Adsorption and Transformation of Four Substituted Anilines in Soil

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^{14}C-labeled substituted anilines were added to soil, and their adsorption and transformation were followed by trapping of volatile products and analysis of the residual radioactivity. If autoclaved and nonautoclaved soils were treated with anilines and incubated for 6 weeks, no CO_2 evolution could be determined from autoclaved soil, but in the nonautoclaved samples CO_2 could be detected in an amount of 7.5, 20.0, 7.6, and 8.4% of the originally applied radioactivity for 4-chloroaniline, 4-chloro-*o*-toluidine, 4-isopropylaniline, and 2,6-dimethylaniline, respectively. Binding to soil varied between 34 and 66% after 24 h of incubation for variously substituted anilines, but after 6 weeks incubation the range of binding between the anilines varied only slightly. However, TLC analysis of the methanolic Soxhlet extract and subsequent extraction by the Bleidner method indicated the formation of different transformation products. Acylation appears to occur easily in soil, as was shown by the isolation and identification of 4-isopropylformanilide and *N*-acetyl-2,6-dimethylanilide from the corresponding anilines.

Many pesticides are degraded to anilinic compounds whose fate in soil and other environments is only partially clarified. If anilines are applied to soil, the greater portion of them is apparently bound by both physical and chemical adsorption. As demonstrated with 3,4-dichloroaniline, it is very difficult to extract the anilines from soil by organic solvents or to obtain their release by acid and alkaline hydrolysis (Chisaka and Kearney, 1970; Bartha, 1971). It seems that anilines are bound to humus or soil organic matter rather than to clay particles (Hsu and Bartha, 1974a).

Several different biological transformation reactions of anilines such as acylation (Tweedy et al., 1970), polymerization (Bartha and Pramer, 1967), and oxidation of the amine to a nitro group (Kaufman et al., 1973) have been described, but a pathway of complete biodegradation has not yet been elaborated. Since anilines are easily bound to soil, the significance of biological participation in the transformation and degradation constitutes a complex problem. Hsu and Bartha (1974b) investigated the biological effects on humus-bound 3,4-dichloroaniline and found that $^{14}CO_2$ is released under aerobic conditions at the rate of 1%/week. In an additional study they concluded that the hydrolyzable portion of the humus-bound radioactive material resulting from 3,4-dichloroaniline degraded at a much faster rate than the residue which they characterized as nonhydrolyzable (Hsu and Bartha, 1976).

In the present study the fate of four pesticide-related anilines was followed in nonautoclaved and autoclaved soil.

MATERIALS AND METHODS

Materials. The origin of the radiolabeled anilines, the position of labeling, and the specific radioactivity are found in Table I. For the incubation experiments the ^{14}C-labeled anilines were diluted with nonlabeled material to a specific radioactivity of 3.3 μCi/mg.

The soil used in these experiments was obtained from Stein (Aargau, Switzerland) and had the following characteristics: pH 7.5 and organic matter, sand, silt, and clay contents of 3.4, 36.6, 28.2, and 35.2%, respectively. The air-dried and coarse-sieved soil used for incubation experiments was reactivated by the addition of water (75 mL of H_2O/300 g of soil) and glucose (6 g/300 g of soil) and incubated for 1 week at 25 °C.

Transformation of Anilines in the Soil and Analytical Procedure. The soil was treated with the ^{14}C-labeled anilines at a concentration of 5 ppm (1.5 mg of a compound added to 300 g of air-dried soil). The anilines were dissolved in 1 mL of ethanol and applied dropwise to the soil which was thoroughly mixed. The soil moistened to 60% of its water-holding capacity was incubated in the dark at 25 °C and water which was lost by evaporation was frequently added during the incubation. Autoclaved soil samples served as controls for the differentiation of biological and nonbiological activity. For this purpose the soil was autoclaved three times for 30 min at 121 °C on three consecutive days. Each treatment was performed at least in duplicate samples.

The soil samples were kept in 1-L flasks which were exposed to a continuous air flow at a rate of approximately 30 mL/min, and the air was subsequently guided through solutions of 0.1 N H_2SO_4 and 2 N NaOH as trapping agents. The trapping solutions were frequently changed and measurements for radioactivity were made. The acid solution was further analyzed after neutralization by extraction with diethyl ether and subsequent thin-layer chromatography (TLC). The NaOH-trapping solution was acidified with H_2SO_4 and the formed gas, presumably CO_2, was absorbed in a solution containing ethanolamine–methanol (1:7, v/v). In all experiments it could be confirmed that the NaOH solution contained the same amount of radioactivity as the radioactivity determined in the ethanolamine–methanol mixture. The absorbed radioactivity in NaOH was also precipitated with a $BaCl_2$ solution to prove its correspondence to $^{14}CO_2$.

At the end of each experiment, one aliquot of the incubated soil was air-dried and then combusted in a stream of oxygen to determine the remaining radioactivity ($^{14}CO_2$ was trapped as previously described). Another aliquot corresponding to 250 g of dry soil was extracted with methanol (700 mL) using a Soxhlet extraction apparatus for 12 h. Radioactivity was then determined in the extracted soil (combustion method) and in the methanol extract. An aliquot of the extract was concentrated under a gentle stream of air in a water bath at about 40 °C to a small volume and analyzed by TLC.

For further identification, the products were purified at least twice by TLC. The chemicals were scraped from the plates and the silica gel was extracted with diethyl ether or methylene chloride. Subsequently they were analyzed by a combination gas chromatograph (flame-ionization

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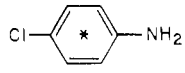
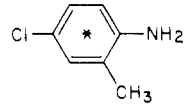
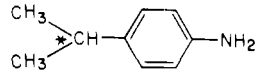
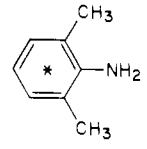
Table I. Characteristics of the ^{14}C-Labeled Anilines Used in This Investigation

aniline and site of ^{14}C labeling	sp. act., μCi/mg	source	code or common name of aniline-based pesticides[a]
4-chloroaniline-*phenyl-U-*^{14}C 	76	The Radiochemical Centre, Amersham, England	monuron (TELVAR) buturon (EPTAPUR) monolinuron (ARESIN)
4-chloro-*o*-toluidine-*phenyl-U-*^{14}C 	108	CIBA-GEIGY Corp., Greensboro, N.C.	chlorodimeform (GALECRON) chloromethiuron (DIPOFENE)
4-isopropyl-α-^{14}C-aniline 	72	CIBA-GEIGY Ltd., Basle, Switzerland	CGA 18 731 (GRAMINON)
2,6-dimethylaniline-*phenyl-U-*^{14}C 	100	Pathfinder Lab., St. Louis, Mo.	CGA 17 020 (TERIDOX)

[a] Trade names are in parentheses.

detector)–mass spectrometer interfaced with a computer. The glass capillary column was Emulphor-O (20 m, 0.36 mm, o.d.), N_2 carrier gas at 30 mL/min, with a linear temperature program of 50–200 °C at a programming rate of 3 °C/min.

Identity of isolated products was verified by cochromatography with authentic standards and by comparing mass spectral fragmentation patterns.

The nonextractable material which remained in the soil after Soxhlet extraction was subjected to Bleidner distillation (Bleidner et al., 1954; Geissbühler et al., 1971). This method combines alkaline hydrolysis and steam distillation of the resulting products which are subsequently extracted with isooctane from the aqueous phase. Twenty grams of dried soil was placed in a 1-L flask and 200 mL of 2.5 N NaOH as well as a few milliliters of Nopco NXZ antifoam were added; 100 mL of isooctane was used as extraction solution and Bleidner distillation was performed for 8 h. Radioactivity was then determined in the NaOH solution, isooctane, and in the nonsoluble dried residue. Isooctane was extracted with 0.1 N HCl; the acid was neutralized with NaOH and extracted with hexane which was concentrated by the method of Kuderna-Danish and analyzed by TLC.

Analytical Methods. Radioactivity was determined on a Packard Tricarb scintillation counter (Model 3375). Quenching was corrected by the AES channels ratio method or by the internal standard method. According to the sample to be analyzed, three different scintillation solutions were used: (1) 500 mL of toluene, 500 mL of dioxane, 300 mL of methanol, 104 g of naphthalene, and 10 g of 2-(4-*tert*-butylphenyl)-5-(4-biphenylyl)-1,3,4-oxadiazole (butyl-PBD) for organic and aqueous solutions; (2) 1000 mL of toluene, 8 g of butyl-PBD and 0.5 g of 2-(4-biphenylyl)-6-phenylbenzoxazole (PBBO) for the $^{14}CO_2$ absorption mixtures; and (3) Insta Gel (Packard Instrument Co., Downers Grove, Ill.) for determination of $Na_2{}^{14}CO_3$ from NaOH traps and silica gel scraped off thin-layer plates.

TLC was performed on precoated plates of silica gel 60 F_{254} with a thickness of 0.25 mm (E. Merck, Darmstadt, Germany). Chloroform–ethanol (9:1, v/v) was usually used as a solvent system. Thin-layer plates were evaluated by a Berthold thin-layer Scanner II (Berthold, Wildbad, Germany), with the Beta-Camera, Model 6000 (Baird Atomic Inc., Cambridge, Massachusetts) or by visualization under UV light (254 nm).

A CEC mass spectrometer (Consolidated Electrodynamics Corporation, Monravia, Calif.), Model 21-110B, was used for mass spectrometric analysis.

RESULTS AND DISCUSSION

^{14}C-labeled 4-chloroaniline, 4-chloro-*o*-toluidine, 4-isopropylaniline, and 2,6-dimethylaniline were incubated at a concentration of 5 ppm for several weeks in autoclaved and nonautoclaved soil. During this time period the evolution of volatile compounds was measured by monitoring an air stream through the incubation flasks whereupon the volatilized compounds were guided through trapping solutions containing 0.1 N H_2SO_4 and 2 N NaOH.

In each instance it was shown that the radiolabeled material which was trapped in the alkaline solution coincided with CO_2, since after acidification of the NaOH solution the evolved gas was absorbed in a solution containing ethanolamine–methanol, and it could be quantitatively precipitated by addition of $BaCl_2$. In all the soil samples which were autoclaved prior to the aseptic application of the aniline, no radioactivity could be detected in the alkaline solution during the entire incubation period; however, in all the nonautoclaved samples a continuous evolvement of CO_2 could be observed but the amount varied considerably among the various anilines. Figure 1 shows that from 4-chloro-*o*-toluidine, the chlorodimeform derived aniline, almost 20% was metabolized to CO_2 within 40 days, whereas the other incubated soils evolved between 7 and 9% of the originally applied aniline as $^{14}CO_2$. This is an interesting observation which suggests that the structure of 4-chloro-*o*-toluidine allows a faster metabolic transformation than those of 4-chloro-, 4-isopropyl-, or 2,6-dimethylaniline.

It has usually been found that CO_2 formation from halogenated anilines occurs slowly (Chisaka and Kearney,

Table II. Adsorption and Biochemical Transformation of Differently Substituted Anilines in Soil after 6 Weeks Incubation

		percent of ^{14}C recovered				
		CO_2	volatiles trapped in 0.1 N H_2SO_4	Soxhlet extract (methanol)	residues in soil (after Soxhlet extraction)	total recov.
4-chloroaniline	autoclaved	0	3.6	16.6	71.0	91.2
	nonautoclaved	7.5	3.4	6.6	72.4	89.9
4-chloro-*o*-toluidine	autoclaved	0	12.2	25.0	55.1	92.3
	nonautoclaved	20.0	2.0	6.2	61.7	90.0
4-isopropylaniline	autoclaved	0	7.0	17.6	66.1	90.7
	nonautoclaved	7.6	1.6	10.0	71.5	90.7
2,6-dimethylaniline	autoclaved	0	57.0	4.0	32.0	93.9
	nonautoclaved	8.4	13.0	8.6	64.7	94.7

Table III. Thin-Layer Chromatography of Methanolic Soxhlet Extract from Soil after 6 Weeks Incubation

		distribution of radioactivity after TLC[a]			
		compd with R_f area lower than applied aniline		R_f area of applied aniline	compd with R_f area higher than applied aniline
4-chloroaniline	autoclaved	0.0 (21)	0.36 (24)	0.50 (39)	0.63 (16)
	nonautoclaved	0.0 (20)	0.36 (10)	0.50 (41)	0.65 (29)
4-chloro-*o*-toluidine	autoclaved	0.0 (14)	0.37 (22)	0.56 (50)	0.66 (14)
	nonautoclaved	0.0 (36)	0.39 (15)	0.56 (30)	0.68 (19)
4-isopropylaniline	autoclaved	0.0 (15)	0.42 (42)	0.56 (30)	0.65 (12)
	nonautoclaved	0.0 (23)	0.42 (13)	0.56 (23)	0.63 (35)
2,6-dimethylaniline	autoclaved	0.0 (12)	0.46 (18)	0.60 (70)	
	nonautoclaved	0.0 (6)	0.34 (40) 0.46 (8)	0.60 (11)	0.68 (35)

[a] Solvent system: chloroform-ethanol (9:1, v/v); R_f values followed by percent in parentheses.

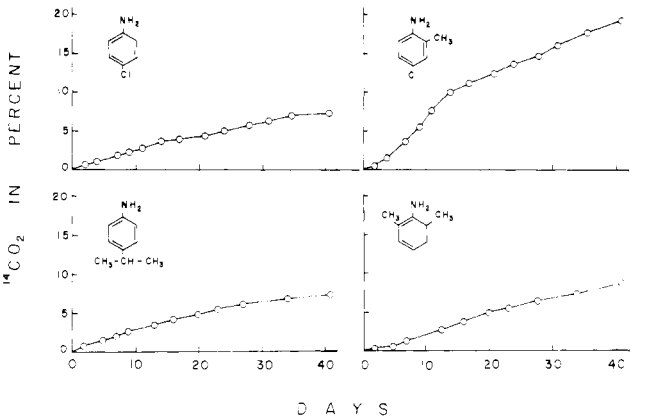


Figure 1. $^{14}CO_2$ evolution from soil treated with differently substituted anilines. $^{14}CO_2$ is presented as percent of the total radioactivity applied to the soil. No $^{14}CO_2$ formation was found in the autoclaved soil samples.

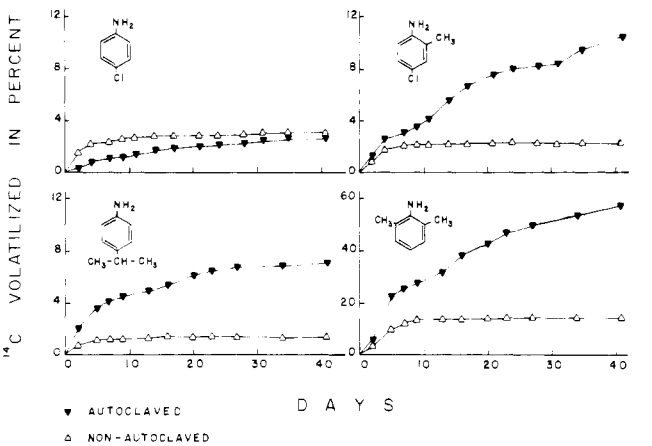


Figure 2. Volatiles trapped in 0.1 N H_2SO_4 from differently substituted anilines during incubation in autoclaved and nonautoclaved soil. The ^{14}C trapped is presented as percent of the total radioactivity applied to the soil.

1970; Bartha, 1971), indicating that ring cleavage of these compounds by microorganisms is not a very common reaction. Very little knowledge exists on the mechanism of ring fission of anilines.

The aeration by a continuous air stream and trapping in an acidic solution revealed that most anilines were bound to a lesser degree in autoclaved than in nonautoclaved soil (Figure 2). After 40 days of incubation 3, 7, 12, and almost 60% of 4-chloroaniline, 4-isopropylaniline, 4-chloro-*o*-toluidine, and 2,6-dimethylaniline, respectively, were volatilized from autoclaved soils. It is especially interesting to note the continuous and considerable release of 2,6-dimethylaniline.

Only during the initial incubation period were the anilines removed by aeration from the nonautoclaved soils, and after 10 days no radioactive compounds could be detected in the acidic trapping solution. The higher

Table IV. Bleidner Distillation of Soil Incubated with Differently Substituted Anilines after Extraction after 6 Weeks Incubation (in Percent of the Nonextractable Radioactivity)

compd		in iso-octane	in 2.5 N NaOH	residue in soil (after distillation)
4-chloroaniline	autoclaved	56.8	34.6	8.8
	nonautoclaved	28.8	58.7	12.5
4-chloro-*o*-toluidine	autoclaved	61.6	30.4	7.9
	nonautoclaved	27.1	62.3	10.6
4-isopropylaniline	autoclaved	47.6	34.5	17.9
	nonautoclaved	28.3	53.9	17.8
2,6-dimethylaniline	autoclaved	21.9	65.6	12.5
	nonautoclaved	8.5	74.9	16.5

volatilization from the autoclaved soil can be due to the alteration of the physicochemical properties of the soil during autoclaving or, more likely, due to the eliminated biological activity which causes the transformation of the anilines or their binding to soil. The latter mechanism was also supported by the fact that methanol-extractable radioactivity was considerably higher for all the compounds in the autoclaved than in the nonautoclaved soils (Table II); there was the exception of 2,6-dimethylaniline, but this can be easily explained if one considers the tremendous loss caused by aeration as it was shown in the acidic trapping reagent.

TLC of the methanolic Soxhlet extract revealed that in both the autoclaved and nonautoclaved samples most of the radioactivity did not coincide with the applied anilines, but several major compounds were formed as determined by scanning of the thin-layer plates (Table III).

Attempts were made to isolate and identify some of the transformation products of the various anilines, but only the compounds with an R_f value between 0.34 and 0.46 resulting from 4-isopropylaniline and from 2,6-dimethylaniline could be identified. In control experiments, degradation products having the same R_f value were already obtained 24 h after application. The product originating from 4-isopropylaniline which was determined in the chemical ionization mass spectrum with methane and methanol-*d* as the reagent gases showed the presence of one exchangeable hydrogen atom, and major m/e peaks were observed at 164, 148, and 122. The mass spectrum determined with electron impact ionization had major m/e peaks at 163, 148, 120, 91, 77, and 65 and coincided with the mass spectrum of 4-isopropylformanilide.

The chemical with an R_f value of 0.46 isolated from the methanol extract of soil treated with 2,6-dimethylaniline showed m/e peaks at 163, 121, 120, and 106 and the spectrum was identical with that of *N*-acetyl-2,6-dimethylanilide. The reason for the formation of the different acylation products from these anilines is not known.

It was not possible to establish whether the formation of acylated products is caused by chemical or biological factors. Experiments were performed in which untreated soil was extracted with methanol using the Soxhlet method and subsequently the methanol extract was carefully reduced to approximately one-tenth of the original volume which was incubated with 4-isopropylaniline. During incubation for several days, a continuous increase in the formation of 4-isopropylformanilide (as indicated by TLC analysis) could be determined. Although this observation appears to support the concept that chemical factors generate the acylation reaction, it is felt that further experiments are needed to provide clearer evidence.

The radioactivity which cannot be extracted from soil by Soxhlet extraction can be designated as "bound" residue. In additional short-time experiments, where various anilines were applied to nonautoclaved soil which was analyzed after 24 h, 34, 49, 52, and 66% of the radioactivity applied was bound to the soil for 4-chloro-*o*-toluidine, 4-chloroaniline, 4-isopropylaniline, and 2,6-dimethylaniline, respectively. Since during this time period little biological transformation can be expected, it is very likely that this initial binding takes place physicochemically without the active participation of soil microorganisms. From the figures in Table II, it is evident that the amount of the total nonextractable radioactivity is changed relatively little during the 6-week incubation period compared to the initial 24 h.

In order to obtain a better characterization of the bound residue, an attempt was made to submit the extracted soil to Bleidner distillation, which simultaneously uses alkaline hydrolysis and steam distillation. It has to be pointed out that hydrolysis can cause a transformation in the identity of a certain bound compound, but the determination of the remaining radioactivity in the isooctane, NaOH, or soil fraction can help to indicate the different nature of the bound radioactivity. In the short-time experiments, nearly all of the bound radioactivity could be solubilized, and in the case of 4-chloroaniline, 4-isopropylaniline, and 4-chloro-*o*-toluidine most of the label was present in the isooctane, whereas the radioactivity originating from 2,6-dimethylaniline was primarily found in NaOH. Analysis of the radioactivity from isooctane was performed by TLC, and in each case it was possible to determine that all the radioactive material coincided with the originally applied aniline.

After 6 weeks incubation the nonextractable radioactivity in the autoclaved and nonautoclaved soil was, with the exception of 2,6-dimethylaniline, in the same order of magnitude. However, the nature of this radioactivity was clearly different in autoclaved and nonautoclaved soil (Table IV). The autoclaved soil samples showed a similar distribution as in the short-time experiment, whereas little radioactivity from the nonautoclaved soil was found in the isooctane. These results indicate that not only the radioactivity which can be easily solubilized, but also the bound radioactivity is susceptible to microbial attack and is further metabolized.

Hsu and Bartha (1974a) found that only one-half of the bound residue from chloroanilines was liberated by hydrolysis under acidic or alkaline conditions. Since it was possible to release a considerably higher amount of radiolabeled material from soil with the Bleidner method, it appears that the difference of hydrolyzable compounds depends on the method applied. Consequently, it may be difficult to distinguish clearly between hydrolyzable and nonhydrolyzable aniline for routine analysis as suggested by Hsu and Bartha (1976).

It can be concluded from the experiments that when anilines reach the soil, they are to a large extent bound and a portion of them is transformed by mechanisms other than microbial activity. The formation of acylated products after an incubation period of only 24 h could be explained by an extracellular enzymatic or chemical reaction, and the isolation of various products after extraction of sterile samples clearly indicated the nonbiological transformation capability of soil towards anilinic compounds. $^{14}CO_2$ evolvement from the ring-labeled compounds gives evidence of ring cleavage, and since this was only observed in nonautoclaved soils, biological participation in the breakdown of anilinic products appears certain. However, despite some reports of aniline degradation by microorganisms (Walker and Harris, 1969; Bachofer et al., 1975), the pathway of ring fission in the soil environment is still not elaborated.

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Equilibrium and Kinetics of Adsorption of Picloram and Parathion with Soils

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The kinetics of adsorption of pesticides on soils is examined utilizing a flow-type system. The pesticide–soil systems included picloram and parathion reacting with Palouse silt loam and Panoche clay loam. Values of the relative adsorption constant, k_o, which is independent of the initial solution concentration, flow rate, and soil mass at 25 °C were 0.644, 0.441, 0.546, and 0.359 for the reactions picloram with Palouse silt, parathion with Panoche clay, parathion with Palouse silt, and picloram with Palouse silt acidified to pH 3, respectively. From the temperature dependence of k_o, the activation energies, E_a, were 2.7, 1.3, and 4.3 kcal/mol for the first three systems. Mechanisms of interaction based on experimental results and thermodynamic considerations emphasize the importance of organic matter for picloram adsorption and both clay and organic matter in the adsorption of parathion. Properties of the pesticides and the soil components were considered in proposing the mechanisms.

Picloram (4-amino-3,5,6-trichloropicolinic acid) was introduced in 1963 as a potent, plant growth regulator and herbicide (Hamaker et al., 1963; Laning, 1963). Its agronomic value has been recognized because of its effective control of brushes and woody plants (Robison, 1967) and its low toxicity to aquatic, avian, and mammalian species (Lynn, 1965). It is rather persistent in the environment (Dowler et al., 1968) and hence its movement in soil became an important subject for research (Scifres et al., 1969; Davidson and Chang, 1972).

Parathion (*O,O*-diethyl *O*-*p*-nitrophenyl phosphorothioate) was introduced in 1947 as an insecticide. It is one of the major substitutes for DDT after the latter was banned in 1972 in the United States. It is a highly toxic chemical to most organisms (Hygienic Guide Series, 1969; Yasuno et al., 1966). A human exposure to 2 to 15 mg/m^3 parathion in the air might depress cholinesterase activity by 25% (Hygienic Guide Series, 1969). Parathion is considered a relatively nonpersistent pesticide in the environment (Lichenstein and Schulz, 1964). However, long-term persistence of parathion in soil at a low level (0.06 μg/g) was observed 15 years after the last application (Voerman and Besemer, 1970; Stewart et al., 1971; Iwata et al., 1973). This long persistence probably involved an adsorption mechanism which protected the pesticide from further degradation.

Pesticides in the soil exist under dynamic conditions involving infiltration, diffusion, adsorption, volatilization, chemical reactions, etc. The purpose of this work is to devise simple experimental and mathematical procedures to obtain data on the rate of adsorption of pesticides under varied dynamic conditions. Such experimental conditions will better approximate the actual situation in the field. Activation parameters were evaluated from the kinetic data obtained at different temperatures. The activation energy and entropy of activation, X-ray and equilibrium adsorption results, and the chemical and physical properties of the substances were used to gain some insight into the mechanisms of adsorption under dynamic conditions.

EXPERIMENTAL SECTION

Materials. All chemicals were reagent or analytical grade except where stated otherwise. Analytical grade 4-amino-3,5,6-trichloropicolinic acid (picloram) of specific purity greater than 99% by weight was obtained from the Dow Chemical Company. A stock solution of 1.66×10^{-4} M was prepared by dissolving the pure acid in an equivalent amount of potassium hydroxide in 1 L of distilled water. A 2.07×10^{-4} M stock solution of picloram was prepared with ^{14}C labeled at the carboxyl carbon (Dow Chemical Company) having a specific activity of 4.13 μCi/mg. Reaction solutions of various concentrations with specific activities ranging between 0.207 to 0.828 μCi/L were prepared from these two stock solutions. Ionic strength of the solution was maintained at 0.03 M with calcium chloride. In the kinetic experiments performed at pH 3, the solutions were initially adjusted to 0.30 N in H_3^+O by HCl.

Parathion was supplied by the Monsanto Company as an analytical standard with a GLC assay of 98.5% purity. Analytical grade parathion with ^{14}C labeled at the 2,6-positions of the benzene ring (specific activity of 1.47 μCi/mg) was supplied by Tracerlab. Stock solutions of 6.88×10^{-3} M of unlabeled parathion and 1.72×10^{-3} M of labeled parathion were prepared in nanograde acetone. Aqueous solutions of 3.44×10^{-5} M were prepared by pipeting 4.5 and 2.0 mL of the unlabeled and labeled solution, respectively, into a 1-L volumetric flask. Distilled water was added and the acetone was evaporated on a warm water bath (70 °C) with a stream of purified nitrogen

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