

Effect of Water upon Malathion Adsorption onto Five Montmorillonite Systems

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The adsorptive behavior and stability of malathion on Na-, Ca-, Cu-, Fe-, and Al-montmorillonite were investigated using both infrared spectroscopy and x-ray diffraction techniques. At relative humidities exceeding 40%, malathion quickly penetrated the interlayer region of the montmorillonite and was adsorbed as a double layer, giving an expansion of 5.6 to 6.5Å. The mechanism of adsorption was through a hydrogen bonding interaction between the carbonyl oxygen atoms and the hydration water shells of the saturating cations. In dehydrated systems, a direct ion-dipole interaction occurred between the carbonyl oxygen atoms and the saturating cations. The magnitude of both interactions increased with cationic valence. Changes in the hydration status of the clay system produced marked reversible alterations in the spectrum of adsorbed malathion that were attributed to orientation and interaction effects. No degradation of adsorbed malathion was observed in this study.

Polon and Sawyer (1962) and Yost *et al.* (1955a,b) reported that high sorptive minerals such as montmorillonite tended to promote malathion degradation more than low sorptive carriers such as kaolinite. They proposed theories for both acidic and alkaline degradation although no breakdown products were reported. Faust and Suffet (1966) stated that the rates of hydrolysis and types of hydrolytic products formed from organophosphate insecticides are determined by the presence of catalytic agents, temperature, pH, and the ionic strength of the system.

Konrad *et al.* (1969) have recently reported that the malathion degradation rate in soils was directly related to the extent of its adsorption. They believed that degradation occurred by a chemical mechanism catalyzed by adsorption, and that 50 to 90% of the added malathion was degraded in 24 hr in both sterile and nonsterile soil systems. They proposed two degradative pathways for malathion, one involving cleavage of the ethyl ester linkages, and the other involving the thiol ester linkage. They believed that the thiol ester cleavage was the predominant pathway.

The major objectives of this research project were to investigate the effect of five saturating cations (Na⁺, Ca²⁺, Cu²⁺, Fe³⁺, Al³⁺) and moisture content upon the adsorptive behavior and stability of malathion on montmorillonite clay, and to see if montmorillonite would serve as a model system to catalyze the degradation of malathion similar to that observed in soil systems (Konrad *et al.*, 1969).

MATERIALS AND METHODS

Preparation of Reference Clays. The reference clays used in this study were obtained from Ward's Natural Science Establishment, P.O. Box 1712, Rochester, N.Y., 14603, and are designated Montmorillonite No. 25 (Bentonite), Upton, Wyo., John C. Lane Tract, and Kaolinite No. 2, Macon, Ga., Birch Pit.

The clays were suspended in distilled water, treated with H₂O₂ to remove organic matter, and the less than 2 μ fraction was separated by sedimentation. This fraction was passed through a Sharpies supercentrifuge to remove the less than 0.1 μ fraction. The 0.1 to 2.0 μ fraction was saturated three times with one of the following 1N salt solutions, NaCl, CaCl₂, CuCl₂, FeCl₃, and AlCl₃, washed until chloride-free (by the AgNO₃ test) with distilled water, and then lyophilized for later use.

Preparation of Clay Films. The appropriate cation-saturated montmorillonite film was made by sedimenting 40 mg of resuspended clay onto a 50 mm diameter aluminum moisture dish. When dry, the film was carefully peeled off the dish and mounted in the infrared cell sample holder. Copper films were sedimented on a polyethylene sheet because of a reaction between copper and aluminum. All kaolinite films were sedimented onto a 25 X 50 X 2 mm IRTRAN-2 window because of their brittleness. Only 10 mg of kaolinite were used to make a film.

Compounds. The purity of the three compounds was as follows: Malathion, 100%; diethyl succinate, b.p. 105-107° C 16 (mm); diethyl mercaptosuccinate, better than 95%. The infrared spectra of eight other related acids and esters were obtained for reference purposes, but were not adsorbed onto the clay.

Sample Application. The three compounds (malathion, diethyl succinate, diethyl mercaptosuccinate) were liquids and were surface-applied to the clay films using a syringe needle. Surface excesses usually disappeared after brief evacuation, or brief equilibration at 100% relative humidity.

In the x-ray diffraction studies, the malathion was either surface-applied to a dried x-ray slide, or a 10-μl aliquot was added to the 20 mg clay sample prior to sedimentation onto the slide.

Equipment. The vacuum system was built around a combination forepump and oil diffusion pump capable of producing an ultimate vacuum of 10⁻⁶ Torr. Greaseless joints and stopcocks were used in the construction to avoid the deposition of stopcock grease on the clay films. A liquid nitrogen cold trap minimized back streaming of pump oil and froze out other vapors. The vacuum system was used to dehydrate the clay films while suspended in the infrared cell, without using heat.

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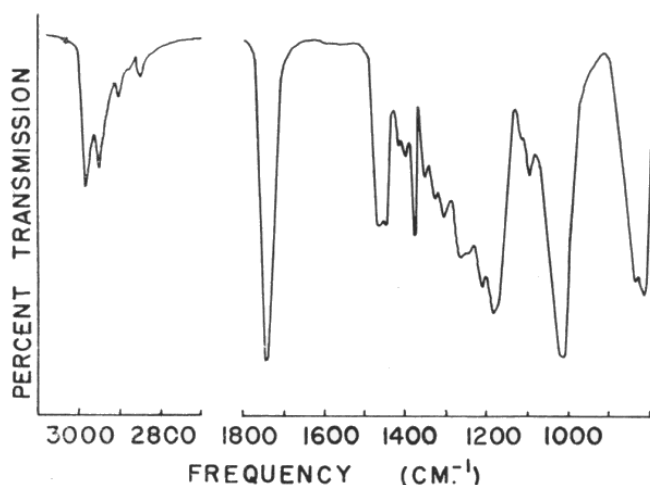


Figure 1. Infrared spectrum of malathion (capillary film)

The infrared cell was custom-built using Pyrex No. 6780 glass with a 50/50 capped, double viton O-ring greaseless joint on the top for entry on the stainless steel sample holder assembly. The path length of the cell was 10 cm and the window aperture was 44 mm. Polished KBr windows (55 X 6.5 mm) were directly sealed onto the cell using a high vacuum leak sealant (Space Environment Laboratories, Boulder, Colo., 80302).

All samples in the study were scanned in the double beam mode using a Beckman IR-12 infrared spectrophotometer. An adjustable beam attenuator was placed in the reference beam when clay films were scanned. The double beam/single beam energy ratio was adjusted to 1.0 at 2200 cm^{-1} and the samples were scanned at 80 cm^{-1} per min. All experiments were conducted at 22.5° C. Periodic scans of the montmorillonite-malathion systems were made during the dehydration process.

X-ray diffractograms were obtained using a General Electric XRD-5 diffractometer. $\text{CuK}\alpha$ was produced at 50 kv and 16 ma. The scanning rate of the goniometer was 0.2° (22 per min). For those samples requiring maximum dehydration, a cylindrical metal container containing P_2O_5 desiccant was placed over the slide holder on the goniometer and dry nitrogen gas was flushed through the container to hasten moisture removal. X-ray diffractograms of the drying samples were periodically obtained until the d spacings became constant. Mylar windows (6.35 X 10^{-4} cm thick) in the container allowed the x-ray beam to pass through the container while excluding water vapor from outside.

RESULTS AND DISCUSSION

Infrared Spectroscopy Studies. In all five montmorillonite systems, malathion was applied to films that had been dried for several minutes by evacuation. The infrared spectrum of malathion (Figure 1), following application onto each of the five montmorillonite systems, was unaltered, indicating that no interaction had occurred. An example of this is shown in Spectrum B, Figure 2 for the Al-montmorillonite-malathion system. This suggested that either malathion entered the interlayer regions of montmorillonite and did not interact, or that malathion remained on the exterior surfaces of the dry clay. An investigation into the effect of relative humidity upon the interaction of malathion with the Cu-montmorillonite system revealed that the number of hydrogen bonded carbonyl groups was very small below 30% relative humidity. X-ray diffraction studies later proved that malathion did not penetrate the interlayer region of montmorillonite in the absence of water molecules.

Spectrum A, Figure 2 shows the infrared spectrum of the Al-montmorillonite film which had been equilibrated twice with D_2O vapor to replace adsorbed water molecules. This was done in only the Al-montmorillonite system to remove the H_2O deformation band (1620 to 1750 cm^{-1} region) which masked some of the carbonyl band perturbations. In actual fact there was an exchange between D_2O and H_2O resulting in the development of an HOD deformation band at 1425 cm^{-1} . Because the clay film was exposed to the atmosphere while malathion was applied, the water deformation band again intensified (Spectrum B, Figure 2). However, the band disappeared when the film was re-exposed to 100% relative humidity D_2O (Spectrum C, Figure 2).

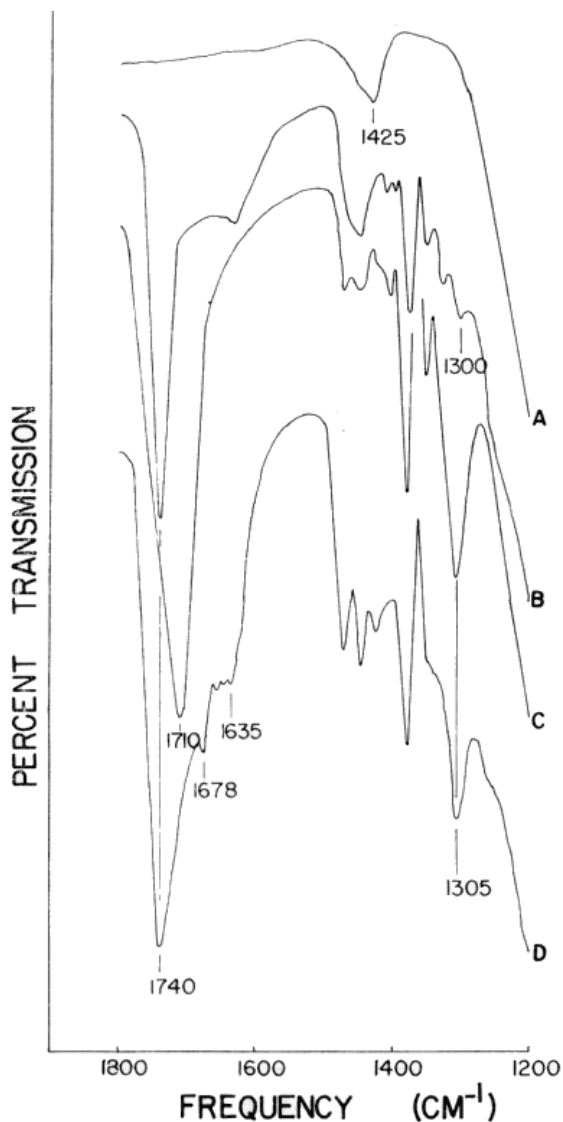


Figure 2. Infrared absorption spectra of the Al-montmorillonite-malathion system

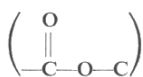
- D_2O treated clay film
- Malathion applied, 5-min evacuation to 15 μ
- Equilibration at 100% R.H. (D_2O) for 13 min, slight evacuation to remove excess D_2O
- Evacuation for 180 hr to $<10^{-4}$ Torr

Table 1. Carbonyl Group Absorption Frequencies of Malathion as Affected by the Saturating Cation and Hydration State of the Montmorillonite

Treatment	Saturating Cation				
	Na ⁺	Ca ⁺²	Cu ⁺²	Fe ⁺³	Al ⁺³
	Wavenumbers, cm ⁻¹				
Hydrated System	1730	1714 1695 ^a	1725 1715	1723 ^a 1714 1695 ^a 1684 ^a	1710
Dehydrated System	1722 1714	1695 1683 ^a	1740 1734 1715 ^a	1740 1660- 1678 1695 ^a 1683 ^a	1740 1678 1635

^a = Shoulder band.

When each of the five montmorillonite-malathion systems were exposed to 100% relative humidity, a relatively intense band developed in the 1300 cm⁻¹ region, and the 1328 cm⁻¹ band irreversibly disappeared (Spectrum C, Figure 2). Except for the Cu-montmorillonite-malathion system, it could not be ascertained whether the 1328 cm⁻¹ band disappeared or was masked by another band. At relative humidities less than 30% in the Cu-montmorillonite-malathion system, it was shown that the 1328 cm⁻¹ band disappeared independently of any change in the surrounding bands. The broad 1300 to 1320 cm⁻¹ band did not appreciably develop until higher relative humidities were attained. At this point, it was not known whether these spectral changes represented a malathion degradation or an interaction between the malathion and the clay-water systems. There are three main cleavage sites in the malathion molecule: the two ethyl ester linkages



and the thiol ester linkage (P—S—C). The methoxy linkage (CH₃—O—P) is not very susceptible to cleavage. Throughout the experiments, the relative intensity and the position of bands in the C—H stretching region remained constant, suggesting that there was no cleavage of the ethyl ester linkages. Such a cleavage would have produced carboxyl groups which have characteristic absorption bands in the 2800 to 3400 cm⁻¹ region of the spectrum. No such bands were ever observed in any of the systems studied.

Because of masking by montmorillonite absorption bands, changes in the P—S absorption bands in the 700 to 100 cm⁻¹ region that might suggest a P—S—C cleavage could not be observed. Therefore a study was made of the infrared spectra of diethyl succinate and diethyl mercaptosuccinate adsorbed on montmorillonite to see if the 1300 cm⁻¹ band observed in the montmorillonite-malathion system developed in these two systems. Konrad *et al.* (1969) have shown diethyl mercaptosuccinate to be a malathion degradation product in soils. All hydrated montmorillonite-diethyl succinate and montmorillonite-diethyl mercaptosuccinate systems developed a 1300 cm⁻¹ region band similar to that observed in the montmorillonite-malathion systems. Since the 1300 cm⁻¹ band appeared in the diethyl succinate system (Spectrum B, Figure 3), its development could not be associated with the P—S—C cleavage in malathion. More likely it was a result of an orientation or interaction effect similar to that reported by Parfitt and Mortland (1968) for 1313 cm⁻¹ band in the montmorillonite-2,5-hexanedione system.

The 1328 cm⁻¹ band of malathion apparently disappeared as a result of the molecule entering the interlayer region of montmorillonite, not a result of a direct interaction with water. The band did not disappear when adsorbed on a hydrated kaolinite system, where there were only exterior adsorptive surfaces.

There were many similarities between the spectra of adsorbed malathion and adsorbed diethyl mercaptosuccinate in the 1200 to 1800 cm⁻¹ region.

In all five montmorillonite-malathion systems the carbonyl group frequency shifted down (from 1740 cm⁻¹) upon exposure to either H₂O or D₂O vapor, indicating a hydrogen bonding interaction between the carbonyl oxygen atoms and the hydration water shells of the cations. Table 1 shows that the magnitude of the perturbation was largely controlled by the saturating cation, with the frequency shift increasing in the following order: Na⁺ < Cu⁺² < Ca⁺² = Fe⁺³ < Al⁺³. It is believed that the positive charge of the saturating cation strongly polarized the hydration water molecules (or D₂O molecules), making some protons more labile and consequently more capable of interacting with the carbonyl oxygen atoms. In other words, the acidity or dissociation of hydration water (or D₂O) molecules increases with cationic valence, thereby forming more energetic hydrogen bonds with carbonyl oxygen atoms.

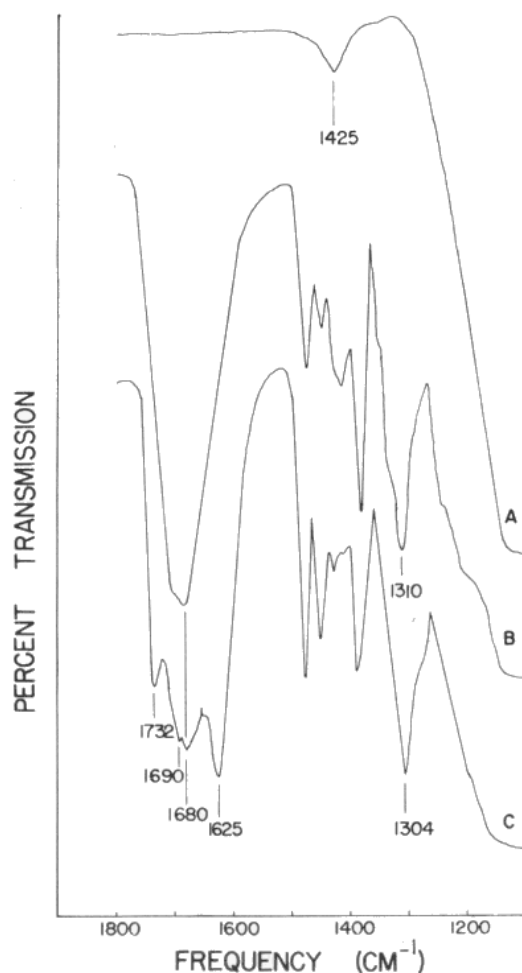


Figure 3. Infrared absorption spectra of the Al-montmorillonite diethyl succinate system

- D₂O treated clay film
- Diethyl succinate applied, equilibration at 100% R.H. (D₂O) for 15 min, slight evacuation to remove excess D₂O
- Evacuation for 120 hr to <10⁻⁴ Torr

However, in each of the five montmorillonite systems there were a few distinct differences. In all adsorbed malathion systems, the intensities of the 1445 and 1465 cm^{-1} bands were considerably greater than the intensity of the 1400 cm^{-1} region bands. In the diethyl mercaptosuccinate systems, the 1400 cm^{-1} bands were more intense than the 1445 and 1465 cm^{-1} bands. In the Na-montmorillonite-diethyl mercapto-succinate system, a band developed at 1293 cm^{-1} , about 10 cm^{-1} less than for the similar band in the malathion system. In the Ca-montmorillonite-malathion system, a strong band developed in the 1215 to 1227 cm^{-1} region depending on the hydration status. The Ca-montmorillonite-diethyl mercaptosuccinate system had an analogous band in the 1230 to 1235 cm^{-1} region, about 8 to 15 cm^{-1} higher. The same 1230 cm^{-1} region band appeared in the Fe-montmorillonite-diethyl mercaptosuccinate system, but did not occur in the Fe-montmorillonite-malathion system.

The next question which arose concerned the sensitivity of infrared techniques for detecting the development of those bands that would indicate the degradation of malathion into diethyl mercaptosuccinate. Probably a fairly substantial amount of malathion degradation, perhaps as much as 30%, might occur before the spectra would clearly show a difference. However, Konrad *et al.* (1969) reported that 50 to 90% of the adsorbed malathion broke down in a soil system within a 24-hr period. It would therefore be expected that if malathion degradation was initiated in these experiments, it would be detected by the end of the 3- to 5-day period over which they were conducted. The observed alterations in the spectrum of clay-adsorbed malathion, when compared to the spectra of possible degradation products, suggested that no breakdown had occurred. These spectral alterations were more suggestive of orientation and interaction effects.

Dehydration of the five montmorillonite-malathion systems by evacuation progressively stripped hydration water molecules from the saturating cations. (At 22.5 °C, some hydration water molecules probably remained with the divalent and trivalent cations following evacuation. The disappearance of the OH deformation band in the 1620 to 1650 cm^{-1} region in the Na-montmorillonite system indicated that evacuation had essentially removed all water molecules from the clay.) The carbonyl oxygen atoms of malathion were able to more closely approach the cations, undergoing very energetic ion-dipole interactions, which resulted in a greater downward shift in the carbonyl group frequency than was the case for the hydrogen bonding interaction. Table 1 shows the perturbed carbonyl group frequencies for the five dehydrated montmorillonite-malathion systems. In both the monovalent and divalent systems (except copper) the entire carbonyl group band shifted down upon dehydration, but in the trivalent iron and aluminum systems, the band split into an unperturbed band at 1740 cm^{-1} and into a low frequency band in the 1635 to 1660 cm^{-1} region. This carbonyl band splitting phenomenon in trivalent montmorillonite systems was observed for adsorbed diethyl succinate (Spectrum C, Figure 3), and diethyl mercaptosuccinate as well as for adsorbed malathion.

Some caution must be exercised in the use of the term "trivalent" as applied to clay-water systems. Jackson (1963) has pointed out that the trivalent aluminohexahydronium monomeric cation, $[\text{Al}(\text{H}_2\text{O})_6]^{+3}$, dissociates as follows:



Since the pH of the montmorillonite used in this study was between 4 and 8, only $[\text{Al}(\text{H}_2\text{O})_6]^{+3}$ and $[\text{AlOH}(\text{H}_2\text{O})_5]^{+2}$ would be of importance. At this time it is not known whether these two forms interact differently with the carbonyl group. Throughout this discussion, the term "trivalent" aluminum will imply an equilibrium mixture of these two forms as dictated by the surface acidity of the clay-water system.

It is postulated that in the trivalent montmorillonite systems, the dehydrated cations were separated by a greater distance than the carbonyl oxygen atoms of the succinate moiety (approximately 4.9 Å). This resulted in a slight lateral movement of the molecule toward one cation, which in turn allowed one carbonyl oxygen to interact much more energetically than the other one. This splitting did not occur in the hydrated trivalent systems because of the considerably larger radius of the hydrated cations. In the monovalent and divalent systems, the increased surface density of the saturating cations would allow both carbonyl oxygen atoms on each molecule to interact equally. Table 1 shows that the dehydrated Cu-montmorillonite-malathion system had a series of bands from 1740 cm^{-1} down to 1683 cm^{-1} . Perhaps the unique coordinating abilities of the copper ions may be related to the development of so many bands.

In the dehydrated trivalent montmorillonite systems, carbonyl group perturbations of up to 115 cm^{-1} (Spectrum C, Figure 3) were observed. The energy involved in this type of interaction is considerably greater than the energy involved in the 60 cm^{-1} or less perturbations observed for hydrogen bonding in the same system. In fact, much of the double bond character of the carbonyl group has given way to a carbon-oxygen bond having considerable bond character. Although this ion-dipole interaction between the carbonyl oxygen and the cation appeared to be quite substantial, it was very reversible. A short exposure of a few minutes to 100% relative humidity quickly rehydrated the cation, and once again the carbonyl oxygen became hydrogen bonded to the hydration water molecules.

With the exception of the 1300 and 1328 cm^{-1} bands, (apparently due to interaction effects) all spectral changes in the montmorillonite-malathion systems as a function of hydration status were reversible, giving rise to the following conclusions. Malathion degradation on the various montmorillonite systems appeared to be minimal over a 3- to 5-day period. To make meaningful conclusions when using infrared spectroscopy to study clay-organic interactions, it is necessary to have control over the hydration status of the clay system. If the hydration status of the clay varies between experiments, comparisons of band perturbations may be meaningless.

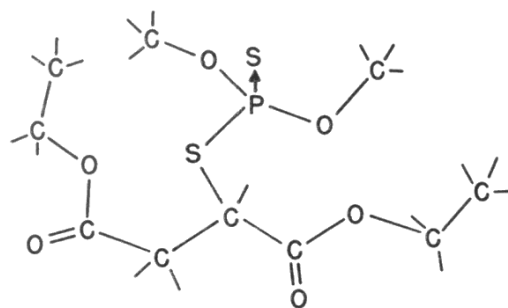
X-ray Diffraction Studies. The purposes of the x-ray diffraction studies were to discover the circumstances under which malathion could enter the interlayer regions of dehydrated montmorillonite, and to see whether malathion formed one or two molecular layers on the interlayer surfaces.

The d spacing of all five dehydrated montmorillonite systems, to which malathion was surface-applied, remained constant over a 24-hr period, indicating that no malathion had penetrated the interlayer region. Upon exposure to water vapor (100% relative humidity) the d spacing increased by 6.0 to 7.0 Å, depending on the particular system. Subsequent drying over P_2O_5 and

flushing with dry N₂ reduced the d spacing to 15.5 to 16.3Å, depending on the system (about a 5.6 to 6.5Å expansion). Previously, Meyers (1968) reported a d spacing of 13.8Å, while Berigari (1967) reported a 16.7Å spacing for the adsorption of a malathion monolayer. The data in this study suggest that the 15.5 to 16.3Å spacing represented a layer of malathion adsorbed on each interlayer surface of montmorillonite.

Configuration and Orientation of Adsorbed Malathion. Little discussion concerning the orientation and configuration of malathion adsorbed onto montmorillonite has been made, other than the assumption that it is a planar molecule. By using a stereomodel structure of malathion it was discovered that there are four possible planar configurations with carbonyl oxygen separation distances ranging from 4.7 to 5.8Å. Of the four configurations, the one shown in Figure 4 appears to be the most probable because it is the most compact model having no steric hindrances, and the carbonyl oxygen atoms (separated by 4.9Å) are on the opposite side of the molecule to the phosphorodithioate entity and therefore are easily accessible for interactions.

The stereomodel suggested a monolayer thickness of approximately 2.5Å. Thus, the 5.6 to 6.5Å expansion of the clay lattice observed in the x-ray diffraction studies could accommodate a double layer of malathion, accounting for about 5.0Å, with the remainder (0.6 to 1.5Å) being accounted for by interlayer cations and their partial hydration shells. Possibly at very low malathion concentrations, the molecules might be alternately adsorbed on opposite interlayer surfaces which, upon collapse of the lattice, would give a d spacing of only one monolayer, consistent with the 13.8 Å d spacing reported by Meyers (1968).



DISTANCE BETWEEN CARBOXYL OXYGENS = 4.9 Å
Figure 4. Possible configuration of malathion

ACKNOWLEDGMENT

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