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Phototransformations of solid pentachlorophenol

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Abstract

The phototransformations of thin layers of pentachlorophenol (PCP), an insectide and herbicide, have been investigated in the laboratory in open air under irradiation at wavelengths >290 nm, i.e. corresponding to the sunlight UV region. The PCP disappearance rate was much higher when a 50 v / v% methanol / water mixture instead of pure methanol was used as the PCP deposition medium; changes in the product distribution also resulted although the products were the same. Analyses by GC / MS showed that tetrachlorophenols, hexachlorobenzene and pentachlorobenzene, in this order, were the monocyclic products that reached the highest amounts. Other C_6-membered products were trichlorophenol isomers and tetrachlorobenzene isomers. Hexachlorocyclopentadiene and a tetrachlorocyclo pentadiene isomer as well as five other C_5-membered cyclic products containing carbonyl groups, among which dichloromaleic anhydride was the most abundant, were also identified. Moreover, polychlorinated-*p*-dioxins and biphenylethers were formed, in particular octachlorodibenzo-*p*-dioxin reached a significant amount. With respect to PCP photodegradation in water the essential difference was the absence of products corresponding to the substitution of Cl by OH with possible subsequent oxidation to quinonic derivatives. Reactions based on the removal of one of the PCP chlorine atoms as the primary photochemical process are tentatively suggested to account for the formation of the main primary products. Consequences for the environment are also very briefly discussed. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Phototransformation; Pentachlorophenol; Monocyclic products

1. Introduction

For many years pentachlorophenol (PCP) has been widely used for its fungicide, bactericide and insecticide action, especially for wood preservation (termite control) [1–3]. It has also found application as a herbicide [3] in rice and sugar production, because of its toxicity to some plants and animals at low levels [4]. The extensive use of PCP has exposed the aquatic and terrestrial environment to pollution. Although nowadays its production, sale and application is forbidden in some countries, e.g. in Germany, PCP is still found in the total environment [5]. Studies have dealt with the photodegradation of PCP in water [6–8,10] and hexane solutions [11]. However, to our knowledge, the phototransformation of solid PCP has not been reported. The solubility of PCP in water is only 80 mg l^{-1} [3] and, accordingly, studies have shown that PCP is adsorbed on soils to a large extent [12–15].

Consequently, to have a better idea of the fate of PCP in the environment we thought of interest to investigate the photodegradation of this pesticide in the solid state, and particularly to identify and quantify the principal products. This study is preliminary to an investigation of the influence of some soil constituents on the photodegradation of adsorbed PCP.

2. Experimental

2.1. Reagents

PCP, dichloromaleic anhydride, pentachlorobenzene, hexachlorobenzene, trichlorophenol isomers, tetrachlorocatechol, tetrachloro-1,2-benzoquinone, tetrachloro-1,4-benzoquinone, 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone (chloranilic acid) were purchased from Aldrich at the highest purity available. 1,2,3,4,6,7,8,9-Octachlorodibenzo-*p*-dioxin, decachlorobiphenylether and 2,2′,3,3′,4,4′,5,5′,6-nonachlorobiphenylether were purchased from Promochem, while 2,3,4,5-tetrachlorophenol and 2,3,4,6-tetrachlorophenol were supplied by Jansen. Fenitrothion (*O*,*O*-dimethyl-*O*-4-nitro-*m*-tolyl phosphorothioate) was obtained from Institute of Organic and

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Industrial Chemistry (Warsaw, Poland) and tetradecane from Fluka. Acetone and methanol were provided by Sigma–Aldrich and Rathburn with a purity of 99.9% and 99.8%, respectively. Water purified by inverse osmose and deionization (MilliQ-Plus Waters System) was used.

2.2. Irradiation experiments

PCP irradiation was carried out in a Pyrex-glass cylindrical reactor open to air. PCP was deposited (see the following paragraph) on the bottom of this reactor, which had a flat surface of about 11 cm^2. The reactor was placed below an high pression mercury lamp Philips HPK 125 W and a water-circulating cell (2.2 cm thick) which was interposed between the lamp and the reactor to avoid heating the PCP layer. An optical filter, cutting the wavelengths below 290 nm, was used to limit the irradiation to the UV domain of the solar spectrum. The incident UV light power on the PCP layer was approximately 37 mW cm^{-2}; it was measured by a United Detector Technology, Model 21, powermeter.

For each irradiation experiment 11.1 mg (ca. 42 μmol) of PCP was deposited. For that purpose, PCP was dissolved either in methanol or in a 50% v / v mixture of methanol and water and the solution was poured into the reactor; the PCP solution was evaporated under vacuum (water vacuum pump) for about 1 h. In the case of the methanol / water mixture, the temperature was gently increased up to 348 K to accelerate water evaporation. These procedures allowed one to obtain a visually homogeneous PCP layer.

2.3. Analytical procedures

After irradiation, the products were extracted with acetone. Approximately 6 ml of acetone was added to the sample and the resulting solution was sonicated for 5 min (30 W, 47 kHz); the procedure was repeated three times. Two internal standards were then introduced and the solution volume was adjusted to 20 ml by adding acetone. Tetradecane and fenitrothion were employed as internal standards to quantify either the PCP monocyclic products or the bicyclic products, respectively.

PCP was analyzed, without sample concentration, using the splitless injection mode, with a Varian gas chromatograph, model 3400 CX, equipped with a temperature programmable injector, a FID detector and a CP-SIL-5CB (25 m × 0.25 mm) capillary column. The oven temperature was programmed as follows: 338 K (3 min) – 288 K min^{-1} – 493 K (0 min) – 278 K min^{-1} – 543 K (10 min); the temperature injector program was: 308 K (0.50 min) – 423 K min^{-1} – 543 K (31 min); the detector temperature was 593 K.

To analyze the products the acetone solutions were evaporated to 0.5 ml by use of a rotavapor. A HP 5890 series II gas chromatograph connected to a quadripole HP 5971 A was used. The capillary column was the same as that utilised in the Varian apparatus. The injector (splitless mode) and the detector temperatures were 573 K. Two oven temperature programs were used for the quantification of the bicyclic and monocyclic products: 393 K (1 min) – 293 K min^{-1} - 493 K (5 min) - 278 K min^{-1} - 573 K (39 min), and 318 K (1 min) - 293 K min^{-1} - 338 K (1 min) - 278 K min^{-1} - 563 K (2 min), respectively.

3. Results and discussion

3.1. Kinetics of PCP disappearance

The kinetics of PCP disappearance is shown in Fig. 1. At the beginning it corresponded to a first-order kinetic law in the case of the deposition of PCP from a methanol / water mixture. In that case the photolytic rate decreased after ca. 6 h of irradiation. The decrease was expected because the irradiation layer was then constituted from PCP and a substantial proportion of degradation products (see below). The PCP disappearance was much faster when PCP was deposited from a methanol / water mixture than when it was deposited from a pure methanolic solution: after 16 h of irradiation ca. 60% and 12% of initial PCP were respectively degraded (Fig. 1). Due to the lower volatility of water compared with that of methanol, it is possible that traces of water did not evaporate and could have influenced the rate of the single reaction steps. The difference might originate from a weakening of the C–Cl bonds of PCP due to residual water. The decrease in bond strength would make the primary photochemical process easier (vide infra Eq. (1) and [16]). Note, however, that the amount of residual water was insufficient to change the nature of the products (see Section 3.2) and in particular to produce hydrolysis reactions which would have led to tetrachlorodihydroxybenzene isomers [6,7,8,10] (not detected; see Section 3.2).

On the other hand, optical microscopy measurements have shown that PCP crystallized differently when it was deposited

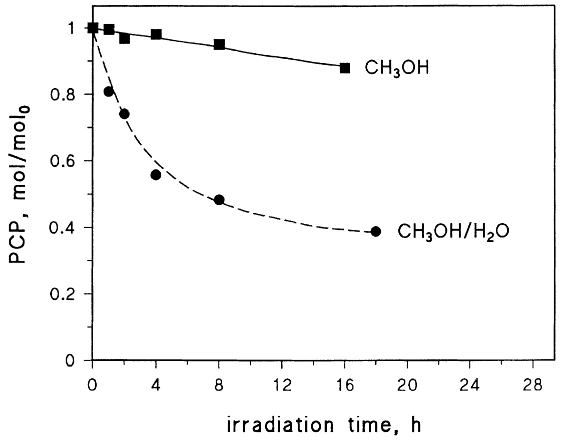


Fig. 1. Effect of the deposition medium on the relative amounts of solid PCP (42 μmol initially) as a function of irradiation (λ > 290 nm) time.

from pure methanol or a methanol / water mixture. In the latter case the PCP crystallites had the same shape (needles) and size, whereas, in the former case the size range of the PCP crystallites was wide. This physical difference may have had an influence on the PCP degradation rate.

From these results it can be inferred that in the natural environment humidity might be an accelerating factor for direct photolysis of solid PCP.

3.2. Pentachlorophenol degradation products

3.2.1. Identifications

Table 1 provides the list of the PCP degradation products which we identified. Specific isomers were identified in a few cases; only the general structure is shown in Table 1. Whether these products were also found previously when PCP photolysis was carried out in water [6–8] or in hexane [11] is also shown in Table 1. In the case of four C_5-membered products the identification was based only on the interpretation of the mass spectra as shown by the letter I in Table 1. Seven intermediate products were identified by comparing the mass spectra and retention times with those of standards and by verifying that the chromatographic peak area increased when the authentic compound was added to the sample analyzed. The letter L in Table 1 means that the spectra were not only interpretated but also compared with those present in the mass analyzer library; in these cases quality match higher than 95% was obtained. All the products in Table 1 were found when PCP was deposited from both a methanol / water solution and a methanol solution, but their distribution varied.

Concerning the identifications some comments are made hereafter. First, two chromatographic peaks, due to tetrachlorophenol (TCP) isomers, were present. Comparison with standards showed that the one with retention time $t_r = 32.2$ min corresponded to the 2,3,5,6-TCP isomer (TCP1); this compound was a PCP impurity: in the case of PCP deposited from methanol / water its amount increased during the photodegradation, whereas, for PCP deposited from methanol its amount was progressively reduced. The second peak, with $t_r = 32.4$ min, was due either to 2,3,4,5-TCP or to 2,3,4,6-TCP or to both isomers (TCP2). The response factor for each of them was found to be the same. Second, the origins of three chromatographic peaks, at $t_r = 18.5$ min, at $t_r = 28.8$ min and at $t_r = 45.2$ min, corresponding to mass peaks at $m/z = 378$ (heaviest mass in these spectra), 396 and 518 respectively, were not determined.

Some products that were detected during the photodegradation of PCP in aqueous solution [6–8] were not found during that of solid PCP. That was the case for the *ortho* and *para* isomers of tetrachlorodihydroxybenzene [8]; although we cannot infer the absence of these products directly from the chromatograms because the peaks of corresponding standards were not separated from the broad peak due to PCP, the lack of the characteristic mass peaks at $m/z = 246$ and 248 was conclusive. This was substantiated by the absence of the related quinones, i.e. tetrachlorobenzoquinones and 2,5-dichloro-3,6-dihydroxy-1,4-benzoquinone [8]. Also, no polychlorodibenzofurans [7] were detected by our analyses. Together with the differences included in Table 1, the absence of these products shows that distinct photodegradation pathways occur depending on the PCP state. In particular, substitution of Cl by OH takes place easily in aqueous solution as a result of the polarization of the photoexcited C–Cl bond by a water molecule [16].

In hexane [11] apart from hexyl derivatives, the only products were chlorinated phenols corresponding to successive reductive dechlorinations. The absence of bicyclic products [11] might be due to the dilution; however, as bicyclic products were observed for PCP aqueous solutions [6,7,9], the analytical conditions used in [11] can also be suspected to account for this difference.

3.2.2. Kinetic variations in products amounts

Figs. 2 and 3 show the temporal variations of the monocyclic products for each deposition procedure. The presence of maximums in some curves and the lag time for dichloromaleic anhydride formation clearly indicate that consecutive reactions occurred. The amount of products have been made dimensionless by dividing them by the initial amount of PCP (mol_0) for the monocyclic products and twice this quantity for the bicyclic products. TCP2 was the product that reached the highest amount, corresponding to about 0.85% or 10% of initial PCP depending on whether the deposition medium was methanol or the methanol / water mixture, respectively.

The quantification of the bicyclic products was carried out only in the case of PCP deposited from a methanolic solution (Fig. 4). The response factors in the mass quadrupole of heptachlorodibenzo-*p*-dioxins and nonachlorobiphenylether were considered as being equal to respectively those of octachlorodibenzo-*p*-dioxin (OCDD) and decachlorobiphenyl ether that were used as standards. Comparison of Figs. 2 and 4 shows that, after irradiating for 16 h, OCDD reached the second highest amount after TCP2.

These analyses show that exposure of solid PCP to sunlight in the presence of air leads to many products. Some monocyclic products are supposed to have a lessened toxicity with respect to PCP either because of a smaller number of chlorine atoms or the presence of carbonyl groups or both. However, the formations of HCB, polychlorodibenzo-*p*-dioxins and polychlorobiphenylethers clearly illustrate that PCP must be handled with great care to avoid releasing significant quantities of it in the environment and therefore to generate still more toxic by-products.

3.2.3. Tentative formation mechanisms for the main products

As shown in Figs. 2 and 3, TCP2, HCB and PCB, were the monocyclic products whose amounts were the highest in this

Table 1
List of solid PCP degradation products (independent of the solution used for depositing PCP)

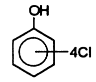
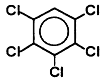
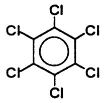
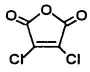
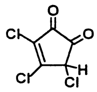
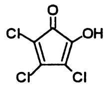
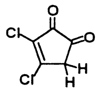
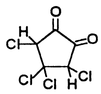
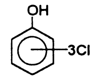
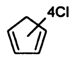
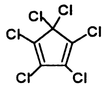
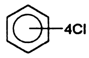
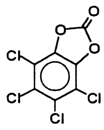
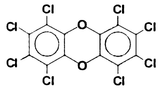
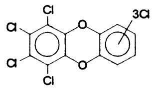
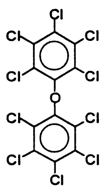
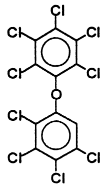
Products	Structures	Identification methods and retention time (min)	Products formed during photolysis in water	Products formed during photolysis in hexane
Tetrachlorophenol (TCP)		S (32.2, 32.4)	[8]	[11]
Pentachlorobenzene (PCB)		S (31.9)		
Hexachlorobenzene (HCB)		S (37.0)		
Dichloromaleic anhydride (DCFD)		S (13.5)	[8]	
Tetrachlorocyclopentenedione (1)		I (20.4, 23.4)		
Trichlorooxocyclopentadienol (2)		I (24.6, 26.6)		
Dichlorocyclopentenedione (3)		I (19.5)	[8]	
Tetrachlorocyclopentanedione (4)		I (23.2)		
Trichlorophenol (TriCP)		S (26.2, 26.9)	[8]	[11]
Tetrachlorocyclopentadiene (1,3-CPTC)		L (20.4)		
Hexachlorocyclopentadiene (1,3-CPHC)		L (25.9)		
Tetrachlorobenzene (TCB)		L (26.4, 26.5)		
3,4,5,6-tetrachloro-*o*-phenylene cyclic carbon acid (CATCOP)		L (36.4)		
Octachlorodibenzo-*p*-dioxin (OCDD)		S (55.1)	[7]	
Heptachlorodibenzo-*p*-dioxin (HpCDD)		L (42.7, 44.4)	[7]	
Decachlorobiphenylether (DCDPE)		S (49.9)		

Table 1 (continued)

Products	Structures	Identification methods and retention time (min)	Products formed during photolysis in water	Products formed during photolysis in hexane
2,2′,3,3′,4,4′,5,5′,6-nonachlorobiphenylether (NCDPE)		S (42.4)		

Methods of identification: S = mass spectrum and t_R in agreement with those of standards; I = interpretation of the mass spectrum; L = interpretation and comparison of the mass spectra with those in the mass analyzer library.

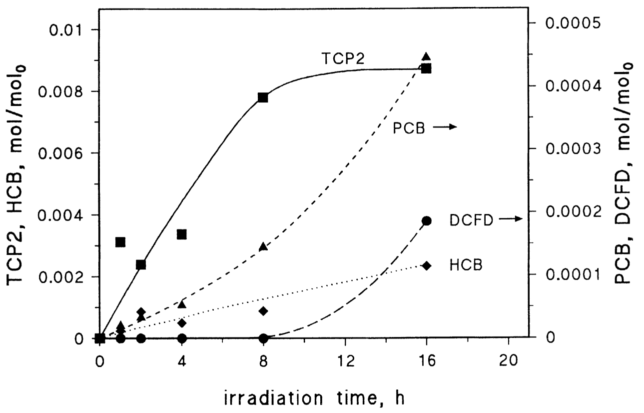


Fig. 2. Kinetic variations in the relative amounts of some monocyclic photoproducts of PCP (42 μmol initially) deposited from a methanolic solution.

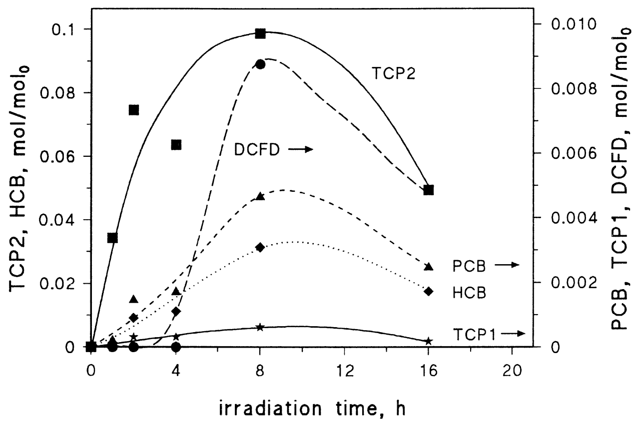


Fig. 3. Kinetic variations in the relative amounts of some monocyclic photoproducts of PCP (42 μmol initially) deposited from a 50% v / v methanol / water solution. Note that the ordinate scales are different from those in Fig. 2.

order. Moreover, their kinetic variations within the first hours of irradiation indicated that they were primary products. They correspond to the substitution of Cl by H (TCP) or OH by Cl (HCB) or OH by H (PCB).

The C–Cl bonds are the more fragile in chlorophenols although the O–H bond is not very much stronger. Therefore

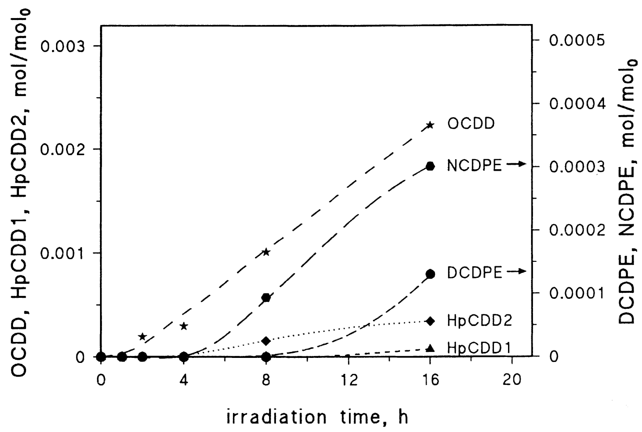
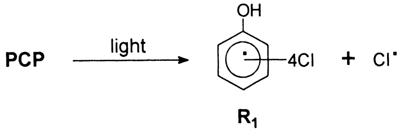


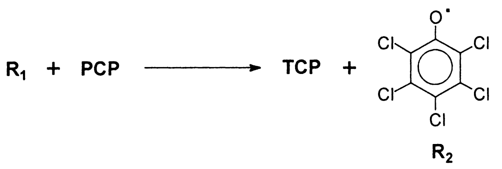
Fig. 4. Kinetic variations in the relative amounts of some bicyclic photoproducts of PCP (42 mol initially) deposited from a methanolic solution.

the following reaction could be the most probable initial photolytic event.



(1)

Propagation might be suggested to occur through the reactions:



(2)

and

$$Cl^{\bullet} + PCP \rightarrow HCB + {}^{\bullet}OH \quad (3)$$

then

$$Cl^{\bullet} + TCP \rightarrow PCB + {}^{\bullet}OH \quad (4)$$

which account for the formations of TCP, HCB and PCB, the latter product being generated in smaller amounts (Figs. 2 and 3); note that the curve pattern in Fig. 2 indicates PCB to be a secondary product consistently with (Eqs. (2) and (4)). Further dechlorination (Table 1) would involve reactions analogous to reaction Eq. (1) with an intermediate product instead of PCP.

OCDD might be the result of termination reactions such as:

$$R_1 + R_2 \rightarrow \text{OCDD} + \text{HCl} \qquad (5)$$

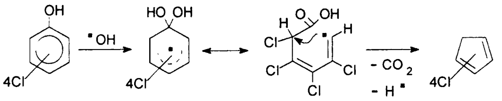
$$2R_2 \rightarrow \text{OCDD} + 2\text{Cl}^{\bullet} \qquad (6)$$

or a reaction between R_1 radical and PCP

$$R_2 + \text{PCP} \rightarrow \text{OCDD} + \text{HCl} + \text{Cl}^{\bullet} \qquad (7)$$

OCDD could lose a chlorine atom by photoreduction to produce the two isomers of heptachlorodibenzo-*p*-dioxin. Heptachlorodibenzo-*p*-dioxin could also be formed by condensation between PCP and TCP [7]. In both the cases, it is a secondary product in agreement with the experimental results shown in Fig. 4.

Pentachlorocyclopentadiene might be formed from TCP as tentatively suggested in Eq. (8).



(8)

Further, chlorination or dechlorination and oxidation of this product would lead to the other C_5-membered products (Table 1). The kinetic curves (Figs. 2 and 3) clearly show that one of these products, dichloromaleic anhydride, is a secondary product, which was probably formed through dichloromaleic acid.

Radical R_1 might also add dioxygen yielding the corresponding peroxy radical. Subsequent coupling of two peroxy radicals and elimination of one O_2 molecule might produce bicyclic aromatic peroxides. No attempt was made to detect these unstable products.

Although reactions (Eqs. (1)–(4)) are plausible and allow one to account for the main products, there are some discrepancies between these reactions and the absence of some products according to our analyses. For instance, the reaction of PCP with a ·OH radical formed via reactions (Eqs. (3) and (4)) should produced dihydroxytetrachlorobenzene isomers; as already mentioned these products were not detected contrary to what was observed in aqueous solution [6–8,10].

4. Conclusion

A series of C_6-membered and, to a lesser extent, C_5-membered monocyclic products as well as products with two phenyl rings are formed on irradiating solid PCP at UV wavelengths that are present in the solar spectrum at the earth's surface. All these products contain several chlorine atoms. Our results complete previous results relating to PCP degradation in aqueous [6–8,10] or organic [11] solutions. Although the products of PCP phototransformations are also photodegraded, the present results clearly illustrate that the use of PCP must be minimized and that research is needed to design safer chemicals to be substituted to PCP in its various uses.

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