Degradation in Soils of Ciodrin, an Organophosphate Insecticide

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The rates of ciodrin degradation in soils followed first-order kinetics and were related to the extent of initial insecticide adsorption by the soils. Rates of the reactions were slower in electron-beam-sterilized soils; however, this rate decrease was due to decreased ciodrin adsorption resulting from the irradiation treatment and not from retardation of microbial degradation processes. First-order rate constants for ciodrin degradation were related directly to adsorption and were the same for sterile and nonsterile soils for constant adsorption in a given soil. Between soils, even at constant adsorption, the rates of ciodrin degradation were variable, ranging from a $t_{1/2}$ value of 2.0 hours in a Poygan silty clay loam (66% adsorption) to 71 hours in an Ella loamy sand (53% adsorption). In aqueous soil-free systems $t_{1/2}$ values for ciodrin degradation were 180, 410, and 540 hours at pH 9, 6, and 2, respectively.

The ready susceptibility of organophosphate insecticides to degradation has contributed recently to their increasing agricultural use. This increase is based partly on the implication that the rapid degradation of these compounds minimizes residue problems. Little information is available on general mechanisms and specific products of degradation and the possibility of the accumulation of toxic residues persists. Certain organophosphates are known to degrade by both chemical and microbial pathways. The degradation of diazinon is principally by chemical hydrolysis (Konrad *et al.*, 1967), while malathion has been observed to degrade by both chemical and microbial means (Hindin, 1963; Matsumura and Boush, 1966). Earlier investigations on the soil degradation of diazinon have shown adsorption on the clay and organic colloids of the soil to be the major catalyst in degradation (Konrad *et al.*, 1967). Other factors which can affect the rates of hydrolysis and types of hydrolytic products formed from organophosphate insecticides are temperature, pH, and the ionic strength of the system. The most important perhaps is pH (Faust and Suffet, 1966).

This investigation was initiated to determine the mechanisms and products of degradation of ciodrin, α-methylbenzyl 3-(dimethoxyphosphinyloxy) *cis*-crotonate, in soils and water.

MATERIALS AND METHODS

The three soils used are described briefly in Table I.

Analytical grade ciodrin and ciodrin labeled with ^{14}C in the *O*-methyl position were obtained from the Shell Development Co.

Analytical procedures were similar to those employed for measurement of diazinon degradation in soil suspensions (Konrad *et al.*, 1967). These methods involved extraction with benzene and verification by gas chromatography that the ^{14}C-activity extracted arose entirely from ciodrin. Occurrence of water-soluble degradation products was determined as the difference between total and benzene-extractable ^{14}C-activity.

Other Methods. Hydrolysis reactions in aqueous systems were conducted at pH 2.0 and 9.0 by adjustment of pH with HCl and NaOH; aqueous solutions remaining after benzene extraction were extracted with 1-butanol at pH 3.5 and 0.5 by adjustment of the pH with HCl; and extent of microbial degradation was determined by comparison of nonsterile soils with soils sterilized by electron beam irradiation using 5×10^6 rads (Midwest Irradiation Center, Rockford, Ill.). Sterility was checked by plating the soils on soil extract agar (Allen, 1959) and streptomycin–rose bengal media (Martin, 1950).

RESULTS AND DISCUSSION

Aqueous ciodrin solutions (200 ml.; 5 p.p.m.) equilibrated with sterile and nonsterile Poygan sicl (pH 7.2), Kewaunee c (pH 6.4), and Ella ls (pH 3.8) soil samples (50 grams each) showed a very rapid initial decrease in ciodrin concentration resulting from adsorption (Figures 1 and 2). Following the initial decrease due to adsorption, the solution concentration of ciodrin continued to decrease at a somewhat slower rate because of degradation. Values of intact ciodrin remaining for early stages of incubation are included in Figure 2; however, because of the number of points and their close proximity to the ordinate they were omitted from Figure 1 and are presented in Table II. Following the initial rapid decrease in ciodrin concentration during the early stages of incubation, a distinct decrease in the slopes of the first-order plots is evident (Table II and Figures 1 and 2). This change in slope is attributed largely to a shift of the principal process occurring from one of adsorption to one of degradation. Since the rates of both adsorption and degradation are so rapid, quantitative determination of the inflection point, where the rate change due to degradation occurs, is difficult to obtain. For this reason the extent of adsorption was measured by extrapolating the degradation curves to zero time and using this to account for adsorption. This value in all cases was less than the total ciodrin adsorption. However, because of the rapid rate of ciodrin degradation in the Poygan and Kewaunee soil systems, it is conceivable that adsorption and degradation occur concurrently in the initial stages

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Table I. Half Lives and First-Order Rate Constants for Ciodrin Degradation in Soils as Related to Adsorption

Soil Sterility	Clay Content, %	Organic Matter Content, %	pH	Adsorption, %	$t_{1/2}$, Hr.	k, Hr.$^{-1}$	Ratio k-Adsorption
				Poygan Silty Clay Loam			
Nonsterile	33.6	10.0	7.2	66	2.00	0.346	526×10^{-5}
Sterile	33.6	10.0	7.2	34	3.75	0.185	544×10^{-5}
				Kewaunee Clay			
Nonsterile	48.7	3.8	6.4	60	5.50	0.126	210×10^{-5}
Sterile	48.7	3.8	6.4	54	6.00	0.115	213×10^{-5}
				Ella Loamy Sand			
Nonsterile	5.2	1.6	3.8	53	71.0	0.0098	18.8×10^{-5}
Sterile	5.2	1.6	3.8	42	77.0	0.0090	21.4×10^{-5}

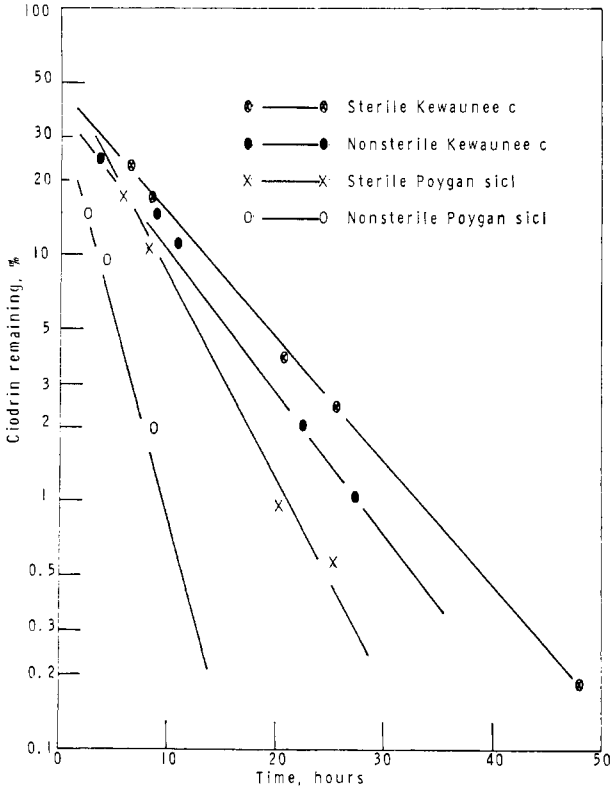

Figure 1. Rates of ciodrin degradation in nonsterile and sterile samples of a Poygan silty clay loam and a Kewaunee clay

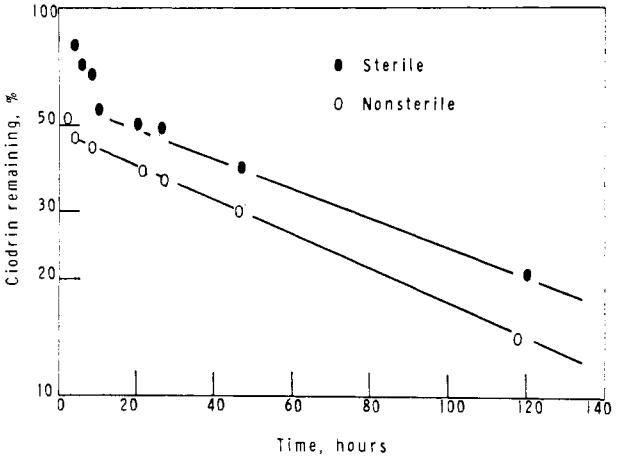

Figure 2. Rates of ciodrin degradation in nonsterile and sterile samples of an Ella loamy sand

of incubation and a true measure of the adsorption equilibrium is impossible to obtain. This pattern of adsorption and degradation is similar to that observed for diazinon (Konrad *et al.*, 1967).

Intact ciodrin was extracted from aqueous samples with benzene and the amount of water-soluble degradation products was taken to be equivalent to the ^{14}C-activity remaining in the aqueous phase following benzene extraction. Following the initial decrease due to adsorption the ^{14}C-activity in the aqueous solutions increased continuously until at the termination of the experiment all of the added ^{14}C-activity was accounted for in water-soluble degradation products. No loss of ^{14}C-activity was observed in any of the soil systems. Thus, following adsorption, ciodrin degradation products were released into the solution and were not themselves adsorbed. For all three soils, the amount of remaining intact ciodrin and ^{14}C-activity in the benzene extracts was the same at each stage of degradation, indicating that no ^{14}C-labeled benzene-soluble degradation products accumulated in the system.

The linearity obtained by plotting remaining intact ciodrin on a logarithmic scale against time on a linear scale showed that ciodrin degradation in soils proceeded by first-order kinetics. Representation of the rate of a first-order reaction is by half lives. The half lives of ciodrin in the soil systems used are shown in Table I. The half-life values are based on the disappearance of ciodrin from solution and do not take into account any

Table II. Intact Ciodrin Remaining in Solution in Soil Systems for Early Stages of Incubation

Incubation Time, Hr.	% Intact Ciodrin Remaining in Solution					
	Poygan sicl		Kewaunee c		Ella ls	
	Sterile	Nonsterile	Sterile	Nonsterile	Sterile	Nonsterile
0.50	92.8	75.5	88.4	84.0	96.0	89.6
1.00	71.6	43.1	61.7	65.3	86.5	75.4
2.00	51.3	15.0	51.2	...	78.7	50.8
3.75	...	9.2	...	23.5	...	46.0

secondary reactions involving intermediate or final products in solution.

In each of the three soil systems, the rate of ciodrin degradation was related to the extent of initial adsorption. The first-order rate constant for atrazine degradation ($k = 0.693/t_{1/2}$) is directly proportional to the extent of initial atrazine adsorption (Armstrong and Chesters, 1968). The ratio of k to initial ciodrin adsorption was determined for the three soil types on nonsterile and sterile samples which had been sterilized by electron-beam irradiation. The result of sterilization was to decrease markedly the adsorptive capacity of the soil for ciodrin, probably resulting from changes in the extractability of soil organic carbon following irradiation sterilization (Cawse, 1967; Salonius *et al.*, 1967). Thus, if the ratio of k to adsorption is constant for the sterile and nonsterile samples of a particular soil, it would imply that for a given soil k is directly proportional to the extent of ciodrin adsorption. From Table I the constancy of the k-adsorption ratio can be seen. However, this value varies greatly between soil types, indicating that if the extent of adsorption is the same for different soil types the rate of ciodrin degradation between soils may vary considerably. For example, the $t_{1/2}$ value and k-adsorption ratio show that the rate of degradation of ciodrin in the Ella soil is approximately one twentieth of that in the Poygan soil even for the same extent of adsorption in the two soils. The differences in rates of degradation between the Ella and Poygan soils at the same adsorption value may be due to several factors. The high acidity of the Ella soil systems probably retards the rate of degradation. The adsorption sites on the Ella soil may be different from those of the Poygan soil and are not so effective in the catalysis of ciodrin degradation. However, as is most likely, the Ella system has sufficient acidity that the acid groups of the soil organic matter remain protonated, whereas many of these groups are likely to be dissociated in the Poygan and Kewaunee soils and the mechanism of adsorption in the Ella soil is different than in the other two soils.

From the structure of ciodrin (Figure 3), hydrolysis of the two carboxyl ester linkages is the most likely mechanism of degradation. When this hypothesis is used as a model, two different pathways of degradation are possible, depending upon the relative rates of hydrolysis of the two ester linkages (Figure 3). Complete hydrolysis of ciodrin—i.e., hydrolysis of both ester linkages—

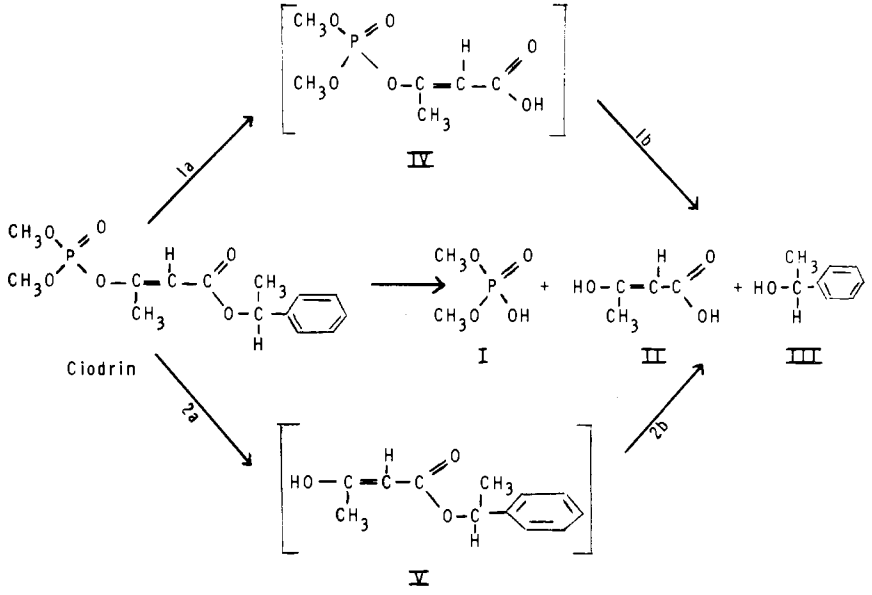

Figure 3. Hypothesized ciodrin degradation pathways

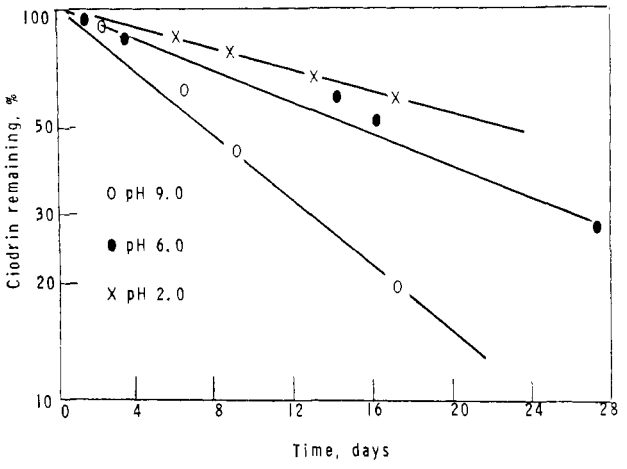

Figure 4. Effect of pH on ciodrin hydrolysis in aqueous systems

results in the formation of degradation products I, II, and III. In pathway 1, if reaction 1b is slower than 1a, intermediate IV will accumulate. Similarly, if reaction 2b is slower than 2a, product V will accumulate. The possibility of hydrolysis of the P-O-C bonds of the ciodrin methoxyl groups also exists. However, upon benzene extraction of the partially degraded ciodrin only intact ciodrin was found in the extract, indicating that no ^{14}C-methanol was formed in the reaction. This agrees with the observation that the alkoxyl groups of diazinon are resistant to hydrolysis (Konrad *et al.*, 1967). Furthermore, the extraction of inorganic phosphates from soils is usually accomplished in acid systems, on the basis that the organophosphate fraction will be neither extracted nor transformed during the procedure (Mehta *et al.*, 1954).

Since hydrolytic reactions can be catalyzed by acid and/or alkali, an investigation was conducted to determine the effect of pH on ciodrin hydrolysis in aqueous soil-free systems (Figure 4). Ciodrin hydrolysis is most rapid in alkaline systems and acidity has an inhibitory effect on the reaction.

The $t_{1/2}$ values for ciodrin hydrolysis at pH 2.0, 6.0, and 9.0 are 540, 410, and 180 hours, respectively. Comparison of these half lives with those obtained in soil systems shows that at pH values near neutrality the rates of degradation in soil systems are approximately two orders of magnitude greater than in the soil-free aqueous systems at pH 6.0. Thus, a mechanism other than pH must prevail in order to explain the much greater rate of ciodrin degradation in soils. Benzene extracts of the soil-free aqueous systems and soil systems were very similar—i.e., all the ^{14}C-activity could be accounted for as intact ciodrin and the reactions approximated first-order kinetics.

Because hydrolysis of both carboxylic ester linkages is likely, an intermediate probably is produced which might accumulate in the systems. Both product I and intermediate IV can exist simultaneously and cannot be distinguished solely on the basis of benzene extractability of ^{14}C-label. It is necessary to distinguish between product I and intermediate IV to establish the complete pathway of ciodrin degradation. If the presence of intermediate IV can be established in both

Table III. Extractability of ^{14}C Degradation Products of Ciodrin with 1-Butanol at pH 3.5 and 0.5

Ciodrin Degradation, %	Intact Ciodrin, %	1-Butanol Extractability, %		Ratio of Butanol Extractability, pH 3.5 to pH 0.5
		pH 3.5	pH 0.5	
		Poygan Silty Clay Loam, Nonsterile		
50.5	49.5	19.2	9.0	2.13
100.0	0.0	3.7	64.5	0.058
		Kewaunee Clay, Nonsterile		
55.2	44.8	13.7	12.7	1.08
91.0	9.0	9.6	57.3	0.17
		Ella Loamy Sand, Nonsterile		
55.1	44.9	20.5	16.2	1.27
85.3	14.7	17.9	24.2	0.74
		Aqueous Solution at pH 2.0		
30.0	70.0	13.7	9.0	1.52
39.4	60.6	11.2	9.8	1.14
		Aqueous Solution at pH 6.0		
25.4	74.6	7.6	4.7	1.62
72.8	27.2	17.4	31.2	0.56

the soil-free aqueous and soil systems, it can be concluded that pathway 1 is the predominant means of ciodrin degradation. If, however, intermediate IV cannot be established in these systems, the reaction proceeds either by hydrolysis of both carboxylic ester linkages at equal rates or by pathway 2 and intermediate V would accumulate. The presence of intermediate V cannot be established in these systems because of the position of the ^{14}C-label.

Both degradation product I and intermediate IV have acidic characteristics and partition between water and 1-butanol differently, depending on the pH of the system. One pH unit below its pK_A value, an acid will be sufficiently protonated to allow 90% to partition into 1-butanol. The estimated pK_A values of degradation product I and intermediate IV are 2.1 (by comparison to phosphoric acid) and 4.5 (by comparison to crotonic acid), respectively. Based on these estimated pK_A values, separation should be achieved by sequential extraction with 1-butanol at pH 3.5 and 0.5. The 1-butanol extractions were preceded by benzene extraction at pH 7 to remove intact ciodrin remaining in the system. At pH 3.5, intermediate IV will partition into 1-butanol, while at pH 0.5 degradation product I, along with any intermediate IV not extracted at pH 3.5, will partition into the butanol. Table III shows the results of 1-butanol extraction at pH 3.5 and 0.5 and the ratio of pH 3.5- to pH 0.5-extractable ^{14}C-activity. In all systems, as the extent of degradation increases—i.e., the amount of intact ciodrin remaining, as determined by benzene extraction, decreases—the ratio of pH 3.5- to pH 0.5-extractable ^{14}C-activity decreases. This ratio is a measure of the accumulation of intermediate IV, and is smallest in systems where the rate of degradation is rapid (Poygan and Kewaunee soil systems) or where the extent of degradation is more complete, indicating that there is little accumulation of intermediate IV in these systems. In the Ella soil and the soil-free aqueous systems the rate of degradation is slow enough to allow accumulation of IV, as shown by the higher values for the ratio of pH 3.5- to pH 0.5-extractable ^{14}C-activity at levels of ciodrin degradation similar to those found in the Poygan and Kewaunee soils. This change in the ratio pH 3.5- to pH 0.5-extractable ^{14}C-activity as degradation progresses is evidence of the presence of intermediate IV in both the soil-free aqueous and soil systems. Thus, pathway 1 apparently is the predominant pathway of ciodrin degradation in both soils and water. Further evidence that ciodrin degradation proceeds by pathway 1 is shown by the presence of small amounts of 3(methoxyphosphinyloxy) crotonic acid (intermediate IV) as a metabolite in the blood of goats sprayed with ciodrin (Chamberlain, 1964).

Thus, dimethylphosphoric acid (product I, Figure 3), *cis*-hydroxycrotonic acid (product II), and 1-phenylethanol (product III) are the final degradation products of ciodrin degradation in soils. The stability of the final products and of intermediate IV which accumulates to various extents in soils raises the question as to whether the effective toxicity of ciodrin is due to the parent compound or to a combination of ciodrin with its intermediate and/or final degradation products.

LITERATURE CITED

Allen, O. N., "Experiments in Soil Bacteriology," p. 5, Burgess Publishing Co., Minneapolis, 1959.
Armstrong, D. E., Chesters, G., *Environ. Sci. Technol.* **2,** 683 (1968).
Cawse, P. A., *J. Sci. Food. Agr.* **18,** 389 (1967).
Chamberlain, W. F., *J. Econ. Entomol.* **57,** 329 (1964).
Faust, S. D., Suffet, I. H., *Residue Revs.* **15,** 44 (1966).
Hindin, E., "Analysis of Organic Pesticides by Gas Chromatography," Washington State University, Final Progress Report to PHS Grant No. WP–00215, 1963.
Konrad, J. G., Armstrong, D. E., Chesters, G., *Agron. J.* **59,** 591 (1967).
Martin, J. P., *Soil Sci.* **69,** 215 (1950).
Matsumura, F., Boush, G. M., *Science* **153,** 1278 (1966).
Mehta, N. C., Legg, J. O., Goring, C. A. I., Black, C. A., *Soil Sci. Soc. Am. Proc.* **19,** 443 (1954).
Salonius, P. O., Robinson, J. B., Chase, F. E., *Plant Soil* **27,** 239 (1967).

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