Clays and Clay Minerals, Vol. 29, No. 1, pp. 53–59, 1981.

STABILITY OF PARATHION ON ATTAPULGITE AS AFFECTED BY STRUCTURAL AND HYDRATION CHANGES[1]

ZEV GERSTL AND BRUNO YARON

Division of Soil Residues Chemistry, Institute of Soils and Water
ARO, Volcani Center, P.O. Box 6, Bet Dagan, Israel

Abstract—The structure and hydration status of attapulgite clay after heating at elevated temperatures and the stability of parathion on these clays was studied. Using infrared spectroscopy and scanning electron microscopy it was found that the bound water was lost in two steps, at 250° and 450°C, with the first step being largely reversible. At 650°C the structure began to dissolve releasing significant amounts of Mg, and a decrease in aggregate porosity was noted. At 850°C an amorphous phase was formed bearing little resemblance to the original attapulgite. Parathion was stable on all of the preheated clays when kept at 25°C for 190 days. The reactions of parathion on the preheated clays was studied at 110°C. Hydrolysis of parathion was found to be minimal. Isomerization was the main reaction occurring on the Ca-attapulgite, whereas on an organo-clay no isomerization was observed. A mechanism for the isomerization reaction is proposed which entails a distortion of the phosphate moiety of the pesticide by the oxygen of the ligand water resulting in the conformational changes necessary for the isomerization to take place. On the organo-clay such a conformation was not possible; hence no isomerization occurred.

Key Words—Attapulgite, Dehydration, Infrared spectroscopy, Isomerization, Parathion, Scanning electron microscopy, Thermal treatment.

INTRODUCTION

Among the many compounds which are altered on clay surfaces, the organophosphate pesticides have received a great deal of attention (Polon and Sawyer, 1962; Mingelgrin *et al.*, 1975; Yaron, 1978). In all the above studies hydrolysis of the phosphate ester bond of the adsorbed pesticide was the observed mechanism. As pointed out by several workers (Saltzman *et al.*, 1976; Mingelgrin *et al.*, 1977), the ligand water of the exchangeable cation has a profound influence on this reaction. Rosenfield and Van Valkenburg (1965) and Mingelgrin and Saltzman (1979) also reported the degradation of organophosphate pesticides via molecular rearrangements on montmorillonite. As in hydrolysis, the nature and hydration status of the clay greatly affect the reaction.

Water molecules in attapulgite, which is widely used as a dust diluent in pesticide formulations, differ from those in other clays in that they are important elements of the structure (Grim, 1968). The loss of bound water in attapulgite results in structural changes (Preisinger, 1963). The effect of heating on the various forms of water in attapulgite and the resulting structural changes in the mineral have received a great deal of attention (Serna *et al.*, 1977; Mifsud *et al.*, 1978; Van Scoyoc *et al.*, 1979). However, the exact conditions under which these changes occur are in dispute. This may be due to inadequate control of experimental conditions and to the use of samples from different sources. The effect of the hydration status and structure of attapulgite on the adsorption and desorption of parathion (0, 0-diethyl O-p-nitrophenyl phosphorothioate) was reported by Gerstl and Yaron (1978) who found that attapulgite differs from kaolinite and montmorillonite in its adsorption of parathion from both aqueous and non-aqueous solvents. Since the rearrangement products of parathion were found to be more toxic to mammals than parathion itself (Joiner *et al.*, 1973), it is of importance to know if such a process is possible in attapulgite-parathion complexes and if so, to study the factors affecting this process. The present work reports on the relationship between the hydration status and structure of attapulgite and the stability of adsorbed parathion.

EXPERIMENTAL

Materials

High purity parathion (98%) and C^{14}-labeled parathion (Amersham Radiochemicals Centre) were used for all the experiments. Attapulgite (Diluex) purchased from Floridin Company (Quincy, Florida) was used. Characterization of the clay by X-ray powder diffraction and infrared analysis showed it to be similar to untreated Georgia attapulgite as reported in the literature (Van Olphen and Fripiat, 1979).

Analytical methods

C^{14} activity was counted with a Packard 3003 liquid scintillation spectrometer. The scintillation liquid contained 60 g of naphthalene, 4 g of PPO (2,5-diphenyloxazole), 0.2 g of POPOP [2,2-p-(phenylene)bis(5-phe-

[1] Contribution 240-E, 1980 series.

Copyright © 1981, The Clay Minerals Society

https://doi.org/10.1346/CCMN.1981.0290108 Published online by Cambridge University Press

Table 1. Properties of attapulgite clays used in the present study.

Pretreatment		Water loss,[2] (%)	Surface area (m^2/g)	CEC (meq/100 g)	Major X-ray diffraction spacing (Å)	Mg released (mmole/100 g)
Air dry[1]	Hydrated	—	40	31	10.64	3.0
HDMA	Organo	3.5[3]	146	29	—	—
Heated to:						
110°C	Partially dehydrated	11	146	29	10.64	1.4
250°C	Dehydrated	15	161	32	9.7	1.4
450°C	Anhydride	19	98	34	9.7	5.0
650°C	Transition	21	85	21	—	16.0
850°C	Amorphous	24	13	4	N.P.[4]	0.0

[1] Relative humidity 52%.
[2] Calculated as the loss in weight of the clay per unit dry weight at each temperature.
[3] Dried over P_2O_5.
[4] Not present; X-ray diffraction pattern was diffuse, indicating noncrystalline materials.

nyloxazole)], 100 cm^3 of methanol, and 20 cm^3 of ethylene glycol diluted to 1 liter with dioxane. Parathion in both organic and aqueous solutions was determined with this scintor.

Procedure

Clay preparation. $CaCO_3$ was removed from the raw clay by shaking a clay suspension overnight with H^+-saturated IR-120 cation-exchange resin. This procedure removes $CaCO_3$ without damaging the clay as might be expected if acid were used for carbonate removal (Satyabrata Ray *et al.*, 1957). After separation from the resin, the clay was washed four times with 1 N $CaCl_2$ (pH 6.5) and thereafter with deionized water until no chloride was detectable in the supernatant liquid with $AgNO_3$. The clay was then freeze-dried, ground in an agate ball mill and passed through a 250-μm sieve. The pretreatments consisted of heating the Ca-attapulgite at various temperatures up to 850°C. X-ray powder diffraction (XRD) of the freeze-dried clay showed no signs of montmorillonite and only traces of quartz. A sample of the ground Ca-attapulgite was washed with an ethanolic solution of hexadecyltrimethylammonium bromide (HDMA) to prepare an organoclay in a similar manner.

Mg-release. The amount of Mg released from the clay structure after heating to elevated temperatures was determined by atomic absorption spectroscopy analysis of dithionite-citrate-bicarbonate extracts according to the procedure of Mehra and Jackson (1960).

Infrared studies

Infrared (IR) spectra of the preheated clays were obtained on KBr discs prepared at 9 tons pressure. Self-supporting films of attapulgite could not be prepared. A Perkin-Elmer Model 257 Infrared Grating Spectrometer was used throughout the study. The preheated clays were kept over P_2O_5 until mixing with the KBr (dried at 110°). Separate samples were rehydrated in a desiccator at 52% R.H. before preparation of the KBr discs.

Scanning electron microscopy (SEM)

Aqueous suspensions (1% by weight) of the preheated clays were shaken for 18 hr followed by ultrasonic vibration for 5 min. A dilute suspension (50 ppm) was then deposited on grids and left to dry at room temperature. The grids were coated with gold and scanned in a Cambridge Instruments Model 180 scanning electron microscope.

Stability studies

Parathion-attapulgite complexes were prepared by shaking the clay with a hexane solution of parathion for 24 hr followed by slow evaporation of the solvent. Extraction of the parathion from the clay was accomplished with 10 ml of acetone:benzene (1:1) and shaking for 1 hr. After centrifugation, 8 ml of the supernatant was transferred to an Erlenmeyer flask, and after evaporation of the solvent the residue was reextracted with 5 ml of water and 5 ml of hexane with each phase being checked for radioactivity as described above. The stability of parathion when adsorbed by the various attapulgites was determined as follows: Complexes were kept in an incubator at 25°C for up to 190 days prior to analysis. Freshly prepared complexes were heated at 110°C for various periods of time. Parathion and its metabolites were extracted as described above. The organic phase was spotted on TLC plates (silica gel, containing fluorescein) and developed with petroleum-ether:chloroform:methanol (7:3:0.3). The separated bands were visualized under UV light, scraped off, eluted with water:hexane (1:2), and counted. The parathion extracted from the heated complexes was divided into four fractions: P = unaltered parathion; I = the thiolo isomer of parathion; H = hydrolysis products of parathion and its isomer; and L = losses which were

https://doi.org/10.1346/CCMN.1981.0290108 Published online by Cambridge University Press

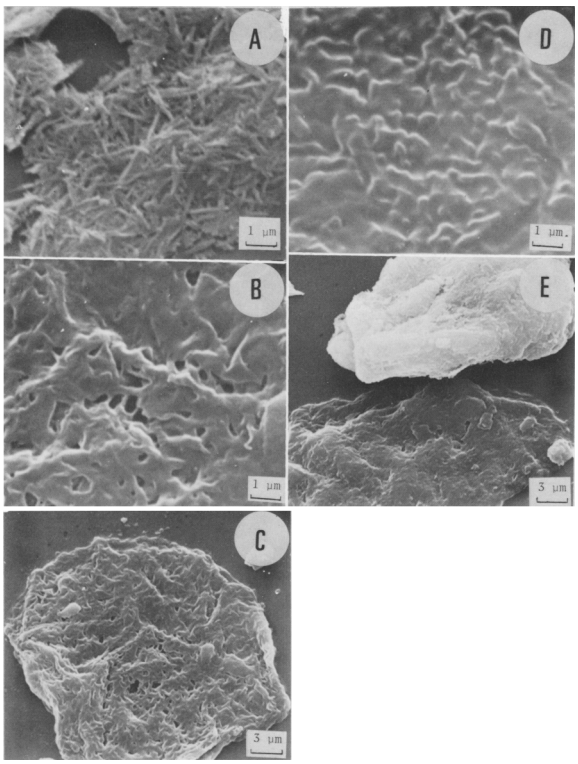


Figure 1. Scanning electron micrographs of attapulgite after heating at elevated temperatures and redispersion in water. (A) hydrated clay (representative of the partially dehydrated, dehydrated, and anhydride clays), (B) and (C) transition clay (650°), (D) and (E) amorphous clay (850°C).

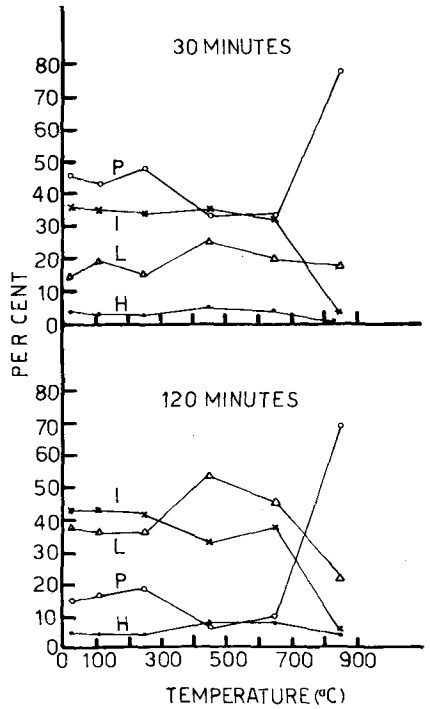


Figure 2. Effect of preheating attapulgite at elevated temperatures on the isomerization of adsorbed parathion (concentration = 1000 µg/g) at 110°C after 30 and 120 min. P = parathion, I = isomer, H = hydrolysis product, L = losses.

taken as the difference between the amount of parathion added and the amount recovered in the first three fractions.

RESULTS

Changes in the chemical properties of attapulgite

The changes in some of the chemical properties of attapulgite after heating at elevated temperatures are presented in Table 1 along with names by which they will be referred to. The cation-exchange capacity (CEC) was fairly constant at about 30 meq/100 g and was found to decrease only after heating the mineral at 650°C. The amount of Mg released from the clay structure increased slightly at 450° and reached a maximum at 650°C.

Changes in hydration status

The water lost at 110°C was completely regained upon rehydration, whereas only 90% of the water lost from the dehydrated clay was regained. After heating at 450°C only 35% rehydration was achieved, whereas at 650° and 850°C the extent of rehydration was minimal. The IR spectra of heated and rehydrated attapulgite are similar to those obtained by other workers (Hayashi *et al.*, 1969; Van Scoyoc *et al.*, 1979) and have been discussed elsewhere (Gerstl, 1979). The interpretation of the spectra is discussed below.

Structural changes

The specific surface area (SSA) increased upon heating the sample to 250°C whereupon it decreases (Table 1). The surface area of the hydrated clay as measured by o-phenanthroline adsorption (Lawrie, 1961) was 140 m^2/g; all the other values were within several m^2/g of those measured by N_2 adsorption. The XRD data (only the major XRD spacing is given in Table 1) showed an initial shift in the principal reflection of the dehydrated clay from 10.6 Å to 9.7 Å. The peak intensities of the anhydrous clay decreased. The patterns of the thermal decomposition products show no peaks of attapulgite, but some small peaks of enstatite (?) or gehlenite (?) could be seen. IR vibrations at 1030 and 981 cm^{-1}, associated with the clay structure, merged upon heating and formed a new band at 1020 cm^{-1} which disappeared at 650°C. The original bands reappeared upon rehydration even after heating at 250°C, but not after heating at 450°C.

The SEM results are presented in Figure 1. The fibrous nature of the clay and its "haystack" structure

https://doi.org/10.1346/CCMN.1981.0290108 Published online by Cambridge University Press

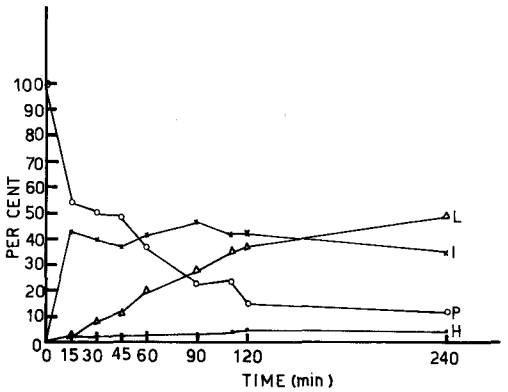


Figure 3. Kinetics of parathion isomerization on hydrated attapulgite at 110°C. (Legend as in Figure 2.)

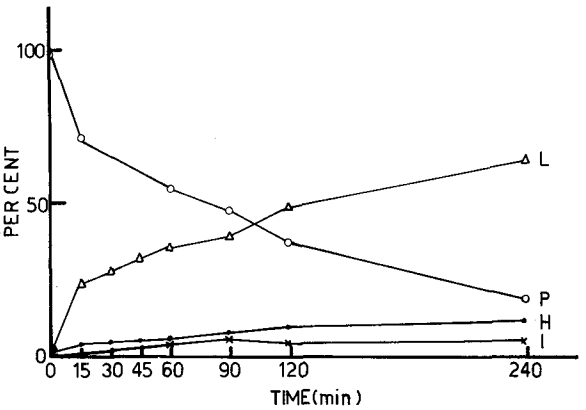


Figure 4. Kinetics of parathion isomerization on an organo-attapulgite (hexadecyl trimethylammonium) at 110°C. (Legend as in Figure 2.)

and porosity are observable in the hydrated clay and are typical of attapulgite heated to 110°C, 250°C, and 450°C, indicating that the external morphology of attapulgite is fairly stable. Because the samples were prepared in aqueous solution, it is conceivable that external changes occurred between 110°C and 450°C, but that they are reversible and were not observed. At 650°C dissolution of the clay was observed, and the original fibrous nature of the attapulgite was discerned with difficulty. The aggregate porosity was greatly reduced, and after heating at 850°C the material resembled a melt with no observable internal porosity and showed no semblance of the original attapulgite fibers.

Parathion-attapulgite incubation experiments

Long term incubation experiments of the various preheated clays with parathion (initial concentration = 30,000 μg/g) showed that after 190 days at 25°C nearly no hydrolysis had occurred (Table 2). On the other hand, when parathion-attapulgite complexes were heated at 110°C isomerization of parathion was noted (Figure 2). After 120 min, isomerization accounted for slightly more than 40% of the original parathion on the hydrated, partially dehydrated, and dehydrated clays. Slightly less isomerization of parathion was noted in the anhydrous clay, whereas a sharp decline in isomerization in the amorphous clay was observed. In all the above samples hydrolysis was of minor consequence, never exceeding 8%. The kinetics of isomerization of the hydrated and organo-clay are compared in Figures 3 and 4. Practically no isomerization occurred on the organo-clay, whereas hydrolysis, although of minor importance, was twice that of the hydrated clay. In the hydrated clay isomerization was complete after 15 min, but the amount of unaltered parathion recovered was always less than that recovered from the organo-clay.

Table 2. Hydrolysis of parathion on attapulgite surfaces preheated to elevated temperatures after 190 days at 25°C.

Temperature	25°C	110°C	250°C	450°C	650°C	850°C
% hydrolysis	0.8	0.4	1.3	2.5	1.1	1.2

DISCUSSION

Effect of heating on structure and hydration state of attapulgite

Three types of water molecules are generally found in attapulgite. Zeolitic water is loosely held in the microchannels of the structure; bound or crystal water is coordinated to magnesium ions; and hydroxyl water is part of the clay structure (Henin and Caillere, 1975). The present results show that most of the zeolitic water was lost at 110°C without significant changes in the properties of the clay. The cation-exchange capacity, major XRD spacing, and amount of Mg released were similar for the hydrated and partially hydrated clay. Water molecules in the hydrated clay which were still present despite the customary degassing procedure prevented adsorption of N_2. Thus, the specific surface area of the hydrated clay as determined by N_2 adsorption was less than one third of that of the clay heated to 110°C.

In contrast to the loss of zeolitic water, the loss of bound water affected the properties of the clay. After heating the sample to 250°C, the SSA increased by 10% as more water molecules were lost, enabling N_2 (and o-phenanthroline) to be adsorbed. A shift in the major XRD spacing from 10.6 Å to 9.7 Å took place and signified the formation of the anhydrous phase (Thorenz, 1976). On heating to 450°C, the continued water loss resulted in a decrease of the SSA possibly due to morphological changes in the clay which physically prevent N_2 molecules from reaching adsorption sites. A small amount of Mg was released at this temperature sug-

https://doi.org/10.1346/CCMN.1981.0290108 Published online by Cambridge University Press

gesting a possible weakening of the clay structure. The loss of bound water, which links the octahedral and tetrahedral layers, resulted in a tilting of the clay structure to the "anhydride" form (Preisinger, 1963; Longchambon, 1937).

The loss of part of the bound water at 250°C was only partially reversible; only 90% of the water lost was regained. After heating at 450°C, only 35% rehydration was accomplished, some of which is certainly due to zeolitic or first-stage bound water, indicating the irreversible formation of the anhydride. These results were supported by the IR data and are similar to those of Van Scoyoc *et al.* (1979).

Bands at 1030 and 981 cm^{-1} and at 775 and 790 cm^{-1} arose from structural vibrations of the Si–O–H angle deformation and Si–O vibration (Mendelovici, 1973). The bands at 1030 and 981 cm^{-1} merged upon heating into a new band at 1020 cm^{-1}, an effect that was reversible at 250°C but not at 450°C. Similar merging of bands was found for attapulgite after 5 hr of acid attack during which the octahedral layer was dissolved (Mendelovici, 1973; Nathan, 1969). The release of Mg, caused by a weakening of the octahedral layer upon irreversible formation of the anhydride at 450°C, supports the thesis that dissolution had begun at this temperature.

Upon heating the sample to 650°C, the amount of Mg released from the structure increased to 16 mmole/100 g (Table 1) which is equivalent to nearly 7% dissolution of the crystal structure. Miller *et al.* (1963) reported that the release of Mg by attapulgite reaches maxima at 500° and 750°C. With the release of Mg, the clay can be considered to have undergone dissolution similar to that reported for HCl, as mentioned above. The clay still retained its fibrous habit but to a reduced extent, as evidenced by the SEM results. Upon heating at 850°C, structural water was lost and an X-ray- and IR-amorphous phase of negligible surface area and CEC was obtained. At this point, it is postulated that a phase transformation had occurred after destruction of the attapulgite structure. These steps were verified by SEM studies as shown in Figure 1.

Stability of parathion-attapulgite complexes

IR studies conducted by Prost *et al.* (1975) showed that parathion is bound to attapulgite via H-bonds between the NO_2 group of the pesticide and the hydrogens in water molecules of the hydration shell of the adsorbed cation. Upon dehydration these bonds were not observed, whereas a change in the P-S moeity of the pesticide molecule was observed, which may be due to a direct linkage with the adsorbed cation itself. The water of the exchangeable cation is known to have a profound influence on the hydrolysis reaction in kaolinite (Saltzman *et al.*, 1976; Mingelgrin *et al.*, 1977). Because the external surface of attapulgite, especially the anhydrous phase, may contain surface hydroxyls similar to those of kaolinite (Serna *et al.*, 1977), the possibility exists that parathion hydrolysis could occur on attapulgite. The results of Table 2, however, indicate the stability of adsorbed parathion. While the slightly greater hydrolysis of the anhydrous clay may be due to the exposure of such surfaces upon tilting of the attapulgite structure, the differences are too small to be significant.

The ability of clays to induce isomerization in an organophosphate was reported by Rosenfield and Van Valkenburg (1965) who observed that bentonites dried at elevated temperatures induced degradation of Ronnel (a thiophosphate) through a molecular rearrangement. Parathion is reported to convert only gradually to the thiolo isomer when heated to 100°C (Melnikov, 1971). Infrared spectra of pure parathion heated at 100°C under vacuum did not differ from those of unheated parathion except for decreased intensities. Mingelgrin and Saltzman (1979) found that isomerization of parathion occurred on montmorillonite surfaces, but not on kaolinite surfaces. In the present study, isomerization occurred on the hydrated clay but not on the organo-clay. These differences are the direct result of the nature of the clay's surface. The organo-clay held parathion strongly by "hydrophobic bonding" in a quasi-organic layer (Gerstl and Yaron, 1978), whereas in the Ca-saturated clays bonding was via the exchangeable ions and/or the water of hydration (Prost *et al.*, 1975). Thus, the isomerization and hydrolysis of parathion on attapulgite surfaces can be explained by the proposed sequences of Mingelgrin and Saltzman (1979) who found that the reaction that occurs on a surface (either direct hydrolysis as in kaolinite, or isomerization as in bentonite) will depend on the compound's configuration on the surface. Fest and Schmidt (1973) pointed out that even small energy changes may affect the conformation of phosphate on surfaces and thereby considerably alter the chemical reactivity of the compound. Distortion of the phosphate moiety by the oxygen of the ligand water towards a trigonal bipyramid structure puts the three P–O bonds of parathion into one plane, enabling the S–C bond of the isomer to form more easily. Since no hydrolysis products were found on the hydrated clay it may be assumed that the isomer was stable at 110°C in accord with the results of Mingelgrin and Saltzman (1979). On a surface such as organo-attapulgite this sequence does not apply, as there was no interaction between the parathion and the ligand water.

Mingelgrin and Saltzman (1979) observed that heating montmorillonite prior to incubation with parathion at 22°C for 60 days increased the relative rate of isomerization. They attributed this reaction to the decreased moisture content, but not total dehydration, of the preheated clays. The present study found that isomeriza-

https://doi.org/10.1346/CCMN.1981.0290108 Published online by Cambridge University Press

tion of parathion occurred even in partially dehydrated attapulgite. In dehydrated and anhydrous attapulgite the presence of retained bound water or surface hydroxyls can account for the continued isomerization. The slight increase in isomerization after heating the clay to 650°C, as compared to 450°C, resulted from the appearance of new surfaces due to the loss of structural water. These new surfaces were most probably oxides of Si and Mg resulting from the dissolution of the attapulgite structure and were also responsible for increased adsorption of parathion from aqueous solutions by attapulgite preheated to 650°C (Gerstl and Yaron, 1978). With the complete loss of the hydroxyl water at 850°C and the formation of an amorphous phase, isomerization was restricted, and the main pathway for parathion loss was volatilization or fixation.

SUMMARY

Heating at elevated temperatures significantly changed the structure and the state of water molecules in the attapulgite structure. Zeolitic water was easily lost at 110°C, resulting in little or no change in the clay. The loss of the bound water in two steps at 250° and 450°C produced striking changes in the state of the water associated with attapulgite, whereas the loss of the hydroxyl water above 650°C resulted in the destruction of the attapulgite structure.

Although parathion was stable on attapulgite surfaces at room temperature, it underwent isomerization, but not hydrolysis, at elevated temperatures. The isomerization reaction resulted from the ability of parathion to interact with ligand water or surface hydroxyls, which allowed the necessary bonds to form. On an organo-clay such a configuration was not possible and no isomerization occurred.

REFERENCES

Fest, C. and Schmidt, K. J. (1973) *The Chemistry of Organophosphorus Pesticides:* Springer Verlag, Berlin, 339 pp.

Gerstl, Z. (1979) Attapulgite-parathion interactions: PhD thesis, Hebrew University of Jerusalem, 103 pp.

Gerstl, Z. and Yaron, B. (1978) Adsorption and desorption of parathion from attapulgite as affected by the mineral structure: *J. Agri. Food Chem.* **26,** 569–573.

Grim, R. E. (1968) *Clay Mineralogy, 2nd ed:* McGraw-Hill, New York, 384 pp.

Hayashi, H., Otsuka, R., and Imai, N. (1969) Infrared study of sepiolite and palygorskite on heating: *Amer. Mineral.* **53,** 1613–1624.

Henin, S. and Caillere, S. (1975) Fibrous minerals: in *Soil Components,* Vol. 2, J. E. Gieseking, ed., Springer Verlag, New York, 335–349.

Joiner, R. L., Chambers, H. W., and Baetcke, K. P. (1973) Comparative inhibition of boll weevil, golden shiner and white rat cholinesterases by selected photoalteration products of parathion: *Pestic. Biochem. Physiol.* **2,** 371–376.

Lawrie, D. C. (1961) A rapid method for the determination of approximate surface area of clays: *Soil Sci.* **92,** 188–191.

Longchambon, H. (1937) X-ray diagram: *C. R. Acad. Sci. Paris* **204,** 55–58.

Mehra, O. P. and Jackson, M. L. (1960) Iron oxide removal from soils and clays by a dithionite-citrate system buffered with sodium bicarbonate: *Clays & Clay Minerals* **7,** 317–327.

Melnikov, N. N. (1971) *Chemistry of Pesticides:* Springer Verlag, New York, 480 pp.

Mendelovici, E. (1973) Infrared study of attapulgite and HCl treated attapulgite: *Clays & Clay Minerals* **21,** 115–119.

Mifsud, A., Rautureau, M., and Fornes, V. (1978) Etude de l'eau dans la palygorskite à l'aide des analyses thermiques: *Clay Miner.* **13,** 367–379.

Miller, J. G., Haden, W. L. Jr., and Oulton, T. P. (1963) Oxidizing power of the surface of attapulgite clay: *Clays & Clay Minerals* **12,** 381–395.

Mingelgrin, U., Gerstl, Z., and Yaron, B. (1975) Pirimiphos ethyl-clay surface interactions: *Soil Sci. Soc. Amer. Proc.* **39,** 834–837.

Mingelgrin, U. and Saltzman, S. (1979) Surface reactions of parathion on clays: *Clays & Clay Minerals* **27,** 72–76.

Mingelgrin, U., Saltzman, S., and Yaron, B. (1977) A possible model for the surface-induced hydrolysis of organophosphorus pesticides on kaolinite clays: *Soil Sci. Soc. Amer. J.* **41,** 519–523.

Nathan, Y. (1969) Dehydration of palygorskites and sepiolites: *Proc. Int. Clay Conf., Tokyo, 1969,* L. Heller, ed., Israel Univ. Press, Jerusalem, 91–98.

Polon, J. A. and Sawyer, E. W. (1962) The use of stabilizing agents to decrease decomposition of malathion on high-sorptive carriers: *J. Agri. Food Chem.* **10,** 244–248.

Preisinger, A. (1963) Sepiolite and related compounds: its stability and application: *Clays & Clay Minerals* **10,** 365–371.

Prost, R., Gerstl, Z., Yaron, B., and Chaussidon, J. (1975) Infrared studies of parathion-attapulgite interactions: in *Behavior of Pesticides in Soils,* M. Horowitz, ed., Israel-France Symposium, Publ. 62, 1977, The Volcani Center, Bet Dagan, Israel, 27–32.

Rosenfield, C. and Van Valkenburg, W. (1965) Decomposition of (0,0-dimethyl-0-2,4,5 trichlorophenyl) phosphorothioate (Ronnel) adsorbed on bentonite and other clays: *J. Agri. Food Chem.* **13,** 68–72.

Saltzman, S., Mingelgrin, U., and Yaron, B. (1976) The role of water in the hydrolysis of parathion and methyl parathion on kaolinite. *J. Agri. Food Chem.* **24,** 739–743.

Satyabrata Ray, H. R., Gault, H. R., and Dodd, C. G. (1957) The separation of clay minerals from carbonate rocks: *Amer. Mineral.* **42,** 681–686.

Serna, C., Van Scoyoc, E., and Ahlrichs, J. L. (1977) Hydroxyl groups and water in palygorskite. *Amer. Mineral.* **62,** 784–792.

Thorenz, J. (1976) *Practical Identification of Clay Minerals:* G. Lelotte, Dison, Belgium, 90 pp.

Van Olphen, H. and Fripiat, J. J. (1979) *Data Handbook for Clay Materials and Other Non-Metallic Minerals:* Pergamon Press, Oxford, 346 pp.

Van Scoyoc, G. E., Serna, C. J., and Ahlrichs, J. L. (1979) Structural changes in palygorskite during dehydration and dehydroxylation: *Amer. Mineral.* **64,** 215–223.

Yaron, B. (1978) Some aspects of surface interactions of clays with organophosphorus pesticides: *Soil Sci.* **125,** 210–216.

(Received 14 March 1980; accepted 2 July 1980)

https://doi.org/10.1346/CCMN.1981.0290108 Published online by Cambridge University Press

Резюме—Исследовались структура и состояние гидратации аттапулгитовой глины после нагревания при повышенных температурах, а также стабилность паратиона на этих глинах. Путем инфракрасной спектроскопии и электронного сканирующего микроскопа было обнаружено, что связанная вода освбождалась в двух этапах, при температурах 250°C и 450°C, причем первый этап был преймущественно реверсивный. При 650°C структура начинала растворяться, освобождая значительное количество магния, а также наблюдалось уменьшение пористости аггрегатов. При 850°C формировалась аморфная фаза, которая только в небольшой степени напоминала исходный аттапульгит. Паратион был стабильныи на всех предварительно нагретых глинах, если они содержались при температуре 25°C в течение 190 дней. Реакции паратиона на нагретых глинах были исследованы при температуре 110°C. Гидролиз паратиона был минимальный. Изомеризация являлясь главной реакцей для Ca-аттапульгита, в то время, как она не наблюдалась для органоглины. Для реакции изомеризации предложен механизм, который определяет искажение фосфатовой половины пестицида кислородом аддендовой воды, результатом чего является изменение формы необходимые для изомеризации. Для органо-глины такая форма невозможна, и в этом случае изомеризация не происходит. [E.C.]

Resümee—Es wurde der Struktur- und Hydratationszustand von Attapulgit-Ton nach dem Erhitzen auf erhöhte Temperaturen sowie die Stabilität von Parathion an diesen Tonen untersucht. Die Untersuchungen mit Infrarotspektroskopie und Rasterelektronenmikroskopie zeigten, daß das gebundene Wasser in zwei Schritten, bei 250°C und 450°C, abgegeben wurde, wobei der erste Schritt in hohem Maße reversibel war. Bei 650°C begann die Struktur sich zu verändern, indem sie beträchtliche Mengen an Magnesium verlor. Weiters wurde eine Abnahme der Aggregatporosität festgestellt. Bei 850°C wurde eine amorphe Substanz gebildet, die sehr wenig Ähnlichkeit mit dem ursprünglichen Attapulgit aufwies. Parathion war an allen vorerhitzten Tonen bei einer Temperatur von 25°C über 190 Tage stabil. Die Reaktion von Parathion an vorerhitzten Tonen wurde bei 110°C untersucht. Es zeigte sich, daß die Hydrolyse von Parathion minimal ist. Die wichtigste Reaktion, die bei Ca-Attapulgit festgestellt wurde, war eine Isomerisierung, während an einem Organo-Ton keine Isomerisierung beobachtet wurde. Es wird ein Mechanismus für die Isomerisierungsreaktion vorgeschlagen, der eine Deformation des Phosphatrestes des Pestizides durch den Sauerstoff des ligandenwassers nach sich zieht, wodurch sich die Anderungen der Konformation ergeben, die für die Isomerisierung notwendig sind. An dem Organo-Ton war eine derartige Konformation nicht möglich, weshalb keine Isomerisierung auftrat. [U.W.]

Résumé—On a étudié l'état de la structure et d'hydration d'argile attapulgite après échauffement à de hautes temperatures, et la stabilité de parathion sur ces argiles. En utilisant la spectroscopie infra-rouge et la microscopie balaynte électronique on a trouvé que l'eau liée est perdue en deux étapes, à 250° et 450°C, la première étape étant réversible. A 650°, la stucture a commencé à se dissoudre, relâchant des quantités significatives de Mg, et un amoindrissement de la porosité de l'aggrégat a été remarqué. A 850°, une phase amorphe a été formée, ressemblant peu à l'attapulgite d'origine. Le parathion était stable sur toutes les argiles pré-échauffées lorsqu'elles étaient gardées à 25° pendant 190 jours. Les réactions de parathion sur les argiles pré-échauffées ont été étudiées à 110°. On a trouvé que l'hydrolise du parathion était minime. L'isomérisation était la réaction principale se passant sur l'attapulgite-Ca, alors que sur l'argile organique, aucune isomérisation n'a été observée. On propose un mécanisme pour la réaction d'isomérisation, mécanisme qui comprend la distortion de la moitié phosphate du pesticide par l'oxygène de l'eau liante, résultant en les changements conformationnels nécessaires pour que l'isomérisation se passe. Sur les argiles organiques, une telle conformation n'était pas possible; par conséquent, aucune isomérisation ne s'est passée. [D.J.]

https://doi.org/10.1346/CCMN.1981.0290108 Published online by Cambridge University Press