

Decomposition of (*O,O*-Dimethyl-*O*-2,4,5-trichlorophenyl) Phosphorothioate (Ronnell) Adsorbed on Bentonite and Other Clays

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The decomposition of Ronnell is normally a base-catalyzed hydrolysis reaction. When clays treated at elevated temperatures are used as carriers for the toxicant, a new type of decomposition occurs, resulting in a new product. This is believed to be an acid-catalyzed molecular rearrangement reaction. A mechanism for the reaction has been proposed.

PESTICIDAL compositions undergo carrier-catalyzed decomposition of the toxicant when formulated with a clay carrier. A number of adducts inhibit this decomposition (1, 2, 6). Possible correlations between the rate of toxicant decomposition and some physical properties of the clay (6, 8, 11-13) have been studied, but the factors controlling the breakdown are not yet fully understood.

In previous studies, the catalytic effect of different kinds of clays upon the breakdown of thiophosphates has been compared. The physical properties (such as state of subdivision, cationic exchange capacity, water content, impurities, pH, and acidic sites) were compared to see which were most significant in causing degradation. Thus, in previous studies, several physical factors have varied simultaneously. No exact correlation of catalysis with physical properties varying singly is known to have been carried out.

The present investigation studied the degradation of a thiophosphate caused by a single clay as a function of previous history or pretreatment of the clay. This reduced the number of varying physical properties, allowing a greater understanding of the mechanism of the breakdown reaction.

Following a thermal pretreatment, cooling, and grinding of the clay samples, the diluents were impregnated with a thiophosphate and compatibility was studied.

Panther Creek bentonite was chosen for this study because it is especially active as a decomposition catalyst on thiophosphates. Following the investigation of the catalytic effects of bentonite, the effect of thermal pretreatment of four industrially important clays on compatibility with a thiophosphate insecticide was studied.

The thiophosphate of choice, (*O,O*-dimethyl-*O*-2,4,5-trichlorophenyl) phosphorothioate, undergoes clay-catalyzed degradation at a rate admitting of convenient analytical determination.

A predetermined amount of this substance, known as Ronnell (a trademark of The Dow Chemical Co. abroad), was adsorbed onto each clay sample. The decomposition of thiophosphate in each of the clay-Ronnell samples was accelerated by heating each mixture for 70 days at 50° C. Resulting decomposition was assayed by infrared spectroscopy.

Decomposition of Ronnell on Thermally Treated Bentonite

Pretreatment of Bentonite. Bentonite was treated with the salts of several polyvalent metals and with HCl. Metals were selected which adsorb easily onto the clay by ion exchange. Each cation form thus prepared was then subdivided, and the subdivided samples of each form were subjected to one of four thermal treatments, one at room temperature and three by heating. It was anticipated that heating would cause a thermal transition in the lattice structure of the clay and a stepwise thermal release of bound water.

A 500-gram sample of commercial Panther Creek bentonite was acidified for 9 days at room temperature in 8 liters of 0.1*N* HCl, with occasional stirring, to replace all available exchangeable cations with H⁺. Next the sample was filtered, and the clay residue washed with 10⁻³*N* HCl. The acid-exchanged clay residue was divided into five portions. One received no further treatment at this point. Each of the other four was soaked for 15 days with occasional stirring in a 0.1*N* aqueous solution of FeCl₃, AlCl₃, MgCl₂, or CaCl₂. Five clay samples were obtained, loaded by ion exchange with, respectively, H⁺, Fe⁺³, Al⁺³, Mg⁺², and Ca⁺². Upon completion of the exchange, each sample was separately filtered, washed with water, and air-dried.

Each clay sample was divided into four portions. Five samples, each representing one of the ion loadings, were heated to 300° C. for 24 hours and then cooled in a desiccator. Similarly, the other five-sample groups were heated to 750° and 950° C., respectively, while the last was held at room temperature.

There resulted 20 clay samples representing the five indicated ion loadings and the four temperature treatments. A comparable sample of untreated commercial Panther Creek bentonite was provided as sample number 21.

Each sample not already in a finely divided form was then ground to 20- to 30-mesh with mortar and pestle.

Physical Properties of Pretreated Bentonite. The cation exchange capacity of each of the 21 clay samples (without Ronnell) was ascertained, using the method of Weidhaas (10).

Form	Cation Exchange Capacity, Mg./100-Gram Sample
Al	58
Ca	59
Fe	56
H	61
Mg	60

X-ray diffraction patterns were prepared and data calculated for each sample. From these data it was ascertained that the unheated clay had the lattice structure typical of a montmorillonite clay (of which bentonite is one form). It was low in quartz, had a lattice spacing of 14 Å., and was in the hydroxyl form characteristic of a natural clay.

The sample heated to 300° C. had the 14-Å. lattice spacing intact, and was predominantly in the oxide form.

In the sample heated to 750° C., the lattice spacing was 9.5 Å. and the crystal structure was that of aluminum silicate.

In the sample heated to 950° C., the lattice structure typical of the clay had collapsed completely. Among the substances present in predominating quantities were mullite, spinel, and cristobalite. In the general collapse, internal capillarity was obliterated.

The surface pK_a of each clay was determined by adding about 0.2 gram of clay to a mixture of 0.2 mg. of Hammett indicator dye in 2 ml. of hexane in a test tube. The hexane was selected as a nonpolar solvent which would not in-

Table I. pH of Clay Slurries

Clay	Temp., °C.	pK _a	pH of Slurry
Unheated Ca		>3.29	4.7
	Room	0.43-1.52	3.5
	300	1.52-3.29	2.3
	750	1.52-3.29	3.55
Mg		>3.29	5.55
	Room	0.43-1.52	3.2
	300	1.52-3.29	2.55
	750	1.52-3.29	3.2
Al		>3.29	4.9
	Room	0.43-1.52	2.6
	300	1.52-3.29	2.85
	750	1.52-3.29	3.2
H		>3.29	4.4
	Room	0.43-1.52	3.12
	300	1.52-3.29	2.75
	750	1.52-3.29	2.5
Fe		>3.29	4.2
	Room	0.43-1.52	3.90
	300	1.52-3.29	2.7
	750	1.52-3.29	2.85
		>3.29	4.4

fluence the apparent surface acidity at any of the clay sites. The three Hammett indicators used to determine the surface acid strengths of each clay and the respective pK_a's determined are (9):

Indicator	Color Change with Acid	pK _a
1. <i>p</i> -Dimethyl-aminoazo-benzene	Yellow-red	3.29
2. Benzeneazodi-phenylamine	Yellow-violet	1.52
3. <i>p</i> -Nitrobenzene-azo-(<i>p</i> '-nitro)-diphenylamine	Orange-violet	0.43

The pH of a 1 to 4 slurry of each clay in water was also determined, using a pH meter (Table I).

To gross physical observation, all the clays were dry solids, their apparent hardness and brittleness increasing with treatment temperature. They were of a generally dark, burnt red color, those treated at a higher temperature being darker. These characteristics were independent of ion exchange treatments.

Impregnation of Clays with Ronnel. Approximately two thirds of each of the 21 clay samples was employed to study the catalytic decomposition of the thiophosphate.

To each of the portions used in the decomposition study was added 25% of its weight of melted technical Ronnel assaying 93.2%, and the Ronnel was thoroughly and intimately mixed into the clay to give a homogeneous mixture containing 18.6% Ronnel by weight. No wetting or dispersing agents or other additives were used. As a result, 21 Ronnel-loaded samples were obtained, with no two alike.

A portion of each Ronnel-loaded sample was then removed immediately for analysis, and the remainder of each was held in an oven at 50° C. Portions were removed and analyzed at 14, 30, and 70 days.

Table II. Decomposition of Ronnel at 125° F. on Clay Surfaces Treated with Cations and Subjected to 24 Hours at Elevated Temperatures

Sample	Temp., °C.	Assay (Average of Duplicates)				Decomposition Product
		Initial	14 days	30 days	70 days	
Unheated and not subjected to cation exchange		13.13	8.2	6.6	4.1	Trichlorophenol
	Room	18.90	11.45	7.9	3.75	Trichlorophenol
	300	12.18	3.95	2.4	1.25	Both
	750	16.10	13.5	12.15	10.4	Both
H		17.73	17.25	17.4	16.2	Rearrangement
	Room	17.70	13.1	10.4	0.65	Trichlorophenol
	300	12.50	5.55	4.25	2.25	Both
	750	16.33	14.1	13.3	10.9	Both
Ca		17.73	17.1	17.15	16.6	Rearrangement
	Room	17.18	11.6	8.8	4.9	Trichlorophenol
	300	12.40	4.75	3.25	2.15	Both
	750	14.93	11.2	10.2	9.25	Both
Mg		17.65	16.35	16.8	15.9	Rearrangement
	Room	16.25	7.35	2.65	0.25	Trichlorophenol
	300	12.18	3.9	2.95	2.05	Both
	750	14.95	12.15	11.05	7.85	Both
Al		18.30	18.25	17.9	17.2	Rearrangement
	Room	16.45	8.45	6.9	1.4	Trichlorophenol
	300	10.98	3.0	1.75	0.75	Both
	750	14.18	12.15	10.55	8.1	Both
Fe		17.58	17.85	17.45	16.1	Rearrangement

Table III. Weight Losses on Heating

Clay	Original Weight of Clay, G.	Weight of Clay after Heating, G.	% Loss
Celatom MN 39	7.85	6.91	12
Barden clay	16.44	14.23	13.42
Bentonite	25.53	19.92	22.0
Attaclay	16.42	14.27	13.1

Analytical Work One gram of each of the 21 Ronnel-loaded samples described above was extracted with 50 ml. of CS₂ until equilibrium was attained. The extract solutions were scanned from 2 to 16 microns, in a 0.9-mm. cell in an attempt to identify decomposition products, and assayed by comparison with a Ronnel standard solution at 10.3 microns.

The assays and general nature of the decomposition products are stated in Table II. An absorbance maximum not characteristic of unmodified Ronnel nor of trichlorophenol (the decomposition product normally expected) at 7.8 microns was observed in the spectra of some samples.

Decomposition of Ronnel on Solid Carriers Heated to 950° C.

Samples and Treatment. Samples of a diatomaceous earth, a kaolinite, a bentonite, and an Attapulgit were heated at 950° for 24 hours and cooled to room temperature in a desiccator, and weight losses were determined.

An amount of molten Ronnel, one third of the dehydrated weight of each clay and assaying 97.3% purity, was added to each clay and intimately mixed into it, giving a homogeneous mixture

Table IV. Decomposition of Ronnel at 125° F. on Clays Previously Heated to 950° for 24 Hours

Clay	Ronnel Assay			
	Initial	14 days	30 days	70 days
Celatom MN 39	24.4	23.3	24.2	22.7
Barden clay	23.5	22.3	22.2	20.8
Bentonite	24.6	23.5	24.7	24.0
Attaclay	23.4	22.3	23.7	24.0

containing 24.3% Ronnel by weight and providing four Ronnel-loaded materials.

Analytical Work. The weight losses from the heating of the clays before addition of Ronnel are shown in Table III.

A portion of each Ronnel-loaded material was removed for infrared analysis immediately and the remaining portions were placed in an oven at 50° and held at this temperature. Small amounts were removed and analyzed after 14, 30, and 70 days' heating (Table IV). The analytical procedure was that used for Ronnel on bentonite.

The pH and pK_a of these clay samples were determined in the manner described earlier.

Clay (950° C.)	pK _a	pH of Slurry
Barden clay	0.43-1.52	4.35
Celatom	0.43-1.52	4.75
Bentonite	>3.29	5.12
Attaclay	>3.29	5.85

While these clays are only slightly acidic according to the pH meter, the strength of the acidic surface sites is sufficient to give an acidic reaction from benzeneazodiphenylamine.

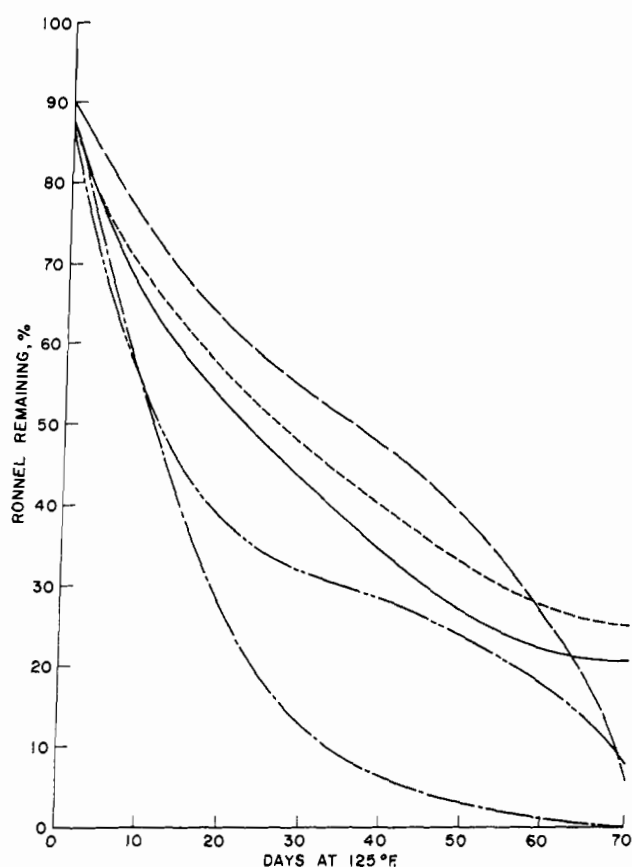


Figure 1. Decomposition of Ronnel adsorbed on bentonite left at room temperature

— H^+ form
 - - - Ca^{+2} form
 . . . Mg^{+2} form
 - · - Al^{+3} form
 - - - Fe^{+3} form

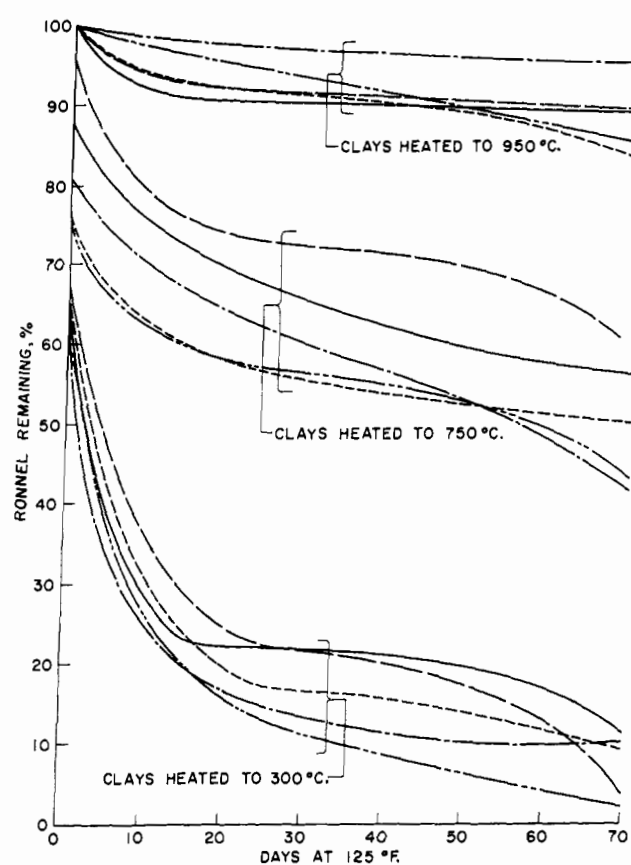


Figure 2. Decomposition of Ronnel on bentonite heated to elevated temperatures

— H^+ form
 - - - Ca^{+2} form
 . . . Mg^{+2} form
 - · - Al^{+3} form
 - - - Fe^{+3} form

Results

X-Ray Data. The lattice spacing of 14 Å. in the unmodified clay and that heated to 300° C. indicates that each pair of aluminum silicate lattice layers is separated by a molecular layer of water. The 300° thermally treated clay represents a transitional state in which all free water has been driven off and the process of driving the elements of water from between the aluminum silicate layers has begun. The remaining water remains bound in a mono-molecular layer within the lattice.

The lattice spacing of 9.5 Å. in the sample heated at 750° C. indicates aluminum silicate with all water removed, the lattice layer spacing essentially collapsed, but the aluminum silicate crystal structure remaining. The sample heated at 950° shows the effect of extensive structural changes and the beginning of the formation of a glass. This sample is conspicuously more brittle than the others.

Cation Exchange Data. The cation exchange capacities of samples of clay that had been treated only by acidification, and washing, reaction with an ionic

salt, all falling within the range of 56 to 61 mg. per 100-gram sample, were so nearly within the limits of error of the method of determination of capacity (± 3 mg. per 100 grams) that the differences are deemed insignificant. Cation exchange capacities of the clays modified by heating at various temperatures were not determined, in view of the slight differences among the unmodified clays on which the determination was made.

Small amounts of added iron have previously been shown to increase the decomposition of DDT (3), but the results of the analysis presented in Table II and Figures 1 and 2 indicate that the small amounts picked up by the present clay through ion-cation exchange have little or no effect on Ronnel.

Table I indicates that, irrespective of the cation loading, the clay acidified and treated by exchange with any of the

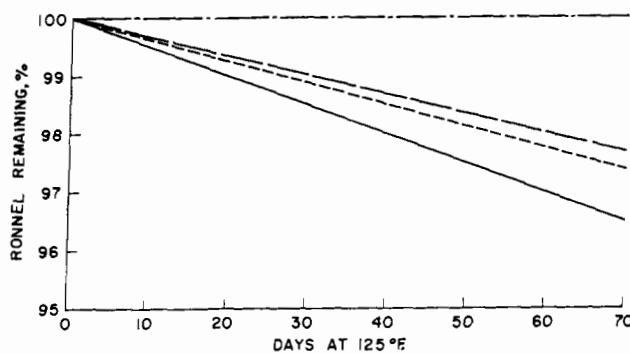


Figure 3. Decomposition of Ronnel on clays heated to 950° C.

— Barden clay
 - - - Bentonite
 . . . Celatom
 - · - Attaclay

ions at room temperature tends to be substantially more acidic than the same clay with the same ion loading after heating, and that the acidic properties decrease as the upper limit temperature of heating increases.

Decomposition Data. Figures 1 and 2 show the four families of curves for the decomposition of Ronnel on the clay products resulting from the four thermal treatments.

An inverse correlation can be noted between pK_a value and the decomposition of Ronnel (Figures 1 and 2).

A comparison of the decomposition rates of Ronnel on the approximately 20-mesh and 100-mesh particles described above shows that the state of gross subdivision cannot be a factor of much significance, since the 20-mesh and 100-mesh particles give results within experimental error. This may be because the total surface area consists largely of capillaries and intraparticulate fissures and varies little with grinding.

As a crude approximation, the decomposition observed in 14 days at 50° will indicate the decomposition to be expected in one year at room temperature.

Discussion

From the foregoing factual conclusions, certain hypotheses can be stated.

Although previous workers (4, 5, 8, 13) have pointed out the effects of water content on the character of the clay and consequent decomposition of adsorbed pesticides, the present study shows that total water content, determined by the per cent loss in weight of the clays on ignition shown in Table III, cannot control the rate of decomposition of the insecticide. Celatom and Barden clay (when not heat-treated) are two of the least catalytically active carriers for use with thiophosphates, while unheated Attaclay and bentonite bring about the most decomposition. Yet, Attaclay, Barden clay, and Celatom have very similar total water contents, while bentonite has an appreciably higher value. The division of activity does not occur according to total water content *per se*. The explanation for this observed fact may lie in the distinction between free and bound water. Water bound into the crystal lattice of the clay, effectively water of crystallization, assists in bringing the toxicant into close contact with the decomposition sites within the capillary structure of the clay, while free water may actually act as an insulator, being adsorbed to a thickness of several molecules over all the interior of capillary surface.

Making this distinction, one can see that free water added to a formulation as an aqueous solution of a wetting or dispersing agent is not necessarily detrimental. Previous observation (4, 8, 13) has been that when a carrier contains more water than normal, the final in-

cremental amount may actually be beneficial. In current commercial calcination processes clays are heated to elevated temperatures but not long enough to establish equilibrium. The water driven off in these calcination processes is largely the free water. The bound water—a thin layer and perhaps a monolayer coating the capillary surfaces—appears to be the real cause of the decomposition catalysis. The increased decomposition of pesticide adsorbed on air-dried Attaclay (4), as compared to the undried material, despite decreased decomposition of a chemically similar pesticide on a "specially dried" Attaclay (12) reflects this distinction.

The heat treatment of the clays at 300° drives off the free water. The remaining clay is far more catalytically active than the original material. As the clay is heated to a still higher temperature, the remaining bound water is also driven off, leaving the dry, collapsed lattice, which loses much of its catalytic activity in this further transition. An equally gradual transition in the decomposition product formed from a thiophosphate (Table II) occurs concurrent with the lattice transition.

The alternative decomposition product, identified in Table II as the "rearrangement" product, has a prominent infrared absorption peak at 7.8 microns. It was tentatively identified as *O*-methyl-*S*-methyl-*O*-(2,4,5-trichlorophenyl) phosphorothioate. The clays equilibrated at 950° give only this latter decomposition product, and no trace of the usual trichlorophenol.

Such a rearrangement product had never been previously observed from the decomposition of a formulated thiophosphate. Previous work has always yielded only hydrolysis products.

The consistent and spectacular distinction in the pH of the active clay before and after the complete removal of the bound water ties into this argument nicely. A basic, uncalcined clay contains an abundance of OH— radicals—perhaps the best known catalyst for the hydrolysis of esters. The more chemically bound water present, the faster hydrolysis appears to take place on a particular clay. Any toxicant existing as an ester can be expected to decompose by this normal hydrolysis mechanism when it comes into contact with free OH— on the clay surface.

The surface areas of the clays would be expected to correlate with decomposition, and appear to do so if internal capillary area is considered. The room temperature sample contains appreciable adsorbed water which will fill the smaller capillaries and reduce the effective surface area. The 300° clay will have all this adsorbed water removed. The remaining bound water holds the lattice in place and maintains the capillary structure, permitting many very fine

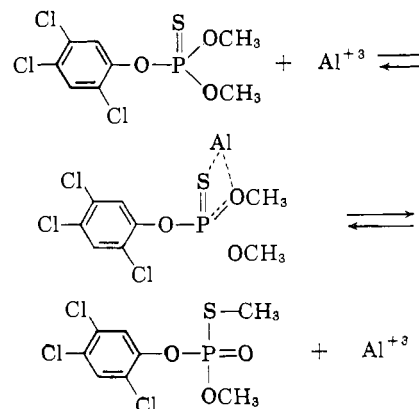
capillaries to exist as areas of close contact between the clay and toxicant. In the 750° material, many of these capillaries have collapsed. The glassy minerals in the 950° material have so little surface that the toxicant composition heated to 950° has a wet appearance.

After the calcination at 950°, all OH— is gone, and the clay has become a mixture of metallic oxides and SiO₂, which is shown above to be distinctly acidic. The decomposition product becomes entirely one of molecular rearrangement rather than hydrolysis.

The molecular rearrangement reactions such as the one now encountered differ from a base-catalyzed hydrolysis in two important respects.

A base-catalyzed hydrolysis goes to completion, since one of the products (methanol, in the case of the decomposition of Ronnel) has appreciable vapor pressure and escapes. The molecular rearrangement, catalyzed preferentially by a Lewis acid (7), approaches an equilibrium (since no product nor reactant is removed), the position of which is determined by the relative thermodynamic stability of the possible arrangements.

A base-catalyzed hydrolysis, in the presence of a limited amount of catalyst, can behave as a zero-order reaction. This can make the relative amount of toxicant lost much greater for a dilute dust than for a concentrated wettable powder. The rearrangement, on the other hand, will approach its equilibrium with first-order kinetics; further, since it is reversible, the utilization or absorption of one molecular arrangement by an insect, or its removal by preferential dissolution in any solvent, can shift the equilibrium and reverse the direction of the reaction. Specifically, in the case of Ronnel, hydrolysis can produce trichlorophenol or methanol, with methanol being approximately twice as likely as trichlorophenol (because there are two methyl and only one trichlorophenyl groups). All of the methanol will escape and be unavailable to reverse the reaction. The mechanism of decomposition of Ronnel by molecular rearrangement should not produce any alternative products which would volatilize. The proposed mechanism is:



It is postulated that the strong Lewis acid forms a tetrahedral configuration

with the S, O, and CH₃, bringing CH₃ close to S and resulting in rearrangement.

The necessary strong Lewis acid will in most cases probably be free Al³⁺, as shown here. The volatilization of all OH⁻ can be expected to produce a number of structures in the clay crystal analogous to lattice defects such as those found in metals. As the clay is heated to extreme temperatures, probably in the range of 1300° to 1400° C. in the case of kaolinite, a process similar to the annealing of a metal can be expected to take place, during which these defects should gradually be eliminated, and after which the clay becomes a glassy mass which should possess no catalytic or absorptive properties and no internal surface. The number of strong Lewis acid sites is probably not large, but their strength is indicated by the pK_a of Barden clay and bentonite, less than 1.52, although the pH of the slurry is greater than 4.

This type of reaction can be expected to occur to a greater extent in the case of Barden clay than most other clays, since natural Barden clay has a much greater crystallinity than many others. The "lattice defect," when it occurs, thus must migrate further before it encounters its opposite member, eliminating

itself. The more amorphous Attaclay and bentonite will eliminate the lattice defect more readily.

To some extent, the cationic exchange capacity of a clay is a measure of the regularity of its crystal structure. A low cationic exchange capacity is to be expected to be associated with a regular structure, with few sites at which ions may exchange. In the natural clay, a low cation exchange capacity should be concomitant with few sites for chemisorbed water, which tends to mean less catalytic decomposition by a hydrolysis mechanism. In clay heated at 950° C. for 24 hours, the very regularity of the original crystal which produces the low cationic exchange capacity will give rise to a long migration distance for the lattice defect, which will encourage the molecular rearrangement.

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HERBICIDE DEGRADATION

Microbial Degradation of Selected Herbicides in Soil

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EPTC, amitrole, amiben, and ipazine are degraded by the microflora of soil. C¹⁴O₂ was not released microbiologically from soil receiving tagged propazine, atrazine, or simazine. The susceptibility of chlorobenzoates to decomposition is related to the number of chlorines on the aromatic ring. A technique for determining the ability of a specific soil population acting on one aromatic herbicide to destroy a structurally related compound is described, and the method is used to show that a 2,4-D-metabolizing microflora of soil is inactive on MCPA and 2,4,5-T and that benzoate-metabolizing microorganisms are inactive on monochlorobenzoates. The resistance of dichlorophenols to microbial destruction is associated with the presence of a chlorine in the position meta to the phenolic hydroxyl. Seed inoculation with a 4-(2,4-DB)-utilizing *Flavobacterium* protected alfalfa in sterile soil amended with the herbicide, but little protection was observed in nonsterile soil.

DESPITE an increasing concern with the persistence and residual effects of herbicides and the dominant position occupied by microbiological agencies in environmental detoxication, little information is available on the chemicals which are metabolized and inactivated by the soil inhabitants. The present communication summarizes a

series of studies designed to determine the role of soil microorganisms in the degradation of herbicidal compounds. The substances investigated include thiocarbamates, triazines, chlorinated benzoates, chlorophenols, and phenoxy compounds.

Unequivocal evidence for the participation of the subterranean microflora in the degradation of thiocarbamate, benzoate, and phenylacetate herbicides has yet to be established, and

microorganisms active upon these pesticides have not been obtained in monoculture. Amitrole, however, appears to be broken down microbiologically, and increases in soil temperature and organic matter level enhance the decomposition (13). The microbiological contribution to the detoxication of the triazine herbicides remains uncertain. Destruction of the triazines has been attributed, in part at least, to microbiological agencies (5, 15). Other

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