uptake from soil contaminated by runoff. Periodic analyses of the soil of the treated plot indicated that essentially all (>95%) of the radioactive material detected was located near the surface (0–7.5 cm deep). Residues in that layer on Aug 3, Sept 7, Nov 2, and Dec 4, 1979, were 0.3 ± <0.1 (SE), 1.1 ± <0.1, 0.7 ± <0.1, and 0.3 ± <0.1 ppm, respectively. Although the nature of these radioactive residues was not determined, their levels clearly declined progressively with time after treatments were terminated.

Although our studies have shown that single applications of RH-0994 are not unusually persistent either on foliar surfaces or in the plant system following absorption, they do indicate that season-long multiple applications may result in the appearance of residues in seeds and other parts of treated plants. Based on the extractability of the radiocarbon in seeds, it seems almost certain that the residues are not in the form of RH-0994 or its intact ester derivatives.

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Photodecomposition of Pentachlorophenol in Water

Anthony S. Wong[1] and Donald G. Crosby*

Exposure of aqueous pentachlorophenol (PCP) solutions to either sunlight or laboratory ultraviolet light resulted in rapid degradation at pH 7.3 and slower degradation at pH 3.3. Displacement of chloride by hydroxide produced tetrachlorocatechol, tetrachlororesorcinol, and tetrachlorohydroquinone which subsequently were air-oxidized to chloranil, hydroxyquinones, and eventually 2,3-dichloromaleic acid (DCM). This acid photodecomposed more slowly to carbon dioxide, chloride, and unidentified organic fragments. Photoreduction of PCP to tetra- (TCP) and trichlorophenols also occurred, as did formation of a cyclic diketone, $C_5H_2Cl_2O_2$. Examination of local field waters revealed PCP and TCP but no DCM.

Pentachlorophenol (PCP) is a major industrial chemical and pesticide used worldwide for the protection of wood and wood products against insects and microorganisms. It also has received extensive use in rice and sugar production and in water treatment. Most of its uses offer the potential for water pollution, and, indeed, PCP has been found in natural waters in such widely separated places as Hawaii (Bevenue et al., 1972), Delaware (Fountaine et al., 1976), The Netherlands (Wegman and Hofstee, 1979), and West Germany (Weber and Ernst, 1978).

Aqueous solutions of PCP absorb strongly within the sunlight region of the spectrum (λ_{max} 320 nm); Hiatt et al. (1960) and Mitchell (1961) first mentioned the photodecomposition, and Kuwahara et al. (1966a,b, 1969) isolated tetrachlororesorcinol, chloranilic acid, and complex chlorinated ethers following the irradiation of relatively concentrated (2%) aqueous PCP solutions. Crosby and Hamadmad (1971) also observed PCP photoreduction to tri- and tetrachlorophenols in organic solvents.

The purpose of the present work was to investigate the rate of PCP photodecomposition in dilute aqueous solutions more nearly characteristic of current use, to identify photodecomposition products, and to suggest degradative pathways by which the products may be explained.

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MATERIALS AND METHODS

Materials. Most reagents and intermediates were purchased from chemical supply houses and were used as received; solvents were redistilled shortly before use. Pentachlorophenol (Puriss, Aldrich Chemical Co.) was recrystallized 3 times from benzene, mp 188.5 °C, and was homogeneous on gas chromatography (GLC). Diazomethane was generated from *N*-methyl-*N*-nitroso-*p*-toluenesulfonamide (de Boer and Backer, 1963).

Pentachlorophenyl chloroacetate was prepared from PCP and chloroacetyl chloride (Kupryszewski and Wojnowski, 1962), mp 120–130 °C.

Tetrachlororesorcinol was prepared by dissolving 1 g of 3-chloro-5-methoxyphenol (Aldrich) in 125 mL of redistilled carbon tetrachloride and introducing chlorine gas slowly for 30 min. The solvent was removed by vacuum evaporation, the solid residue was fused with pyridine hydrochloride (5 g) for 1 h at 210 °C, the resulting cake was dissolved in 200 mL of 5% aqueous HCl and extracted into ethyl ether, and the combined ether extracts were evaporated. Recrystallization of the crude product twice from water gave an 80% yield of white crystals, mp 140.5 °C (140–141 °C; Heilbron, 1965), *m/e* 246 with an isotope

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cluster indicating four chlorines.

Irradiation. Irradiation experiments were conducted in borosilicate glass flasks exposed to summer sunlight at Davis, CA, in similar flasks exposed to six F40BL ultraviolet lamps in a cylindrical mounting (Crosby and Wong, 1973), or in 1.5-L photoreactors (Crosby and Tang, 1969). Rate measurements were made in the smaller photoreactors wrapped with plastic tubing through which chilled water was circulated to maintain the reaction temperature at 26 ± 1 °C. Solutions were prepared in distilled water, filtered water from a nearby rice field, or Carmody wide-range (citrate–borate–phosphate) buffers.

In a typical experiment, pure PCP (100 mg) was dissolved in 1 L of buffer at pH 3.3 or 7.3, the solution was irradiated, and aliquots were removed to monitor the disappearance of the PCP. For product determination, the irradiation was terminated at the desired degree of degradation, the pH was adjusted to 10 with sodium hydroxide solution, and neutral products were extracted into benzene. The aqueous portion was made strongly acidic with sulfuric acid and extracted with ether, the extract washed with a small volume of water and dried over sodium sulfate, and the ether solution evaporated to a volume of ~1 mL for subsequent chromatography. Dark controls were run concurrently.

Tetrachlorohydroquinone, tetrachlororesorcinol, tetrachlorocatechol, and 2,3-dichloromaleic acid (DCM, generated from its anhydride) were irradiated in the same manner to determine rates and product distribution.

Separation and Identification. The concentrated ether extract, whose acidic constituents represented most of the degraded PCP, was subjected to GLC on an F & M Model 720 gas chromatograph equipped with a thermal conductivity detector and a 60 × 0.6 cm stainless steel columm containing 1% DEGA on Chromosorb G, temperature programmed from 75 to 200 °C at 10 °C/min. The eluted photoproducts were collected in glass capillary tubes as they emerged, removed with ether, and their spectral and chemical properties compared with those of standards whenever possible.

Thin-layer chromatography (TLC) was conducted on 20 × 20 cm glass plates coated with silica gel G, 1 mm thick, containing zinc silicate phosphor. Solvent A was 2-propanol–ammonium hydroxide (7:3 v/v), and solvent B was benzene–hexane (1:1). Infrared (IR) spectra were measured in 1.5-mm KBr pellets, ultraviolet (UV) spectra in water or ethanol in 1-cm cuvettes, and nuclear magnetic resonance (NMR) spectra in deuterioacetone with a Me_4Si standard.

The neutral extract was evaporated to small volume and analyzed on a Finnigan Model 3000 gas chromatograph–mass spectrometer (GC–MS) with a 150 × 0.2 cm glass column containing 2% OV-1 on 60–80-mesh Chromosorb W programmed from 150 to 240 °C at 10 °C/min with an He flow of 25 mL/min.

Rate Measurements. Aliquots (25 mL) of irradiated solutions were acidified to pH 2 with sulfuric acid; remaining PCP was extracted into an equal volume of hexane, the tetrachlorodiols into 3 separate volumes of ether, and DCM into 4 separate volumes of ether. In each case, the combined extracts were dried over sodium sulfate and made up to 100 mL with ether, and a 5-mL aliquot was methylated with ethereal diazomethane. The methylated phenols were analyzed on a Varian Model 1400 gas chromatograph with an electron-capture detector and a 180 × 0.6 cm glass column containing 5% SE-30 on 80–100-mesh Chromosorb W at 150 °C or 10% DC 200 on 80–100 Gas-Chrom Q at 150 °C, and dimethyl dichloromaleate was analyzed on the same columns at 140 °C. Recovery was 95% for the phenols and 85% for DCMA.

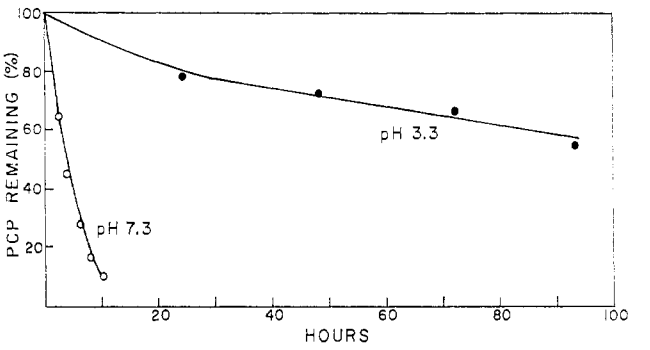


Figure 1. PCP photodegradation rates at 26 °C and pH 3.3 and 7.3 (F40BL lamps). Initial concentration was 100 mg/L (3.8×10^{-4} M).

Trapping Experiment. DCM (2.0 g) was dissolved in 1 L of deionized water from which carbon dioxide had been carefully removed by repeated boiling and cooling under nitrogen. High-purity oxygen was introduced into the solution while it was irradiated, and the effluent gas was passed into a trap containing carbonate-free sodium hydroxide solution. Aliquots of the irradiated solution were analyzed for chloride by titration with a standard silver nitrate solution (0.0144 N) and potassium dichromate indicator. The trapped carbon dioxide was precipitated as barium carbonate and weighed.

Chloroacetic Acid Analysis. The aqueous sample was acidified with dilute sulfuric acid and extracted with three 25-mL portions of dichloromethane, and the combined extracts were treated under vigorous stirring with a sequence of 0.1 g of PCP, 0.2 mL of phosphorus oxychloride, and 0.5 mL of pyridine. The mixture was maintained at room temperature for ~3 h, evaporated to 10 mL under nitrogen, rinsed into separatory funnel with 250 mL of hexane, and washed with three 50-mL portions of 5% aqueous sodium hydroxide followed by equal volumes of 5% hydrochloric acid. After being dried over sodium sulfate, the extract was brought to 100 mL with hexane, an aliquot reduced to small volume to remove final traces of dichloromethane, and the pentachlorophenyl chloroacetate measured by GLC on a 1800 × 0.2 cm glass column containing 2% QF-1 on 60–80-mesh Gas-Chrom Q at 170 °C and N_2 flow at 40 mL/min. Standard recovery was 80%, with picogram sensitivity on an electron-capture detector.

Water Analysis. Water samples (1 L) were collected from field sites in Northern California, acidified to pH 2 with sulfuric acid, and extracted with three 200-mL portions of ether, and the combined extracts were dried over sodium sulfate, condensed to 1 mL, and analyzed directly by GC–MS on a 150 × 0.6 cm glass column of 3% OV-1 on 60–80-mesh Chromosorb W programmed from 70 to 225 °C at 10 °C/min. The limit of detection was below 1 μg/L, and recovery was 85–95% at the microgram per liter level. Retention times and mass spectra were compared to those of standards, and calibration curves were based on total-ion current.

RESULTS

Laboratory irradiation of buffered solutions of PCP (0.38 mM, 100 mg/L) under both acidic and alkaline conditions resulted in the degradation rates shown in Figure 1; the half-life at pH 3.3 was ~100 h, while at pH 7.3 it was only 3.5 h. Dark controls remained unchanged. Photodegradation in filtered rice-field water or in the presence of tryptophan as a sensitizer resulted in the same rates, while

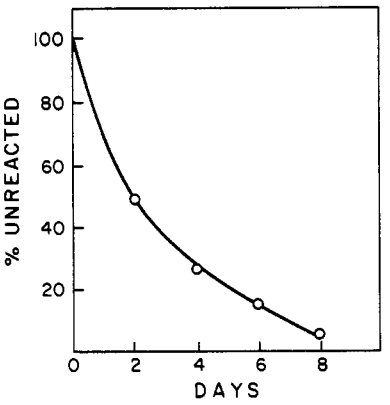


Figure 2. PCP photodegradation rate at pH 7.3 (sunlight, July 1974). Initial concentration was 100 mg/L (3.8×10^{-4} M).

Table I. Spectral Data for Compound 3

spectral characteristic	interpretation
IR: 1718, 1730 cm^{-1}	C=O
1600 cm^{-1}	C=C
2940, 1458 cm^{-1}	CH_2
1379, 1200 cm^{-1}	C=C–OH
UV: λ_{max} 260 nm	C=C–C=O
MS: *m/e* 164 (Cl_2 cluster)	M^+ ($C_5H_2Cl_2O_2$)
m/e 129 (Cl cluster)	M – Cl ($C_5H_2ClO_2$)
m/e 122 (Cl_2 cluster)	Cl–C=C(Cl)–C=O (C_3Cl_2O)
m/e 94 (Cl_2 cluster)	Cl–C=C–Cl
m/e 87 (Cl cluster)	Cl–C=C–C=O (base)
m/e 42 (no Cl)	CH_2C=O
NMR: δ 3.76	

exposure in pH 7.3 buffer to outdoor July sunlight resulted in a half-life of 48 (total elapsed) h and total disappearance within 10 days (Figure 2).

Extraction and gas chromatography of the acidic photolysis products at the point where 50% of the initial PCP had been degraded revealed a complex mixture (Figure 3). The mass spectrum of compound 1 showed a molecular ion at *m/e* 166 with a Cl_2 isotope cluster indicating a formula of $C_4Cl_2O_3$. The IR spectrum showed prominent carbonyl absorptions at 1790 and 1778 cm^{-1} typical of a five-membered cyclic anhydride (Nakanishi, 1962), and NMR confirmed the lack of H. Mass and IR spectra proved identical with those of an authentic specimen of 2,3-dichloromaleic anhydride. As the compound had appeared in the acidic fraction, it was assumed to have been formed from the corresponding dichloromaleic acid (DCM) during GLC, and methylation of the original ether extract before GLC indeed provided dimethyl 2,3-dichloromaleate, identical with an authentic specimen.

The quantity of **2** was sufficient only for a mass spectrum which revealed a simple fragmentation and a molecular ion at *m/e* 108. The GLC retention time and mass spectrum indicated a chloropropionic acid but it was not

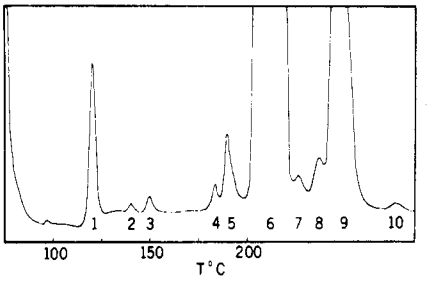
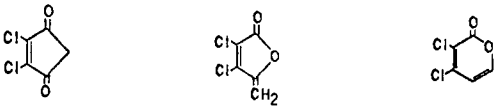


Figure 3. Gas chromatogram of PCP photodegradation products.

confirmed against standards.

Compound **3** also was present in only small amounts and exhibited the spectral properties shown in Table I. The molecular ion at *m/e* 164 (Cl_2 cluster) fitted an empirical formula of $C_5H_2Cl_2O_2$, and spectral properties and the mass fragmentation suggested **3a–c** as possible structures.



3a 3b 3c

Compounds **4** and **5** provided mass spectra (*m/e* 230, Cl_4) corresponding to $C_6H_2Cl_4O$, suggestive of tetrachlorophenols, and GLC retention, mass spectra, and IR spectra confirmed them to be 2,3,5,6- and 2,3,4,6-tetrachlorophenol, respectively. Compound **6** was unchanged PCP, and **7** and **8** could not be resolved sufficiently to allow unambiguous characterization.

Compound **9** provided a mass spectrum (*m/e* 246, Cl_4) corresponding to the formula $C_6H_2Cl_4O_2$ and an IR spectrum showing strong OH absorption. The isolated crystalline solid melted at 140.5 °C, corresponding to that of tetrachlororesorcinol (TCR) (mp 141 °C; Heilbron, 1965), and its identity was confirmed by comparison with a synthetic standard. Compound **10** had very similar spectral characteristics and was shown to be the isomeric tetrachlorocatechol (TCC) by comparison with a standard. Repeated attempts to isolate the unstable chlorodiol, tetrachlorohydroquinone (TCH) (perhaps **8**), were unsuccessful.

Thin-layer chromatography of the extractives in benzene–hexane (solvent B) provided a yellow band at R_f 0.60 representing 2,3,5,6-tetrachloro-*p*-benzoquinone (chloranil, **11**). The residue at the origin, extracted into ether and methylated with diazomethane, exhibited a retention time and mass spectrum (Table II) identical with those of authentic (methylated) 2,5-dichloro-3,6-dihydroxy-*p*-benzoquinone (chloranilic acid, **13**). Solvent A caused degradation of **11**.

Each tetrachlorodiol subsequently was irradiated at pH 7.3 (Figure 4). TCH no longer was detectable after 3 h,

Table II. Photodegradation Products of PCP

compd no.	elution temp, °C[a]	M^+, *m/e*	empirical formula	proposed identity
1	120	166 (Cl_2)	$C_4Cl_2O_3$	2,3-dichloromaleic acid[b]
2	138	108 (Cl)	$C_3H_5ClO_2$	chloropropionic acid
3	149	164 (Cl_2)	$C_5H_2Cl_2O_2$	4,5-dichloro-1,3-cyclopentanedione
4	180	230 (Cl_4)	$C_6H_2Cl_4O$	2,3,5,6-tetrachlorophenol
5	188	230 (Cl_4)	$C_6H_2Cl_4O$	2,3,4,6-tetrachlorophenol
6	200	266 (Cl_5)	C_6HCl_5O	pentachlorophenol
9	200	246 (Cl_4)	$C_6H_2Cl_4O_2$	tetrachlororesorcinol
10	200	246 (Cl_4)	$C_6H_2Cl_4O_2$	tetrachlorocatechol
11		244 (Cl_4)	$C_6Cl_4O_2$	tetrachloro-1,4-benzoquinone
13	180 (3.2 min)	237 (Cl_2)	$C_8H_6Cl_2O_4$	3,6-dichloro-2,5-dihydroxy-1,4-benzoquinone[c]

[a] See the text for GLC conditions. [b] As anhydride. [c] As methyl ether.

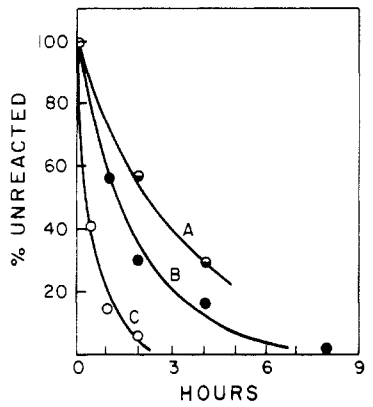


Figure 4. Photodegradation rates of tetrachlorocatechol (A), tetrachlororesorcinol (B), and tetrachlorohydroquinone (C) at 26 °C and pH 7.3. Initial concentration was 200 mg/L (8.1×10^{-4} M).

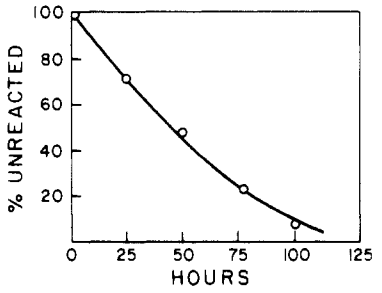


Figure 5. DCM photodegradation rate at 26 °C and pH 7.3 (F40BL lamps). Initial concentration was 86 mg/L (4.7×10^{-4} M).

or TCC after 8 h, and GC–MS in both instances gave peaks representing the corresponding trichlorodiol (*m/e* 212), trichloroquinone (*m/e* 210), DCM anhydride (*m/e* 166), and **3** (*m/e* 164). While TCC solution was stable in the dark, TCH spontaneously decomposed to chloranil, 2-hydroxy-3,5,6-trichlorobenzoquinone (**12**), chloranilic acid (**13**), and DCM. TCR photolysis primarily produced small amounts of two trichlororesorcinols (*m/e* 212) and **3**; while stable in the dark, it, too, was undetectable after ~8 h of irradiation.

DCM absorbed and was degraded in the sunlight region (Figure 5), but repeated isolation attempts failed to provide any photolysis products, either directly or after methylation. A specific search for chloroacetic acid likewise was unsuccessful. However, when DCM was irradiated in carbon dioxide–free water, the generation of both chloride ion and carbon dioxide could be monitored (Figure 6).

With the exception of some chloranil, the neutral extract from PCP photolysis normally yielded no products. At high initial PCP concentrations (1000 mg/L), a small proportion of 1,2,3,4,6,7,8,9-octachlorodibenzo-*p*-dioxin (OCDD) could be detected by GC–MS (*m/e* 456) (Crosby and Wong, 1976), but, if present, OCDD or its acidic "predioxins" (Rappe and Nilsson, 1972) were below our limits of analytical detection in other experiments.

Water samples from suspected high-exposure sites were analyzed with the hope of verifying PCP photodecomposition products under field conditions (Table III). Relatively high levels of PCP were observed in surface ponds and agricultural drainage water in the vicinity of a local wood-treatment plant, while any levels in downstream river water were below detectability. PCP in the pond water was confirmed by GC–MS, as were 2,3,4,6-tetrachlorophenol (TCP) and a dichlorophenol; nearby (dark) well water contained only PCP. However, while DCM also should have been detectable at the microgram per liter level (Figure 3), none was observed.

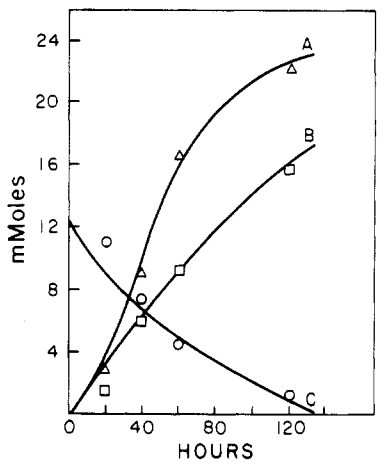


Figure 6. Generation of carbon dioxide (A) and chloride ion (B) from DCM (C).

Table III. PCP Content of Natural Water Samples

sample type (no.)	location	PCP, μg/L
surface pond water (7)	Oroville, CA	1-800 (av 227)
agricultural drainage (1)[a]	Oroville, CA	20
domestic well water (50)	Oroville, CA	<1-50
Sacramento River (1)[a]	Sacramento, CA	<1

[a] Triplicate.

DISCUSSION

The photochemical decomposition of PCP is obvious. A colorless aqueous solution (pH 9) placed outdoors in sunlight soon turns violet and then fades through brown, red, and yellow to colorless again. The same but slower process also can be followed analytically at pH 3.3 and 7.3 where PCP ($pK_a = 5.3$) is 99% unionized or 99% ionized, respectively (Figure 1). After the solution has stood sealed in sunlight for 2–3 weeks, neither PCP nor any other organic substance is detectable.

Identification of the photolysis products (Table II) explains these observations and provides the key to the degradative process (Figure 7). The first step represents a photonucleophilic substitution of hydroxide for chloride to provide the three possible tetrachlorodiols (Crosby et al., 1972; Crosby and Wong, 1976). TCH and TCC then are air-oxidized to the corresponding (red) quinones (Reiner et al., 1978), followed by further displacement of chloride to form the purple hydroxytrichloroquinones (Hancock et al., 1962) and orange dichlorodihydroxyquinones (chloranilic acids). TCR, which cannot form a quinone directly, presumably must undergo chloride displacement first. Tetrachlorophenols and trichlorodiols also are formed early by photoreduction (Crosby and Hamadmad, 1971; Crosby et al., 1972) but can be expected to undergo later photonucleophilic and photooxidation reactions.

The oxidative ring cleavage of catechols by periodate is well-known, and Karrer and Tests (1949) converted *o*-chloranil to *cis,cis*-tetrachloromuconic acid with perphthalic acid. A similar oxidation of the chloranilic acids would result in the observed (colorless) 2,3-dichloromaleic acid and hypothetical chloroacetic acid, but the specific photochemical oxidant remains unknown. Karrer and Testa (1949) also isolated dichlorobutenolides from *o*-chloranil oxidation, and the presence of a hydroxylactone also is suggested by the work of Tiedje et al. (1969).

The calandra formula (Calandra, 1932) indicated that compound **3**, $C_5H_2Cl_2O_2$, was monocyclic and contained

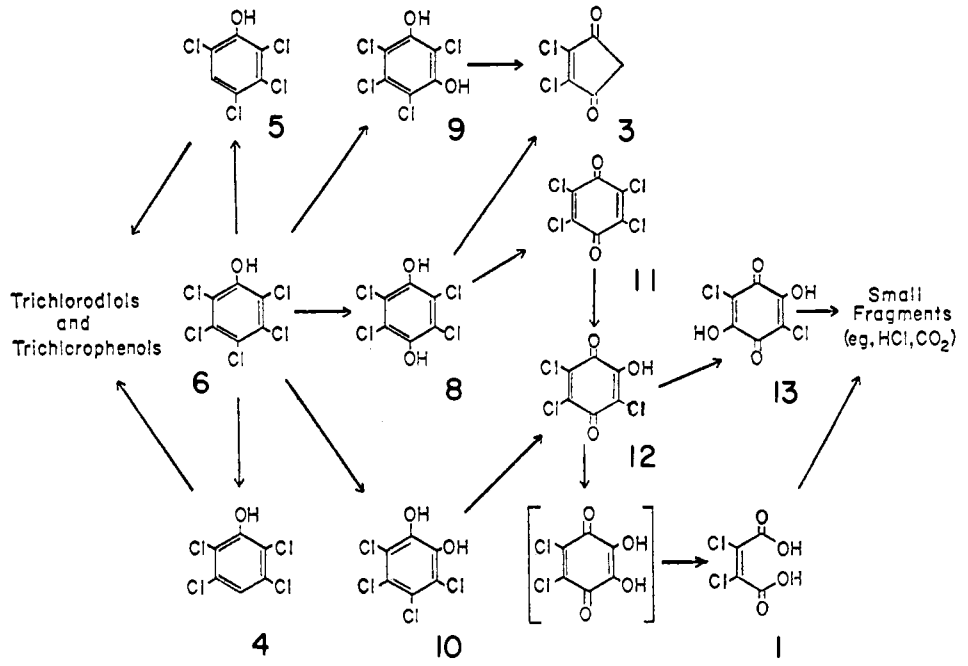


Figure 7. PCP photodegradation scheme.

three double bonds; three types of compounds were suggested (**3a**, **3b**, and **3c**). While a butenolide such as **3b** would be attractive due to recognition of this class as microbial metabolites of chlorophenols (Tiedje et al., 1969), their 1800-cm^{-1} carbonyl absorption in the IR ruled them out (Tiedje et al., 1969; Wells, 1963). Pyrones such as **3c** were unlikely because of their strong UV absorption near 300 nm (Roedig and Märkl, 1960) and the prominent M − CO in their mass spectra (Porter and Baldas, 1971) which was all but missing with **3**. However. all the spectral data were consistent for **3a**, including the strong CH_2 absorption at 1458 cm^{-1}, the absence of C=CH near 800 cm^{-1}, and the major mass spectral fragments at m/e 42 (CH_2CO) and m/e 122 (M − CH_2CO) characteristic of a cyclic ketone (Budzikiewicz et al., 1964). The UV and IR data reported in the literature for **3a** (McBee et al., 1956) were identical with those of compound **3**, and direct spectral comparison with an authentic standard confirmed structure **3a**.

The measurement of CO_2 and chloride during photolysis of DCM (Figure 6) indicated that a stable two-carbon unchlorinated fragment also was generated, as both chlorines and two carbons can be accounted for. However, a specific search for the more obvious possibilities (oxalic, glycolic, and glyoxylic acids) failed to detect them, and, in fact, no terminal organic product could be isolated.

This research demonstrates for the first time the photochemical cleavage of an aromatic ring under environmental conditions and its subsequent mineralization, although similar conversion of PCP to chloride ions and carbon dioxide by microorganisms has been reported by Suzuki (1977).

As with microbial degradation (Kaufman, 1978), PCP photodegradation proved to be primarily oxidative, and the rapid photochemical generation and cleavage of other oxidizable phenols eventually may prove to be a general and significant phenomenon in nature. However, analysis of PCP-containing natural waters failed to detect oxidized products such as DCM, although reduced products were observed by us and by others (Pierce and Victor, 1978; Weber and Ernst, 1978; Wegman and Hofstee, 1979). It seems likely that pH has a pronounced influence on the diol-forming (ionic) process (Crosby et al., 1972) while the (radical) reduction process would be influenced more by the level of organic H donors in the water and might predominate in an acidic, high-BOD environment. Further, the action of natural sensitizers (Plimmer and Klingebiel, 1971) cannot be excluded in field degradations, although the laboratory photolysis rates remained unchanged when rice-field water was substituted for the buffer.

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Metabolism of *cis*- and *trans*-Cypermethrin in Rats. Balance and Tissue Retention Study

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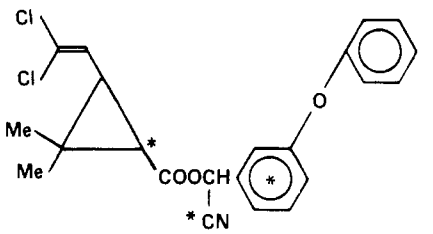
The fate of the cis and trans isomers of the pyrethroid insecticide cypermethrin (NRDC 149), α-cyano-3-phenoxybenzyl 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate, has been studied in rats (1–5 mg/kg) by using three forms of radiolabeling (benzyl-^{14}C, cyclopropyl-^{14}C, and cyano-^{14}C). Radioactivity derived from the benzyl-^{14}C and cyclopropyl-^{14}C labeling was rapidly eliminated, mostly in the urine. Tissue residues were generally very low, e.g., 0.01 μg/g in brain, with the exception of fat (~1 μg/g). Residues derived from the cis isomer tended to be higher than those derived from the trans isomer. The rate of depletion of the residues derived from [benzyl-^{14}C]-*cis*-cypermethrin was rapid ($t_{1/2}$ was less than ~1 day) from all tissues except fat, from which radioactivity was eliminated with a half-life of 11–12 days. This residue was largely due to unchanged *cis*-cypermethrin. [*cyano*-^{14}C]Cypermethrin afforded radioelimination and distribution characteristics similar to those reported for the cyanide ion.

Cypermethrin (NRDC 149, I) is one of the pyrethroid α-cyano-3-phenoxybenzyl esters which combine high insecticidal activity with a degree of photostability suitable for use in the field (Elliott, 1976). Part of the successful development of this compound is a study of its mammalian toxicology which includes a knowledge of its biotransformation in experimental animals. It is a complex molecule in terms of stereochemistry, and furthermore, as it is an ester, its fate in biological systems must be studied by using a radiolabel in both the acid and alcohol moieties. Cypermethrin possesses three chiral carbon atoms and is therefore a mixture of eight isomers. It was discovered some years ago (Abernathy and Casida, 1973) that the relative orientation of the ethenyl group and the carboxylic group on the cyclopropane ring of the pyrethroid insecticides has a dominant effect on the rate of enzymatic hydrolysis of these compounds. Hence, the traditional "cis" and "trans" nomenclature is still in common use. In the rat metabolism study reported here, two isomer mixtures were used; these are referred to as the cis and trans isomers throughout. C-1 (cyclopropyl) and C-α (benzyl) were racemic. Three positions of ^{14}C labeling were utilized: the cyclopropyl group, the 3-phenoxybenzyl group, and the cyano group:



I (cypermethrin ; * = ^{14}C–labelling)

MATERIALS AND METHODS

Chemicals. [*benzyl*-^{14}C]-*cis*- and *trans*-cypermethrin [α-cyano-3-phenoxy[^{14}C]benzyl 3-(2,2-dichlorovinyl)-2,2-dimethylcyclopropanecarboxylate, I] (34 μCi/mg) were synthesized at the Shell Biosciences Laboratory. [*cyclopropyl*-^{14}C]Cypermethrin (cis and trans mixture) (9.6 μCi/mg), the separate cis and trans isomers (11.1 μCi/mg), and [*cyano*-^{14}C]cypermethrin (7.13 μCi/mg) were obtained from the same source. All compounds were analyzed by thin-layer chromatography (TLC) on Merck silica gel F_{254} plates developed in toluene and were either >99.5% pure or purified by further TLC in toluene before use. The isomeric composition of some of the compounds was

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