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SURFACE REACTIONS OF PARATHION ON CLAYS[1]

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Abstract—The adsorption-catalyzed degradation of parathion on clay surfaces is a hydrolysis process, proceeding either directly or through a rearrangement step. The rate and mechanism of degradation are dependent on the nature of the clay, its hydration status, and saturating cation. A mechanism for parathion degradation at adsorption sites on clay surfaces, in the absence of a liquid phase, is proposed.

Key Words—Adsorption, Catalysis, Hydrolysis, Insecticide, Parathion.

INTRODUCTION

Parathion (O,O-diethyl O-p-nitrophenyl phosphorothioate) is one of the most widely used plant and soil insecticides. Its metabolism in both biotic and abiotic media proceeds through one or more of the following reactions: isomerization, hydrolysis, oxidation, reduction (Melnikov, 1971). Clays are well known as potential catalyzers of various kinds of reactions of the adsorbed molecules (Mortland, 1970; Theng, 1974). As clay-parathion complexes are often formed, either in soils or in formulations using clays as carriers, their effect on parathion conversion may play an important role in parathion alteration in the environment.

The catalytic effect of clays on the metabolism of some organophosphate pesticides, such as malathion, dursban, diazinon, ronnel, zytron, and pyrimiphos ethyl, was reported by Polon and Sawyer (1962), Mortland and Raman (1967), and Mingelgrin et al. (1975). The only degradation mechanism observed in all these cases was the hydrolysis of the phosphate ester bond of the adsorbed molecule. Such factors as the nature of the clay, the moisture content, the saturating cations, and the incubation temperature, were found to affect the rate of the process. In recent years, some results on kaolinite-parathion interactions were reported. Kaolinite was found to enhance parathion degradation; this process also proceeds by the hydrolysis of the phosphate ester bond (Saltzman et al., 1974; Mingelgrin et al., 1977).

Rosenfield and Van Valkenburg (1965) observed that various homoionic bentonites, dried at elevated temperatures (300–950°C), induced the degradation of a thiophosphate (ronnel), the process occurring through a molecular rearrangement. The possible rearrangement products of parathion are known to be much more toxic to mammals than is the parent compound (Joiner et al., 1973). Therefore, it is important to check if such a process is possible in the case of clay-parathion complexes and, if so, to understand its mechanism and study the specific conditions favoring it.

MATERIALS AND METHODS

The clays used in this study were Wyoming bentonite (B-235, Fisher Scientific Co., Fair Lawn, N.J., U.S.A.) and kaolinite (Peerless No. 2, R. T. Vanderbilt, Export Corp., Norwalk, Conn., U.S.A.). The clays investigated were the natural commercial bentonite (which is a Na-saturated clay), and homoionic Ca-bentonite and Ca-kaolinite, prepared by a method described by Shainberg and Otoh (1968). Other materials used as adsorbents were silica gel and anionotrop and cationotrop aluminum oxide (chromatography grade, activity grade I, M. Woelm, Eschwege, W. Germany).

Parathion-^{14}C, labeled in the alkyl chain (Amersham Radiochemical Center, Arlington Heights, Illinois, U.S.A.), and high grade parathion (Analabs, Inc., North Haven, Conn., U.S.A.) were used; paraoxon (Koch Light Labs., England), diethyl thiophosphoric acid, ammonium salt (Ciba-Geigy, AG, Basle, Switzerland), and p-nitrophenol (BDH, Poole, England), were used as standards.

Procedure

The persistence of parathion when adsorbed on various adsorbents was investigated by two procedures:

a) Clay-parathion-^{14}C complexes were prepared by shaking for 30 min 0.3 g air-dried clay with 5 ml hexane solution containing 10,000 ppm parathion-^{14}C. The supernatant was checked for parathion, and discarded; the clay was washed with 5 ml hexane, which was also checked for parathion and discarded. The clay-parathion complex obtained was dried in an air stream, and divided into subsamples of 0.05 g, which were incubated in an oven, at different temperatures, for various periods of time. After incubation the samples were extracted twice, each time for 1 hr, with 4 ml hexane, together with 2 ml deionized water.

b) The clays were dried for 24 hr at 110° and 200°C and clay-parathion complexes were prepared by adding

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Table 1. Composition of the hexane extracts of parathion complexes (TLC data).

Adsorbent	Pretreatment	Incubation conditions		Components[1]	
		Temp (°C)	Time	Parathion	SEP
Bentonite (crude)	none	180	10 min	—	m
Ca-bentonite	none	180	10 min	—	m
Ca-kaolinite	none	110	10 min	s	w
Aluminum oxide cationotrop	none	110	2 min	m	—
Aluminum oxide anionotrop	none	110	2 min	m	—
Silica gel	none	140	10 min	s	w
Bentonite (crude)	none			s	m
	110°C			s	m
	200°C	22	60 days	m	w
Ca-bentonite	none			s	m
	110°C			m	m
	200°C			m	s
Ca-kaolinite	none			m	w
Aluminum oxide cationotrop	none		50 days	w	—
Aluminum oxide anionotrop	none			m	—

[1] The letters s (strong), m (medium), and w (weak) denote the relative intensities of the spots.

parathion to the predried, as well as to air-dried clays. The samples were kept in a desiccator and checked at various intervals. The preparation and the extraction procedures were similar to those described previously. All incubations were in the absence of a liquid phase.

Analytical methods

Several analytical methods were used to identify and quantitate parathion and its metabolites in both the water and hexane used for extraction.

Thin-layer chromatography. Silica gel, fluorescein-containing precoated plates (Riedel-De-Haën AG, Seelze-Hannover, W. Germany), were activated for 1 hr at 105°C. The extracts were spotted and the spots were either air-dried or dried with the aid of an air stream. The solvent systems used were petroleum ether:chloroform:methanol, 7:3:0.3 for the hexane extracts, and 6:2:2 for the water extracts. The spots were viewed under UV light and after spraying with a palladium chloride solution, and an additional spray with NaOH (Lichtenstein and Schulz, 1964). Parathion, paraoxon, diethylthiophosphate, and p-nitrophenol solutions were used as standards.

Infrared spectroscopy. Hexane extracts were applied as continuous bands on TLC plates and developed as described previously. The separated bands were scraped off and eluted with water:hexane, 1:2. The concentrated hexane extracts were evaporated on AgBr windows and the IR spectra were recorded. Parathion and paraoxon standards were run in a similar way. These two analytical methods were used for the separation and identification of parathion metabolites.

Gas-liquid chromatography. Five μl aliquots of the hexane extracts and standard solutions were injected into a gas chromatograph equipped with a glass column 90 cm long, filled with 3.4% QF-1 + 6.2% DC-200 on Gaschrom Q. The operating conditions were 225°, 205°, and 225°C for the inlet, column, and detector, respectively, and the flow rate of the gas carrier (N_2) was 70 ml/min. Under these conditions, a good separation of parathion, paraoxon, and O,S-diethyl O-p-nitrophenyl phosphate was obtained.

^{14}C-counting. Both water and hexane extracts obtained from the experiment in which labeled parathion was used, were checked in the presence of a scintillation fluid containing 60 g naphthalene, 4 g PPO, 0.2 g POPOP, 100 cc methyl alcohol, and 20 cc ethylene glycol to 1 liter dioxan. The last two methods were used to quantitate parathion and its metabolites, which were identified by TLC and IR spectroscopy.

Apparatus. The IR spectra were recorded on a Perkin-Elmer 257 infrared spectrophotometer; for the radioactivity measurements a Packard model 3003 Tricarb scintillation spectrometer was used. Gas-liquid chromatography was performed by a Packard gas chromatograph equipped with an alkali flame ionization detector.

RESULTS AND INTERPRETATION

The behavior of parathion as affected by temperature was checked by IR spectroscopy by heating pure parathion at 180°C for up to 2 hr in a heating cell. No alterations in the spectra were noted, other than a decrease in the intensity of all the peaks, due to volatilization. However, incubation of clay-parathion complexes at similar or lower temperatures resulted in marked and rather fast modifications of the adsorbed parathion.

Thin-layer chromatography. All the hexane extracts obtained from parathion incubated with different adsorbents and in different conditions were checked by

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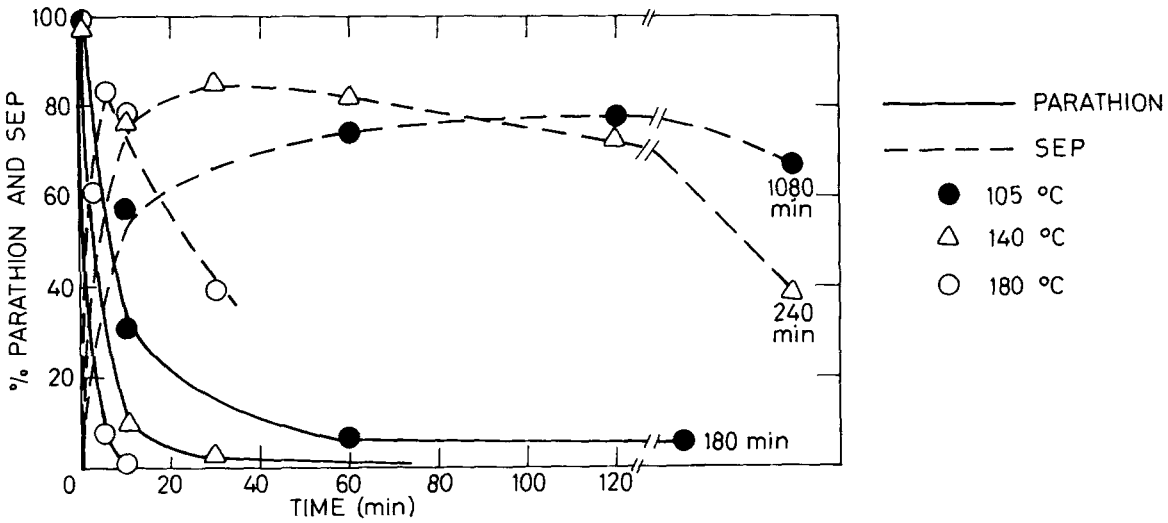


Fig. 1. Parathion loss and SEP evolution at various temperatures on Ca-bentonite.

TLC. Some representative data are given in Table 1. The qualitative nature of the TLC data enables the comparison between the intensities of the spots obtained from one sample, but less so between different samples. Only one or two spots could be detected in all the samples investigated. One of them (Rf 0.87) was identified as parathion (O,O-diethyl O-p-nitrophenyl phosphorothioate), by using a standard parathion solution, while the second (Rf 0.56) was identified as the parathion isomer, O,S-diethyl O-p-nitrophenyl phosphate (SEP). This identification was carried out by isolating the metabolite by TLC, and comparing its IR spectra with the IR spectra of standards (Joiner and Baetcke, 1974).

The qualitative analysis of the hexane extracts shows that SEP is always found in the presence of bentonites in which under some specific conditions it could be the predominant or the only compound present. Relatively small amounts of SEP were also found in the hexane extracts obtained from kaolinite and silica gel, and no such compound was detected in the case of the aluminum oxides investigated.

The TLC examination of the water extracts indicated that 2–3 spots are separated by the solvent system used. Two of the spots, with Rf 0.56 and Rf 0.16, were identified as p-nitrophenol (PNP) and diethyl thiophosphate (DETP), respectively. A more polar, unknown, compound (Rf 0.12) could be seen by UV-light and gave a brownish-yellow color upon spraying with the detection reagents, which indicates the presence of a S atom. This spot was tentatively identified as the phosphate hydrolysis product of SEP. This identification is supported by the fact that it appeared after SEP was formed and degraded. For example, in the water extract of ben-

Table 2. Composition of the water extracts of parathion complexes (TLC data).

Adsorbent	Pretreatment	Incubation conditions		Components[1]		
		Temp (°C)	Time	PNP	DETP	Unknown
Bentonite (crude)	none	180	10 min	m	—	s
Ca-bentonite	none	180	10 min	m	—	s
Ca-kaolinite	none	110	10 min	m	m	m
Aluminum oxide cationotrop	none	110	2 min	m	m	w
Bentonite (crude)	none			w	vw	—
	110°C			w	vw	—
	200°C			vw	vw	—
Ca-bentonite	none	22	60 days	w	m	vw
	110°C			vw	w	vw
	200°C			vw	vw	vw
Ca-kaolinite	none			m	w	m
Aluminum oxide cationotrop	none	22	50 days	s	s	m
Aluminum oxide anionotrop	none			m	m	m

[1] The letters s (strong), m (medium), w (weak) and vw (very weak) denote the relative intensities of the spots.

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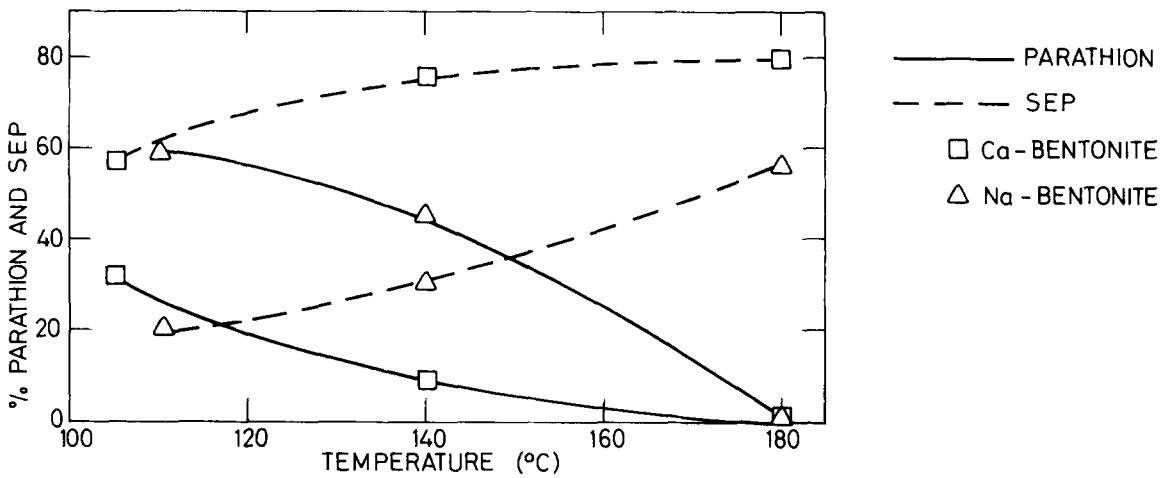


Fig. 2. Comparison between parathion loss and SEP evolution on Na- and Ca-bentonite.

tonites heated at 180°C for 10 min this spot is rather strong (Table 2 and Figure 1).

Table 2 gives some of the representative results obtained by the TLC analysis of the water extracts. The presence of either DETP or the unknown polar compound, or both, is an indication of the degradation mechanism. DETP is the phosphate-containing, hydrolysis product of parathion, while the polar, unknown, water-soluble compound seems to be the hydrolysis product of SEP, which was identified in the hexane extracts. Both SEP and parathion hydrolysis produces p-nitrophenol. The results obtained suggest that the degradation pathway is dependent on both the nature of the adsorbents and the incubation conditions. In bentonite-parathion complexes incubated at temperatures above 100°C no DETP, but only the unknown more polar compound and PNP were detected. Under similar conditions, Ca-kaolinite and aluminum oxide yielded both DETP and the unknown compound. This indicates that under these conditions, formation of SEP and its subsequent hydrolysis is the predominant mechanism for bentonites, while for kaolinite and aluminum oxide this mechanism and direct parathion hydrolysis seem to proceed simultaneously, with direct hydrolysis of parathion dominating in the case of the aluminum oxide. The rate of hydrolysis was about 5 times larger on the cationotrop as compared with the anionotrop aluminum oxide.

With all the adsorbents except the crude bentonite, long term incubation for 50–60 days at room temperature resulted in a degradation pattern similar to that mentioned previously in the case of kaolinite and aluminum oxides (the aluminum oxide cationotrop is one of the most active adsorbents in promoting parathion hydrolysis). On the other hand, the water extracts of the Na-bentonite complexes, irrespective of the predrying temperature, displayed only weak spots of DETP, and no spots of the unknown polar compound could be detected. With the homoionic Ca-bentonite direct parathion hydrolysis seems to be the dominant process in the air-dried samples, whereas in samples preheated at higher temperatures the relative importance of this degradation pathway declined (Table 2).

Gas-liquid chromatography—^{14}C-counting. The information obtained by TLC was used further to quantitate the rate of these processes by a combined GLC-^{14}C counting technique. In the hexane extracts in which parathion only was detected by TLC, this compound was measured by ^{14}C-counting. When both parathion and SEP were present in the same extract, the total amount of both compounds was accounted for by ^{14}C counting. In these extracts two peaks were obtained by GLC. One of the peaks (Rt 4.2 min) was identified as parathion and quantitatively measured by using standard parathion solutions. The retention time of the second peak was 8.2 min. The amount of SEP was calculated as the difference between the total amount of ^{14}C labeled compound and the amount of parathion found by GLC. The results obtained in such a way for Ca-bentonite-parathion complexes heated at different temperatures are presented in Figure 1.

The increase in temperature leads, as expected, to an increase in the rate of the degradation process, which in the case of bentonite proceeds through the formation of the rearrangement product SEP. The stability of this product is highly temperature-dependent. After 5 min at 180°C SEP concentration declined sharply, whereas at 105°C it was stable even after 18 hr. This shows that, under some conditions, the formation of SEP could be the rate-limiting step in parathion degradation. As the decrease in parathion concentration, the formation and disappearance of SEP, and the formation of the water-soluble hydrolysis product are consecutive reactions, each one with its own kinetics, the order of the overall reaction is complicated. Even the rate of the rearrangement reaction as extracted from the slope of parathion

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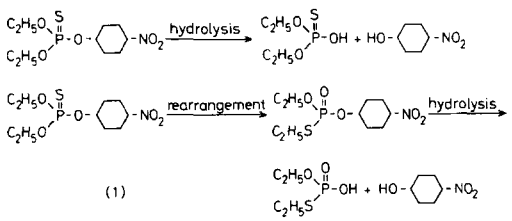
disappearance at time = 0 (Figure 1) does not obey simple zero or first-order reaction kinetics.

The effect of the saturating cation of the bentonites may be inferred from Figure 2, which presents a plot of the amounts of parathion disappearing, and of SEP recovered from bentonites after 10 min of incubation, versus the incubation temperature. Although the effect of temperature is rather similar—by increasing the temperature the amount of parathion decreases and that of SEP increases—there is an obvious difference between the two clays. The fraction of parathion remaining is higher with the crude bentonite, which is Na-saturated, than with the homoionic Ca-bentonite; also the fraction of SEP present is smaller with the Na-clay.

The extent of the hydrolysis of both parathion and SEP was determined from the ^{14}C-counting in the water extracts. However, total ^{14}C recovery (water plus hexane) at temperatures above 110°C decreased with time of heating. The loss in ^{14}C-counting is due to three factors: a) volatilization of parathion and SEP; b) fixation of the phosphate degradation product (Saltzman et al., 1976); and c) formation of volatile products of further degradation. At 180°C the presence of the ethyl mercaptan gas was detected by the lead acetate test.

DISCUSSION

The results obtained show that the adsorption catalyzed degradation of parathion on clays is a hydrolysis process, which proceeds directly and/or through an intermediary step, which was identified as a molecular rearrangement:



(1)

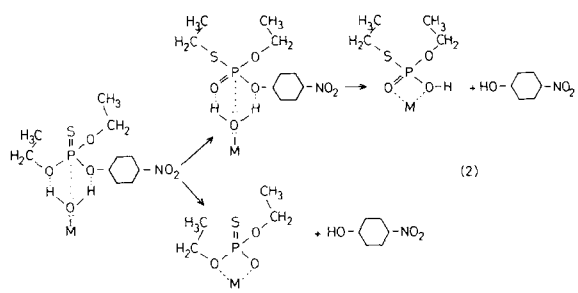
The rearrangement product may be rather long-lived.

The degradation mechanism and the velocity of the process are dependent on the nature of the clay, the saturating cation, and the hydration status of the clay, which is determined by the incubation conditions. The effect of the hydration status is emphasized by the results obtained with predried Ca-bentonite. By reducing the moisture content, the relative rate of the rearrangement reaction increases (Table 1), while the direct hydrolysis rate decreases (Table 2). It should be noted that an IR study of the dehydration of homoionic bentonites demonstrated that Ca-bentonite loses most of its cation hydration water at about 150°C, while some of this water is retained even above 200°C (Mingelgrin and Saltzman, unpublished data).

The results obtained with silica gel and aluminum oxides as adsorbents shed some light on the degradation mechanism, as related to the surface structure. Although the process was very slow in the presence of silica gel, the degradation proceeded through the molecular rearrangement exclusively, and no traces of the water-soluble degradation products were observed. With aluminum oxide, relatively very fast, direct hydrolysis was the predominant mechanism. This provides the explanation for the difference in behavior between bentonite and kaolinite clays. Bentonites, the adsorbing surfaces of which are almost exclusively silica sheets, behaved in a way similar to silica gel, although the specific features of the bentonite surfaces (the presence of counter-cations, the characteristics of the interlayer spaces, etc.) greatly enhanced the velocity of the process, as compared with silica gel. The presence of both alumina and silica surfaces in kaolinite may explain the simultaneous occurrence of the two degradation mechanisms, although direct hydrolysis is the predominant pathway at lower parathion concentrations (Mingelgrin et al., 1977). This is probably due to the stronger adsorbing capacity of alumina surfaces, as compared with silica ones, due to the surface hydroxyls-benzene ring interactions (Sahay and Low, 1974).

The importance of the cation in the degradation process is exemplified by the difference between Na- and Ca-bentonites. Calcium, as the saturating cation, enhances the degradation process, as compared with sodium. This cation effect was also evident with kaolinites (Saltzman et al., 1974). Another indication of the importance of the cation is provided by the much larger rate of hydrolysis on the cationotrop, as compared with the anionotrop aluminum oxide.

Based on the above observations that both the exchangeable cation and hydration status determine the mode of degradation, it may be suggested that ligand water of the exchangeable cation participates in both direct hydrolysis and rearrangement processes through the following mechanism:



(2)

where M is an exchangeable cation.

The above sequence (2) explains both hydrolysis and rearrangement at the same site in the absence of a liquid phase and is in agreement with the previously proposed mode of adsorption on clays (Mingelgrin et al., 1977). The occurrence of direct hydrolysis or rearrangement is a function of the precise conformation of the ester on

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the surface. Minor energy changes may affect the conformation of the phosphate, which in turn may affect considerably the chemical reactivity of the species (Fest and Schmidt, 1973). If the oxygen of the ligand water of the cation distorts the phosphate conformation towards a trigonal bipyramid structure, putting the three P–O bonds of the parathion molecule closer to one plane, the S–C bond will tend to form more easily, as the proper C-atom will get closer to the S-atom. The extent of distortion will depend on the total surface interactions. On the alumina surfaces the tendency towards a trigonal bipyramid structure may be smaller than on the silica surfaces, thus making the direct hydrolysis of parathion the dominant process on these surfaces, and the rearrangement dominant on silica and bentonites. An inductive effect of the conjugated system interaction with the hydroxyl surface may further induce hydrolysis on the alumina surfaces (Mingelgrin et al., 1977). The significantly larger rate of rearrangement on bentonites as compared with silica may result from the increased tendency of all the P–O bonds to get into one plane in the interlayer space, due to steric constraints imposed by the interlayer space.

Finally, it is interesting to note that the peak at 1265 cm^{-1} prominent in the IR spectrum of free SEP and assigned to P=O (Gore, 1950), shifts in the adsorbed SEP to 1282 cm^{-1} (Mingelgrin and Saltzman, 1978). This suggests that the newly formed P=O bond interacts strongly with the surface, in agreement with equation (2). In the region assigned to the P=S bond (Gore, 1950), no such large shift was observed, which is additional support for the mechanism proposed.

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Резюме- Адсорбционно-каталитическая деградация паратиона на поверхностях глины является гидролизным процессом,протекающим непосредственно или через стадию перегруппировки. Скорость и механизм деградации зависят от природы глины,ее состояния гидратации и насыщающего катиона. Предлагается механизм деградации паратиона в местах адсорбции на поверхностях глины,в отсутствии жидкой фазы.

Kurzreferat- Die durch Adsorption katalysierte Degradation von Paration, welches sich auf Tonoberflächen befindet,ist ein Hydrolysenprozeß,der entweder direkt oder durch eine Umlagerungsstufe vor sich geht.Die Geschwindigkeit und der Mechanismus der Degradation hängt von der Natur des Tones und der Kationen und des Tones Hydrationszustand ab.Ein Mechanismus für die Parathiondegradation an den Adsorptionsplätzen auf Tonoberflächen,in Abwesenheit einer flüssigen Phase,wird vorgeschlagen.

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Résumé-La dégradation catalysée par adsorption de parathion sur des surfaces argileuses est un processus d'hydrolyse,découlant soit directement,soit d'une étape de réarrangement.La vitesse et le méchanisme de dégradation dépendent de la nature de l'argile,de son statut d'hydratation,et de son cation de saturation.Un mécanisme est proposé pour la dégradation de parathion à des sites d'adsorption sur des surfaces argileuses,sans phase liquide.

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