Parathion Adsorption by Attapulgite

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the proposal that solanidine and its glycosides can cause birth defects when fed during embryonic differentiation, although the risk of such defects may be quite small. The data (Table I) apparently support this proposal showing that (22R,25S)-5α-solanidan-3β-ol caused relatively high percentages of fetal resorption in as much as resorption and malformation rates are generally closely related. The single abnormal offspring, although not a significant incidence, was a characteristic defect of teratogenic steroids. It is also apparent from the widely different structures of the highly teratogenic compounds, jervine and (22S,-25R)-5α-solanidan-3β-ol, that structural requirements for activity (aside from an unhindered basic nitrogen accessible to the α steroid face) are minimal and that a conventional steroid skeleton fitting this requirement can be highly teratogenic.

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Adsorption and Desorption of Parathion by Attapulgite as Affected by the Mineral Structure

Zev Gerstl* and Bruno Yaron

Adsorption of parathion by pretreated attapulgites was studied in both organic and aqueous media. In organic media the presence of hygroscopic moisture resulted in competition between parathion and water so that an increase in the clay's moisture content reduced parathion adsorption. Heating the clays above 250 °C resulted in structural changes that cause a decrease in parathion adsorption. Adsorption of parathion in aqueous solution was found to be inversely related to the release of parathion from highly loaded clays under equilibrium conditions. Saturating clays with an organocation altered their properties favoring increased adsorption and decreased desorption. The results indicate that pretreatment of the clay might affect both the rate and amount of release to the external environment.

For insoluble or slightly soluble pesticides, dust formulations are commonly used to achieve uniform application to the soil surface; the desired compound is added in combination with a solid diluent (Polon, 1973). Attapulgite is one of the clays commonly used. This mineral is a fibrous clay which differs from the more common layer silicates (montmorillonite, kaolinite) in that it does not consist of discrete platelets, but rather has a rigid three-dimensional structure with microchannels (3.5 × 6

Å) running the length of the structure (Bradley, 1940). It contains three forms of water: zeolitic water, which is lost below 220 °C; crystal water coordinated to magnesium ions in the crystal and lost upon being heated at 225–350 °C; and hydroxyl water of the silicate unit, lost above 400 °C (Haden and Schwint, 1967). Heating the clay to various temperatures, therefore, will have a profound influence not only on the clay's water content but upon its structure as well.

Despite the wide use of attapulgite as a carrier, only little attention has been paid to its interactions with pesticides. Early studies by Fowkes et al. (1960), Polon and Sawyer (1962), and Rosenfield and Van Valkenburg (1965) reported the behavior of several organochlorinated and

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Table I. Properties of Attapulgite Clay after Heating for 24 h at Various Temperatures

Pretreatment temperature		Water loss,[a] %	Surface area, m²/g	CEC[b]	Major x-ray spacing
Air dry[c]	Hydrated		40	31	10.64
Heated to:					
110 °C	Partially dehydrated	11	146	29	10.64
250 °C	Dehydrated	15	161	32	9.7
450 °C	Anhydride	19	98	34	9.7
650 °C	Transition	21	85	21	
850 °C	Amorphous	24	13	4	NP[d]

[a] Calculated as the loss in weight of the clay when heated to each temperature; the organoclay's moisture content was determined by keeping it over P_2O_5 for 2 weeks. [b] Cation-exchange capacity (mequiv/100 g). [c] Relative humidity 52%; moisture content, 11%. [d] Not present; x-ray was diffuse, indicating an amorphous phase.

organophosphorus pesticides on attapulgite. These studies dealt mainly with compatibility between the pesticides and carriers, and attapulgite represented only one of several minerals tested. In general, the mineral used in the studies was either a natural or commercial sample and in only one case (Rosenfield and Van Valkenburg, 1965) were pretreatments applied.

Due to the increased use of clay minerals, including attapulgites, in pesticide formulations in the last few years, studies have been renewed in this field. Parathion (O,-O-diethyl O-p-nitrophenyl phosphorothioate), an organophosphorus insecticide widely used as a crop protection chemical, was selected as a representative pesticide. Infrared studies (Prost et al., 1977) defined the adsorption mechanism of parathion by attapulgite. It was established that adsorption from organic solvents proceeds via H bonds to the hydration water of the adsorbed cation or under certain conditions directly to the cation. The mechanism of parathion adsorption by attapulgite is similar to that observed for adsorption by montmorillonite, which has been described in detail by Saltzman and Yariv (1976). Similar adsorption capacities for parathion were observed for attapulgite and montmorillonite (8 and 10%, respectively), which far exceeded that of kaolinites (Gerstl and Yaron, 1978).

In the present paper results are reported on the adsorption and desorption of parathion on attapulgite when the mineral is preheated at selected temperatures, thereby affecting its structure. These results help in understanding the parathion–attapulgite surface interactions and might lead to improved use of this mineral for formulation purposes.

EXPERIMENTAL SECTION

Materials. High purity parathion (98%) and ¹⁴C-labeled parathion (Amersham Radiochemicals Centre) were used for all the experiments. Preparation of the clay is described under the Procedures section.

Analytical Methods. ¹⁴C activity was counted with a Packard 3003 Tri-Carb 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-phenyloxazole)]; 100 cm³ of methanol; and 20 cm³ of ethylene glycol, brought to 1 L with dioxane. Parathion in both organic and aqueous solutions was determined with this scintor.

X-ray studies were done on powdered samples using Cu Kα radiation on a Philips x-ray diffractometer. Surface area measurements were carried out by N₂ gas adsorption after degassing the samples at appropriate temperatures on a Quantasorb Sorption System (Quantachrome Corp., Greenvale, N.Y.). Surface areas were calculated by the Brunauer, Emmett and Teller (B.E.T.) equation.

Procedure. A. *Clay Preparation.* CaCO₃ was removed from the raw clay by shaking a clay suspension overnight

with H⁺ saturated IR-120 cation-exchange resin. After separation from the resin, the clay was washed four times with 1 N CaCl₂ (pH 6.5) and thereafter with deionized water until no chloride was detectable in the supernatant with AgNO₃. The clay was then freeze-dried and ground in an agate ball mill and passed through a 250 μm sieve. A sample of the ground calcium attapulgite was washed with an ethanolic solution of hexadecyltrimethylammonium bromide to prepare an organoclay in a similar manner.

The pretreatments consisted of heating the calcium attapulgite at various temperatures up to 850 °C. The properties of the clays after heating are presented in Table I.

B. Adsorption Studies. Adsorption was studied by batch experiments using aqueous (0.01 N CaCl₂) and spectroscopic grade hexane solutions of parathion. The concentration range for the aqueous solutions was 1–10 ppm, with a clay–solution ratio of 1:100. For the hexane solutions the concentration ranged from 200 to 10 000 ppm, at a clay–solution ratio of 1:10.

Preliminary kinetic studies showed that adsorption equilibrium was reached after several hours in both solvents and so an equilibration time of 18 h was chosen for all experiments. Adsorption was determined by the change in concentration of the solution after equilibration.

In order to study the effect of water on the adsorption capacity of the clay, samples were equilibrated in desiccators over saturated salt solutions at different relative humidities (15, 32, 52, 65, 81, and 98%) to obtain a range of moisture contents (6.9, 10.0, 11.1, 14.0, 17.9, and 45.6%, respectively, after heating at 110 °C), and the adsorption of parathion from a 10 000 ppm hexane solution was determined. The moisture contents were determined by the standard method of heating to 110 °C.

C. Desorption Studies. Equilibrium desorption of parathion was accomplished by adding a given amount of parathion to the various clays in hexane solution for 24 h and then slowly evaporating the solvent. The clays were then transferred into flasks containing enough 0.01 N CaCl₂ solution so that in the event that all the parathion desorbed into solution, a concentration of 9–10 ppm would not be exceeded. This suspension was shaken for 24 h, at which time the suspension was centrifuged and the parathion content of the clear supernatant was determined. The initial concentrations of parathion adsorbed on the clay were 0.5, 1, 3, and 5% (w/w).

RESULTS AND DISCUSSION

Adsorption from Organic Media. The adsorption of parathion by attapulgite from organic solutions gives a good measure of the clay's adsorption capacity. Adsorption will, however, be affected by both the polarity of the solvent and the parathion's solubility in it. Previous work (Saltzman and Yariv, 1976) has shown that the solvent best
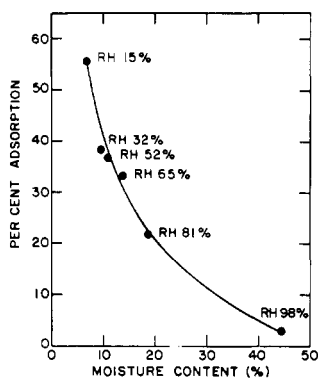
Figure 1. Effect of moisture content upon the adsorption of parathion from hexane solution by attapulgite (initial solution concentration, 10 000 μg/mL; clay–solution ratio, 1:10.)
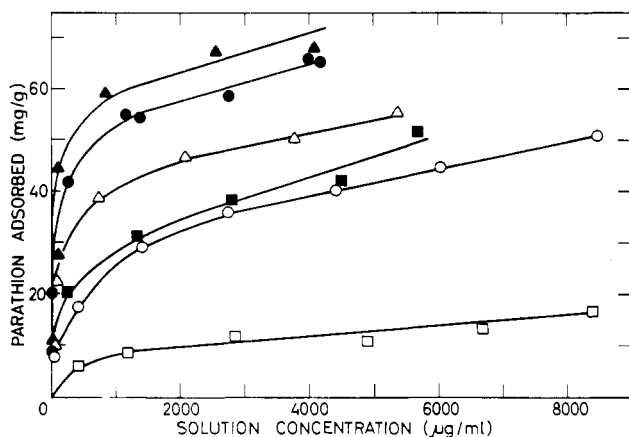

Figure 2. Parathion adsorption by attapulgite from hexane solutions: (O) hydrated; (●) partially dehydrated, (▲) dehydrated, (△) anhydride, (■) transition, (□) amorphous.

Figure 3. Parathion adsorption (at an equilibrium solution concentration of 4000 μg/mL) as a function of the B.E.T. surface area.

Figure 4. Parathion adsorption from aqueous (0.01 N $CaCl_2$) solutions (legend as in Figure 2.)

suited from these aspects is hexane, which is apolar and in which parathion solubility barely exceeds 10 000 ppm. It was necessary to use spectroscopic grade hexane, since even trace amounts (100 ppm) of benzene and other impurities in hexane were found to affect greatly the adsorption of parathion. Kipling (1965) pointed out that, in adsorption from a multisolvent system, preferential adsorption of one of the solvents can affect the adsorption of a soluble species. An analogous effect occurred when water was present on the clay. As seen from the results presented in Figure 1, adsorption decreased with increasing hygroscopic moisture content and was similar to previously reported data for soils (Yaron and Saltzman, 1972). This decrease in adsorption was the result of a decrease in the "free surface area" available for adsorption, since both water and parathion compete for the same adsorption sites. This hydration effect was also responsible for the increase in adsorption relative to a hydrated clay, for the partially dehydrated and dehydrated clays, as seen from their adsorption isotherms in Figure 2. Heating the clay to 110 °C frees a large number of sites previously held by water. Since Ca^{2+} ions do not completely lose their hydration shell until 180 °C (Slabaugh, 1959), further heating to 250 °C resulted in an additional increase in adsorption.

It should be noted that the isotherms presented in Figure 2 are of the L2c (low affinity) and H2 (high affinity) types, according to the classification of Giles et al. (1974). In all cases there was a rapid increase in adsorption followed by a region of linear increase. This linear increase is indicative of a surface where the number of energetically active sites remains constant as adsorption progresses, yet it is highly unlikely that this would occur on attapulgite
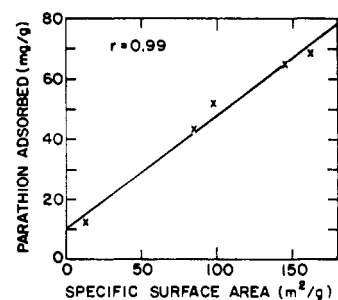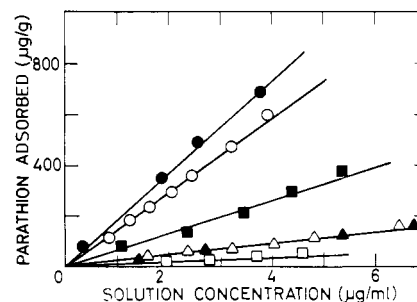
at such high surface concentrations. In adsorption from apolar solvents such as hexane, however, it is difficult to obtain a uniform clay dispersion as in aqueous suspensions, so that the available surfaces in such cases can be very variable and highly dependent on such factors as the particle size of the adsorbent and mode of preparation. In the present study this phenomenon repeated itself in all treatments, whereas in a previous study on a different attapulgite, a plateau was achieved at the higher equilibrium concentrations (Gerstl and Yaron, 1978).

The structural changes which occur in attapulgite at elevated temperatures explain the decreased adsorption observed for these clays. Upon heating to 450 °C crystal water is lost, causing a tilting of the attapulgite structure (analogous to collapse of the platelets in montmorillonite). This was confirmed in part by the shift in the main peak in the x-ray diffractogram from 10.6 to 9.7 Å and by the weakening of the other peaks (Thorez, 1976). The crystal water lost comes from within the microchannels of the clay and does not affect parathion adsorption, since it could not enter pores of such small diameter. Yet heating did decrease the clay's affinity for parathion in relation to the dehydrated clay, most probably due to a decrease in the available surface area for adsorption, resulting from the rotation of the structure to form the anhydride. Since the CEC did not decrease, it seems that the noted decrease in surface area was due more to physical blockage, that is, prevention of the apolar N_2 molecules from reaching certain adsorption sites. It was not until 650 °C that the CEC decreased due to actual structural and phase transitions, which are completed at 850 °C with the formation of an amorphous mineral phase. These structural changes bring about changes in the clay's specific surface area which are reflected in the clay's adsorption capacity for the pesticide. When the amount of parathion adsorbed (at an equilibrium solution concentration of 4000 μg/mL, chosen arbitrarily) was plotted as a function of the surface area, a linear relationship was observed (Figure 3). An exception was the hydrated clay, where adsorbed water prevented N_2 adsorption (resulting in a lower surface area), but did not affect parathion adsorption, which proceeds
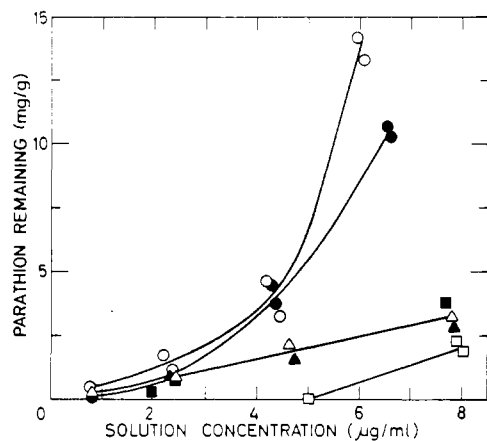
Figure 5. Equilibrium desorption isotherms for the various clays into aqueous (0.01 N CaCl₂) solution (legend as in Figure 2.)

via H bonds to the water molecules.

Adsorption from Aqueous Media. The adsorption isotherms from aqueous solution (Figure 4) can be grouped into those with K_d (mL/g) values above 100 and those with values below 100. The first group includes the hydrated and partially dehydrated clays, while the latter group includes the remaining samples.

The partially dehydrated sample exhibited a slightly greater affinity for parathion than did the hydrated clay. Saltzman (1977) found that when a parathion solution was added to oven-dried magnesium montmorillonite, adsorption was initially greater than on suspended clays but slowly decreased until it reached a value only slightly higher than the suspended system as water slowly replaced the parathion initially adsorbed. This mechanism offers a possible explanation for attapulgite as well.

The tremendous decrease in adsorption by the dehydrated and anhydride samples was originally thought to be the result of the clay's greater preference for water when dried at such temperatures, thereby decreasing parathion's ability to compete for adsorption sites. However, when partially dehydrated and dehydrated clays were resuspended in solution for 24 h prior to addition of parathion, the adsorption was identical with that shown in Figure 4. It would seem, therefore, that heating at 250 °C does cause some structural changes. In fact, some workers (Nathan, 1969; Imai et al., 1969) have reported that formation of the attapulgite anhydride can begin already at about 200 °C. Although these authors do not definitely state that these changes are irreversible at 250 °C, the present results suggest that the changes occurring (whether a shrinking of the ribbon in the *c* direction or tilting of the ribbon-like structure) are irreversible to some extent. Further evidence for irreversibility at this temperature is that the dehydrated clay—when placed in a desiccator at 52% relative humidity—regained only 82% of its weight loss (as opposed to 97% for the partially dehydrated clay).

With increased heating, a surprising increase in adsorption occurred. At 650 °C the clay begins to lose hydroxyl water from its structure and undergoes transition to a new mineral phase. The structure is still that of attapulgite anhydride, but new surfaces of Al, Mg, and Si are likely to appear and have a higher affinity for parathion. These surfaces were almost completely lost upon heating to 850 °C, thereby reducing the adsorption.

Release to an Aqueous Media. Information concerning release from the carrier of the pesticide when present at high loading rates, as affected by the carrier pretreatment, is of importance for studies of the use of attapulgite as a diluent for parathion. Under equilibrium
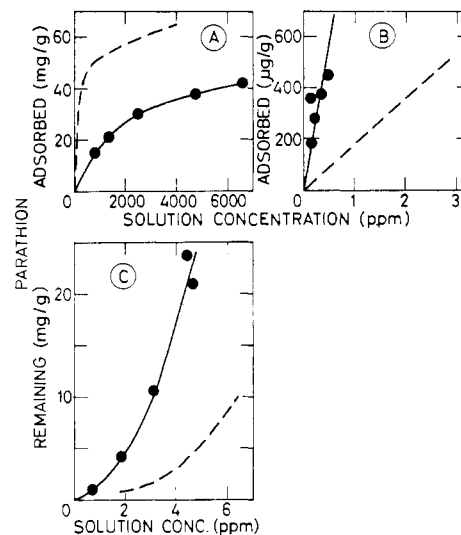

Figure 6. Behavior of parathion on organoattapulgite (hexa-decyltrimethylammonium) (solid line) compared to that of the partially hydrated clay (broken line): (a) adsorption in organic media, (b) adsorption in aqueous media, (c) equilibrium desorption isotherm.

conditions, two characteristic groupings for the release of parathion from pretreated attapulgite were found (Figure 5). Linear desorption was found for the dehydrated, anhydride, transition and amorphous clays, with nearly complete release. On the other hand, the hydrated and partially dehydrated clays exhibited nonlinear release and retained relatively large amounts of parathion. The results imply that the release of parathion to the external environment can be controlled by the pretreatment of the clay.

Organoattapulgite. The nature of the clay's surface was altered, in contrast to the thermal pretreatment, by replacing calcium as the exchangeable cation with an organic cation. The organoclay did not have any special affinity for parathion in organic media, as seen in Figure 6a. In adsorption from aqueous solutions (Figure 6b), however, it was clear that adsorption by the organoclay was greater than by the other clays. On clays saturated with organic cations a "quasiorganic" layer was formed, thus increasing the clay's affinity for other organic compounds. It should be pointed out, however, that attapulgite saturated with tetramethylammonium cations showed very weak adsorption of parathion, similar to the dehydrated and anhydride forms of the clay. Mortland (1978) has explained this phenomenon as being due to the relative size of the organic cations and adsorbing species. For large organic molecules, such as parathion, it is necessary to have a large organic cation to form an appropriate organic phase on the clay's surface. While the hexadecyltrimethylammonium cation provides such a phase for parathion, the smaller tetramethylammonium cation does not.

As with the thermally treated clays, the release of parathion to aqueous suspension under equilibrium conditions was correlated with its adsorption from water and was retained quite strongly, indicating that water was less able to displace parathion from the organoclay than from the nontreated attapulgite (Figure 6c).

SUMMARY AND CONCLUSIONS

Two different effects were responsible for the variation in adsorption capacity of pretreated attapulgite. The presence of hygroscopic moisture (hydration effects) reduced the adsorption of parathion so that heating up to 250 °C to remove this water increased adsorption. Above

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this temperature, structural changes in the clay reduced adsorption by reducing the surface area available for adsorption.

In aqueous solutions an inverse relationship was found between the adsorption of parathion and the release of parathion from highly loaded clays under equilibrium conditions.

The presence of an organic cation on the clay's surface altered the clay's behavior in aqueous solution, favoring increased adsorption and decreased desorption.

The results indicate that pretreatment of the clay can affect the rate of pesticide release and the amount released to the external environment.

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Kinetic Study of Reversible Conversion of Methyl 1-(Butylcarbamoyl)-2-benzimidazolecarbamate (Benomyl) to Methyl 2-Benzimidazolecarbamate (MBC) and n-Butyl Isocyanate (BIC) in Organic Solvents

Mikio Chiba* and Eugene A. Cherniak

The decomposition of benomyl (B), methyl 1-(butylcarbamoyl)-2-benzimidazolecarbamate, in chloroform, dichloromethane, ethyl acetate, benzene, ethanol, methanol, and dioxane was studied spectrophotometrically at 25 °C. The mechanism of decomposition in all the solvents is represented by: B (k_{21}) $\rightleftarrows$ MBC + BIC (k_{12}) where MBC is methyl 2-benzimidazolecarbamate and BIC is n-butyl isocyanate. Values of the specific rates k_{12} and k_{21} have been obtained for all the solvents studied. The values of k_{12} show no correlation with existing solvent parameters, but k_{21} values seem to be larger for less polar solvents. Kinetic and spectrophotometric evidence for the establishment of equilibrium has been obtained and the values of the equilibrium constant K seem to be larger for more polar solvents. Also, the largest value of the percentage of intact benomyl at equilibrium is found for benzene while the smallest value is found for methanol. The significance of these kinetic studies to the meaningful analysis of benomyl is discussed.

The fungicide benomyl (methyl 1-(butylcarbamoyl)-2-benzimidazolecarbamate) is reported to be unstable in aqueous media and breaks down rapidly to methyl 2-benzimidazolecarbamate (MBC) (Clemons and Sisler, 1969; Peterson and Edgington, 1970). Baude et al. (1973), however, demonstrated by using ¹⁴C-labeled benomyl that benomyl is rather stable in water and on plants after application. Chiba and Doornbos (1974) reported a rapid degradation of benomyl in organic solvents and its deg-

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radation product was confirmed to be MBC. At the 170th National Meeting of the American Chemical Society in Chicago, 1975, Chiba reported that the degradation of benomyl is very fast in organic solvents when the solution is prepared, but the reaction soon reaches equilibrium. The degradation in water, on the other hand, is rather slow and is influenced by agents employed to disperse benomyl in water. Chiba concluded that the generally accepted view that benomyl rapidly degrades in water may not be correct. Previous workers had failed to recognize that benomyl is rapidly decomposed in organic solvents during ordinary extraction procedures even though intact benomyl residues existed in or on plant tissues and in water.

According to Austin et al. (1976) the solubility of benomyl in water was 3.8 ppm at 20 °C and the half-life of