Arch. Environm. Contam. Toxicol. 9, 135–146 (1980)

Archives of Environmental Contamination and Toxicology

Photodecomposition of DDA[1]

G. W. Ware,[2] D. G. Crosby,[3] and J. W. Giles[3]

Abstract. The photodecomposition of aqueous solutions of 2,2-bis (*p*-chlorophenyl) acetic acid (DDA) was slow in sunlight and rapid in the laboratory, producing *p,p'*-dichlorobenzophenone (DCB), *p*-chlorobenzaldehyde, *p*-chlorophenol, and several unidentified polar products. *p,p'*-Dichlorobenzilic acid, and *p,p'*-dichlorobenzhydrol gave rise to the same photoproducts, while bis-(*p*-chlorophenyl) methane (DDM) and chlorobenzilate were converted only to DCB. DCB and *p*-chlorobenzaldehyde proved to be resistant to photodegradation but gradually produced *p*-chlorobenzoic acid which, in turn, formed *p*-hydroxybenzoic and benzoic acids, probably the last environmentally detectable links in the long chain of DDT degradation to CO_2 and water.

High pressure liquid chromatography (HPLC) proved to be ideal for separating and quantitating the parent compounds and their photoproducts directly from the aqueous photolysates or from methanol solutions of the isolates and standards.

More than four billion pounds of 1,1,1-trichloro-2,2-bis(*p*-chlorophenyl) ethane (DDT) were released into the environment during almost four decades, but Woodwell *et al.* (1971) have estimated that only about 10 percent of it presently can be accounted for. Their proposed explanations for this discrepancy ignore the environmental breakdown of DDT, although its metabolism and other forms of degradation have been studied more extensively than those of most other pesticides (Menzie 1969, 1974).

2,2-bis(*p*-Chlorophenyl) acetic acid (DDA) (Figure 1) is recognized as perhaps the universal DDT metabolite in microorganisms, plants, insects, and higher animals. It forms in both aerobic and anerobic bacteria (Wedemeyer 1966, Guenzi and Beard 1968, Pfaender and Alexander 1972), in fungi (Engst and Kujawa 1967), in many genera of insects including the grain weevil,

[1] Contribution to Regional Project W-45, Environmental Distribution, Transformation, and Toxicological Implications of Pesticide Residues. University of Arizona Agricultural Experiment Station journal series No. 2931.

[2] Department of Entomology, University of Arizona, Tucson, AZ 85721.

[3] Department of Environmental Toxicology, University of California, Davis, CA 95616.

0090–4341/80/0009–0135 $02.40

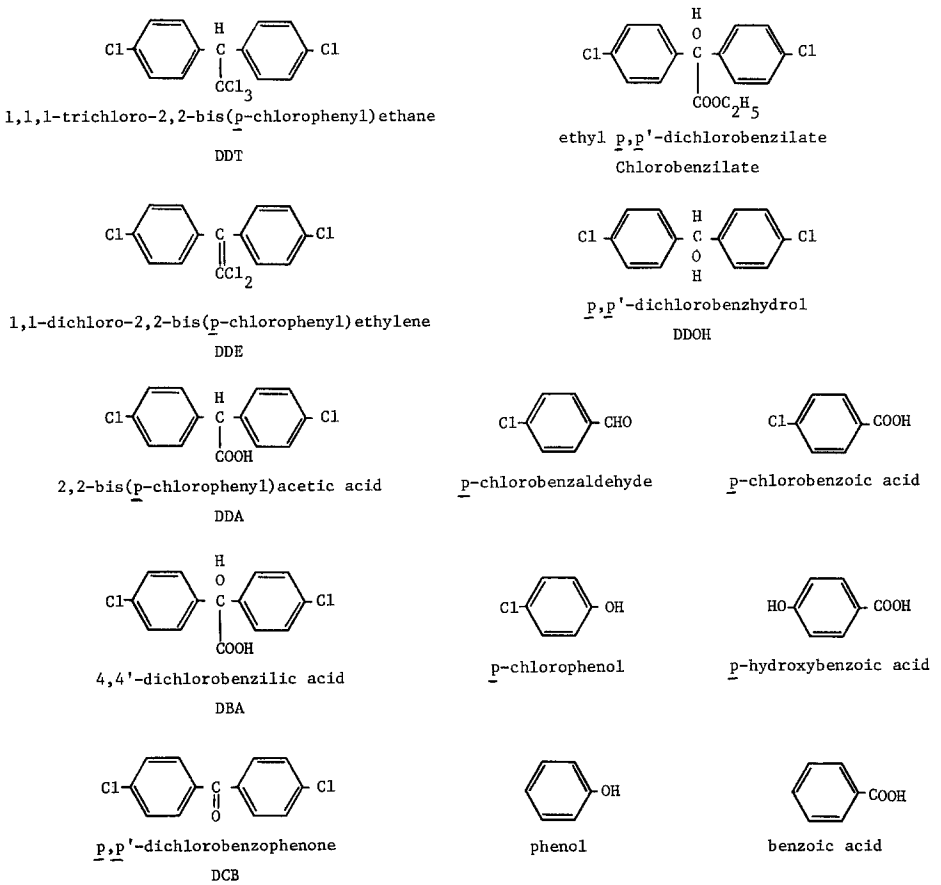

Fig. 1. Structures of DDA and related products

Sitophilus granarius (Rowlands and Lloyd 1969), human body louse, *Pediculus humanis corporis* (Perry *et al.* 1963), and tobacco budworm, *Heliothis virescens* (Vinson and Brazzel 1966), in higher plants such as spinach and cabbage (Zimmer and Klein 1972), and in both birds and mammals, including man (Abou-Donia and Menzel 1968, Menzie 1974). It also has been reported as a metabolite of 1,1-dichloro-2,2-bis (*p*-chlorophenyl) ethane (DDD) in mammals (Bowery *et al.* 1965) and insects (Plapp *et al.* 1965), and usually is accompanied by *p,p'*-dichlorobenzophenone (DCB).

DDT is also converted readily into DDA by purely chemical action. It is a photodecomposition product when DDT or 1,1-dichloro-2,2-bis (*p*-chlorophenyl) ethylene (DDE) is irradiated in methanol with ultraviolet (UV) light (Plimmer *et al.* 1970) or in water with either UV light or sunlight (Crosby *et al.* 1975, Leffingwell and Crosby 1978). It is the major product when DDT is hydrolyzed by alcoholic potassium hydroxide (Horning 1967), tin and aqueous ammonium chloride (DeLoach and Hemphill 1971), or by aqueous dioxane alone (Singh and Maliyandi 1969). Again, it is often accompanied by DCB.

DDA emerges, then, as a key intermediate in the environmental degrada-

tion of DDT and its relatives to structurally simpler, nontoxic forms. The objectives of our research were to determine the rates and products of DDA photolysis in water under both indoor and outdoor conditions and to estimate its contribution to the environmental destruction of DDT.

Experiment

Materials

The organic chemicals and reagents were of the purest commercial grade available, but they were recrystallized where necessary for high pressure liquid chromatography (HPLC). Identities were confirmed by melting point or mass spectrum in comparison to values expected from the literature, and by postulating their structures from mass spectral fragmentation patterns.

DDA (Aldrich Chemical Company), m.p. 166–168°C, *p*-chlorobenzoic acid, and *p*-hydroxybenzoic acid (Matheson, Coleman and Bell), m.p. 215–216°C, were purified by dissolving in excess 0.1 *M* potassium carbonate solution. Each solution was filtered and extracted twice with benzene. The aqueous layer was acidified with aqueous hydrochloric acid, filtered, and the precipitated acid washed with water and dried under vacuum. *p,p'*-Dichlorobenzilic acid (DBA) was prepared as described by Leffingwell and Crosby (1978). DCB (Heyden Newport Chemical Co.) was recrystallized twice from benzene, m.p 144–146°C; bis (*p*-chlorophenyl) methane (DDM) (Eastman Organic Chemicals) was recrystallized three times from methanol, m.p. 52.5°C; and p,p'-dichlorobenzhydrol (DDOH) (Aldrich Chemical Company) was recrystallized three times from ethanol, m.p. 90.5–91.5°C. *p*-Chlorobenzaldehyde (Matheson, Coleman, and Bell), *p*-chlorophenol (Eastman Organic Chemicals), and ethyl *p,p'*-dichlorobenzilate (Ciba-Geigy chlorobenzilate, technical grade, 98%) were used as received.

Methanol (Burdick and Jackson Laboratories) mixtures with demineralized water were used as the eluting solvent for HPLC.

Irradiation

Solutions for irradiation were prepared by dissolving or suspending the desired compound (100-200 mg/L) in distilled water containing enough sodium hydroxide to provide an initial pH of approximately 8.0.

Two types of experiments were conducted. In one series, each of the test compounds was individually stirred and aerated in 1-L Erlenmeyer flasks exposed to late summer or fall sunlight (Davis, CA) for periods of 10 to 60 days. In some instances, the flasks were stoppered to retain volatile photoproducts, while others were covered with a watch glass taped in position. These long experiments in sunlight were not accompanied by dark controls.

A companion series was irradiated in the laboratory in 1-L Erlenmeyer flasks exposed to the continuous irradiation from a 275 W General Electric RS Sunlamp placed 4 cm from the flask. Both types of exposure lasted from 24 to 137 hr. In one instance, a DDA solution was irradiated for two weeks in a sunlight-simulating photoreactor (Crosby and Tang 1969c) with an 8W BL fluorescent blacklight (peak intensity near 340 nm).

Extractions

Following irradiation, aqueous photolysates were separated into acidic, phenolic, and neutral fractions. Neutrals and phenols were removed by buffering the photolysate with $NaHCO_3$ and extracted with chloroform; acids were extracted into chloroform from the remaining aqueous fraction after acidification with HCl; phenols were separated from the neutrals by extracting the chloroform solution with NaOH. The acidified fraction was reextracted, evaporated to dryness under nitrogen, and redissolved in methanol for photoproduct identification and quantification with HPLC.

Table 1. HPLC Retention times of DDA and related compounds[a]

Compound	Solvent system (methanol:water)	Flow rate (ml/min)	Retention time (minutes: seconds)
p-Hydroxybenzoic acid	75:25	1.0	1:48
Benzoic acid	75:25	1.0	1:57
4,4′-Dichlorobenzilic acid (DBA)	75:25	1.0	2:00
p-Chlorobenzoic acid	75:25	1.0	2:15
Phenol	75:25	1.0	2:25
DDA	75:25	1.0	2:35
p-Chlorophenol	75:25	1.0	2:45
p-Chlorobenzaldehyde	75:25	1.0	3:07
p,p′-Dichlorobenzhydrol (DDOH)	75:25	1.0	5:12
4,4′-Dichlorobenzophenone (DCB)	75:25	1.0	6:30
bis(*p*-Chlorophenyl) methane (DDM)	75:25	1.0	10:20
p-Hydroxybenzoic acid	30:70	1.0	2:20
Benzoic acid	30:70	1.0	2:50
p-Chlorobenzoic acid	30:70	1.0	4:30
p-Hydroxybenzoic acid	40:60	0.8	2:07
Benzoic acid	40:60	0.8	2:30
p-Chlorobenzoic acid	40:60	0.8	3:00

[a] 30 cm Bonapak C_{18} reverse-phase column

Analytical Systems

DDA and its photoproducts were analyzed on a Waters Associates High Pressure Liquid Chromatograph equipped with a Model 440 UV absorbance detector and a 30 cm Waters Bondapak C_{18} reverse-phase column. The solvent system for gross separations consisted of 75:25 (v/v) methanol-water filtered through a 0.5 μ Millipore FH filter. The various acids were separated with 30:70 or 40:60 (v/v) methanol-water, with flow rates varying from 0.8 to 1.0 ml/min (Table 1). Since these systems easily separated all but the polar (largely unidentified) photoproducts, identification was usually established by comparison of retention times for two or more solvent combinations of methanol and water with those of authentic specimens or by gas chromatography-mass spectrometry (GCMS) where feasible.

Several polar photoproducts were isolated by HPLC, their solutions taken to dryness with a rotary evaporator, and the residues methylated with ethereal diazomethane prepared from *N*-methyl-*N*-nitroso-*p*-toluene-sulfonamide (Aldrich Chemical Company) according to manufacturer's directions.

Mass spectra were measured on a Finnigan Model 3200 Gas Chromatograph Mass Spectrometer equipped with a Finnigan Model 9500 gas chromatograph and 1.5 m × 6 mm id glass column containing 5% OV-17 on 60/80 mesh Chromosorb G, temperature-programmed from 75° to 250°C at 10°C/min.

Material Balance

A DDA photolysis experiment of 137 hr was designed to provide a total accounting of products. DDA (1000 mg) was dissolved in 1.0 L of distilled water and adjusted to pH 8.0 with NaOH. The round-bottom 2-L flask used in the experiment was positioned four cm from a 275 W General Electric Model RS sunlamp and cooled with an electric fan. The system was closed and swept at 5 L/hr with an air stream previously passed through two fritted-glass air scrubbers which contained 200 ml each of 5 *M* NaOH to remove all carbon dioxide. Volatile organics were collected on a 3.0 g column of Amberlite XAD-4 polystyrene granules, 20/50 mesh, inserted in the exhaust air stream.

In the final stage, the air was passed through a fritted air scrubber which contained 150 ml of 0.5 *M* barium hydroxide solution to collect the generated CO_2; the $BaCO_3$ precipitate was dried and weighed. Photoproducts which remained in solution were measured as described above.

Results

Repeated attempts to separate and quantitate DDA photoproducts by gas chromatography and electron-capture detection generally proved unsatisfactory because of their polarity and instability. However, HPLC proved to be ideal for this purpose in that the parent compounds and their photoproducts could be identified and quantified directly from the aqueous photolysates or from methanol solutions of the isolates and standards.

The photodecomposition of aqueous solutions of DDA was rapid under laboratory conditions and slow in fall sunlight (Table 2). A 20-L borosilicate glass bath which contained 12 L of water and 500 mg of DDA retained 45% of the original DDA after six weeks of outdoor exposure to October-November sunlight. The indoor photoreactor (8 W fluorescent blacklight) decomposed 99.5% of the DDA in two weeks of continuous irradiation, while an earlier study in a similar 40 W blacklight photoreactor indicated that DDA had a half-life of 12 to 14 hr (Figure 2).

In most instances, DCB was the principal product and amounted to as much as 23% of the starting material at one point. It formed rapidly in both sunlight and UV light, with insoluble crystals appearing within two hr in the latter case. However, both it and the similarly stable *p*-chlorobenzaldehyde were easily lost by volatilization from the surface of the reaction mixture, and 55% of the aldehyde produced in an aerated photolysis experiment was recovered as vapor during a period of 5.5 days. Both DCB and *p*-chlorobenzaldehyde were identified as photoproducts of DDA by GCMS.

DDM was rapidly converted to DCB in either UV or sunlight, as well as in the dark, and chlorobenzilate also was converted to DCB with UV. DCB proved to be resistant to photodegradation but gradually produced *p*-chlorobenzoic acid and small quantities of unidentified acids and phenolics. DDA, DBA and DDOH gave rise to DCB, *p*-chlorobenzaldehyde, and a group of polar photoproducts.

p-Chlorobenzaldehyde was slowly converted to *p*-chlorobenzoic acid under intense laboratory UV and very slowly in sunlight. With either light source, *p*-chlorobenzoic acid solutions soon became bright- and then dark-yellow, perhaps as a result of the formation of quinones. As expected (Crosby and Leitis 1969a), *p*-hydroxybenzoic and benzoic acids also were seen as photoproducts of *p*-chlorobenzoic acid. Similarly, *p*-chlorophenol solutions became yellow under intense UV, resulted in substantial quantities of unidentified acids and phenolics, and probably included phenol and hydroquinone (Crosby and Wong 1973). The yellow color was probably due to quinone production.

Quantitation of the photoproducts revealed the ease with which DDA decomposed in the presence of water and UV light. Table 2 compares the results of five DDA photolysis experiments, all conducted in different ways. The most complete degradation took place with fluorescent blacklight during 14 days of exposure, and this was the only experiment which produced measurable quan-

Table 2. Summary of DDA photolysis

Irradiation	Time (Days)	DDA (mMoles)	Conc. (mM)	Recovery (mMoles)[a]							
				DDA	DCB	CBZ	CBA	HBA	BZA	Total	%
Sun (open)	44	1.780	0.15	0.811	0.092	ND	0.002	T[b]	ND	0.905	51
Sun (closed)	45	0.178	0.35	0.071	0.043	0.010	T	ND	ND	0.124	70
Sun (open)	58	0.142	0.35	0.038	0.022	0.008	T	ND	ND	0.068	48
Sunlamp (closed)	5.5	3.557	3.56	2.668	0.263	0.038	0.039	0.002	ND	3.010	85
Blacklight (open)	14	0.096	0.35	0.000	0.009	0.002	0.013	0.001	0.008	0.033	34

[a] CBZ = *p*-chlorobenzaldehyde, CBA = *p*-chlorobenzoic acid, HBA = *p*-hydroxybenzoic acid, BZA = benzoic acid

[b] Trace

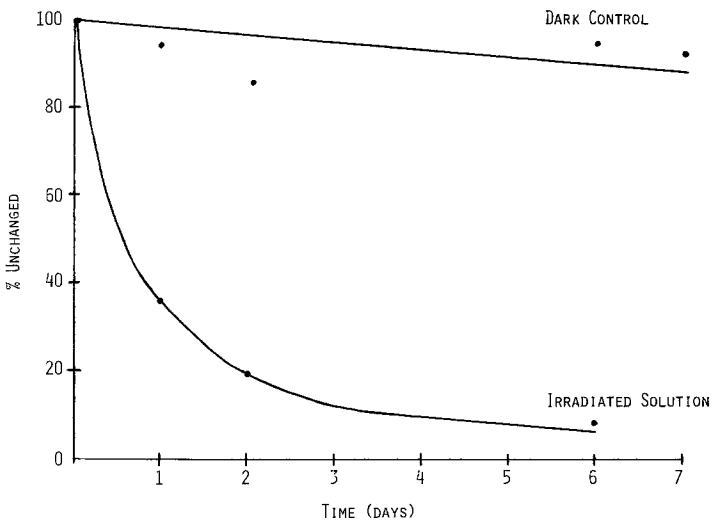

Fig. 2. Photodecomposition rate of DDA in water in a 40 W fluorescent blacklight photoreactor. (Initial Concentration 20 mg/L, 30°C.)

tities of the benzoic acid reported to be produced in 90% yield in the photolysis of *p*-chlorobenzoic acid in a similar apparatus (Crosby and Leitis 1969a). One experiment, which attempted to account for the lost DDA, resulted in a material balance of 85%; CO_2 (collected as $BaCO_3$) represented 33% of the amount expected from complete loss of the DDA carboxyl group, but, as 75% of the initial DDA was recovered unchanged, more extensive breakdown of the photoproducts may have occurred.

Sampling at 30-minute intervals, followed by direct injection into HPLC, showed the formation of DCB, *p*-chlorobenzaldehyde, and unidentified polar products within the first sampling period. During the complete breakdown of DDA, there would typically appear three peaks, the first representing a mixture of polar materials (P), a second *p*-chlorobenzaldehyde (CBZ), and a third DCB (Figure 3). The results from both sunlamp and sunlight irradiations differed somewhat, but this was probably due to a loss of volatile materials and the quantities of the lesser photoproducts produced in the sunlight. Refined HPLC analysis demonstrated that four of the early polar products were *p*-chlorobenzoic acid, *p*-hydroxybenzoic acid, benzoic acid, and *p*-chlorophenol. Other products sought but not detected in the first peak were phenol, benzoquinone, hydroquinone, benzaldehyde, maleic acid, chloromaleic acid, *p*-chloroperbenzoic acid, and dihydroxybenzoic acid; certain compounds in this group may be transient products in the complex set of reactions, but they were never isolated in sufficient quantities to be identified.

To determine a sequence in which such products might be formed, similar laboratory and/or sunlight irradiation experiments were conducted with DCB and 12 other demonstrated or suspected intermediates, and the results are presented in Table 3. In attempts to resolve the unidentified polar fraction, the phenolic group from DDA photolysis in a closed system was collected from

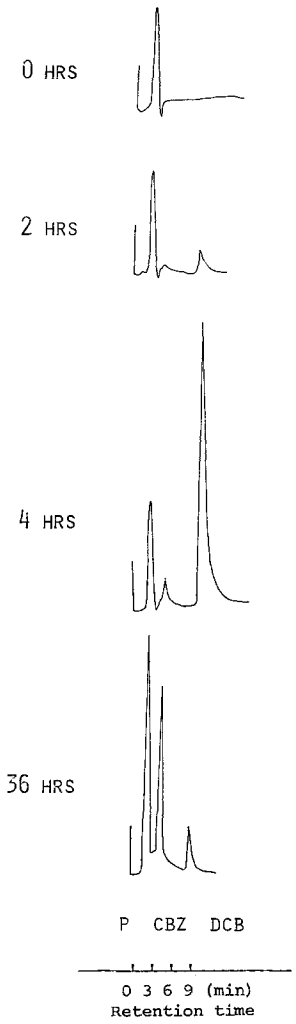

Fig. 3. Typical HPLC traces of photoproducts resulting from the irradiation of a Pyrex flask of DDA solution with a 275 W sunlamp

HPLC following repeated injections, concentrated, and methylated. Mass spectra were obtained for three compounds having respective masses of 254, 244, and 222; while isotopic clusters characteristic of chlorine were absent (so also were the M-15 and M-30 or M-31 fragments signifying *O*-methyl) and the compounds remain unidentified. However, other compounds in this same group yielded spectra which indicated oils, phthalate esters, and other photoproducts.

Discussion

DDA is among the most water-soluble of DDT derivatives, and it readily dissolves at the alkaline pH common to most natural waters. Unlike DDT or DDE, it does not volatilize from water under these conditions but tends to be ex-

Table 3. Summary of photolysis products

Compound irradiated	Products						
	DCB	CBZ[a]	CBA	HBA	BZA	Unidentified polar products	Unidentified neutrals
p,p'-Dichlorobenzilic acid	X	X				X	X
p,p'-Dichlorobenzhydrol	X	X				X	
bis(*p*-Chlorophenyl) methane	X					X	
p,p'-Dichlorobenzophenone						X	
Chlorobenzilate	X					X	
p-Chlorobenzaldehyde			X				X
Benzaldehyde					X		
p-Chlorophenol						X	
Benzoic acid	Stable						
p-Hydroxybenzoic acid	Stable						
p-Chlorobenzoic acid				X		X	
Hydroquinone						X	
Benzoquinone						X	

[a] See Table 2 for abbreviations

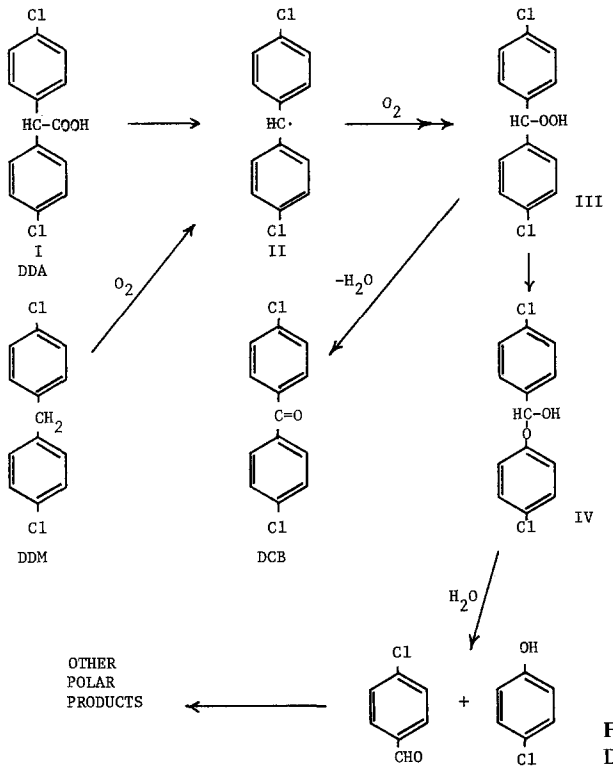

Fig. 4. Proposed mechanism of DDA photodecomposition

tracted from soil, sewage sludge, excreta, or other substrates as it is formed. Thus, the effect of light on alkaline solutions of DDA has particular significance to the environmental fate of DDT. Because direct photoreaction is slow, it would not be surprising to find that the reaction is accelerated by photosensitizers in natural waters.

DDA was photolyzed to DCB, *p*-chlorobenzaldehyde, and *p*-chlorophenol, and these conversions may be rationalized by known reaction mechanisms (Figure 4): (1) photochemical generation of the bis(*p*-chlorophenol) methyl radical, II (Joschek and Grossweiner 1966) (2) reaction of this radical with dissolved oxygen and formation of the hydroperoxide III by H-abstraction (Crosby and Tang 1969d; Crosby and Leitis 1969b) (3) dehydration of III to DCB (Kornblum and de La Mare 1951) and, possibly, (4) rearrangement of III to the hemiacetal IV (Davies 1961), which would be hydrolyzed under our reaction conditions to *p*-chlorobenzaldehyde and *p*-chlorophenol.

The photodecomposition of several other environmental degradation products of DDT, including DDM, DDOH and DBA (V) was examined under the same conditions. Despite a careful search for other products, DDM gave only DCB and did so even in the dark. As the intermediate hydroperoxide (III) generated from DDM would be the same as the one predicted above from DDA (Hock and Lang 1944), the absence of aldehyde places the mechanism of Figure 4 in doubt.

Both 4,4′-dichlorobenzylic acid and DDOH underwent photolysis even more rapidly than did DDA, and all three provided the same analytical results suggesting a common intermediate. Formation of 1-hydroxyhydroperoxide represents one possible intermediate (Brown *et al.* 1955), and the decomposition reactions in alkaline solution which would convert it to DCB as well as to *p*-chlorobenzoic acid and *p*-chlorophenol are well documented (Davies 1961). However, the formation of *p*-chlorobenzaldehyde remains unexplained by this mechanism.

Microbial transformation of DDA is a definite possibility when several days or weeks are involved; however, both DCB and *p*-chlorobenzaldehyde were evident in DDA solutions after only 4 to 6 hr of sunlight exposure.

DCB and *p*-chlorobenzaldehyde were both relatively stable and volatile, but, irradiated individually in a closed container to maximize reaction times, each was slowly photooxidized to *p*-chlorobenzoic acid. As expected (Crosby and Leitis 1969a), this acid formed *p*-hydroxybenzoic and benzoic acids—the stable substances we consider to be the terminal residues in DDA photodecomposition and probably the last environmentally detectable links in the long chain of DDT degradation to produce CO_2 and water.

References

Abou-Donia, M. B., and D. B. Menzel: The metabolism in vivo of DDT, DDD, and DDE in the chick by embryonic injection and dietary ingestion. Biochem. Pharmacol. **17**, 2143 (1968).

Avramoff, M., and Y. Sprinzak: Reactions of active methylene compounds in pyridine solution. V α-Hydroperoxyesters. J. Amer. Chem. Soc. **85**, 1655 (1963).

Bowery, T. G., P. E. Gatterdam, F. E. Guthrie, and R. L. Rabb: Metabolism of insecticide residues, fate of inhaled C^{14}-TDE in rabbits. J. Agr. Food Chem. **13**, 356 (1965).

Brown, N., M. J. Hartig, M. J. Roedel, A. W. Anderson, and C. E. Schweitzer: Cycloalkanone peroxides (I) Cyclohexanone peroxide by oxidation of cyclohexanol. J. Amer. Chem. Soc. **77**, 1756 (1955).

Crosby, D. G., and E. Leitis: Photodecomposition of chlorobenzoic acids. J. Agr. Food Chem. **17**, 1033 (1969a).

Crosby, D. G., and E. Leitis: Photolysis of chlorophenylacetic acids. J. Agr. Food Chem. **17**, 1036 (1969b).

Crosby, D. G., and C. S. Tang: Photodecomposition of 3-(*p*-chlorophenyl)-1,1-dimethylurea (Monuron). J. Agr. Food Chem. **17**, 1041 (1969c).

Crosby, D. G., and C. S. Tang: Photodecomposition of 1-naphthaleneacetic acid. J. Agr. Food Chem. **17**, 1291 (1969d).

Crosby, D. G., and A. S. Wong: Photodecomposition of *p*-chlorophenoxyacetic acid. J. Agr. Food Chem. **21**, 1049 (1973).

Crosby, D. G., J. T. Leffingwell, and K. W. Moilanen: Transformations of environmental contaminants by light. Environmental Quality and Safety **4**, 175 (1975).

Davies, A. G.: Organic Peroxides. London: Butterworths (1961).

DeLoach, H. K., and D. D. Hemphill: Effect of cooking utensil composition and contents on reductive dechlorination of DDT to DDD. J. Assoc. Off. Anal. Chem. **54**, 1352 (1971).

Engst, R., and M. Kujawa: Enzymic decomposition of DDT by a fungus. II. The course of enzymic DDT decomposition. Nahrung **11**, 751 (1967). (Chem. Abs. **68**. 7442 (1968)).

Guenzi, W. D., and W. E. Beard: Anaerobic conversion of DDT to DDD and aerobic stability of DDT in soil. Soil Sci. Soc. Amer. Proc. **32**, 522 (1968).

Hock, H., and S. Lang: Autoxydation von Kohlenwasserstoffen, IX Mitteil: Über Peroxyde von Benzol-Derivaten. Ber. **77B**, 257 (1944).

Horning, E. C., ed: Organic synthesis, Coll. Vol. III. p. 270. London: John Wiley and Sons (1967).

Joschek, H. I., and L. I. Grossweiner: Optical generation of hydrated electrons from aromatic compounds. II. J. Amer. Chem. Soc. **88**, 3261 (1966).

Kornblum, N., and H. E. De La Mare: The base catalyzed decomposition of a dialkyl peroxide. J. Amer. Chem. Soc. **73**, 880 (1951).

Leffingwell, J. T., and D. G. Crosby: Private Communication (1978).

Menzie, C. M.: Metabolism of pesticides. Special report. Wildlife No. 127, U.S. Dept. Interior, Bur. Sport Fisheries and Wildlife, Washington, DC (1969).

Menzie, C. M.: Metabolism of pesticides—an update. Special Scientific Report. Wildlife No. 184, U.S. Dept. Interior, Fish and Wildlife Service. Washington, DC (1974).

Perry, A. S., S. Miller, and A. J. Buckner: The enzymatic *in vitro* degradation of DDT by susceptible and DDT-resistant body lice. J. Agr. Food Chem. **11**, 457 (1963).

Pfaender, F. K., and M. Alexander: Extensive microbial degradation of DDT *in vitro* and DDT metabolism by natural communities. J. Agr. Food Chem. **20**, 842 (1972).

Plapp, F. W., Jr., G. A. Chapman, and J. W. Morgan: DDT resistance in *Culex tarsalis* Coquillet: cross resistance to related compounds and metabolic fate of C^{14}-labelled DDT analog. J. Econ. Entomol. **58**, 1064 (1965).

Plimmer, J. R., U. I. Klingebiel, and B. E. Hummer: Photooxidation of DDT and DDE. Science **167**, 67 (1970).

Rowlands, D. G., and C. J. Lloyd: DDT metabolism in susceptible and pyrethrin-resistant *Sitophilus granarius* (L.) (Coleoptera, Curculioninae). J. Stored Prod. Res. **5**, 413 (1969).

Singh, J., and M. Malaiyandi: Dechlorination of *p,p'*-DDT in aqueous media. Bull. Environ. Contam. Toxicol. **4**, 337 (1969).

Vinson, S. B., and J. R. Brazzel: The penetration and metabolism of C^{14}-labeled DDT in resistant and susceptible tobacco budworm larvae, *Heliothis virescens* (F.) J. Econ. Entomol. **59**, 600 (1966).

Wedemeyer, G.: Dechlorination of DDT by *Aerobacter aerogenes*. Science, **152**, 647 (1966).

Woodwell, G. M., P. P. Craig, and H. A. Johnson: DDT in the biosphere: Where does it go? Science, **174**, 1101 (1971).

Zimmer, M., and W. Klein. Beitrage zur Okologischen Chemie-XXXVII. Ruckstandsverhalten und Umwandlung von *p,p'*-DDT-^{14}C und seiner Analogen *p,p'*-DDD-^{14}C in hoheren Pflanzen. Chemosphere **1**, 3 (1972).

Manuscript received November 24, 1978; accepted May 31, 1979.