodegradation products in 100 ppm hexane solution after 33.3 min xenon lamp irradiation at various wavelengths.

No.	Product	Retention time (min)	Wavelength (nm)															
			199.8	212.8	226.2	239.2	252.6	265.6	279.1	292.1	305.6	318.6	332.0	345.0	358.4	371.4		
I	PCP	15.890 ^{a)}	0.996	0.882	0.788	0.332	0.073	0.030	0.044	N/D	0.009	0.008	0.226	0.815	0.991	1.000		
II-1	2,3,4,5-TeCP	24.107 ^{b)}	0.013	0.039	0.091	0.110	0.104	0.092	0.109	0.033	0.011	0.140	0.294	0.041	0.008	N/D		
II-2	2,3,4,6-TeCP	24.218 ^{b)}	0.002	0.006	0.036	0.037	0.024	0.011	t	N/D	N/D	N/D	N/D	N/D	t	N/D		
II-3	2,3,5,6-TeCP	23.913 ^{b)}	0.002	0.006	0.044	0.070	0.059	0.045	0.016	t	t	N/D	0.001	0.002	N/D	N/D		
III-1	2,3,4-TrCP	9.353 ^{a)}	N/D ^{c)}	N/D	N/D	0.009	0.038	0.016	0.005	N/D	N/D	N/D	N/D	N/D	N/D	N/D		
III-2	2,4,5-TrCP	9.761 ^{a)}	N/D	N/D	N/D	N/D	0.012	0.006	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D		
III-3	3,4,5-TrCP	13.867 ^{a)}	N/D	N/D	N/D	N/D	0.004	t ^{d)}	0.009	0.006	0.004	0.041	0.004	N/D	N/D	N/D		
IV-3	3,4-DCP	10.519 ^{a)}	N/D	N/D	N/D	N/D	N/D	N/D	0.004	0.003	0.005	N/D	N/D	N/D	N/D	N/D		
V	3-MCP	6.834 ^{a)}	N/D	N/D	N/D	N/D	N/D	N/D	0.004	0.005	0.015	N/D	N/D	N/D	N/D	N/D		
VI-1	Unknown	18.296 ^{a)}	N/D	N/D	0.004	0.006	0.010	0.006	0.007	N/D	N/D	0.007	0.008	N/D	N/D	N/D		
VI-2	Unknown	18.536 ^{a)}	N/D	N/D	0.006	0.016	0.011	0.009	0.006	0.007	N/D	0.009	0.010	N/D	N/D	N/D		
VI-3	Unknown	19.202 ^{a)}	N/D	N/D	N/D	0.005	N/D	N/D	N/D	N/D	N/D	0.004	0.008	N/D	N/D	N/D		

a) GC-MS condition 1.

b) GC-MS condition 2.

c) not detected.

d) trace.

Fig. 3 Mass spectra of PCP (I) and its photodegradation products.

I: PCP, II: TeCP, III: TrCP, IV: DCP, V: MCP.

of PCP (I) chlorine atoms by the hexyl group of the solvent were observed at longer retention times than that of PCP (I) on GC-MS (Fig. 2, compounds VI). Unknown products (VI) which had isotope ions of m/z 314, 316, 318 and 320 were tentatively identified as three isomers of monohexyltetrachlorophenol based on the mass fragmentations (Table 2). The photodegradation products in the 10 ppm solution of PCP (I) were the same as those in the 100 ppm solution, except DCPs (IV) and unknown products (VII). In the 10 ppm solution, two other isomers of DCPs, 2,4-DCP (IV-1) and 3,5-DCP (IV-2), were identified, but 3,4-DCP (IV-3) was not found. Besides the three alkylated products which were found in the 100 ppm solution, three other unknown products which had isotope ions of m/z 280, 282 and 284 were observed in the 10 ppm solution, and they were identi-

fied as isomers of monohexyltrichlorophenol (VII) based on the mass fragmentations (Table 3).

Recovery rates of PCP (I) in hexane solutions at various wavelengths are shown in Tables 2 and 3. After 33.3 min irradiation the maximal degradation of PCP (I) was observed at 292.1 nm in the 100 ppm solution and in a range of 252.6 nm to 318.6 nm in the 10 ppm solution, where the energy intensities were 4.171×10^6 erg/cm²·min and 1.227×10^6 to 8.021×10^6 erg/cm²·min (Table 1), respectively. At these wavelengths, PCP (I) was completely degraded. As shown in Table 2, the main degradation product was 2,3,4,5-TeCP (II-1), followed by 2,3,5,6-TeCP (II-3). 2,3,4,6-TeCP (II-2) was also identified as a photodegradation product in a range of 199.8 nm to 279.1 nm. TrCPs (III-1, 2 and 3), DCP (IV-3) and MCP

Table 3 Recovery rates (shown in relative intensities) of PCP (I) and its photodegradation products in 10 ppm hexane solution after 33.3 min xenon lamp irradiation at various wavelengths.

No.	Product	Retention time (min)	Wavelength (nm)															
			199.8	212.8	226.2	239.2	252.6	265.6	279.1	292.1	305.6	318.6	332.0	345.0	358.4	371.4	384.9	
I	PCP	15.890 ^{a)}	0.964	0.822	0.084	0.043	N/D	N/D	N/D	N/D	N/D	N/D	0.163	0.613	0.996	0.985	1.000	
II-1	2,3,4,5-TeCP	24.107 ^{b)}	0.034	0.119	0.092	0.034	0.009	0.051	0.012	t	t	0.066	0.226	0.052	0.029	0.012	N/D	
II-2	2,3,4,6-TeCP	24.218 ^{b)}	t ^{c)}	0.065	0.065	0.016	0.006	0.012	0.001	N/D	N/D	N/D	N/D	0.001	0.001	0.001	N/D	
II-3	2,3,5,6-TeCP	23.913 ^{b)}	0.002	0.057	0.069	0.015	0.004	0.024	0.002	N/D	N/D	N/D	0.001	0.006	0.005	0.002	N/D	
III-1	2,3,4-TrCP	9.360 ^{a)}	N/D ^{d)}	N/D	0.034	0.037	0.045	0.024	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	
III-2	2,4,5-TrCP	9.756 ^{a)}	N/D	N/D	0.016	0.016	0.013	0.007	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	
III-3	3,4,5-TrCP	13.867 ^{a)}	N/D	N/D	0.006	0.007	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	
IV-1	2,4-DCP	6.580 ^{a)}	N/D	N/D	0.009	0.026	0.024	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	
IV-2	3,5-DCP	10.210 ^{a)}	N/D	N/D	0.003	0.005	0.006	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	
V	3-MCP	6.834 ^{a)}	N/D	N/D	N/D	0.004	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	N/D	
VI-1	Unknown	18.296 ^{a)}	N/D	0.005	0.007	0.010	0.006	0.006	0.007	N/D	N/D	0.007	0.005	N/D	N/D	N/D	N/D	
VI-2	Unknown	18.536 ^{a)}	N/D	0.009	0.017	0.015	0.009	0.010	0.015	0.007	0.006	0.025	N/D	N/D	N/D	N/D	N/D	
VI-3	Unknown	19.202 ^{a)}	N/D	0.007	0.006	N/D	N/D	N/D	N/D	N/D	N/D	0.006	N/D	N/D	N/D	N/D	N/D	
VII-1	Unknown	16.314 ^{a)}	N/D	N/D	N/D	0.006	0.005	N/D	N/D	N/D	N/D	N/D	0.005	N/D	N/D	N/D	N/D	
VII-2	Unknown	16.619 ^{a)}	N/D	N/D	N/D	0.006	0.006	0.010	N/D	N/D	N/D	N/D	0.011	N/D	N/D	N/D	N/D	
VII-3	Unknown	16.787 ^{a)}	N/D	N/D	N/D	0.004	0.004	0.004	N/D	N/D	N/D	N/D	0.014	0.003	N/D	N/D	N/D	

a) GC-MS condition 1.

b) GC-MS condition 2.

c) trace.

d) not detected.

(V) were found only in a range between 239.2 nm and 332.0 nm. Unknown products (VI-1, 2 and 3) were found in a wide range of 226.2 nm to 332.0 nm. In the 10 ppm solution (Table 3), the main photodegradation products varied depending upon the irradiation wavelengths. The main products were 2,3,4,5-TeCP (II-1) in ranges of 199.8 nm to 226.2 nm and 318.6 nm to 371.4 nm, 2,3,4-TrCP (III-1) in a range of 239.2 nm to 265.6 nm, and the unknown compound (VI-2) in a range of 279.1 nm to 305.6 nm. TrCPs (III-1, 2 and 3), DCPs (IV-1 and 2) and MCP (V) were also found at wavelengths between 226.2 nm and 265.6 nm, but the ranges of wavelengths effective to photodegradation were different from those in the 100 ppm solution. The wavelengths of minimal photodegradation of PCP (I) were 358.4 nm in the 100 ppm solution and 371.4 nm in the 10 ppm solution. The above results suggest that PCP (I) is easily photodegraded in the environment, particularly in the oil layer of the surface, as

286.1 nm is the shortest wavelength ever recorded on the earth surface.¹³⁾

Although many kinds of chlorinated phenols were identified as the photodegradation products of PCP (I), only a few products, such as 2,3,4,5-TeCP (II-1), 2,3,4,6-TeCP (II-2) and 2,3,5,6-TeCP (II-3), would be expected in natural environment conditions.

The possible photodegradation pathways of PCP (I) in the hexane solutions are shown in Fig. 4.

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Fig. 4 Possible photodegradation pathways of PCP (I) in hexane solutions.

—: in 10 ppm solution, ----: in 100 ppm solution.

要 約

ヘキサン溶液中におけるペンタクロロフェノールのキセノンランプによる光分解

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ペンタクロロフェノールはキセノンランプ照射下で容易に光分解を受け, 33.3分照射下において, 100 ppm 溶液で 292.1 nmで, 10 ppm 溶液では 252.6 nm から 318.6 nm の間で完全に分解した。光分解反応は, 還元的脱塩

素および塩素と溶媒分子との置換反応であった。脱塩素生成物として 2,3,4,5-テトラクロロフェノール (TeCP), 2,3,4,6-TeCP, 2,3,5,6-TeCP, 2,3,4-トリクロロフェノール (TrCP), 2,4,5-TrCP, 3,4,5-TrCP, 2,4-ジクロロフェノール (DCP), 3,4-DCP, 3,5-DCP および 3-モノクロロフェノールが GC-MS により同定された。また置換反応生成物として, 3種のモノヘキシルテトラクロロフェノールおよび3種のモノヘキシルトリクロロフェノールが同時に同定された。