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THE EFFECT OF SOIL MINERAL PHASES ON THE
ABIOTIC DEGRADATION OF SELECTED
ORGANIC COMPOUNDS

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Shingara S. Sandhu, Chairman
Division of Natural Science and Mathematics
and Computer Science
Claflin College
Orangeburg, South Carolina 29115

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THE EFFECTS OF SOIL MINERAL PHASES ON THE ABIOTIC DEGRADATION OF SELECTED ORGANIC COMPOUNDS

Background

Microbial and chemical transformations of organic chemicals in soil and water are important processes that directly affect their environmental distribution, persistence and toxicity. During the past decade, studies of heterogeneous chemistry have burgeoned. A major impetus for environmentally related research in this area has been the need for reliable estimates of lifetimes of pollutants in the soil, surface and groundwater. Abiotic conversion of organics may be fairly common, especially hydrolysis and oxidation reactions (1,2). When transformations are rapid, measurements of adsorption and degradation are rendered by nonequilibrium conditions.

The mobility and fate of nonvolatile organic compounds in the soil environment are largely determined by sorption and degradation reactions. Although soil microorganisms are known to degrade a large variety of organic contaminants, abiotic chemical reactions are also important for some compounds and have recently received increased attention (3,4,5). These reviews indicate that many organic reactions, including hydrolysis, elimination, substitution, redox, and polymerization, can be catalyzed or facilitated by surfaces in soils. The principle soil properties that affect the rates of heterogeneous catalysis are surface charge, structural characteristics of the clay minerals, exchangeable cations, and hydration status of the surface.

The abiotic transformation of organic compounds in soils is generally related to the Bronsted or Lewis acid characteristic of mineral surfaces (3,4,6,7,8,). Acidity in the Bronsted sense refers to the ability of the mineral surface to act as a proton donor. High surface acidity has been attributed to exchangeable cations which polarize coordinated water molecules and induce proton dissociation. The principle factors which influence the acid strength of these reactive sites are soil moisture content and charge to size ratio of the exchangeable cations (5). The surface acidity at low moisture levels can be 2-3 units less than that of bulk water in equilibrium with the delay at saturation (8,9).

Mineral surfaces can also act as Lewis acids by accepting electrons from adsorbed organic molecules, thus promoting redox transformations (3). Lewis acid sites can be either exchangeable cations on the planar surface or structural cations on the edge surface of the mineral crystal. The reactivity of these sites with regard to organic compounds increases with decreasing moisture content. This is due to the competition of water molecules with organic compounds for the Lewis acid site(s).

Several studies on the adsorption and degradation of organic chemicals and pesticides in soil and in pure mineral systems have been reported. Studies on the nonbiological degradation of pesticides in soil indicate that the precise understanding of the nature of pesticide reactions at the solid-liquid interface is difficult due to the complexity of the solid surface and their interaction with water (10). However, it was reported that surface-induced degradation could play a dominant role in the fate of pesticides in soil. Heterogeneous reactions have been reported to contribute heavily to the transformation of organic chemicals in the environment (11). The sorbed chemicals were found to undergo hydrolysis and reduction in anaerobic sediments.

Kinetic (11) models were applied to the data to illustrate the degradation mechanisms. Soil was found to catalyze the oxidation of aniline, azobenzene, azoxybenzene, phenazine and acetanilide (12). Nitrobenzene, Penzoquinone and unidentified species were the possible products. Substantial quantities of bound residues were also formed. Freundlich constants for several intermediate products were reported (12). In other studies, the degradation mechanisms and kinetics of chemical changes were defined for aldicarb which is an effective nematode and insecticide (13). It appears that microbial oxidation is an important degradation mechanism in the surface soil, but the breakdown of aldicarb residues to noncarbamates is largely the result of chemical hydrolysis.

Dragun and Hilling (14) hypothesized that abiotic degradation of organic chemicals in soil and clay catalyzed reactions depends on the physiochemical nature of the chemicals which have been categorized into four groups. Group 1 comprises those aromatic chemicals having weak electron-donating substituent fragments ($0 < p < 0.5$) in association with and electron-withdrawing substituent fragments. Group 2 comprises those aromatic chemicals which have strong electron-donating substituent fragments ($0 < p < 0.5$). Group 3 comprises those aromatic chemicals which have only electron donating substituent fragments. Group 4 comprises those chemicals which have extensive conjugation. Dragun and Hilling also indicated the relationship between the lower solubility limit and chemical structure by using simple kinetic theory. The guidelines designed by these authors (14) have been useful in predicting the behavior of organic chemicals in soil.

Physiochemical factors also play a significant role in the polymerization reaction of aniline in soil (15). McBride et al. (16) investigated the role of soluble Al in

catalyzing the abiotic oxidation of organic compounds by monitoring the slow oxidation of aerated aqueous solutions of catechol containing Al, which increased the rate of oxidation leading to the formation of colored polymeric products. The role of Al in promoting oxidative polymerization is based on the concept that Al tends to stabilize semiquinone radicals at low pH. It may also provide a bridge between the reduced and oxidized species during charge transfer reactions. Oxidation and polymerization of phenolic compounds are promoted by mineral surfaces (17,18,19). While various mechanisms have been proposed to explain this phenomenon, experimental results have been inconsistent. For example, there is both positive and negative evidence that layer silicate clays are catalysts for oxidation of organic compounds (18,19,20,21). It is difficult to determine the mechanism by which layer silicates enhance the oxidation of organic compounds since one or more of the following mechanisms could promote the reaction:

1. Direct electron transfer between structural Fe (III) and adsorbed phenol.
2. Adsorption of protons generated by oxidation of the phenol.
3. Increased probability of interaction between molecular oxygen and the phenol due to the presence of a surface.
4. Oxidation of the phenol by impurities of Mn and Fe oxides in the silicate.
5. Preferential adsorption of the oxidative product relative to the unoxidized phenols.

The mechanisms for the adsorption and oxidation of phenolic compounds by Fe and Mn oxides were investigated by Fourier transform infrared (FTIR) spectroscopy and by measuring the oxygen consumption by the suspension of these oxides. Through the method of FTIR, direct coordination of phenolics with oxides were

observed, and degradation rates were obtained for the consumption of oxygen and the release of Fe^{2+} and Mn^{2+} into the solution (22). The kinetics of adsorption and degradation for several aromatic compounds was measured at two temperatures (23) through accelerated soil solution contact. A mechanistic adsorption-catalyzed degradation model was evaluated (23) to mathematically uncouple these processes.

PROPOSED RESEARCH

Tetraphenylborate (TPB) is used to precipitate radioactive ^{137}Cs from high-level nuclear waste water at the Defense Waste Processing Facility (DWPF) operated by the United States Department of Energy (USDOE) at the Savannah River Plant (SRP), Aiken, SC (24). The process is a part of the procedure for the glassification of high-level nuclear waste in preparation for its long-term geological disposal. The decontaminated waste water contains millimolar quantities of TPB that will be processed into salt concretions. The transportation and use of large amounts of TPB (Table I) can potentially result in the release of TPB into soil or aquatic environments. TPB has been used in a variety of laboratory applications (25,26,27). However; it has not been previously used in industry on a large scale. Previous study (28) has shown that TPB degrades in soils to initially form diphenylborinic acid (DPBA) and biphenyl. The degradation of TPB appears to be an abiotic process as its degradation was observed in sterilized soils, collected from several locations in South Carolina (29). DPBA is not the final product of TPB abiotic-degradation via abiotic pathways. It does not accumulate in the soils, but rather appears to degrade further into other unidentified compounds which subsequently degrade into inorganic boron (29).

Table I. Projected Usage of Tetraphenylboron at the Savannah River Plant

PROJECTED USAGE TETRAPHENYLBORON	
<u>YEAR</u>	<u>ANNUAL USAGE</u> (metric tons)
1991	25,000
1992	300,000
1993	260,000
1994	360,000
1995	540,000

The reaction mechanism and the specific soil surfaces mediating the chemical degradation of TPB in soils are not known. Soils present a heterogeneous surface with a variety of organic and inorganic active sites. The preliminary studies indicate that the degradation of TPB is abiotic and is catalyzed by soil mineral surfaces. The soil is a multiphase system containing silicate minerals, nonsilicate minerals, liquid phase and various kinds of organic matter. Mechanisms of abiotic degradation cannot be formulated from the soil-related degradation. The factors which promote the abiotic degradation need to be investigated. The degradation studies of TPB is of special interest to the DOE which will utilize this chemical in the processing of radioactive wastes. TPB as well as its intermediate product, DPBA, have been reported to be toxic to microorganisms (30) and plants, dependent on soil or water environments for their survival and growth (29,31,32).

OBJECTIVES OF STUDIES

Tetraphenylborate and diphenylboronic acid are contaminants of concern at the SRP. However, the factors controlling their rates of abiotic degradation are not fully understood. The effects of several variables such as moisture levels, temperature, type of adsorbing surface and organic matter are not clearly known.

The contribution from various surface sites (Si, Al, Fe, Mn, organic matter) needs to be evaluated in order to be able to predict the rate of transformation in the surface and lower horizons in various soil types. In addition, the intermediate products derived from decomposition of TPB need to be identified and their persistence evaluated. The initial work done at SREL (24) provided a basis for the design of investigations conducted on the abiotic degradation of TPB and DPBA.

The major objectives of the proposed research were to determine the effects of soil mineral phases on the rates of surface facilitated degradation of Tetraphenylborate and diphenylboronic acid. In addition, experiments were conducted to identify the products of the abiotic degradation of TPB and DPBA in soils. Since previous work (29) suggested that the initial reactions involved oxidation of TPB by electron transfer to Lewis acid sites, this study focused on the effects of major redox active solid phases in minerals. Kaolinite is the predominate clay mineral in SRP soils and was the principle solid phase component in the experimental systems. However; a comparative study with montmorillonite was also conducted. Various Fe and Mn oxide phases were used to elucidate their role in affecting the rates of degradation of the organoborates. Previous work indicated that the rates of degradation were slow in saturated systems; however, these rates were considerably enhanced by the higher concentrations of the oxide surfaces. The oxides employed in this study included well crystallized mineral phases such as goethite, corundum, manganite and rutile.

Previous studies at SREL have shown that DPBA is the initial product of surface facilitated degradation of TPB in soils. The DPBA produced subsequently degraded abiotically. However, the products of this reaction were not identified. After several weeks of TPB degradation an increase in inorganic boron concentration was observed. One of the objectives in the proposed study was to identify the products of DPBA degradation. Based on the results of past experimental data, a large amount of DPBA was added to kaolinite mineral to facilitate recovery and identification of degradation products. Reaction mixtures were extracted with an organic solvent. These extracts were analyzed using HPLC. However further confirmation of intermediate products is required by use of mass spectrometry.

Materials and Methods

Adsorbate clay minerals, KGa-2 (poorly crystallized kaolinite, Warren County GA) and SWY1-(Na-montmorillonite, Crook County Wyoming) were procured, from the Department of Geology, University of Missouri, Columbia, Missouri. The physico-chemical characteristics of these minerals along with other necessary information is given in Table II and III. Manganite, corundum, goethite and rutile minerals were purchased from Ward's Natural Science Establishment, Inc., Rochester, New York. Tetraphenylboron (TPB), diphenylborinic acid (DPBA), biphenyl (BP), phenylboric acid (PBA), and phenol were obtained from Aldrich Chemical Company, Inc. Milwaukee, WI. All chemicals were of AR quality. No further purification of chemicals was done. The clay minerals were cleaned of carbonates, soluble salts, organic matter, and free iron oxides and were saturated with Ca and Na (33) prior to their use as substrate in this study.

One hundred microliter (100 μ L) of solution containing requisite quantities of organoborates was added to an appropriate portion of the solid phase adsorbate in borosilicate glass centrifuge tubes with teflon lined screw caps. After thorough mixing, samples were incubated at room temperature (24°C). At a predetermined time the entire contents of the tube were equilibrated with 4.0 mL of acetonitrile by manual shaking for fifteen (15) minutes, after which the contents of the tube were centrifuged for 30 minutes at 10,000 rpm in Fisher Centrifuge TM centrifuge. The supernatant liquid was passed through a 0.2 μ m nylon syringe filter and analyzed using high performance liquid chromatography (HPLC). The HPLC analysis was performed using a Hewlett-Packard model 1050 liquid chromatograph, with a UV100 variable wavelength detector, autosampler, LC chem station and a VYDAC-C 18

Table II.

CHARACTERISTICS OF MINERALS

CHARACTERISTICS	KAOLINITE	MONTMORILLONITE
Code Name	KGa-2	SWY-1
	%	%
Si 02	43.900	62.900
Al2 03	38.500	19.600
Ti 02	2.080	0.090
Fe2 03	0.980	3.350
Fe 0	0.150	0.320
Mn 0	n.d	0.006

Table III.

CHARACTERISTICS OF MINERALS

CHARACTERISTICS	KAOLINITE	MONTMORILLONITE
Code Name	KGa-2	SWY-1
	%	%
Mg O	0.030	3.050
Ca O	n.d	1.680
Na ₂ O	<0.050	1.530
K ₂ O	0.065	0.530
P ₂ O ₅	0.045	0.049
S	0.020	0.040
F	0.020	0.111
CEC, Meq/100g	3.3	76.4
SURFACE AREA	23.5	31.82
M ₂ /g		

reverse phase column. The solvent system employed was water (HPLC grade), adjusted to pH 3.2 with H_3PO_4 and acetonitrile. The elution program was a 20 min. gradient from 95:5 water/acetonitrile to 100% acetonitrile at a flow of 1 mL min^{-1} . The UV detector sensitivity was generally 0.02 to 0.04 absorbance units for a full-scale deflection, monitored at 230 nm with an injection volume of 20 μL . The organoborates added to one set of minerals were extracted within the first about five minutes which has been recognized as time zero extraction.

RESULTS AND DISCUSSION

Degradation of tetraphenylboron and Diphenylborinic Acid

Theory

The present study indicates that the degradation of TPB and DPBA is a consecutive chain reaction as indicated below (equations I & II). The reactions leading to the disappearance of TPB and DPBA move through a number of steps, forming several intermediates, prior to their conversion into inorganic boron compounds and probably carbon dioxide. No attempt was made to measure carbon dioxide during this work. However; it is hypothesized, based on the flow of reactions, that carbon dioxide is probably one of the ultimate end product of this chain reaction. Undoubtedly additional study is required to probe this hypothesis. It is believed that the final product for the degradation of TPB and DPBA is the same

Assuming no reverse reaction and that the intermediates do not compete for the surface active reaction sites, a rate equation of the following kind can be derived.

$$\frac{d[\text{TPB}]}{dt} = -k_1 [\text{TPB}]$$

$$[\text{TPB}] = [\text{TPB}]_0 e^{-k_1 t} \text{-----III}$$

[TPB] is concentration of TPB at time t.
 [TPB]₀ is concentration of TPB at time zero
 k₁ is forward rate reaction constant
 and t is time of reaction
 $t_{1/2} = \frac{0.693}{k_1}$
 t_{1/2} is half life for the reaction

The data reported here was collected by use of HPLC under parameters listed in the methods and material section of this report.

Twenty microliters of TPB (1.5 um/mL), DPBA (1.563um/ml), BP (0.3125 Um/mL) MPBA (0.0775 Um/mL) & phenol (0.3125 um/mL) were injected into HPLC to obtain the estimate on the sensitivity of the instrument. The chromatograms thus obtained are shown in the figures 1-5. The peak area followed a linear relation with TPB concentration (figure 6). The chromatogram for the mixture, containing the above mentioned concentrations of organoborates and organic compounds, is given in figure 7. The retention time for each of these chemicals is given in Table IV. The chromatogram (figure 7) indicates that an excellent separation of DPBA, BP, MPBA & Phenol was achieved by use of the HPLC techniques applied in the present study. The retention time (t_r) was used for the identification of degradation products of TPB and DPBA. The peak area was indicative of the quantitative estimates of each of the degradation products generated in the reaction system as well as the parent organoborates, TPB & DPBA remained in the system at any specific time interval during the experimental period.

Figure I. Chromatogram of Tetraphenylboron(TPB)

Figure 2. Chromatogram of Diphenylboronic acid (DPBA)

Figure 3. Chromatogram of Biphenyl (BP)

Figure 4. Chromatogram of Phenylboronic acid (MPBA)

Figure 5. Chromatogram of Phenol

Figure 6. Relation of Peak Area vs TPB Concentration

STANDARD CURVE

Table IV.

RETENTION TIME OF STANDARDS, (SEPARATE AND MIXTURE)

Name	Formula	Formula Weight	Retention Time
PhenylBoric Acid	$C_6H_5 B(OH)_2$	121.93	8.407
Phenol	$C_6H_5 OH$	94.11	9.272
Tetraphenylboron Sodium	$(C_6H_5)_4 BNa$	342.23	14.661
Diphenylborinic Acid Ethanolamine Ester	$(C_6H_5)_2 BOCH_2 CH_2 NH_2$	225.10	16.251
Biphenyl	$C_6H_5 C_6H_5$	154.21	18.348
Benzene	C_6H_6	78.11	?

Figure 7. Chromatogram of Diphenylboronic acid (DPBA), Biphenyl (BP), Phenylboronic acid(MPBA), and Phenol.

Degradation of Tetraphenylboron by Non Clay Minerals: The kaolinite and montmorellonite clay minerals used in the current study contained significant amounts of oxides of aluminum iron, manganese and titanium (Table II). Consequently it was considered useful to evaluate the role of goethite, corundum, manganite and rutile in the degradation of organoborates. All these minerals were ground to pass through a standard sieve #60. Zero point five gram of each mineral except manganite received 12 mm/kg of TPB. Manganite received 10 mm/kg of TPB. Data on the degradation of TPB facilitated by theses minerals is shown in Table V. Corundum was most effective in the initial degradation (48.75% TPB disappeared) of TPB followed by goethite (39.58% TPB disappeared) and rutile (8% TPB disappeared). Manganite was not only the least effective in carrying out the initial TPB degradation, but the amount of TPB in the system remained steady during the time interval (0-48 hrs) used in this study. Most of TPB added to goethite disappeared within 24 hours. This was followed by rutile which was instrumental in leading to the continuous degradation of TPB. However the overall rate of degradation of TPB by goethite was much higher than by rutile (Table V).

Degradation of Tetraphenylboron By Kaolinite and Montmorillonite

The TPB concentrations decreased exponentially with time in kaolinite and montmorillonite clays (Figure 8 & 9). About 15 percent of the initial TPB remained in clays at the end of the experimental period. The degradation rate of TPB on kaolinite was much higher than on montmorillonite (Tables X & XI). Over 80% of TPB added to kaolinite disappeared in 8 hours whereas it took over 12 days for montmorillonite to achieve that level of TPB degradation . (Figures 8 & 9).

Table V.

AMOUNT OF TETRAPHENYLBORON (TPB) REMAINING IN THE SYSTEM

MINERALS Hours	Amount of TPB added, MM/kg			
	10	12	12	12
	MANGANITE $\text{MnO}(\text{OH})_2$	GOETHITE Fe_2O_3	CORUNDUM Al_2O_3	RUTILE TiO_2
0	9.995	7.25	6.15	11.04
2	8.91	5.98	6.91	10.41
8	8.85	4.71	6.26	9.38
16	8.23	4.25	6.48	6.05
24	8.06	0.42	6.63	5.72
48		0.12	6.64	2.99

Kaolinite is composed of one layer of silica tetrahedra and a sheet of aluminum octahedra where an aluminum atom is linked to six oxygen atoms and/or hydroxal groups through coordinate covalent bonds. Due to the presence of one silica sheet and one alumina sheet, kaolinite is known as 1:1 mineral. Its structure suggests that metal (Al) ions are likely to be exposed to perform the function of Lewis acid. Montmorillonite is composed of two sheets of silica tetrahedra and one sheet of aluminum octahedra which is sandwiched between the two sheets of silica tetrahedra thus limiting or inhibiting the role of metal ions as a Lewis acid as the metal ions are not exposed to act as surface active sites.

The elements in group III A; especially boron and aluminum form 3 coordinate Lewis acids capable of accepting an electron pair and increasing their coordination number (34). Commonly used Lewis acids of aluminum are dimers, which probably are similar in structure to the aluminum octahedra sheet which contributes to the synthesis of kaolinite and montmorillonite clay minerals.

The data presented in Table V clearly indicated the role of corundum in facilitating the degradation of TPB. Based on the literature search (23) and the data collected in this study it appeared that kaolinite, due to its exposed metal ions, which have been hypothesized (29) as potential sites for the redox decomposition of TPB, provided an ideal substrate for the surface catalyzed degradation of TPB. Contrary to this, montmorillonite did not provide an ideal surface conditions for the acceptance of electrons that needed to be donated by TPB during its redox reaction. Consequently the degradation of TPB in montmorillonite was slow.

Degradation of TPB by sodium saturated kaolinite and montmorillonite was slow as compared to calcium saturated minerals. The degradation of TPB by

Figure 8.

DEGRADATION OF TPB BY KAOLINITE

Figure 9.

DEGRADATION OF TPB BY MONTMORILLONITE

uncleaned minerals appeared close to the average of sodium and calcium saturated minerals. The data collected for uncleaned kaolinite and montmorillonite was very interesting, as the rate of TPB degradation for uncleaned kaolinite was much faster than uncleaned montmorillonite, even though kaolinite contained, as compared to montmorillonite lower quantities of Fe_2O_3 , FeO and MnO , which traditionally have been considered active Lewis acids. On the other hand kaolinite contained higher amounts of Al_2O_3 and TiO_2 which provided active surface for TPB degradation. Figures 8 and 9 indicate that the initial degradation of TPB on clay mineral was relatively fast. This was followed by a considerable lag period, after which the rate of reaction for the degradation of TPB increased again. It was obvious that the rate of degradation of TPB continued to vary with time

Effect of Argon and Oxygen on the Degradation of TPB

An appropriate amount gm of (0.50) uncleaned kaolinite was transferred to two sets of centrifuge tubes. Both sets were purged with argon, plugged and allowed to sit overnight. The contents of the centrifuge tubes were purged again (next morning) with argon prior to each centrifuge tube receiving 12.0 mm/kg of TPB which was mixed with substrate. Tubes were purged again with argon, plugged and allowed to incubate at room temperature. TPB from each tube was extracted at pre-determined time and quantified in accordance with the method described in the section on methods and materials.

The results for this analysis are shown in figure 10. The data clearly indicate that purging of samples with argon completely retarded the further degradation of TPB, probably by eliminating the supply of air to the active surface sites where redox reaction was facilitated. After twenty four hours the argon from the samples was

Figure 10.

EFFECT OF ARGON AND OXYGEN ON THE DEGRADATION OF TPB BY KAOLINITE

purged and replaced with oxygen. The TPB of each centrifuge tube, purged with oxygen, was determined at predetermined times. The results shown in figure 10 indicated that the degradation of TPB was initiated immediately after the samples were purged with oxygen, which replaced argon from the tubes. In about eight hours remaining TPB disappeared from centrifuge tubes, purged with oxygen. The data indicate that the initial degradation of TPB related to the metal ions acting as Lewis acid which received a pair of electrons from TPB. The absence of air/oxygen inhibited the rejuvenation of active surface sites which had been reduced and were responsible for catalyzing the degradation of TPB. The oxygen pumped into the system restored the vitality of the active sites by oxidation which resulted in the initiation of TPB degradation again. It might be hypothesized that the rate of TPB degradation was controlled by the availability and diffusion of Air/oxygen into the substrate that provided the active sites for chemical reactions.

TPB Concentrations and TPB Degradation

The effect of TPB concentrations on the rate of TPB degradation is shown in table VI. It is clear from this data that increasing the concentration of TPB led to a decrease in the percentage of TPB degraded by kaolinite. It was difficult to ascertain the significance of this fact. However, when the concentration of TPB was increased from 6 mm/kg to 24 mm/kg, the initial amount of TPB degraded by kaolinite decreased from 3.47 mm/kg to 2.2mm/kg (Table VI).. This was presumed to mean that overloading the surface sites where reaction activities were occurring resulted in poisoning those sites temporarily. It was obvious that doubling the concentration of TPB on the same amount of substrate did not double the rate of reaction, indicating that degradation of TPB was driven by the availability of active sites rather than the

Table VI.

EFFECT OF TPB CONCENTRATION ON TPB DEGRADATION

Hours	TPB ADDED MM/KG	6		12		24	
		TPB REMAINING	% DEGRADED	TPB REMAINING	% DEGRADED	TPB REMAINING	% DEGRADED
0		2.53	57.8	8.15	32	21.8	18.76
2		2.14	59.4	7.63	36.4	22.3	18.63
8		2.07	65.5	6.42	46.5	40.8	14.20
16		0.674	88.8	1.98	83.5	55.5	10.68
24		0.357	94.0	.274	97.7	97.2	.663
48		0.280	95.3	.266	97.8	98.2	.406

amount of TPB added to kaolinite.

Effect of Kaolinite on TPB Degradation

In order to ascertain the role of surface active sites in the degradation of TPB, 100 uL of solution containing 6.0 um of TPB was mixed with three sets of centrifuge tubes. Each set contained 0.25, 0.5 and 1.0 gs of kaolinite. The TPB from each tube was extracted and quantified in accordance with the previously described methodology. The data shown in Table VII indicate that the rate of TPB degradation increased from 26.6% for 0.25 gs of kaolinite to 51.5% for 1.0 gs of kaolinite. Generally higher amounts of substrate led to increased percent of degradation of TPB. This trend was followed through 16 hours of sampling beyond which the amount of TPB remaining in this system was about the same and percentage degradation at the end of 24 hours was about 97 percent. This indicated that irrespective of the amount of kaolinite used for these experiments about 97% TPB had been degraded by 24 hours. A small but measurable quantity of TPB remained in the system even beyond 48 hours of sampling. It was interesting to point out that doubling the amount of kaolinite did not double the degradation of TPB.

Effect of Temperature on the Degradation of TPB

Chemical reactions are accelerated by an increase in temperature. In many cases, the rate of a reaction in a homogeneous system approximately doubles by an increase in temperature of only 10°C (35). The present system was a heterogeneous system which contained kaolinite, corrupted with TPB, as well as several degraded intermediates of TPB. Surface active sites of kaolinite provided a medium to catalyze the reaction. In addition TPB and kaolinite air/oxygen appeared to have played an important role in the reaction system. The rate of TPB degradation generally

Table VIII.

EFFECT OF TEMPERATURE ON TPB DEGRADATION

Weight of Kaolinite gs Hours	0.25				0.50				1.0			
	32 DEG C		24 deg C		32 deg C		24 degC		32 deg C		24 deg C	
	TPB	%	TPB	%	TPB	%	TPB	%	TPB	%	TPB	%
0	9.33	22.2	8.81	26.6	6.69	44.3	8.15	32.0	4.49	62.6	5.82	51.5
2	7.50	37.5	8.61	28.3	4.21	64.9	7.63	36.4	4.02	66.5	4.36	63.7
8	1.30	89.2	5.68	52.6	0.617	94.7	6.42	46.5	0.335	97.2	4.10	65.8
16	0.437	96.4	4.33	63.9	0.288	97.6	1.98	83.5	0.183	98.5	0.866	92.8
24	0.186	98.5	0.252	97.9	0.189	98.4	0.274	97.7	0.192	98.4	0.348	97.1
48	0.183	98.0	0.193	98.4	0.210	98.3	0.266	97.8	0.150	98.8	0.204	98.3

Table VII.

EFFECT OF KAOLONITE ON TPB DEGRADATION

Weight of Kaolinite gs Hours	0.25		0.50		1.0	
	TPB	%	TPB	%	TPB	%
0	8.81	26.6	8.15	32.0	5.82	51.5
2	8.61	28.3	7.63	36.4	4.36	63.7
8	5.68	52.6	6.42	46.5	4.10	65.8
16	4.33	63.9	1.98	83.5	0.866	92.8
24	0.252	97.9	0.274	97.7	0.348	97.1
48	0.193	98.4	0.266	97.8	0.204	98.3

increased (Table VIII) as temperature was raised from 24°C to 32°C. However; this was a complex system and the rate of reaction did not double as was expected for every 10°C rise in temperature for homogeneous reactions. Additional study is required to fully evaluate the role of temperature in the degradation process as well as its relationship with the diffusion of air/oxygen to the active sites where actual reaction occurred.

Degradation of Diphenylborinic Acid (DPBA) by Kaolinite

The requisite amount (24 mm/kg) of DPBA was added to kaolinite. DPBA was extracted at a predetermined time schedule and quantified as described previously. The amount of DPBA remaining at a specified time interval is shown in Figure II. Generally, the degradation DPBA followed a similar pattern as described for TPB. There was an initial fast reaction followed by a considerable lag period. There was no appreciable decrease in the amount of DPBA at 8 hours sampling as compared to 2 hours sampling. The rate of reaction considerably increased between 8 and 16 hour sampling as is indicated by Figure II. Over 96% of DPBA degraded by 24 hour sampling time. The reaction appeared to have followed a linear relations for the measurements made at 8, 16 and 24 hours.

Kinetics of Degradation of TPB and DPBA

Several studies (23, 36) investigating the abiotic degradation of organic compounds aniline, benzoic acid, phenol, deurion etc. on mineral surfaces have shown that the overall reactions followed first order kinetics. A pseudo first order rate expression was applied by Mills et. al (29) to test that hypothesis. The data (29) did not follow the first order reaction rate law. Several methods (36) are available for determining the rate laws from the raw kinetic data, given the concentration as a

DEGRADATION OF DIPHENYLBORINIC ACID

Figure 11.

function of time. Some of the available methods were applied to the data collected in the present study. It appears that the data reported did not show a perfect obedience to any of the traditionally available rate laws.

A first order reaction rate equation (equation III) was derived for TPB degradation, presuming that there was no reverse reaction and the intermediates did not compete of surface active sites where reaction was catalyzed. A similar equation for the degradation of DPBA could be obtained. The kinetics data for TPB degradation on the kaolinite and mountmorillinite surface are shown in figures 12&13.

The plots consisted of log of the TPB remaining in the system [$\log C$] as a function of time. A similar plot (Figure 14) was obtained for the degradation of DPBA on kaolinite surface where $\log [DPBA]/[DPBA]$ (equation III) was plotted as a function of time. It was apparent from these plots that the data did not obey the first order rate reaction law. Each of the curves can be reasonably dissected into three linear components. The initial reaction was relatively fast as in some cases; up to about 60% of TPB disappeared by the time first measurement (Time Zero) was made. This was followed by a considerable lag period. After this period the rate of reaction increased again. Similar results have been reported in the literature (23 & 37) where it was suggested that the abiotic degradation of parathion on kaolinite proceeded by both a rapid and a slow reaction. It was difficult to refute that assertion (37). However; several logical and valid interpretations could be derived based on the data reported here. The deviation from linearity in the first order model was at least partially caused by the competition for the surface active sites not only by DPBA, but also by a number of other organic compounds (BP, PBA and phenol) which were detected in the reaction system and were found to under degradation. The system changed from a

simple TPB/kaolinite system to a complex multi-phase organic compound/kaolinite-system- where the degradation of several of the intermediates was also taking place. Several of the organic and organoborate compounds were detected in the system which obviously refuted the hypothesis that the intermediates did not compete for the surface active sites on kaolinite and montmorillinite. The competition by intermediates for surface active sites may be one of the several reasons that the data do not obey any of the kinetic rate laws. Initial reaction was fast as there was no competition from the intermediate products for the surface active sites. The surface active sites played an important role in facilitating the degradation of organic compounds as the degradation continued to increase with the increasing amount of kaolinite (Table VIII) for the same concentration of TPB.

The degradation, of TPB, and DPBA as well as other intermediates detected in the system, appeared to be a redox reaction; where metal ions acting as Lewis acids would require a concomitant reduction and a decrease in the concentration of reactive sites as the reaction proceeded. These sites needed regeneration (oxidation) so that they could continue to play their part in oxidizing TPB, DPBA etc. This was found to be true since the degradation of TPB was completely retarded when the system was purged with argon (Figure 10). The degradation of TPB resumed immediately on purging the same system with oxygen. It appeared that the rate of degradation of TPB was higher for oxygen purged system when compared to systems which were exposed to normal air in the laboratory. It was obvious, as hypothesized in the literature (23), that oxygen played a vital role in the degradation of organoborates. However; additional study is required to quantify the role of oxygen in the degradation of organoborates.

Figure 12.

Figure 13.

KINETICS OF TPB DEGRADATION BY MONTMORILLONITE

Figure 14.

Table X. KINETIC PARAMETERS FOR THE DEGRADATION
OF TETRAPHENYLBORON (TPB) BY KAOLINITE

TREATMENT	Na	Uncleaned	Ca
REACTION RATE UM/HR	0.485	0.650	0.564
HALF LIFE $t_{1/2}$ HRS	4.85	NA	2.75
REACTION RATE CONSTANT (k) 10^{-2} /HR	15.40	NA	25.20

Table XI. KINETIC PARAMETERS FOR THE DEGRADATION
OF TETRAPHENYLBORON (TPB) BY MONTMORILLONITE

TREATMENT	Na	Uncleaned	Ca
REACTION RATE UM/HR	0.019	0.024	0.057
HALF LIFE t 1/2 HRS	96.0	24.0	10.0
REACTION RATE CONSTANT (k) 10-2 /HR	0.72	2.89	6.90

The raw data did not obey overall first order reaction rate law. However if the plots of Figures 12-14 were broken into three segments, then each segment appeared to follow the first order reaction rate law. Presuming that first order reaction rate law was obeyed, several kinetic parameters for the degradation of TPB by kaolinite and montmorillonite were calculated and are given in Tables X & XI. The data given in these tables indicated that the reaction rate for the degradation TPB was much higher on kaolinite surface than on montmorillonite surface. In general Ca saturated kaolinite and montmorillonite provided degradation surfaces for TPB which were significantly superior than the other surfaces used in the current studies.

Mechanisms of TPB and DPBA Degradation

Electrochemical techniques of oxidation, using platinum electrodes, applied by Geske (38) indicated that TPB initially degraded into DPBA and biphenyl (BP). Similar results were also obtained by chemical oxidation of TPB by ceric (39) and iridate ions (40). Mills et. al (23) hypothesized the formation of TPB radicals and carbonation in the initiation of the oxidation process. Two (23) hypothesis have been projected in the literature for the degradation of TPB and formation of intermediate products. The metal ions in the clay minerals or in soil act as Lewis acids accepting a pair of electrons leading to the oxidation of TPB as well as many of its degradation intermediates. The metal ions which undergo reduction during this process need to be oxidized by their interaction with oxygen. Alternatively, reaction of TPB with H^+ results in the initial formation of triphenylboron and benzene. Triphenylboron is unstable and decomposes to form phenyl diphenylborinate $[(C_6H_5)_2 BO C_6H_5]$ which hydrolyses to yield phenol and DPBA. Although these compounds (benzene, triphenylboron) could readily be detected by the analytical method employed, none was detected in any of

Table IX.

TETRAPHENYLBORON SODIUM DEGRADATION PRODUCTS (HPLC ANALYSIS BASED)

RETENTION TIME
AVERAGE OF 5 RUNS

t_r

DEGRADED PRODUCT

8.407	PHENYLBORIC ACID
9.207	PHENOL
14.661	TETRAPHENYLBORON SODIUM
16.251	DIPHENYLBORINIC ACID ETHANOLAMINO
18.348	BIPHENYL

the several experiments. The surface active sites of kaolinite and montmorillonite required the availability of H^+ for them to act as a Bronsted acids and to become proton donor. The present study used dry minerals. No moisture was added to the mineral surfaces. All dilutions of TPB & DPBA were made in $CH_3 CN$. Under the conditions employed in the present research, polarization of water resulting in the generation of H^+ was highly unlikely.

The degradation products of TPB and DPBA are shown in table IX. These products were easily detectable and identifiable by the HPLC, using retention time as one of the techniques employed for the identification of organic compounds in the system. These products (table IX) were consistently detected as intermediates for the degradation of TPB. Degradation of DPBA produced phenylboric acid (PBA) and phenol which persisted in the system even after DPBA & TPB had completely disappeared. It was concluded from the data collected through out the tenure of this work that the degradation of TPB & DPBA is a redox reaction. Possible flow of reaction leading to the formation of various intermediates is given below. (No attempt was made to balance the equations).

The oxidation was perceived to proceed via the following mechanism involving the formation of TPB radicals and carbocation.

Literature Cited

1. Goring, C.A., D.A. Laskawski, J. W. Hamaker and R. W. Meekle, Principles of pesticide degradation in soil. In R. Hague and V.H. Freed eds., Environmental Dynamics to Pesticides, Plenum Press, New York. Pp. 135-172 (1975).
2. Khan, S.V., Pesticides in the soil environment. Elsevier Scientific Publ. Co. New York. Pp. 411-428 (1969).
3. Voudriaw, E.A. and M. Reinhard, Abiotic organic reactions at mineral surfaces. Chap. 22, p. 462-486, In J.A. Davis and K.F. Hayes (eds.), Geochemical processes at mineral surfaces, ACS Symposium Series 323, American Chemical Society, Washington, DC (1986)
4. Laszlo, P., Chemical reactions on clays. Science, 235: 1473-1477 (1987).
5. Saltzman, S. and U. Mingelgrin, nonbiological degradation of pesticides in the unsaturated zone. Chap. 11, p. 153-161, In B. Yaron, G. Dagan, and J. Goldsmith (eds.), Pollutants in Porous Media, Springer-Verlag, NY (1984).
6. Mortland, M.A. and K. V. Raman, Surface acidity of smectites in relation to hydration, exchangeable cation, and structure. Clay Miner., 16:393-398 (1968).
7. Solomon, D.H., B.C. Loft and J. D. Swift, Reactions catalyzed by mineals. IV. The mechanism of the benzidine blue reaction on solicate minerals. Clay minerals, 7:389-397(1968).
8. Theng, B.K.G., Organic reactions catalyzed by clay minerals, Chap. 7, p.261-291, In The Chemistry of Clay Organic Reactions, John Wiley and sons, NY (1974).

9. Karickhoff, S.W. and G. W. Bailey, Protonation of organic bases in a clay-water system. *Clays Clay Miner.* 24:170-176 (1976).
10. Armstrong, D.E. and J. G. Kanard, Nonbiological degradation of pesticides. In Guenzi W. D. (ed) *Pesticides in soil and water.* Soil Sci. Soc. Am., Madison, WI. Pp. 123-131 (1974).
11. Zepp, R.G., P. F. Schlotzhaun and R. M. Sink, Photosensitized transformation involving electron energy transfer in natural waters: Role of humic substances. *Envir. Sci. Tech.* 19, 74-81(1985).
12. Pillai, P., C. S. Helling and J. C. Dragun, Soil catalyzed oxidation of aniline, *Chemosphere*, 11, 299-317(1982).
13. Lightfoot, E.N., P.S. Thomas, R.L. Jones, J. L. Hansen and R. R. Romine, Laboratory studies on mechanisms for degradation of aldicarb, aldicarb sulfoxide and aldecarb sulfone. *Envir. Toxicology and Chemistry*, 6, 337-394 (1987).
14. Dragun, J. and C. S. Helling, Physiochemical and structural relationship of organic chemicals undergoing soil and clay catalyzed free-radical oxidation. *Soil Sci.* 139, 100-111 (1986).
15. Ballog, J.M., S.U. Liu and E. G. Deune, Transformation of 2-6 diethylaniline, *Soil Sci.*, 143, 56-65 (1987).
16. McBride, M.B., E.J. Silkora and L. G. Wesselink, Complexation and catalyzed oxidative polymerization of catechol by aluminum in acid solutions. *Soil Sci. Soc. Am. J.* 52:985-993 (1988).
17. Kyuma, K. and K. Kawaguchi, Oxidative changes of polyphenols as influenced by allophone. *Soil Sci. Am. Proc.* 28:371-374 (1984).

18. Kumuda K. and H. Kato, browning of pyrogallal as affected by clay minerals. I. classification of clay minerals based on their catalytic effects on the browning reaction of pyrogallal. *Soil Sci. Plant. Nutr.* 116:195-200 (1970).
19. Thompson, T.D. and J. F. Mall, Oxidative power of smectites measured by hydroquinone. *Clays Clay Miner.* 21:337-350 (1973).
20. Filip, Z., W. Flaig and E. Rietz, Oxidation of some phenolic substances as influenced by clay minerals. *Soil Org. Matter Stud. Proc. Symp.* 2:92-96 (1973).
21. Wang, T. S. C., S. W. Li and Y. L. Ferng, Catalytic polymerization of phenolic compounds by clay minerals. *Soil Sci.* 126:15-21 (1978).
22. McBride, M. B., Adsorption and oxidation of phenolic compounds by iron and manganese oxides. *Soil Sci. Soc. Am. J.* 61:1466-1472 (1987).
23. Dao and T. L. Lavy, A kinetic study of adsorption and degradation of aniline, benzoic acid, phenol, and Diuron in soil suspensions. *Soil Sci.* 143:66-72 (1987).
24. Mills, G. L., D. Schwind and D. C. Adriano, Preconcentration and analysis of tetraphenylboron and diphenylborinic acid in natural waters using C reverse-phase liquid chromatography. *Chemosphere*, 17, 937-942 (1988).
25. Flaschka H. and A. J. Bernard, J. In Reilly ed., *Advances in Analytical Chemistry and Instrumentation*. Interscience, New York, Pp. 1-118 (1960).
26. Jalicoeur, C., N.D. The and A. Cabarra, *Can J. Chem.*, 49:2008-2013 (1971).
27. Arnatt, S and S. C. Abrahams, *Acta Cryst.* 11,449-450 (1958).

28. Adriano, D. C., G. L. Mills, J. L. Afre and R. J. Hart, Proceedings of the International Conference on Environmental Contamination, United Nations Environment (1985).
29. Mills, G.L., D. Kaplan, D. Schwind, and D. Adriano, Surface-facilitated chemical degradation of tetraphenylboron in soil. J. Environ. Qual. In Press. (1989).
30. Shann, J. R., P. M. Bertsch and S. M. Presnell. J. Environ. Qual. (submitted) (1989).
31. Burkman, W. G., D. C. Adriano and J. L. Afre. Phytoavailability of boron from organic sources. J. Environ. Qual., 15:416-421 (1987).
32. Kaplan, D. I., W. G. Burkman and D. C. Adriano. Response of loblolly pine (*Pinus taeda* L.) seedlings to soil-applied organo-borates. 37:73-83 (1988).
33. Klute, Arnold. Methods of Soil Analysis Part I Physical and Mineralogical methods. American Society of Agronomy, Inc. Medison, WI. 53711 (1965).
34. Miessler Gary L. and Tarr, Donald A., Inorganic Chemistry, pp. 230-250 Prentice Hall, Englewood Cliffs, New Jersey , 1990.
35. Robinson, W.R. Odom, J.D. and Holtzelaw, Jr. H. F., Chemistry , concepts and models, D.C. Heath and Company, Lexington Mass. 1992.
36. El-Amanay, M. M. and Mill, T. , Hydrolysis Kinetics of Organic Chemicals on montmorillonite and kaolinite surfaces as related to moisture conten. clays clay Miner, 32: 67, 1984.
37. Yaron, B. and Saltzman S., Soil Parathion surface intraction. Residue Rev. 69: 1, 1978.

38. Geske, D. H., The electrooxidation of the tetraphenylborate, an example of a secondary chemical reaction following the primary electrode process J. Phys. Chem. 63: 1062, 1959.
39. Geske, D.H., Evidence for the formation of biphenyl by intermolecular dimerization in the electrooxidation of tetraphenylborate ion. J. phys. chem., 66:1743, 1962.
40. Onak, T., Four Coordination Organoborates In. Organoborate chem. pp 136-163. Academic Press, New York, 1975.

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