

## DISSERTATION ABSTRACT

### **THE EFFECT OF WATER UPON MALATHION ADSORPTION ONTO FIVE MONTMORILLONITE SYSTEMS.**

by

Bruce T. Bowman, Ph.D.

Thesis Advisor: Professor R.S. Adams, Jr.

The adsorptive behavior and stability of malathion on Na-, Ca-, Cu-, Al-, and Fe-montmorillonite was investigated, using both infrared spectroscopy and x-ray diffraction techniques. Malathion was surface-applied to thin montmorillonite films and a series of infrared spectra were obtained of the systems as they were dehydrated by evacuation.

Malathion penetration of the interlayer regions of montmorillonite was very slow below 30 % relative humidity. At relative humidities exceeding 40 %, penetration occurred within minutes, resulting in a hydrogen bonding interaction between the carbonyl oxygen atoms and the cationic hydration water shells. The magnitude of the carbonyl group frequency perturbation increased with the valence of the saturating cation;  $\text{Na}^+$  ( $10 \text{ cm}^{-1}$ ) <  $\text{Cu}^{+2}$  ( $15 \text{ cm}^{-1}$ ) <  $\text{Ca}^{+2} = \text{Fe}^{+3}$  ( $25 \text{ cm}^{-1}$ ) <  $\text{Al}^{+3}$  ( $30 \text{ cm}^{-1}$ ). It is postulated that water molecules wedged open the interlayer space allowing malathion molecules to migrate into the interlayer space.

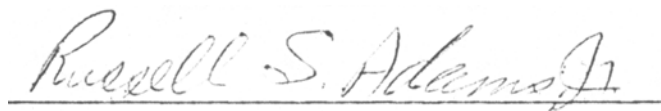
In all hydrated montmorillonite-malathion systems a relatively intense infrared absorption band developed in the  $1300 \text{ cm}^{-1}$  region, suggesting either a degradation reaction or an interaction effect. Malathion is subject to cleavage at the ethyl ester linkages or at the thiol (P-S-C) ester linkage. No ethyl ester linkage cleavage was observed because the C-d stretching bands remained

constant in position and in intensity relative to the remainder of the spectrum throughout the experiments. Since P-S vibrations occur coincidentally with clay absorption bands in the 700 to 1000  $\text{cm}^{-1}$  region, it was impossible to determine whether these bands were altered, thereby suggesting a thiol ester linkage cleavage. Infrared spectra of diethyl succinate and diethyl mercaptosuccinate adsorbed onto the five montmorillonite systems all developed the 1300  $\text{cm}^{-1}$  region band suggesting that it was due to an interaction or orientation effect rather than a P-S-C cleavage. A careful comparison of the adsorbed malathion and diethyl mercaptosuccinate spectra showed some small but distinct differences. On the basis of these comparisons, no malathion degradation was detected over a three to five day period. It should be emphasized that there were many reversible changes in the spectrum of adsorbed malathion, controlled by the hydration state of the system.

Dehydration of the montmorillonite-malathion systems by evacuation progressively stripped hydration water molecules from the saturating cations, allowing the carbonyl oxygen atoms of malathion to more closely approach the cation for ion-dipole interactions. Being of greater energy, this interaction lowered the carbonyl group frequencies by 45 to 115  $\text{cm}^{-1}$  (the latter figure was for diethyl succinate). Such large perturbations suggested a carbonyl group having considerable single bond character. In the dehydrated trivalent montmorillonite systems, the carbonyl group frequencies (of malathion, diethyl succinate and diethyl mercaptosuccinate) split onto a high frequency band (near 1740  $\text{cm}^{-1}$ ) as well as the low frequency band mentioned above. It is postulated that the lower cation surface density in the trivalent system placed the dehydrated cations too far apart for both carbonyl groups to simultaneously interact, resulting in the molecule shifting toward one cation. Rehydration quickly returned the system to the original hydrogen bonded state.

A stereomodel of the malathion molecule suggested four possible planar configurations with the carbonyl oxygen atoms separated by 4.7 to 5.8 Å (depending on the configuration). The most

probable of these was a compact, steric hindrance-free model where the carbonyl oxygen atoms were on the opposite side of the molecule to the phosphorodithioate entity and were separated by 4.9 Å. The monolayer thickness appeared to be approximately 2.5 Å. X-ray diffraction studies showed that malathion expanded the interlayer space of montmorillonite by 6.0 to 7.0 Å depending on the system. Probably a monolayer of malathion adsorbed to each interlayer surface of the clay accounting for at least 5 Å. The other 1 to 2 Å could be accounted for by the partially hydrated saturating cation.

A handwritten signature in cursive script, reading "Russell S. Adams, Jr.", is written above a horizontal line.

Approved by

Thesis Advisor



**THE EFFECT OF WATER UPON MALATHION ADSORPTION ONTO  
FIVE MONTMORILLONITE SYSTEMS**

A Thesis

Submitted to the

Faculty of the Graduate School

of

The University of Minnesota

by

Bruce T. Bowman

in. partial fulfillment of the requirements

for the degree of

Doctor of Philosophy

December, 1969



## ACKNOWLEDGMENTS

The author wishes to express his sincere appreciation to Dr. R. S, Adams, Jr., Associate Professor of Soil Science, University of Minnesota, for his guidance and interest throughout the course of this investigation and for his assistance during the preparation of this dissertation.

Appreciation is expressed to Dr. R. H. Dowdy, ARS, SWORD, USDA, for his technical assistance and for permission to use the infrared spectrophotometer.

Special appreciation is expressed to Dr. S. W. Fenton, Professor of Organic Chemistry, University of Minnesota, for his assistance in the interpretation of infrared spectra during this study.

The author wishes to express his gratitude to the National Research Council of Canada for their financial support throughout the entire program.

The author also wishes to thank his wife, Gail, for her understanding and encouragement throughout this study.

This research was supported in part by SWCRD, ARS, USDA Contract Number 12-14-100-8177(41).

## TABLE OF CONTENTS

Acknowledgments	ii
Table of Contents	iii
List of Tables	v
List of Figures and Diagrams	vi
I. Introduction	1
II. Review of Literature	4
A. Organophosphate Insecticides	4
a. Nomenclature	4
b. Development and Commercial Consumption	8
c. Mode of Action	11
d. Fate of Applied Organophosphate Insecticides	18
B. Malathion	26
a. Chemical, Physical and Biological Properties	26
b. Commercial Formulations and Factors Affecting Their Stability	28
c. Possible Breakdown Products of Malathion	33
d. Behavior of Applied Malathion	37
III. Materials and Methods	45
A. Preparation of Reference Clays	45
B. Infrared Spectroscopy Studies	46
a. Vacuum System	46
b. Infrared Cell and Accessories	46
c. Preparation of Clay Films	49
d. Compounds Used for Study	49
e. Operating Parameters of the Beckman IR-12 Spectrophotometer	51

C. X-ray Diffraction Studies	51
IV. Results and Discussion	53
A. Infrared Spectroscopy Studies	53
a. Na-Montmorillonite-Malathion System	53
b. Ca-Montmorillonite-Malathion. System	59
c. Cu-Montmorillonite-Malathion System	68
d. Al-Montmorillonite-Malathion System	74
e. Fe-Montmorillonite-Malathion System	80
f. Montmorillonite-Diethyl Succinate Systems	84
g. Montmorillonite-Diethyl Mercaptosuccinate Systems	109
h. Kaolinite-Malathion Systems	119
B. X-ray Diffraction Studies	120
C. Configuration and Orientation of Malathion on the Interlayer Surfaces of Montmorillonite	129
V. Summary and Conclusions	139
Bibliography	147

## List of Tables

1. Consumption of Leading Organophosphate Insecticides in the United States, 1964	9
2. Chemical and Physical Properties of Malathion	27
3. Common and Scientific Names of Insecticides	44
4. The Compounds Selected for Investigation	50
5. Relative Humidity Mixtures	73
6. Assignments of Infrared Absorption Frequencies of Diethyl Fumarate and Diethyl Mercaptosuccinate	95
7. Assignments of Infrared Absorption Frequencies of Succinic Acid and Fumaric Acid	96
8. Assignments of Infrared Absorption Frequencies of Dimethyl Succinate	97
9. Assignments of Infrared Absorption Frequencies of Malathion Di-acid and 2,3-Dimethyl Succinic Acid	98
10. Assignments of Infrared Absorption Frequencies of Malathion and Diethyl Succinate	99
11. X-ray Diffraction Data for the Na- and CaMontmorillonite-Malathion Systems	122
12. X-ray Diffraction Data for the Cu- and Fe-Montmorillonite-Malathion Systems	123
13. X-ray Diffraction Data for the Al-MontmorilloniteMalathion System	124
14. Carbonyl Group Absorption Frequencies of Malathion as Affected by the Saturating Cation and Hydration State of the Montmorillonite	144

## List of Figures

1. Photograph of Vacuum Apparatus	47
2. Photographs of Infrared Cell and Sample Holder	48
3. Spectra of the Na-Montmorillonite-Malathion System	54
4. Spectra of the Na-Montmorillonite-Malathion System	56
5. IR Spectra of the Ca-Montmorillonite-Malathion System	60
6. IR Spectra of the Cu-Montmorillonite-Malathion System	69
7. IR Spectra of the Al-Montmorillonite-Malathion System	75
8. IR Spectra of the Fe-Montmorillonite-Malathion System	81
9. IR Spectra of the Fe-Montmorillonite-Malathion System	83
10. IR Spectra of the Na-Montmorillonite-Diethyl Succinate System	86
11. IR Spectrum of Malathion (Capillary Film)	87
12. IR Spectrum of Diethyl Succinate (Capillary Film)	88
13. IR Spectrum of Diethyl Mercaptosuccinate (Capillary Film)	89
14. IR Spectrum of Dimethyl Succinate (Capillary Film)	90
15. IR Spectrum of; A) Hydroxysuccinic Acid. (KBr Pellet) B) Mercaptosuccinic Acid. (KBr Pellet)	91
16. IR Spectrum of Diethyl Fumarate (Capillary Film)	92
17. IR Spectrum of; A) Malathion Di-acid. (KBr Pellet) B) 2,3-dimethyl Succinic Acid (KBr Pellet)	93
18. IR Spectrum of; A) Succinic Acid (KBr Pellet) B) Fumaric Acid (KBr Pellet)	94
19. IR Spectra of the Ca-Montmorillonite-Diethyl Succinate System	101
20. IR Spectra of the Cu-Montmorillonite-Diethyl Succinate System	103
21. IR Spectra of the Al-Montmorillonite-Diethyl Succinate System	105

22. IR Spectra of the Fe-Montmorillonite-Diethyl Succinate System	107
23. IR Spectra of the Na-Montmorillonite-Diethyl Mercaptosuccinate System	111
24. IR Spectra of the Ca-Montmorillonite-Diethyl Mercaptosuccinate System	113
25. IR Spectra of the Cu-Montmorillonite-Diethyl Mercaptosuccinate System	115
26. IR Spectra of the Al-Montmorillonite-Diethyl Mercaptosuccinate System	116
27. IR Spectra of the Fe-Montmorillonite-Diethyl Mercaptosuccinate System	118
28. Photographs of Possible 3-Dimensional Configurations of Malathion Using the Dreiding Stereomodel	130-131
29. Possible 2-Dimensional Configurations of the Malathion Molecule	132-133

## I. INTRODUCTION

Malathion, since its initial synthesis in the early 1950's, has become a widely used organophosphate insecticide on fruit and vegetable crops. Its short lived persistence and high toxicity to insects has made it very acceptable from a pollution viewpoint.

Most of the research done to date has involved the persistence of malathion on small grains or on leaf surfaces, the effects on insects and devising suitable application methods. Polon and Sawyer (1962) and Yost et al. (1955) found 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 breakdown although no breakdown products were mentioned.. Yost et al. (1955) also suggested that metallic salts of copper and iron as well as surface adsorbed water on minerals promoted malathion degradation. According to Faust and Suffet (1966), the rates of hydrolysis and types of hydrolytic products formed from organophosphate insecticides are determined by (i) presence of catalytic agents, (ii) temperature, (iii) pH and (iv) the ionic strength of the system.

Konrad et al. (1969) have recently reported that the rate of malathion degradation in soils was directly related to the extent of its adsorption. They concluded that degradation occurred by a chemical mechanism catalyzed by adsorption and that 50 to 90 percent of the added malathion

$\begin{matrix} \text{O} \\ \parallel \\ (-\text{C}-\text{O}-\text{C}) \end{matrix}$  was degraded in 24 hours in both sterile and non-sterile soil systems. They proposed two degradative pathways for malathion, one involving the cleavage of the ethyl ester linkage and the other involving the thiol ester linkage (P-S-C). They believed that degradation via cleavage of the thiol ester linkage was the more important pathway.

Konrad *et al.* stated that soil sterilization had little effect upon malathion degradation rates and therefore the linear degradation rate was due to non-biological mechanisms. However, intracellular enzymes released at the time of irradiation (if they were not destroyed) could have produced the same linear degradation rate.

Both Berigari (1967) and Meyers (1968) have studied the adsorption of malathion onto montmorillonite using X-ray diffraction techniques, but report somewhat different results. Berigari stated that montmorillonite expanded to give a d spacing of 16.7 Å for a monolayer of malathion, whereas Meyers reported a monolayer d spacing of only 13.8 Å.

The objectives of this research project were several fold;

1. To investigate the effect of several saturation cations ( $\text{Na}^+$ ,  $\text{Ca}^{+2}$ ,  $\text{Cu}^{+2}$ ,  $\text{Al}^{+3}$ ,  $\text{Fe}^{+3}$ ) upon the adsorptive behavior and stability of malathion on montmorillonite clay,
2. To investigate the effect of water upon the stability of malathion adsorbed on the five montmorillonite systems listed above,

3. To see if the degradative pathways of malathion on montmorillonite were similar to those reported by Konrad *et al.* (1969) for several sterile and non-sterile soil systems,
4. To try and resolve the discrepancy between the data of Berigari (1967) and Meyers (1968) as to whether a d spacing of 13.8 Å or 16.7 Å represents a monolayer of malathion on the interlayer surfaces of montmorillonite.

Both infrared spectroscopy and X-ray diffraction techniques were employed in the study since these techniques allowed in situ observations of the various montmorillonite-malathion systems, without destruction of the systems themselves. Desorption of the malathion from the clay was not undertaken. An artificial degradation might have resulted, thereby confusing interpretation of any naturally occurring processes.

## II. REVIEW OF LITERATURE

### A. Organophosphate Insecticides

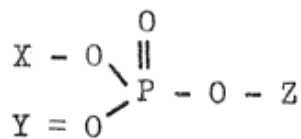
#### a) Nomenclature

The nomenclature of organophosphate insecticides has been somewhat confusing because there has been no internationally accepted standard. Up to 1952, there were at least four systems in use; the British, Swedish, German and American systems. Fortunately in 1952, the British and Americans agreed upon a single system of naming compounds, which today accounts for the majority of economically important products.

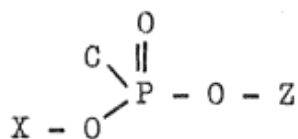
It has become an accepted practice to employ the term organophosphate as a generic term covering all toxic organic compounds containing phosphorus. Terms such as organophosphorus, organic phosphates and organic phosphorus are now considered improper when applied to compounds having insecticidal activity, although the term organophosphorus seems to be accepted for use in organic chemistry texts (Roberts and Caserio, 1964) when referring to derivatives of phosphorus hydrides, oxyacids and oxides.

The first step in naming phosphorus compounds is to consider the atoms attached to the phosphorus atom. Compound (I) is called a phosphate; (II) is a phosphonate; (III) is a phosphorothionate; (IV) is a phosphorothiolate (some authors do not distinguish between the sulfur atoms and call both (III) and (IV) phosphorothioates; they do not distinguish between a thiono sulfur, = S, and a thio sulfur, (- S -); (V) is a phosphorodithioate; and (VI) is a

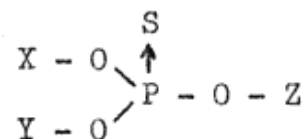
phosphoroamidate. Sometimes authors, in an attempt to distinguish between the thiono and thio sulfur, even when both are present, refer to compound (V) as a phosphorothiolothionate.



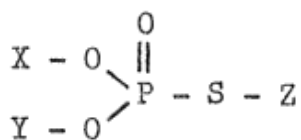
(I)



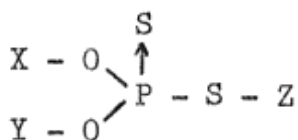
(II)



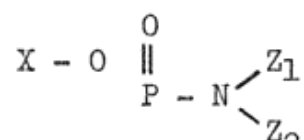
(III)



(IV)

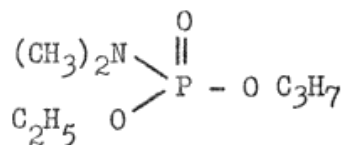


(V)



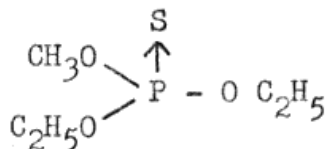
(VI)

The substituents X, Y, and Z are included in the name with an indication of the atom to which they are attached (eg),



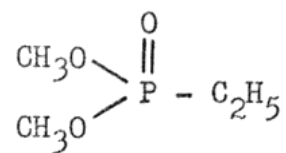
N,N- Dimethyl 0-ethyl 0-n- propyl phosphoroamidate

But in those cases where is no ambiguity, the atom of attachment can be omitted (eg),



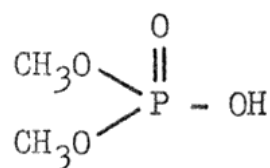
Methyl diethyl phosphorothionate

With the phosphonates containing a P-C bond, by convention, the name of the alkyl group which is attached to the phosphorus atom is written as one word with the acid part (O'Brien, 1960).



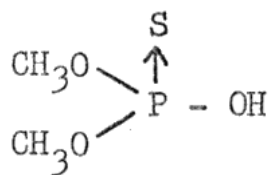
Dimethyl ethylphosphonate

If, in any of the above cases the X, Y or Z of an OX, OY or OZ group is hydrogen, the "hydrogen" should be used in the name (eg),



Dimethyl hydrogen phosphate

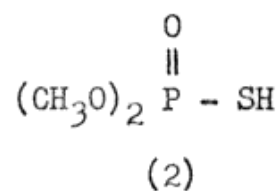
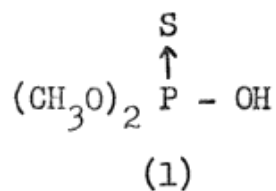
or



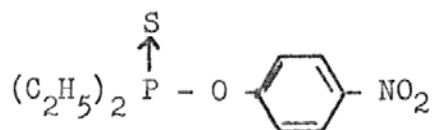
Dimethyl hydrogen phosphorothionate

Often this latter compound has been referred to as just O,O-dimethyl phosphorothionate and sometimes as O,O- dimethyl phosphorothionic acid. Usually in writing, authors choose to ignore the use of "hydrogen" in the name of a compound.

As mentioned above, some authors do not distinguish between the thio and thiono sulfur groups. In some cases there may be a justification for this (eg),



The first could be called dimethyl phosphorothionate, the second, O,O-dimethyl phosphorothionate. But it is uncertain which isomer predominates and so the name O,O-dimethyl phosphorothioate is justifiably used. But compounds such as parathion,



should always be referred to as thionates, not thioates since there is no doubt as to whether the sulfur is  $\text{P} \rightarrow \text{S}$ , or  $\text{P} - \text{S} -$ .

O'Brien (1967) states that most organophosphates can be considered to be esters of alcohols with a phosphorus acid, or as anhydrides of a phosphorus acid with some other acid. Thus parathion is an ester of the acid  $(\text{HO})_3\text{P} \rightarrow \text{S}$  with two molecules of ethanol and one of the weakly acidic "alcohol" p-nitrophenol. In such cases, the chemical name is simply given by naming the alcohols (alphabetically) and then the appropriate phosphorus acid ending, with spaces after each alcohol. Parathion is, then, diethyl p-nitrophenyl phosphorothionate.

Most nomenclature problems with organophosphates arise in naming the side-chain alcohols. Fortunately most commercial compounds are O,O-diethyl and O,O-dimethyl types, and the variety comes in the nature of the third alcohol, often referred to as the leaving group. Thus the general structure of organophosphates may be shown as  $(\text{RO})_2 \text{P} (\text{A}) \text{X}$ , where R = methyl or ethyl, A = sulfur or oxygen, and X can vary a great deal.

The insecticide malathion has received a variety of chemical names by different authors (eg);

1. S- (1,2-dicarbethoxyethyl) O,O- dimethyl dithiophosphate,
2. O,O- dimethyl S-[1,2-bis(ethoxycarbonyl)-ethyl] phosphorodithioate,
3. O,O- dimethyl thiophosphate of diethyl mercaptosuccinate,
4. O,O- dimethyl S- bis(carboethoxy)ethyl phosphorodithioate,

The third name listed is the manner in which Chemical Abstracts refer to malathion and is probably the most accepted one, although the second and the fourth name are often found in the literature. Rather than attempt to give the full chemical name of each organophosphate throughout the body of the thesis, Table 3 lists the common name(s) along with the chemical name(s).

b) Development and Commercial Consumption

The initial work conducted on organophosphates was started in 1934 by Gerhard Schrader of Farbenfabriken Bayer in Germany. Because of their potential application as biological warfare agents, a considerable amount of research was conducted on this class of compound during World War II. It wasn't until after the war in 1947, that Schrader's work was published. Since that time the number of organophosphates has mushroomed, exceeding 50,000 by 1959, although only a small percentage of these found commercial application. The following table 1 gives the consumption of several of the more widely used organophosphates in the United States during 1964 as quoted in The Pesticide Review (1968),

Historically, insecticides have been the major pest control chemicals used by farmers, and in 1964, still accounted for 55 percent of farmers' expenditures for all crop pesticides (Fox *et al.*,

**Table 1. Consumption of Leading Organophosphate Insecticides (active ingredient basis) in the United States, 1964.**

Product	Area of Use			Total	Wholesale Price *
	Crops(1)	Livestock (2)	Other (3)		
	x 1000 lb.	x 1000 lb.	x 1000 lb.	x 1000 lb.	dollars
methyl parathion	9,981	--	4	9,985	8,764,800
parathion	6,138	--	288	6,426	5,654,880
malathion	4,066	602	100	4,768	4,292,200
diazinon	2,277	31	2	2,310	N.A.
azinphosmethyl	2,245	--	28	2,273	N.A.
				25,762	

(1) includes all crops, pasture, rangeland and land in summer fallow.

(2) includes livestock buildings.

(3) includes all other uses except treating seed, stored crops and storage buildings.

\* Calculated using 1965 price level and the quantity shown in the Total column.

N.A. = not available.

1966). In 1966, about 29 percent of all producers of deciduous fruit (excluding apples) and nearly 70 percent of the citrus, apple and tobacco growers used insecticides on their crops. In recent years, insecticides have found increased usage on alfalfa and cotton crops. By 1966, insecticides were used on about two-thirds of the acreage of alfalfa in the Appalachian region, 45 percent in the Southern Plains and 30 percent in the Northeast (Fox et al., 1966). In 1964, farmers applied two-thirds of the total quantity of all insecticides used on farms to three crops - cotton, corn and apples. The cotton market accounted for more than half the total, including about 88 percent of the methyl parathion, 86 percent of the endrin, 70 percent of the DDT and 69 percent of the toxaphene. The corn market accounted for only 10 percent of the total used, including 96 percent of the aldrin, 84 percent of the heptachlor, 80 percent of the phorate and 63 percent of the diazinon.

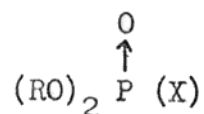
While the rate of growth of the insecticide market is not as spectacular as that for herbicides, insecticide sales continue upward, topping the \$301 million mark in 1967 (Fox *et al.*, 1966). As far as consumption of insecticides is concerned, the chlorinated hydrocarbons such as toxaphene, DDT, carbaryl and aldrin still account for the bulk of the consumption (about four times the sum of the five organophosphates listed in Table 1). Because of the increasing concern for pollution by the more persistent pesticides, namely the organochlorine insecticides, the relative consumption of the less persistent organophosphate insecticides will probably increase.

The search for more effective, safer and more convenient techniques of insecticide application continues. A recent development is the ultra-low-volume (ULV) method of application which is increasing in favor because of economy of manpower, equipment and pesticides. Other methods of insect control are also under study such as the release of male insects sterilized by irradiation, sterilization chemically with chemosterilants, biological control by insect predators, insect parasites and disease organisms and trapping with insect attractants. Techniques involving insect hormones and ultrasonics are also showing some promise for controlling insect behavior. However, at this time these "biological" controls do not give sufficient pest control and for the foreseeable future, chemical insecticides will be required.

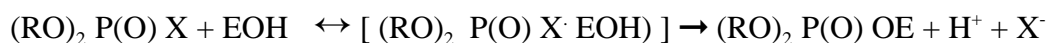
c) Mode of Action

The mode of action of most organophosphate insecticides is widely accepted to be through the interaction of the organophosphate with the OH group of the vital serine molecule, the active site in the cholinesterase enzyme (O'Brien, 1967). The cholinesterase is responsible for hydrolyzing acetylcholine produced in nerve synapses, preventing them from firing continuously.

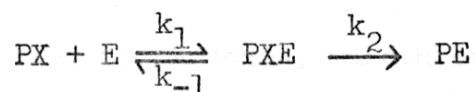
In the course of the interaction between the organophosphate and the cholinesterase, the "leaving" group of the organophosphate is replaced by the cholinesterase. The "leaving" group of the organophosphate can be envisioned as follows; let us assume the following general formula for organophosphates;



where R usually represents a methyl or ethyl group, and X represents the leaving group. (In the case of malathion, the oxygen would be a sulfur atom and X would represent the diethyl mercaptosuccinate moiety.) The overall reaction, as suggested by Main (1964) is



where EOH represents the active site on the serine molecule of the cholinesterase. Essentially, the cholinesterase is phosphorylated by the organophosphate. The reaction involves two steps and can be symbolized as



where  $\text{P} = (\text{RO})_2 \text{P}(\text{O})$ , and  $\text{E} = \text{EOH}$ . The ratio of  $k_1 / k_{-1}$  is referred to as an affinity constant,  $K_a$  and describes the tendency of the organophosphate to combine with the cholinesterase. The second step, described by the monomolecular rate constant,  $k_2$ , indicates the tendency of the organophosphate to phosphorylate the enzyme, thereby destroying its activity.

Using the above equation and the rate constants, kinetic principles can be used to describe the rate at which the organophosphate can be expected to phosphorylate the cholinesterase.

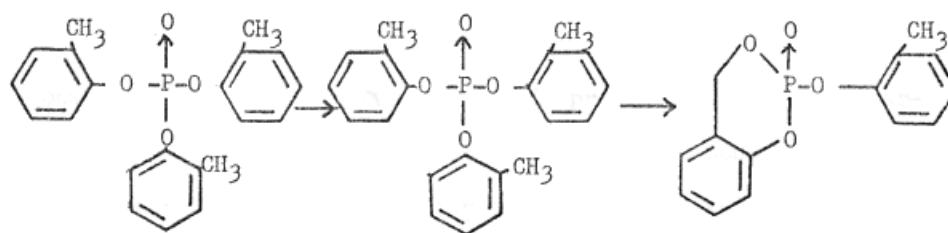
An examination of the inhibitory action of many organophosphates would reveal that approximately 75 percent of them are rather poor inhibitors of cholinesterase in vitro, requiring as much as  $10^{-3}$  to  $10^{-4}$  M to inhibit 50 percent of the cholinesterase in a 15 to 30 minute period.

(O'Brien, 1967). The other 25 percent would prove to be potent inhibitors, requiring only  $10^{-5}$  to  $10^{-9}$  M to achieve the same results in the same time period. This latter group are referred to as "direct inhibitors". Yet when comparisons are made of animals poisoned by organophosphates, the differences between direct inhibitors and the others seem to disappear. The reason is that many organophosphates are "latent inhibitors", owing their effectiveness "in vivo" to the fact that they are converted or "activated" in the body to give compounds which are direct inhibitors.

The most common activation is the conversion of a phosphorothionate (P→S) compound to a phosphate (P→O) compound, (ie) parathion is converted to paraoxon, malathion to malaaxon. This process is referred to as desulfuration. Compounds which are already P→O compounds are usually direct inhibitors and therefore do not require this activation step. Examples are tepp (diethyl phosphoric anhydride) and dichlorvos. The reason that activation is required for most phosphorothionates is explained by the relative electrophilic (electron - withdrawing) nature of the P →S bond and the P →O bonds. The tendency for the OH radical of the cholinesterase to attach itself to the phosphorus atom is greatly reduced when sulfur is attached to the phosphorus because of its inability to withdraw sufficient electrons from the phosphorus atom to make it electropositive. The oxygen atom is sufficiently electronegative to promote this reaction.

A second type of activation process is found in certain phosphoroamidates such as schradan, which undergoes hydroxylation of one of the N-methyl groups as follows (Heath et al., 1955; Spencer *et al.*, 1957).

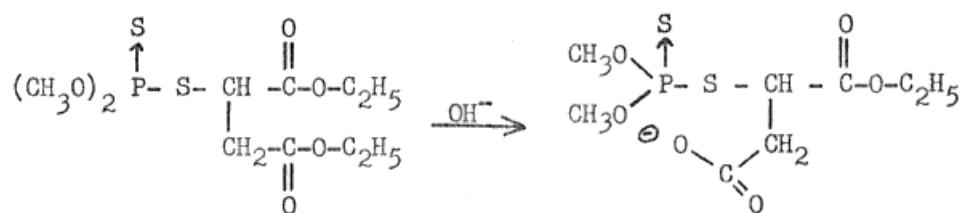




Tri -O-cresyl phosphate

The reason why such a reaction constitutes an activation is not clear.

In the preceding paragraphs it has been demonstrated that the success of organophosphates as cholinesterase inhibitors necessitates the phosphorus atom possessing a certain electropositivity in order to attract the OH group of the enzyme. Under the same circumstances, however, the organophosphate becomes susceptible to alkaline hydrolysis by OH ions in solution. When this reaction occurs, the molecule loses its tendency to phosphorylate the cholinesterase because of the decreased electropositivity of the phosphorus atom. Such an example is malathion when it is hydrolyzed to the p--monoacid.



malathion

malathion p-monoacid

The close approach of the ionized  $\beta$ -carboxyl group to the phosphorus atom reduces the electrophilic nature of the phosphorus. This is referred to as a field effect (O'Brien, 1967).

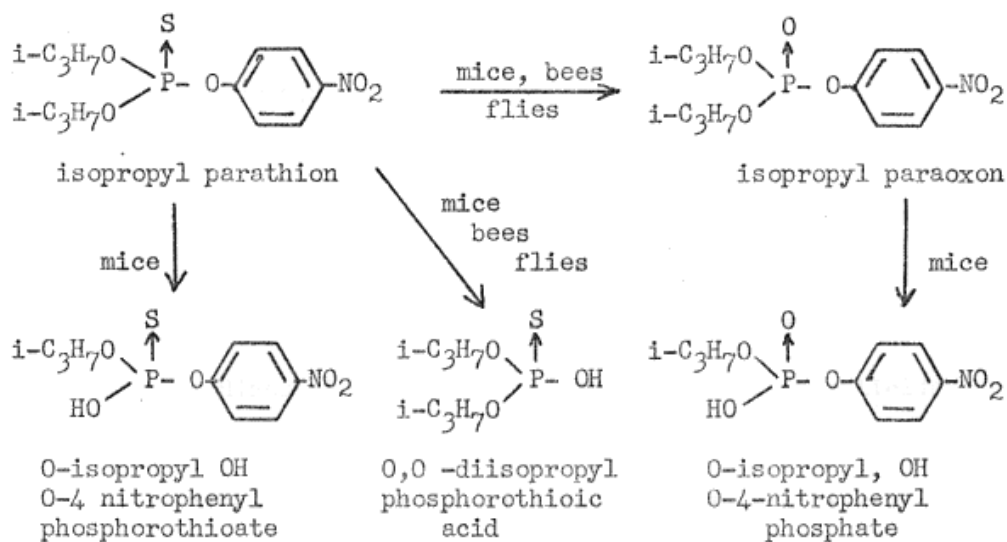
Although O'Brien suggests that alkaline hydrolysis produces the  $\beta$ -monoacid of malathion, Chen et al. (1969) have recently demonstrated that only the  $\alpha$ -monoacid is produced by carboxylesterases both in vivo and in vitro. This casts some doubt upon the importance of the above reaction since it is unlikely that the  $\alpha$ -carboxyl entity could exert a field effect upon the phosphorus atom to the extent that the  $\beta$ -carboxyl would be able to exert.

Recent work reported by Camp and co-workers (Camp *et al.*, 1969a; Camp *et al.*, 1969b) suggested that the selective toxicity of isopropyl parathion and a series of related phosphate, phosphonate and phosphinate esters containing branched alkyl groups, towards the housefly, honey bee and white mouse may be explained only in part by differences in cholinesterase inhibitors and that other factors are also involved in their selective action. With isopropyl paraoxon, the selectivity differences exhibited between the housefly and the honey bee appear to be in part due to the difference in susceptibility of the cholinesterases of the two species to inhibition. Their data for isopropyl parathion suggested that other factors in addition to selectivity in target enzyme inhibition must be considered. They hypothesized that the activation process (converting  $P \rightarrow S$  to  $P \rightarrow O$ ) does not occur to any significant extent in the honey bee, whereas this process is of major significance in the housefly. They conclude that the much greater toxicity of isopropyl parathion in the housefly than in the honey bee is a combination of

- (i) a greater sensitivity of the housefly cholinesterase to isopropyl paraoxon than to honey bee cholinesterase,

- (ii) the much greater degree to which the housefly is able to convert the isopropyl parathion to isopropyl paraoxon (activation) .

They found that the metabolism of isopropyl parathion in the white mouse was more complex than in the two insects. Apparently mice, unlike the two insects, can degrade isopropyl parathion and isopropyl paraoxon by dealkylation of the isopropyl moiety in addition to cleavage of the p-nitrophenoxide - phosphorus bond. Undoubtedly, this additional degradation pathway contributes in part to the low mouse toxicity towards isopropyl parathion (Camp et al., 1969b). They propose the following metabolic pathway for isopropyl parathion for the three species which undoubtedly reflects the relative toxicity of the insecticide to each;



From the standpoint of residue toxicity problems in the soil, it is important to know the relative toxicity of insecticide degradation products towards insects and mammals, and also whether any of the phosphate-containing fragments would have any effect upon the vegetation. The preceding discussion appears to suggest the following points;

- (1) The conversion from a sulfur analog to an oxygen analog (eg. malathion to malaoxon) seems to increase its anticholinesterase activity.
- (2) Any degradation resulting in the phosphorus atom becoming more electronegative results in a lower toxicity.
- (3) Although the conversion from the P →S bond to the P →O bond increases the toxicity, the resulting compound becomes much more susceptible to hydrolysis.
- (3) Mammals possess more degradative pathways than insects for organophosphates, resulting in a lower toxicity.
- (4) It appears that many organophosphates are converted to more toxic compounds after ingestion. There is no one type of conversion responsible for this increased toxicity.

d) Fate of Applied Organophosphate Insecticides

Although insecticides may be applied to the vegetation, or directly onto insects, some part of either the insecticides or their degradation products eventually reach the soil. The first part of this discussion will deal with the fate of insecticides applied to the foliage or to insects, and the second part will cover the ultimate fate of insecticides regardless of their source of application.

Residues on Foliage or on Insects:

Organophosphates applied to the foliage of plants or to insects may undergo one or more of the following interactions;

- (1) absorption by the substrate (with no degradation) with the possibility of returning to the exterior environment at some later time,
- (2) absorption by the substrate with degradation, usually enzymatically,
- (3) degradation on the surface of the substrate, followed by absorption, volatilization, or displacement by water onto the soil surface,
- (4) displacement from the substrate onto the soil surface by water molecules,
- (5) volatilization as the intact molecule.

The first type of interaction was reported by Kansouh and Hopkins (1968). They studied the uptake of  $^{14}\text{C}$ -diazinon aqueous solution by roots of intact bean plants over a five hour period, finding that the uptake varied from 1.5 to 5.0 ml. per plant. About 80 percent of the diazinon absorbed was in the roots while the remainder was translocated to the stem and to the primary and terminal leaves. Upon rinsing the roots and transferring them to nutrient solution, 68 percent of the radioactivity in the plant (mainly from the roots) diffused back into the nutrient solution over a two day period. Over an eight day period, 13.5 percent reaccumulated in the roots. The authors go on to mention that the majority of the  $^{14}\text{C}$  radioactivity in the roots after two days was still diazinon whereas in the primary leaves, 80 percent of the radioactivity was due to a breakdown product, pyrimindinol. Thus it appears that there was a free exchange of diazinon possible across the root membranes, governed by concentration gradients.

Absorption of the organophosphate with degradation is a more frequently reported occurrence than the one discussed above. Shipp *et al.* (1963) reported that methyl parathion sprayed onto cotton persisted on the foliage up to twelve days, the principal site of the residues being in and under the leaf cuticle, not on the leaf surface. The residual half-life of methyl parathion on cotton leaves was about 24 hours with the maximum penetration occurring two hours after application. Four compounds containing  $^{32}\text{P}$  were found in the residue; methyl parathion, methyl paraoxon (dimethyl p-nitrophenyl phosphate), and two unidentified compounds. Brett and Bowery (1958) found that malathion, applied as a four percent spray, was detectable for three days on snap beans, two days on tomatoes and three days on collards. They state that rainfall easily removed malathion from the collards, but made no mention of breakdown products.

Hopkins (1967) studied the effect of three relative humidities (45, 65, 85 percent) upon the rate that malathion deposits disappeared from leaf surfaces. The loss rate was logarithmic and the half-life of the residue at all three humidities occurred at five hours. At this point a divergence occurred because of the increasing persistence at 65 and 85 percent R.H., resulting in 25 percent of the original deposit remaining after 20 hours. At 45 percent R.H., the loss rate did not decrease until after two half-lives (10 hours). He concluded that high relative humidities apparently retard malathion loss from the leaf surface, but this effect did not become apparent until 50 percent of the original deposit had disappeared.

Coffin (1966) studied the fate of malathion and parathion applied to lettuce. Parathion residues decreased from 1.9 to 0.1 ppm. in 4 days, with detectable amounts up to 15 days. Small quantities of paraoxon (O,O-diethyl O-p-nitrophenyl phosphate) and two unidentified metabolites were detected up to two days following application. He hypothesized that they might be the S-ethyl isomer (O-ethyl S-ethyl O-p-nitrophenyl phosphorothioate) and the S-phenyl isomer (O,O-diethyl S-p-nitrophenyl phosphorothioate) formed by isomerization of parathion. Malathion residues decreased from 11.5 ppm. after four hours to less than 0.1 ppm. after 10 days. Malaoxon [O,O-dimethyl S-(1,2-dicarbethoxyethyl)phosphorothioate] and three unidentified metabolites were detected up to 2 days after application. He suggested that they might be the  $\alpha$ -monoacid and O-methyl S-methyl S-(1,2-dicarbethoxyethyl) phosphorodithioate.

Blinn (1968) reported that unlike many other organophosphates, Abate (O,O,O',O'-tetramethyl O,O-thiodi-p-phenylene phosphorothioate) was relatively resistant to degradation on bean leaves. The major metabolic product was the sulfoxide derivative, accounting for less than five percent of the initial dose. Trace amounts of the sulfone derivative and the oxygen analog were also found. With prolonged biotic exposure (28 days), increasing amounts of glucosidic conjugates of the phenolic hydrolysis products from Abate and its sulf oxide and sulf one derivatives were found, accounting for 17 percent of the applied dose.

### Residues in the Soil:

As indicated in the previous section, organophosphate insecticides or their breakdown products may eventually find their way into the soil even though not initially put there. An excellent review of the behavior of insecticides in soils has been written by Edwards (1966). It is beyond the scope of this discussion to deal with the subject in as great detail and instead a brief summary of Edwards' review supplemented by later reports is presented below.

Edwards has arranged all the factors associated with insecticide behavior in soils into four groups, in terms of their relative importance. He considers that the chemical structure and hence the intrinsic stability of the insecticide to be the most important general factor. The most important properties of an individual insecticide would be its solubility and volatility. In general, the entire organophosphate family are inherently unstable in the soil, relative to other classes such as the organochlorine pesticides or the carbamates. Edwards considered the soil type to be a secondary factor in determining insecticide behavior, with organic matter being most important and other properties such as clay content and soil structure assuming secondary importance. He believed that soil moisture, soil temperature, soil microorganisms and cultivation were tertiary factors and that quarternary factors would include formulation and concentration of the insecticide, the mineral content and the soil acidity.

Obviously these divisions in importance must be made on a somewhat arbitrary basis. However, it is questionable whether he should have rated soil microorganisms only of tertiary importance, especially for the organophosphate insecticides which seem very susceptible to degradation via biological means. It is a very difficult factor to properly assess since soil sterilization can not be realistically achieved without irreversibly altering what we consider to be soil (Salonius *et al.*, 1967; Bowman *et al.*, 1967). Although moderate dosages of gamma irradiation will kill the microbial population, considerable amounts of intracellular enzymes are released from the lysed cells in an active state, effectively accomplishing what the living population accomplishes.

Getzin *et al.* (1968) reported the effects of sterilizing by heat and by gamma irradiation upon the degradation of several organophosphate insecticides. All pesticides degraded fastest in non-sterile soils, and malathion, dichlorvos, Ciodrin<sup>R</sup> and mevinphos decomposed much faster in irradiated soil than in autoclaved soil. This research seems to support the idea that indeed some non-living factor, such as intracellular enzymes, had been released into the soil upon irradiation. Getzin *et al.* claim that they have separated a heat-labile substance from the soil which degrades malathion. They do not believe it to be an enzyme since it was not inactivated by 0.2 N NaOH as most enzymes would be. As yet, they have not been able to identify the substance.

Lichtenstein (1968) studied the use of sodium azide and autoclaving upon the persistence of parathion and diazinon in soils. Both sterilizing techniques reduced bacterial numbers in

the soil, resulting in increased parathion persistence. However, diazinon was not detectable in the soil after a two week incubation with sodium azide. It was discovered that in aqueous solution, sodium azide catalyzed the hydrolysis of diazinon into diethyl thiophosphoric acid, 2-isopropyl- 4-methyl- 6-hydroxy- pyrimidine and three other breakdown products. Therefore its use as a soil sterilant is rather questionable.

Matsumura and Bausch (1966) reported that autoclaving was quite effective in reducing the degradation of malathion by a soil fungus, *Trichoderma viride* and a bacterium, *Pseudomonas* sp. Konrad and Chesters (1969) studied the adsorption and degradation of Ciodrin<sup>R</sup> (alpha methylbenzyl 3- dimethoxy phosphinyloxy) cis-crotonate from aqueous solution with two soils. They found that Ciodrin<sup>R</sup> degradation followed first order reaction kinetics and was related to the extent of initial adsorption by the soil. They observed that in electron-beam irradiated soils, the reaction rates were slower. They attributed this rate decrease to decreased Ciodrin<sup>R</sup> adsorption resulting from the irradiation treatment and not from retardation of microbial degradation processes. They believed that the electron-beam modified the nature of the organic matter, decreasing its adsorptive capacity for Ciodrin<sup>R</sup>.

Moisture has been shown by many workers to markedly affect the behavior of the organophosphates in the soil. Harris (1964) demonstrated that at field capacity, diazinon was 65.7, V-C 13 (O-2,4- dichlorophenyl O,O- diethyl phosphorothioate) was 73.3 and parathion was 92.0 times less toxic in much than in sand, but in dry soil there was no obvious correlation between organic matter content and toxicity. V-C 13 and diazinon were less toxic on dry sand

than on dry much. This suggests that in moist soils, inactivation of the insecticide is related to the organic matter content, but in dry soils, inactivation is related to the adsorptive capacity of the mineral fraction.

Swoboda and Thomas (1968) and Lichtenstein (1958) have studied the movement of parathion in soils. Lichtenstein showed that parathion can move by diffusion (presumably in the aqueous phase) and can be lost at the soil-air interface by volatilization. On the other hand, Swoboda and Thomas found that parathion was not effectively displaced from the soil by inorganic electrolytes or by aqueous solutions. However, it readily moved through soil columns when leached with ethanol.

Meyers (1968) studied the movement of phorate and malathion on watershed soils in Indiana, investigating possible contamination of nearby farm ponds. He concluded that malathion had a greater potential for adsorption to the soil colloids than phorate and that phorate presented the greater pollution hazard in ponds. He also discussed the possibility of surface transport of these insecticides by rainwater, emphasizing the need for proper vegetative cover surrounding these ponds.

Recently, Ibrahim *et al.* (1969) reported on the decomposition of Di-Syston {O,O-diethyl S-[2-(ethylthio)ethyl] phosphorodithioate} on different fertilizers. On superphosphate and ammonium nitrate, all but a trace of Di-Syston was oxidized to the oxygen analog sulfone and the oxygen analog sulfoxide. Conversely, it was relatively stable on triple superphosphate

and most of the other materials tested. These results for superphosphate differ with those of Yost et. al. (1955) who found that malathion was quite compatible with superphosphate, but not with rock phosphate. The differences may well reflect inherent differences in the two insecticides.

In summary, organophosphate insecticides, as a class of compound, have relatively short persistence following application to either foliage or to the soil surface. The major factors affecting the persistence of organophosphates include;

- (1) the inherent stability of a particular insecticide,
- (2) active enzymes of plant, insect, or microbiological origin, water vapor which can either displace the insecticide from the substrate or promote its hydrolysis,
- (3) the ionic environment which includes the effects of pH and electrolytes such as superphosphate or ammonium nitrate, or particular ions such as iron or copper,
- (4) the temperature of the surrounding environment.

## B. Malathion

### a) Chemical, Physical and Biological Properties

Pure malathion is a colorless, slightly viscous, high boiling liquid possessing an ester-like odor. Its structure is shown in Figures 28 and 29. The commercially available product, 95 percent grade or better, has similar characteristics to the pure product, but it is a brown or yellow liquid with a characteristic mercaptan-like odor. This odor is due to a slight impurity present in the commercial preparation. Table 2 summarizes the chemical and physical properties of pure malathion.

**Table 2. Chemical and Physical Properties of Malathion.**

---

Molecular Weight	329.2
Boiling Point	156-157 °C (0.70 mm. Hg, slight decomp.)
Melting Point	2.85 °C
Refractive Index ( nD <sup>25</sup> )	1.4985
Vapor Pressure	4 x 10 <sup>-4</sup> mm. Hg (30°C)
Density (25°C)	1.2315 gm./cc.
Solubility - water	145 ppm.
- organic solvents	very soluble, especially in moderately polar solvents; sparingly soluble in highly polar, or non-polar solvents
Stability - light	stable
- temperature	becomes increasingly unstable with increasing temperature above ambient
- metals	slight decomposition in presence of iron
- pH	decomposition when pH < 2, > 9

---

Malathion is a relatively stable compound when stored for long periods of time at room temperature, providing the pH is kept within extremes and that iron is excluded. When solubilized in a water-alcohol, or water-methyl cellosolve solution, almost instantaneous hydrolysis occurs at pH 12. At pH 9. 50 percent hydrolysis occurred in about 10 hours, while at pH 5 to 7, no hydrolysis was observed over a period of 12 days (Yost *et al.*, 1955).

Malathion has a relatively low toxicity to mammals, probably because of their superior ability to lyse the molecule at the carboxylester sites (Matsumura and Bausch, 1966). The LD<sub>50</sub> acute oral toxicity of 95 percent technical grade malathion, the commercial product, against male albino rats is over 2100 mg./kg, of body weight. The highly purified product is even less toxic to mammals (Yost *et al.*, 1955). More recent data quoted by O'Brien (1967) indicate the oral LD<sub>50</sub> for vertebrates to range from 275 mg./kg. (chickens) to 1609 mg./kg. (mice). Topical applications of malathion onto insects give an LD<sub>50</sub> ranging from 0.75 mg./kg. (pea aphid) to 30 mg./kg. (housefly) and 120 mg./kg. (German cockroach). Malathion is an exceptionally useful insecticide because of its much greater toxicity to insects relative to vertebrates. Although malathion is not usually considered injurious to plants, there have been a few exceptions noted (Spiller, 1961).

b) Commercial Formulations and Factors Affecting Their Stability

Since malathion, as with most organophosphates, retains its stability for only a short period of time following field application (in terms of days), it must be combined with a carrier material that will prolong its effectiveness. The carrier material also makes a more uniform application possible because of its greater volume relative to malathion in the application mixture.

As a part of American Cyanamid's development program of malathion, Yost and co-workers (1955) investigated the shelf-life of 60 percent technical grade malathion combined with 8 percent emulsifier and xylene (32 percent) at room temperature. Their data indicate that

a loss of one to three percent malathion would occur over a two year period of storage. Further studies suggested that the shelf-life of malathion may be significantly reduced when formulated with certain anionic-nonionic emulsifier blends. To accentuate stability differences among additives to the emulsifier blends, they stored the mixture at 50°C. The following additives resulted in significant losses of 60 percent technical malathion in one month; triethylamine ( $C_2H_5)_3N$  (1 percent), a mixture of one percent triethylamine with two percent water, a mixture of one percent acetic acid with two percent water, a mixture of one percent  $H_3PO_4$  and two percent water, and a mixture of one percent O,O-dimethyl dithiophosphoric acid and two percent water. They concluded that combinations of moisture and strong acid or base were especially detrimental to the stability of malathion and that prolonged storage at elevated temperatures should also be avoided.

Yost found somewhat different results when he conducted stability studies on flowable and dilute emulsions of malathion (one percent) which were prepared in water buffered to various acidities over the pH range 2 to 7.2. Good chemical stability of the insecticide was obtained for at least seven months. Addition of sugar to the aqueous media had no detrimental effect on the stability of malathion. In fact good chemical stability of malathion was also obtained in a 50 percent flowable emulsion. They postulated that in emulsions of malathion, the emulsifier forms a protective layer on the surface of the malathion oil droplets, thus shielding them from the hydrolytic action of water. They further suggest that a catalytic surface, in addition to moisture, may be required to degrade malathion.

Because of its relative insolubility in water (145 ppm.), malathion is often applied as a wettable powder with the filler or carrier being some type of clay mineral such as attaclay, bentonite or kaolinite. Results suggested that with these fillers, the presence of moisture accelerates the breakdown of malathion, and while pH is also a factor, its effect is least in compositions having low moisture contents. As observed with the emulsifiers, elevated temperatures markedly accelerate the rate of malathion degradation. Yost *et al.* (1955) suggested that the most stable malathion formulations include acidic kaolins, such as Barden clay, a calcined montmorillonite, acidic frianites and diatomaceous earths with result in only a few percent loss of malathion over a 12 month storage period, provided that the pH is in the 4 to 7 range and the moisture content is low.

For certain applications, it is desirable to apply malathion in the form of a dust. In general, the long-term stability of malathion is satisfactory in dilute dust preparations (about five percent). The most promising diluents tested by Yost *et al.* were pyrophyllites, such as Pyrax AAB and Pyrolyte, neutral talcs, gypsum and possibly certain calcium carbonates. They suggested that the higher the purity of the malathion used in preparing these formulations, the better the stability of the formulation may be.

In 1962, Polon and Sawyer reported on a study involving the use of stabilizing agents to decrease malathion decomposition on high-sorptive capacity carriers such as attapulgit and

montmorillonite. The results show that the attapulgite dusts were the least stable, one sample decomposing 64 percent of the added malathion in 30 days (40°C) while a second attapulgite sample, prepared differently, caused a 47 percent decomposition. A montmorillonite carrier decomposed 32.4 percent and three kaolinites decomposed from 14 to 28.5 percent of the added malathion over the same 30 day period at 40°C.

Polon and Sawyer (1962) stated that on the surface of mineral carriers there are acid sites whose strength can be correlated with the decomposition of certain organochlorine insecticides. Malina *et al.* (1956) had previously reported on a method of deactivating mineral carriers for stabilizing heptachlor-dust formulations using oxygen-containing compounds such as glycols to reduce surface acidity. This acid-site theory has also been proposed as the cause of decomposition of some thiophosphate insecticides such as malathion, parathion and methyl parathion. Polon and Sawyer (1962) proceeded to show that merely neutralizing these acid-sites using glycols did not completely eliminate the decomposition of malathion impregnated on attapulgite. They believed that clay properties other than surface acidity must be involved in malathion decomposition and proposed an alkaline-site theory that could account for the hydrolytic cleavage of the P-S-C bond. They proposed that metallic salts (calcium and magnesium) might provide such an alkaline condition on the clay surface. To test their hypothesis, they used over 100 additives and found that a tall oil additive, Indusoil M-28, at a five percent concentration was capable of reducing the breakdown of a five percent malathion-attapulgite dust mixture from the 47 to 64 percent values previously noted above, to

the 18.5 to 28.8 percent range. They also demonstrated that treatment of attapulgite with up to eight percent Indusoil M-28 had no effect upon the surface acidity as measured by Walling's method (1950). Therefore the mode of stabilization is other than neutralization of surface acidity as indicated for the glycol deactivators. Polon and Sawyer also demonstrated that Indusoil M-28 seemed effective in decreasing malathion decomposition with montmorillonite, but might not be commercially feasible because of apparent variations in montmorillonite activity.

As noted previously, the unique combination of insecticidal activity, low mammalian toxicity and rapid disappearance of malathion after application makes it well suited for use on fruits, vegetable and other garden crops. Often it is useful to apply fungicides, fertilizers or other insecticides simultaneously, making the pest control program more effective. It is, therefore, very important that the applied components be compatible with one another over a reasonable period of time. Yost *et al.* (1955) indicate that in dry formulations, malathion is reasonably compatible for one to two years with captan, phygon, spirgon, Delmo Z, basic zinc sulfate and dusting sulfur. Short-term half-life, approximately six months, can be obtained with a large number of other fungicides. Malathion possesses very poor stability when formulated with soluble compounds such as tribasic copper sulfate. Use of certain conditioning agents found in some wettable sulfurs also induces degradation. It is believed that metal ion catalysis, basicity and moisture are among the factors responsible for the poor compatibility of the latter formulations.

Work done on the long-term compatibility of malathion with other insecticides when formulated as a dilute dust (about 20 percent malathion) shows that it is reasonably compatible with organochlorine insecticides such as Karathane and Ovotran (Yost *et al.*, 1955). Fair compatibility was found for toxaphene, Sulphenone and Aramite combinations. Neutral calcium arsenate caused fairly rapid breakdown of malathion during storage.

While it is true that alkaline substances and divalent metal ions in general catalyze or induce decomposition of malathion, especially in its formulations, it can be mixed and used quite successfully in the spray tank with most commercial pesticides including soluble coppers, zineb, ferbam, etc., as well as with mildly alkaline substances. In addition to this, malathion is quite compatible with compositions containing potash, magnesium carbonate, gypsum, superphosphate and urea type plant nutrients. However rapid decomposition occurred in the presence of rock phosphate.

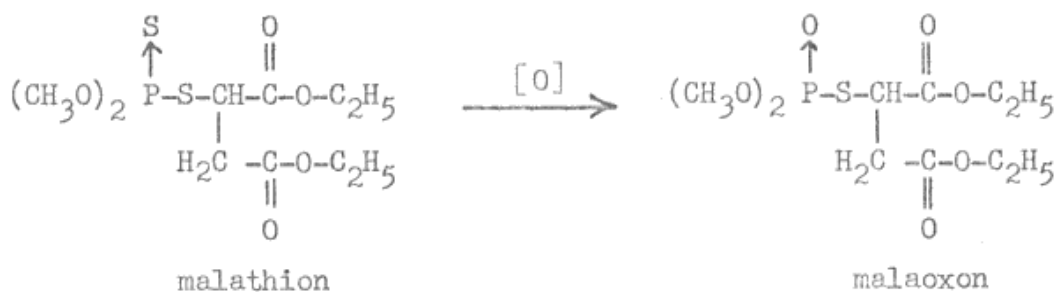
### c) Possible Breakdown Products of Malathion

Malathion is a somewhat difficult compound to use because of its susceptibility to degradation into a variety of breakdown products, depending on its immediate environment. To facilitate discussion, the following review will be divided into nonbiological (chemical) and biological factors responsible for the degradation of malathion,

#### (1) Nonbiological (chemical) Degradation

Several researchers have reported that the stability of malathion in aqueous solution is dependent on pH (Yost *et al.*, 1955; Faust and Suffet, 1966; Konrad *et al.*, 1969). Konrad *et al.*

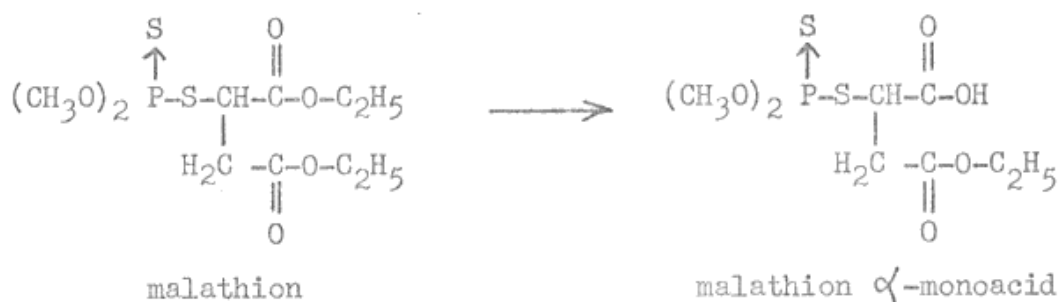




Consequently the previously shown pH sensitive reaction for malathion should also apply for malaoxon. Yost et al. (1955) claimed that malathion was subject to decomposition by certain metallic salts such as copper sulfate and also by elevated temperatures. However no mention was made of possible degradation products.

## (2) Biological Degradation

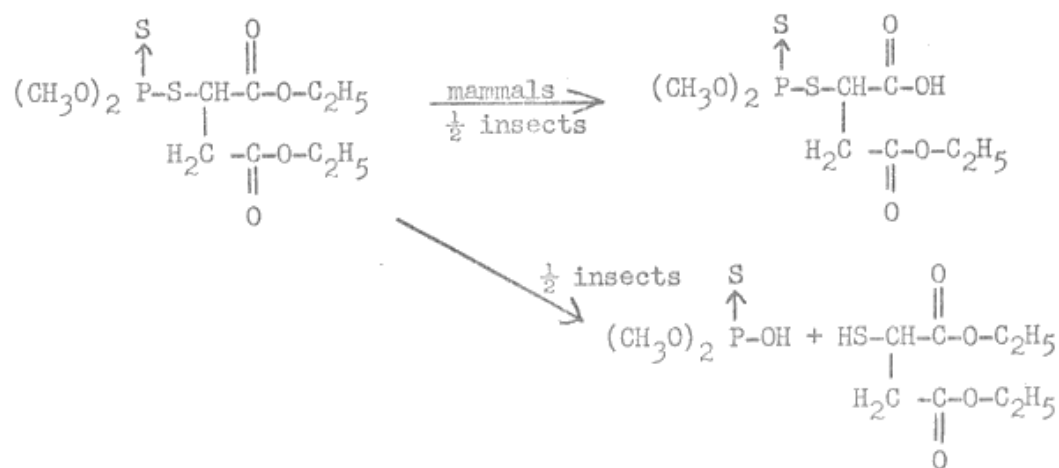
Most researchers have dealt with the biological aspects of malathion degradation. There appears to be three areas of the molecule susceptible to enzymatic attack; the carboxyester linkages, the thiol ester linkage and the methoxyester linkage. Some very recent work by Chen *et al.* (1969) has demonstrated that rat liver carboxyesterase selectively hydrolyzed malathion to only the  $\alpha$ -monoacid (both in vivo and in vitro).



Until this work had been published, it was believed that the carboxyesterases were not specific, resulting in the production of the  $\beta$ -monoacid as well as the  $\alpha$ -monoacid, as intermediate steps to producing malathion di-acid. The question is now raised whether a biologically produced

enzyme from another source has the ability to produce either the  $\beta$ -monoacid, or to convert either monoacid to the di-acid. The data of Chen *et al.* (1969) seemed to be quite convincing that only the  $\alpha$ -monoacid was formed. If this is true, then the production of the di-acid must occur only by non-biological hydrolysis. This would contradict Rowlands' suggested pathway (1964) that carboxyesterases can carry out the second hydrolysis step. Malaoxon would also be subject to hydrolysis by carboxyesterases, producing the oxygen analogs of the  $\alpha$ ,  $\beta$  and di-acids.

It is interesting that different species degrade malathion in different ways. In almost all mammals and about one half of the insects, malathion is hydrolyzed into the alpha-monoacid by carboxy-esterases and in the other half of the insects, phosphatases hydrolyze the sulfur linkage (O'Brien, 1967).



(Note: O'Brien shows the production of the p-monoacid, which, in light of Chen's data, appears incorrect.)

Matsumura and Bousch (1966) found that in the soil, *Trichoderma viride* and a *Pseudomonas* sp. degraded malathion into diethylmalate (diethyl hydroxysuccinate).

This suggests two possibilities; (1) that there are phosphatases capable of cleaving the P-S-C linkage between the sulfur and the carbon, instead of between the phosphorus and the sulfur, as indicated by O'Brien, or (2) that the two organisms did not degrade the malathion, but instead it was degraded non-biologically as proposed by Faust and Suffet (1966) . Matsumura and Bousch also found that some carboxyesterase products and some desmethyl malathion were produced by the two organisms. This would necessitate the presence of a demethylase, capable of removing a methyl group and replacing it with a hydroxyl group. O'Brien (1967) states that cows, rats and dogs also produce demethylase, (It should be noted that recent terminology dropped the "s" in desmethyl malathion and in desmethylase.)

In living biological systems, both chemical and biological degradation mechanisms for malathion operate simultaneously and in fact, probably complement each other to a certain extent. For instance, the P-S-C linkage may be attacked by phosphatases as well as extremes in pH. Under environmental conditions, especially in the soil, it is difficult to isolate chemical mechanisms without having to chemically alter the system to sterilize it, or to deactivate the enzyme systems.

d) Behavior of Applied Malathion

The foregoing sections of this literature review have attempted to compile the chemical and biological properties of malathion, the manner in which it is prepared and used, and the possibilities which exist for its degradation under various environmental conditions. Before

reviewing the literature pertaining to malathion in the soil, it would be useful to summarize the facts presented in the preceding sections which might aid in predicting its behavior in soils.

- (1) High-sorptive capacity minerals such as attapulgite and montmorillonite tend to promote malathion breakdown more than low-sorptive capacity minerals such as kaolinite (Polon and Sawyer, 1962). They have proposed both an acid-site and an alkaline-site theory to explain malathion breakdown. They suggest that the presence of metallic cations such as calcium or magnesium could trigger the breakdown process.
- (2) In acidic (< pH 2) the alkaline (> pH 9) aqueous solutions, malathion is rather quickly hydrolyzed at the P-S-C linkage (Faust and Suffet, 1966; Konrad *et al.*, 1969).
- (3) Temperatures exceeding approximately 30°C accelerate the rate of malathion degradation (Yost *et al.*, 1955). No degradation products were given for thermal degradation.
- (4) Metallic salts of copper and iron seem to promote the degradation of malathion (Yost *et al.*, 1955).
- (5) The water content on the surface of minerals seems to be involved with the degradation of malathion. (Yost *et al.*, 1955).
- (6) Various enzyme systems are capable of cleaving the ester linkages of malathion.

Recently MacNamara (1969) studied the adsorption and desorption of malathion onto H/Al, Ca, Mg and K saturated clay systems and onto humic acid. He found that the K-saturated

clay system adsorbed more malathion than other clay systems, by non-exchange reactions, and that pH had no influence upon the adsorption over the normal soil range. His data also showed that the adsorption of malathion was not related to the percent carbon, pH, cation-exchange capacity or clay content of the A and B horizons of 10 New Jersey soils, but with four selected soils with and without organic matter, malathion adsorption was related to organic matter content. Meyers (1968), in his study of malathion adsorption onto soils and pond sediment, reported that organic matter appeared to have a slightly negative effect upon adsorption. He suggested that perhaps there was a preferential adsorption of water by the adsorbent, thereby increasing the adsorbate concentration in solution. MacNamara did not describe the nature of the organic matter-malathion relationship in his work, although he did show that malathion was easily desorbed from humic acid.

Meyers (1968), MacNamara (1969) and Berigari (1967) all suggested that the adsorption of malathion onto clay was through the carbonyl group. Infrared spectra of malathion-clay complexes showed a decrease in the carbonyl stretching frequency, suggesting hydrogen-bonding. Meyers' (1968) spectrum showed that the carbonyl stretching frequency decreased from 1740 to 1710  $\text{cm}^{-1}$  upon adsorption for the  $\text{H}^+$ ,  $\text{Al}^{+3}$ , and  $\text{Ca}^{+2}$ -saturated systems whereas Berigari (1967) stated that the saturating cation determined the amount of the shift with  $\text{Na} < \text{Ca}^{+2} \leq \text{Al}^{+3} \leq \text{La}^{+3}$ . Parfitt and Mortland (1968) also demonstrated that the saturating cation profoundly affected the extent of the carbonyl frequency shift in ketones. There are some obvious discrepancies among these data which may be due to differing methods of preparation or due to variations in the environment of the malathion-clay systems when the spectra were obtained.

In recent years, several other researchers (Kohl and Taylor (1961); Larson and Sherman (1964); Mortland (1966); Tahoun and Mortland (1966); Parfitt and Mortland (1968)) have studied the interaction of the carbonyl group with montmorillonite clay surfaces. Both Kohl and Taylor and Larson and Sherman interpreted the carbonyl stretching shift to lower wave numbers as indicative of hydrogen bonding with clay lattice hydroxyl groups. However Mortland and his associates have since shown that the carbonyl group of urea, amides and benzoic acid interacts with the water of hydration surrounding the exchangeable metal cations, or directly with the cations themselves. The first type of interaction would be a hydrogen bonding interaction, whereas the second type would represent an ion-dipole interaction (electrostatic).

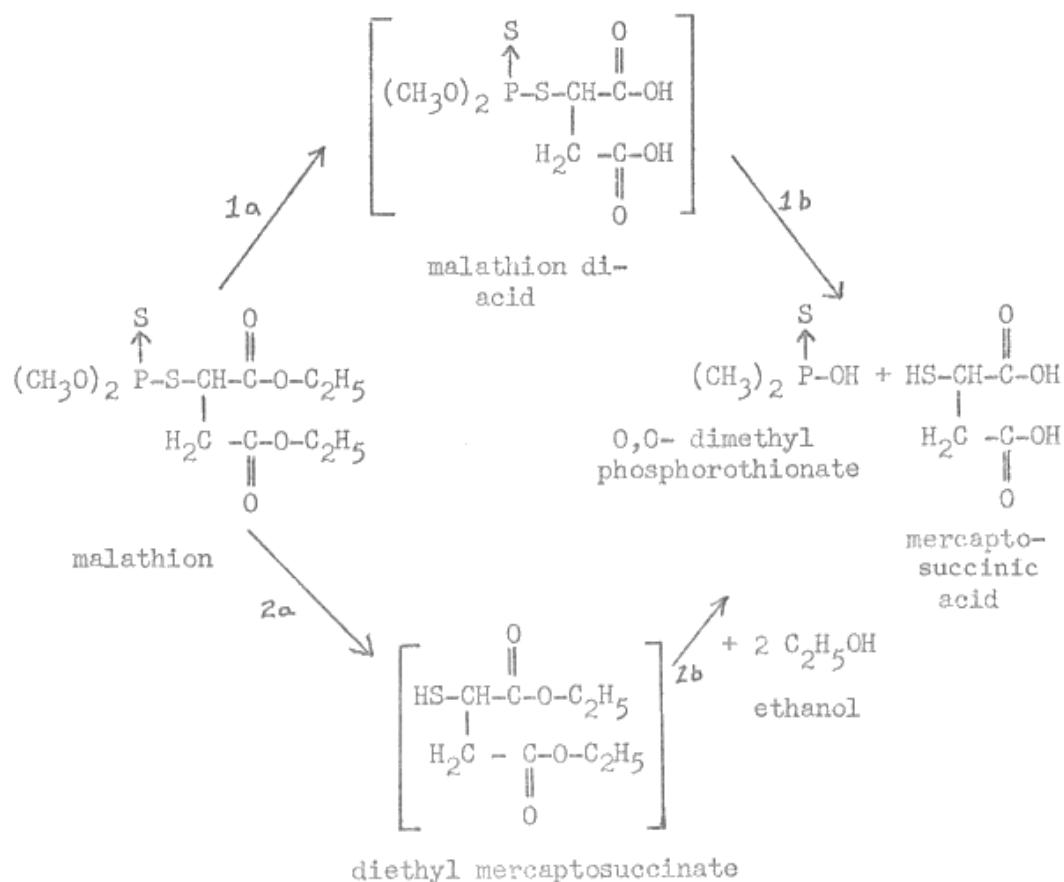
Parfitt and Mortland (1968) have shown that when there were sufficient water molecules surrounding the interlayer cation, hydrogen bond formation occurred with the carbonyl bond, but as this water shell was removed by either evacuation and/or heat, the carbonyl group more closely approached the cation for an electrostatic-type interaction. Because the electrostatic interaction was more energetic than that of hydrogen bonding, the downward shift of the carbonyl stretching frequency was greater. They also reported that the water deformation band at  $1632\text{ cm}^{-1}$  shifted upward to  $1650\text{ cm}^{-1}$  as hydrogen bond formation with the carbonyl group occurred. With the Ca-montmorillonite-acetone system, the water deformation band at  $1625\text{ cm}^{-1}$  shifted upward and split into two bands at  $1640\text{ cm}^{-1}$  and at  $1660\text{ cm}^{-1}$ . This suggested that there was two types of water present; that associated with the Ca-H<sub>2</sub>O-acetone bridges at  $1660\text{ cm}^{-1}$ , and interlamellar water not directly associated with the cation at  $1640\text{ cm}^{-1}$ .

Parfitt and Mortland also stated that hydrogen bond formation lowered the OH stretching frequency. Kohl and Taylor (1961) believed that any frequency shift in the OH stretching frequency of water molecules participating in hydrogen bond formation would not be observed in infrared spectra because of masking by the OH stretching of internal hydroxyl groups and of adsorbed water.

The stability of malathion on clay still seems to be unresolved. Although both Yost *et al.* (1955) and Polon and Sawyer (1962) reported that malathion was degraded on high-sorptive capacity carriers such as montmorillonite, neither Meyers (1968) nor MacNamara (1969) reported any significant malathion degradation during their studies. In fact both researchers used H-saturated montmorillonite which would be quite acidic. Berigari (1967) did report some alteration of malathion recovered from an Al-saturated clay, but not from a Na- nor from a Ca-clay, after three week equilibrium. There is, however, the distinct possibility that the malathion was degraded during the extraction process and that no breakdown had occurred while it was in equilibrium on the clay. He did not specify the nature of the alteration of the extracted malathion.

Very recently Konrad *et al.* (1969) have described the breakdown pathways of malathion in several soils. They proposed that the rates of degradation were directly related to the extent of malathion adsorption, and that degradation occurred by a chemical mechanism catalyzed by

adsorption. Within a 24 hour period, 50 to 90 percent of the malathion degraded in both sterile and non-sterile soil systems, with no lag phase occurring prior to degradation. In aqueous soil-free systems inoculated with a soil extract, a lag phase of seven days occurred, followed by rapid malathion loss, probably due to microbial degradation. They proposed the following pathways for malathion degradation in the soil;



Konrad *et al.* believed that Pathway 2 was the more important means of degradation, although some degradation may proceed via Pathway 1. Although they did not show the half ester in

Pathway 1a, nor in Pathway 2b, they did not preclude the existence of these intermediate steps. At the present time they have no means of distinguishing the half esters from the full esters.

In comparing the work of Konrad *et al.* (1969) with that of Meyers (1968), Berigari (1967) and MacNamara (1969), there is a considerable difference between the natural soil systems and reference clays with respect to malathion stability. Furthermore, the recent work with malathion stability in clay systems does not produce the results that one might predict from the work of Yost *et al.* (1955), or Polon and Sawyer (1962) with mineral carriers for malathion. There appears to be some factors, as yet not well defined, which must be responsible for the breakdown of malathion on clay mineral surfaces. In spite of the fact that Konrad *et al.* (1969) claim that malathion was chemically degraded in the soil, it would be difficult to disprove the presence of some biologically active enzymes not destroyed by irradiation, that could be responsible for malathion breakdown. These enzymes would not exhibit the lag phase normally associated with microbiological activity. Perhaps more investigation into the heat-labile substances and their part in degradation (Getzin and Rosefield, 1968) is also warranted.

**Table 3. Common and Scientific Names of Insecticides.**

<b>Common Names</b>	<b>Scientific Names</b>
malathion	1. O,O-dimethyl thiophosphate of diethyl mercaptosuccinate 2. diethyl mercaptosuccinate, S- ester with O,O-dimethyl phosphorodithioate 3. O,O-dimethyl S-(1,2- bis-(ethoxycarbonyl)ethyl phosphorodithioate
methyl parathion	O,O-dimethyl O-p-nitrophenyl phosphorothioate
parathion	O,O-diethyl O-p-nitrophenyl phosphorothioate
diazinon	O,O-diethyl O-(2- isopropyl-6- methyl-4- pyrimidinyl) phosphorothioate
azinphosmethyl	O,O-dimethyl S-4- oxo-1,2,3- benzotriazin-3(4H)-ylmethyl phosphorodithioate
heptachlor	1,4,5,6,7,8,8-heptachloro- 3a,4,7,7a- tetrahydro-4,7- methanoindene
DDT	1,1,1-trichloro-2,2- bis (p-chlorophenyl) ethane
aldrin	not less than 95% of 1,2,3,4,10,10- hexachloro- 1,4,4a,5,8,8a- hexahydro-1,4- endo-exo-5,8- dimethanonaphthalene
phorate	O,O-diethyl S-(ethylthio) methyl phosphorodithioate
endrin	1,2,3,4,10,10- hexachloro-6,7- epoxy-1,4,4a,5,6,7,8,8a- octahydro-1,4- endo- endo-5,8-dimethanonaphthalene
toxaphene	chlorinated comphene containing 67-69% chlorine
carbaryl	1- naphthyl methylcarbamate
tepp	tetraethyl pyrophosphate
dichlorvos	2,2- dichlorovinyl dimethyl phosphate
schradan	octamethyl pyrophosphoramide
dimefox	tetramethylphosphorodiamidic fluoride
Ciodrin <sup>R</sup>	α(- methylbenzyl 3- hydroxy crotonate dimethyl phosphate
V-C 13 <sup>R</sup>	O-2,4- dichlorophenyl O,O-diethyl phosphorothioate
ABATE <sup>R</sup>	O,O,O',O'- tetramethyl O,O'- thiodi-p-phenylene phosphorothioate
Di-Syston <sup>R</sup>	1. disulfoton 2. O,O- diethyl S-2-(ethylthio) ethyl phosphorodithioate

### III. MATERIALS AND METHODS

#### A. Preparation of Reference Clans.

The reference clays used in this study were obtained from Ward's Natural Science Establishment, Rochester, N. Y., and are designated as follows;

- a) Montmorillonite No. 25 (Bentonite), Upton Wyoming, John C. Lane Tract.
- b) Kaolinite No. 2, Macon, Georgia, Birch Pit.

The clays were crushed to pass through a 2 mm. sieve, suspended in distilled water and treated with 30 percent  $H_2O_2$  until effervescence ceased. Approximately a three percent suspension of each clay was allowed to settle by gravity and the clay suspension ( $< 20$  above a certain depth (calculated from Stokes Law) *was* siphoned off at a given time. This procedure was repeated twice. The less than  $2\mu$  clay was then centrifuged with a Sharples supercentrifuge to remove the less than  $0.1\mu$  clay. The operating parameters were obtained from the publication of Jackson (1956). The  $0.1$  to  $2.0 \mu$  clays were Ca-saturated with 1 N  $CaCl_2$  three times and washed until chloride-free by the  $AgNO_3$  test. The clays were then quick-frozen with liquid nitrogen and then lyophilized and stored over  $P_2O_5$ .

For later experiments, the Ca-saturated clay was resuspended and saturated with 1N solutions of the following cations,  $CaCl_2$ ,  $AlCl_3$ ,  $CuCl_2$ ,  $NaCl$  or  $FeCl_3$ , and then frozen with liquid nitrogen and lyophilized.

## B. Infrared Spectroscopy Studies.

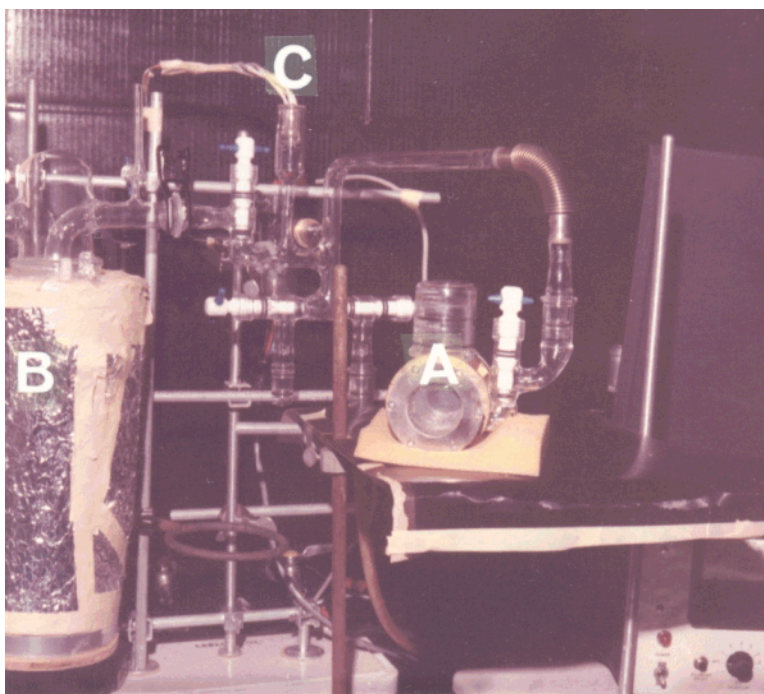
### a) Vacuum System

The vacuum system was built around a combination forepump and oil diffusion pump capable of producing an ultimate vacuum of approximately  $10^{-6}$  Torr. To avoid the slow volatilization of vacuum greases, only greaseless joints and stopcocks were used in the construction. (See Figure 1). The vacuum was monitored with a combination thermocouple ( $10^{-3}$ -1 Torr) -hot ionization gauge ( $10^{-3}$  -  $2 \times 10^{-9}$  Torr). A liquid nitrogen cold trap was situated between the vacuum pump and the remainder of the system to freeze out vapors from the system, as well as to minimize back streaming of the silicon pump oil (Dow Corning DC- 704) .

### b) Infrared Cell and Accessories

The infrared cell was custom-made using Pyrex glass, with a 50/50 capped, double viton O-ring greaseless joint on the top for entry of the sample holder assembly. (See Figure 2). The path length of the cell was approximately 10 cm. and the aperture of the windows was 44 mm. Polished potassium bromide windows (55 x 6.5 mm.) were sealed directly onto the Pyrex glass using a high vacuum leak sealant, Vacseal<sup>R</sup> (produced by Space Environment Laboratories Inc., Box 1061, Boulder, Colorado 80302).

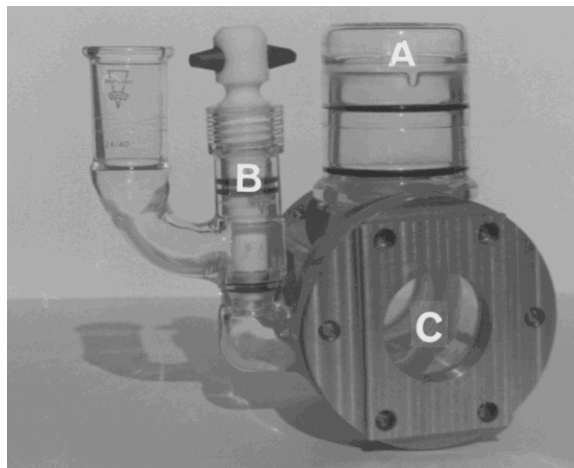
The sample holder was constructed of stainless steel and could be set to give an incidence angle of  $0^\circ$  or  $45^\circ$  for incoming infrared radiation. (See Figure 2). The clay film dimensions, as seen by the incoming infrared beam ( $0^\circ$  incidence) were 28 x 44 mm. When the IRTRAN -2 window was used, it was mounted on the sample holder using special fastening clips.



**FIGURE I. PHOTOGRAPH OF VACUUM APPARATUS.**

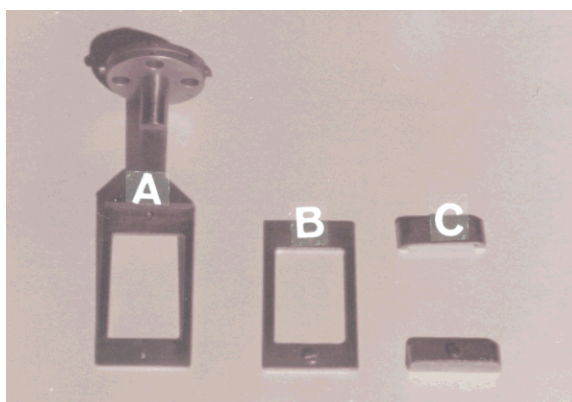
- A. Infrared Cell.
- B. Liquid Nitrogen Cold Trap.
- C. Thermocouple Vacuum Gauge Tube

**Figure 2. Photographs of The Infrared Cell and Sample Holder.**



**Infrared Cell.**

- A. 50/50 Greaseless Joint Cap.
- B. 0-12 mm. Teflon Stopcock.
- C. 50 x 6.5 mm. KBr window.



**Sample Holder.**

- A. Holder.
- B. Clamp to Secure Clay Film to Holder.
- C. Clips to Hold IRTRAN-2 Window.

C) Preparation of Clay Films

Calcium-, sodium-, aluminum- and iron-saturated montmorillonite films were prepared by sedimenting 40 mg. of resuspended, freeze-dried 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. A thin polyethylene film was positioned in the aluminum moisture dish when sedimenting the copper films because of an apparent reaction with the aluminum, resulting in a poorly formed, discolored clay film.

Because of their brittleness, all kaolinite films were sedimented on a 25 x 50 x 2 mm. IRTRAN-2 window (Eastman Kodak, Rochester, N.Y.). The amount of clay used was reduced from 40 mg. to 10 mg. since the films no longer had to be self-supporting.

The compounds used in this study were liquids and were applied to the clay film surface with a syringe needle. This technique resulted in a slight surface excess of the compound which seemed to disappear after exposure to water vapor, or to evacuation for a short period of time.

d) Compounds Used For Study

The compounds used in this study were selected on the basis of their close structural relationships to malathion and on the possibility of being breakdown products of malathion. Table 4 lists the chemicals used, their source and their purity, Figures 11 to 18 show the infrared spectra of these compounds and Tables 6 to 10 show the exact frequencies with some of their assignments.

All of the esters (compounds 1,2,3,4,9) were liquids and the acids were solids (compounds 5,6,7,8,10,11). Infrared spectra of the liquids were obtained by making a capillary film

**Table 4. The Compounds Selected for Investigation.**

	<b>Chemical</b>	<b>Source</b>	<b>Purity</b>
1.	malathion	Unilab Research Corp. Berkeley, Calif.	100%
2	diethyl succinate	Eastman Organic Chemicals Rochester, N. Y.	B.P. 105-107 C (16 mm)
3	diethyl mercapto-succinate	Wateree Chemical Co. Lugoff, S. Carolina	> 95%
4	dimethyl succinate	Eastman Organic Chemicals Rochester, N. Y.	M.P. 18-19 C
5	mercaptosuccinic acid	Aldrich Chemical Co., Milwaukee, Wisc.	M.P. 153-154 C
6	DL- hydroxy succinic acid	" " "	M.P. 131 C
7	succinic acid	Eastman Organic Chemicals Rochester, N. Y.	M.P. 186-188 C
8	2,3- dimethyl succinic acid	Aldrich Chemical Co. Milwaukee, Wisc.	not given
9	diethyl fumarate	Eastman Organic Chemicals Rochester, N. Y.	M.P. 1-2 C
10	malathion di-acid	American Cyanamid Princeton, N. J.	not given
11	fumaric acid	Eastman Organic Chemicals Rochester, N. Y.	98+ %

Note. Infrared spectra of compounds 4 - 11 were used for reference purposes. The behavior of these compounds on clay films was not investigated.

between KBr salt discs. Infrared spectra of the solids were obtained by-using the KBr pellet technique. Approximately 0.125 percent of the solid was incorporated with dry KBr, the mixture thoroughly ground and then pressed (at about 12 tons pressure) into a transparent pellet.

e) Operating Parameters of the Beckman IR- 12 Infrared Spectrophotometer

All samples in the study were scanned in the double beam mode. An adjustable beam attenuator was placed in the reference beam when a clay sample was being scanned. The following procedure was used to obtain spectra;

- 1) Glower current = 0.6 amp.  
Coarse gain = 10  
Fine gain = 0.30  
Period = 2.0  
Slit control = select
- 2) With sample in sample beam, the double beam/single beam energy ratio was adjusted to 1.0 at  $2200\text{ cm}^{-1}$ , a point in the spectrum where absorption due to  $\text{CO}_2$  or  $\text{H}_2\text{O}$  was minimal. The reference beam attenuator and the trimmer comb were used to select the percent transmission in the double beam, so that the most transparent of the clay-malathion spectrum ( $1350$  to  $1500\text{ cm}^{-1}$ ) was approximately at 95 to 100 percent transmission.
- 3) The spectra shown in this thesis were scanned at  $80\text{ cm}^{-1}/\text{minute}$ , unless otherwise noted.

C. X-ray Diffraction Studies.

X-ray diffractograms of malathion - montmorillonite - water complexes were obtained. X-ray slides were made by sedimenting 20 mg. of freeze-dried Ca-, Cu-, Na-, Al-, or

Fe-saturated montmorillonite with distilled water onto a microscope slide. Malathion was added either to the suspension before drying (10  $\mu$ l.) or was applied to the surface of the dried x-ray slide using a syringe needle (in the same manner as in the infrared studies). The montmorillonite x-ray slide was pre-dried over  $P_2O_5$  for approximately 24 hours prior to applying the malathion.

During x-ray diffraction analysis, the sample was kept inside a cylindrical container containing a  $P_2O_5$  desiccant and through which passed dry nitrogen gas. Mylar windows (0.00025 in. thick) in the container allowed the x-ray beam to pass through. By keeping a slight positive pressure with nitrogen gas in the sample chamber at all times, the x-ray slide apparently adsorbed little moisture.

## IV. RESULTS AND DISCUSSION

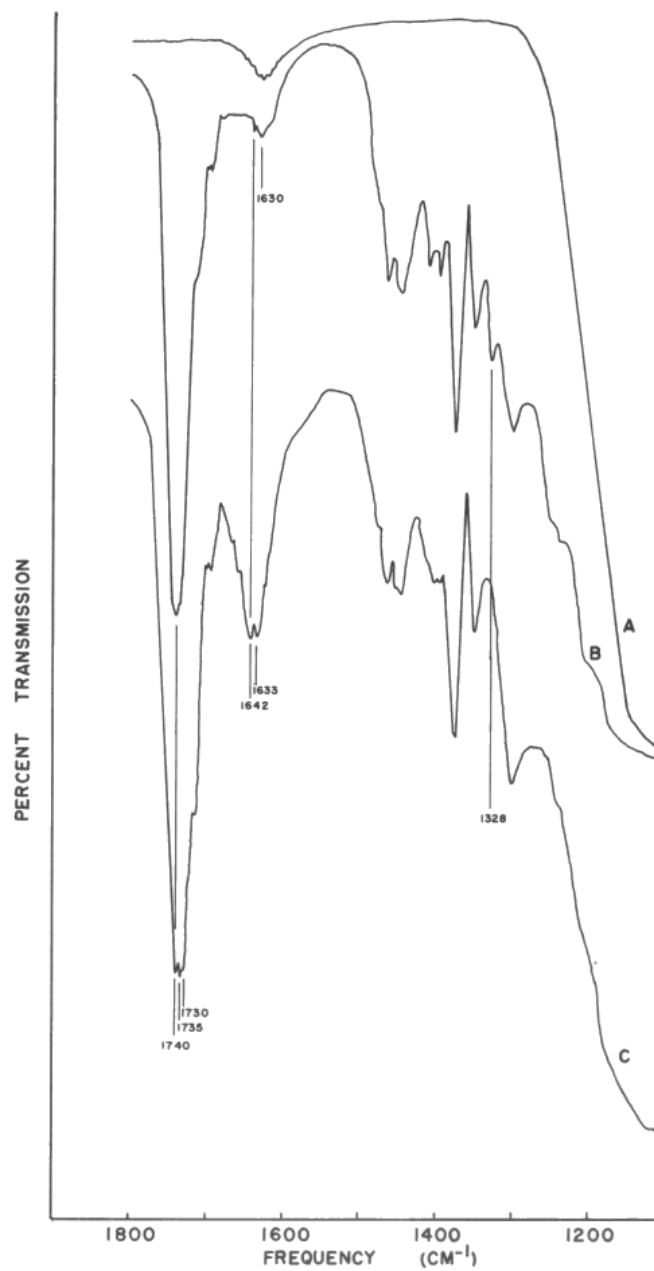
### A. Infrared Spectroscopy Studies.

#### a) Na-Montmorillonite-Malathion System.

Prior to applying malathion, the clay film was evacuated for several minutes and scanned. Spectrum A, Figure 3, is a Na-montmorillonite film. The bending mode of water occurred in the  $1630\text{ cm}^{-1}$  region and was rather weak because of the short evacuation period and also because sodium does not tend to hydrate to any great extent on the interlayer surfaces of montmorillonite. Spectrum B, Figure 3, is the spectrum of Na-montmorillonite after the surface application of malathion. (For the purposes of this discussion, only the  $1100$  to  $1800\text{ cm}^{-1}$  region will be discussed unless some significant change has occurred in another portion of the spectrum.) There has been no interaction of malathion with the clay surface since all absorption bands of malathion occurred at the same frequency as they did in the reference spectrum (Figure 11 and Table 10). Spectrum C, Figure 3, was the same system as in Spectrum B, after equilibrium at 100 percent relative humidity for 32.5 hours followed by a very short evacuation ( $> 1000\ \mu$ ) to remove water droplets from the surface of the clay film that could fog the KBr windows of the infrared cell. The carbonyl group, which in the free state vibrated at  $1740\text{ cm}^{-1}$ , now had a second broader band in the  $1730$  to  $1735\text{ cm}^{-1}$  region. (Throughout this discussion, the term "free" when used to refer to the carbonyl group frequency, will mean its unperturbed frequency.) In addition to the doublet at  $1740$  and  $1735\text{ cm}^{-1}$ , there was also a shoulder at  $1714\text{ cm}^{-1}$ .

**Figure 3. IR Spectra of the Na-montmorillonite-Malathion System.**

- A. Spectrum of Na-Montmorillonite evacuated to 500 $\mu$  for five minutes.
- B. Spectrum of adsorbed malathion after surface application and evacuation to 350 $\mu$  for five minutes.
- C. Spectrum of adsorbed malathion after exposure to 100 percent relative humidity for 32.5 hours and a short evacuation to remove surface-adsorbed water droplets.

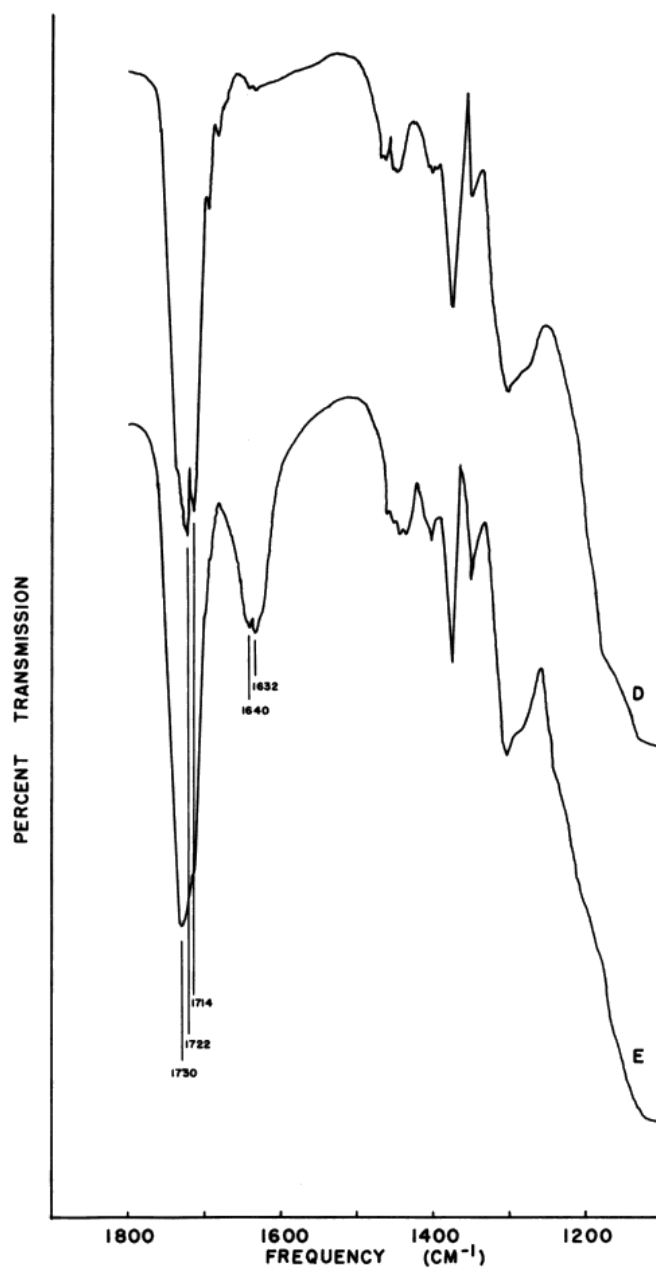


The formation of the 1730 to 1735  $\text{cm}^{-1}$  absorption band was believed to be indicative of hydrogen bonding between a carbonyl group of the malathion molecule and some water molecules associated with the sodium ion on the interlayer surface. Similar hydrogen bonding reactions have been reported by Parfitt and Mortland (1968). The fact that frequency shift was less than 10  $\text{cm}^{-1}$  suggests that the hydrogen bonding energies involved were small. The strength of such a hydrogen bond gives some indication of the acidity or the degree of dissociation of a proton forming an integral part of the hydration sphere of a saturating cation. As the positive charge of the cation increases (i.e. monovalent vs. divalent), its ability to polarize the hydration water increases, making the hydrogen ion more labile. Hence the small perturbation observed for hydrogen bonding in the Na-montmorillonite-malathion system was consistent with the idea that the sodium tends to hydrate to only a limited extent on the interlayer surface. The persistence of the 1740  $\text{cm}^{-1}$  band after exposure to water vapor indicated that there were carbonyl groups present in excess of the hydrogen bonding capacity of the Na-montmorillonite system.

Spectrum D, Figure 4, was obtained for the above described system (Spectrum C, Figure 3) after a 10 hour evacuation period with an oil diffusion pump. The removal of water has shifted the carbonyl frequency to 1722 and 1714  $\text{cm}^{-1}$ . These bands were probably a result of a direct ion-dipole interaction (electrostatic) between the surface-adsorbed sodium ion and the carbonyl group of malathion.

**Figure 4. IR Spectra of the Na-Montmorillonite-Malathion System.**

- D. Spectrum of adsorbed malathion after a 10 hour evacuation.
- E. Spectrum of adsorbed malathion after a 6 hour exposure to 100 percent relative humidity, followed by a short evacuation to remove surface-adsorbed water droplets.



Parfitt and Mortland (1968) reported a somewhat analogous situation for ketone adsorption onto montmorillonite. At the present time, no concrete reason can be advanced for the presence of two bands instead of one. In Spectrum C, Figure 3, there was also a small shoulder band at  $1714\text{ cm}^{-1}$  on the main carbonyl band. One can speculate that perhaps the two carbonyl groups of malathion were not undergoing exactly the same degree of electrostatic interaction, or that some molecules were undergoing a more energetic interaction than others (assuming that both carbonyl groups interacted equally). From theoretical calculations of the surface density of sodium ions on montmorillonite, and of the distance between the carbonyl groups on the malathion molecule (approximately  $4.9\text{ \AA}$ ), the sodium ions should be close enough to interact electrostatically with both carbonyl groups. However upon dehydration, sodium ions tend to migrate from whatever position they assume on the interlayer surface, into the hexagonal holes formed by the oxygen atoms of the tetrahedral layer.

The possibility exists that the  $1714\text{ cm}^{-1}$  band (the more energetic interaction) reflects the ion-dipole interaction with sodium ions that have not sunk into the hexagonal holes whereas the  $1722\text{ cm}^{-1}$  band represents the interaction in which the sodium ions have sunk into the hexagonal holes. The assumption made here is that the carbonyl group could more closely approach the sodium ion on the surface than in the hole, thereby undergoing a more energetic interaction. A second explanation involves a steric hindrance which might interfere with an electrostatic interaction between the sodium ion and the carbonyl group. This possibility seems

somewhat remote, especially for Configuration 29a where there are no other atoms in close proximity to the carbonyl oxygen atoms.

It is interesting to note that upon addition of the water vapor, the water deformation frequency that occurred on the dry clay at approximately  $1630\text{ cm}^{-1}$  (Spectrum A, Figure 3), split into two bands at  $1633$  and  $1642\text{ cm}^{-1}$  (Spectrum C, Figure 3). The  $1642\text{ cm}^{-1}$  band existed as only a spike shoulder before exposure to the water vapor (Spectrum B, Figure 3). Parfitt and Mortland (1968) have suggested that the greater the upward shift of the water deformation band, the more energetic is the interaction. Presumably in this system, the  $1642\text{ cm}^{-1}$  band represented the hydration water that was hydrogen bonded to the carbonyl groups of malathion and the  $1630$  to  $1633\text{ cm}^{-1}$  band represented surface-adsorbed water.

Spectrum E, Figure 4, shows the rehydration of the system in Spectrum D. The main carbonyl band, a result of hydrogen bonding, is once more at  $1730\text{ cm}^{-1}$ , approximately the same position it assumed before the evacuation period. It is possible that a hysteresis effect tended to spread the band out above  $1730\text{ cm}^{-1}$  before evacuation and below  $1730\text{ cm}^{-1}$  upon rehydration.

Upon initial exposure of the dry Na-montmorillonite-malathion system to water vapor (Spectrum C, Figure 3), a small band at  $1328\text{ cm}^{-1}$  irreversibly disappeared. No explanation can be given for this except that the same phenomenon was noted with other cation saturated systems. Further discussion concerning this phenomenon will be presented in a subsequent part

of this dissertation. An inspection of the remainder of the spectrum of malathion on Na-montmorillonite showed no significant deviations from the reference spectrum of malathion, thereby suggesting no breakdown reactions in either the wet or the dry systems.

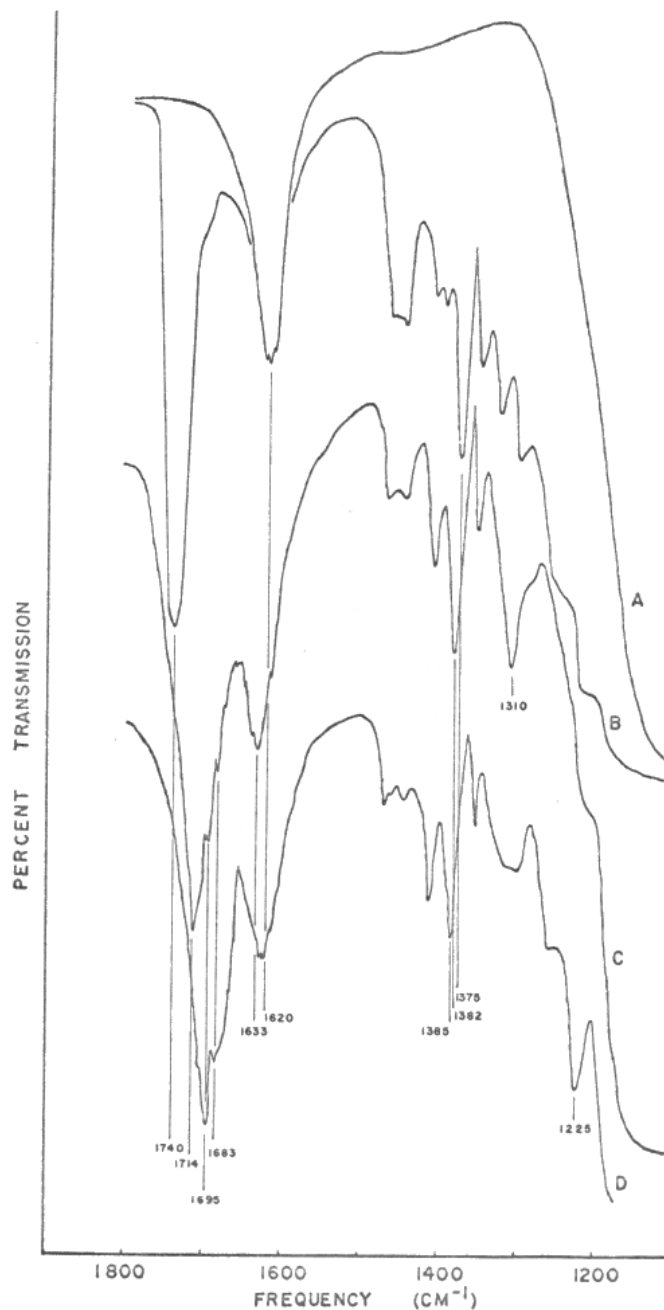
b) Ca-Montmorillonite-Malathion System.

Spectrum A, Figure 5, shows that the water deformation band for Ca-montmorillonite was at  $1620\text{ cm}^{-1}$ . This film had been evacuated to approximately 250 p. for five minutes prior to scanning. Malathion was applied to the surface of the film, the system evacuated to about  $350\mu$  for 10 minutes and then scanned (Spectrum B, Figure 5). As in the Na-montmorillonite system at this point, the spectrum of malathion was almost identical to its reference spectrum (Figure 11 and Table 10). Thus no interaction with the Ca-montmorillonite had occurred.

Spectrum C, Figure 5, is the spectrum of the system after a 44 hour equilibrium period at 100 percent relative humidity, followed by a five minute evacuation to approximately  $500\mu$ . The carbonyl group has shifted down to  $1714\text{ cm}^{-1}$  with two spike shoulders at 1695 and  $1683\text{ cm}^{-1}$ . The  $1714\text{ cm}^{-1}$  band was ascribed to hydrogen bonding with the hydration water of the calcium ions on the interlayer surfaces. The hydrogen bond in the calcium system was considerably stronger than that observed in the sodium system by virtue of the greater frequency shift ( $26\text{ cm}^{-1}$  for the calcium system,  $< 10\text{ cm}^{-1}$  for the sodium system). During this 44 hour equilibrium period, the clay film was periodically scanned. By comparing the intensities of the  $1740$  and  $1714\text{ cm}^{-1}$  peaks, the hydrogen bonding reaction was approximately 30 to 40 percent

**Figure 5. IR Spectra of the Ca-Montmorillonite-Malathion System.**

- A. Spectrum of Ca-Montmorillonite evacuated to  $250\mu$  for five minutes.
- B. Spectrum of adsorbed malathion after surface-application followed by evacuation to  $350\mu$  for 10 minutes.
- C. Spectrum of adsorbed malathion after equilibrating at 100 percent relative humidity for 44. hours, followed by a brief evacuation to remove surface-adsorbed water droplets.
- D. Spectrum of adsorbed malathion after a 5.3 hour evacuation period.



complete after 5.0 hours and more than 90 percent complete after 10.5 hours.

It is important to note that the interlayer hydration water had sufficient capacity to completely hydrogen bond with all the malathion carbonyl groups as indicated by the absence of the  $1740\text{ cm}^{-1}$  band. Perhaps one of the major criticisms of applying the malathion to the surface of the film might be the difficulty in controlling the amount and its distribution, resulting in unreacted localized excesses. Such unreacted excesses would always show up in a spectrum as the  $1740\text{ cm}^{-1}$  band. This would confuse the interpretation of the spectrum, especially upon evacuation of the hydrated system when the reacted portion of the carbonyl groups shifted down to a lower frequency at  $1695\text{ cm}^{-1}$ , as shown in Spectrum D, Figure 5. This particular point becomes very important in a subsequent discussion of the Al-montmorillonite- and Fe-montmorillonite-malathion systems, where the carbonyl group frequency split upon drying the hydrated system, the higher frequency band returning to  $1740\text{ cm}^{-1}$ . Had a surface excess of malathion been present throughout the experiment, it is doubtful that the frequency splitting of the carbonyl group would have been detected.

The hydrated Ca-montmorillonite-malathion system in Spectrum C, Figure 5, required approximately 5.3 hours of evacuation with the oil diffusion pump to give Spectrum D. The bands at  $1695$ ,  $1683$  and  $1669\text{ cm}^{-1}$  were believed to be due to electrostatic interactions between the carbonyl oxygens and the interlayer calcium ions. Since the greater the frequency shift, the more energetic the interaction, one must assume that the  $1669$  and  $1683\text{ cm}^{-1}$  bands represented

a small proportion of the carbonyl groups that interacted more energetically than those creating the 1695  $\text{cm}^{-1}$  band. It is probable that the majority of the interlayer calcium ions were not completely dehydrated by evacuation at temperatures below 25°C and that the 1695  $\text{cm}^{-1}$  band represented a situation where one or two water molecules remained associated with the calcium ion. Hence there are two possibilities that could give rise to absorption bands below 1714  $\text{cm}^{-1}$ ; 1) the remaining hydration water molecules could partially shield the carbonyl group from the cation, resulting in a somewhat less energetic ion-dipole interaction, and/or 2) the acidity of the remaining water molecules surrounding the calcium ion would be somewhat increased since the cation only coordinates with one or two water molecules, rather than with four or six as occurred in the hydrated state. The more labile protons on the residual hydrated water shell would create stronger hydrogen bonds with carbonyl groups, producing a larger frequency shift toward lower wavenumbers. Perhaps only the 1669  $\text{cm}^{-1}$  shoulder band represented a true ion-dipole interaction where all of the hydration water molecules have been stripped from the calcium ion.

The water deformation frequency did not change from 1620  $\text{cm}^{-1}$  upon application of the malathion to the clay as shown in Spectra A and B, Figure 5. This implies that there was no interaction between the surface adsorbed and hydration water, and the malathion carbonyl groups. Either the malathion entered the interlayer region of the montmorillonite and did not interact with the water present, or else the malathion did not enter at all. The latter possibility is the more probable one and is supported by x-ray diffraction data presented later in this

discussion. Spectrum C, Figure 5, indicates that, upon addition of water vapor, the interlayer water deformation frequency shifted up to the  $1633\text{ cm}^{-1}$  region, and that the carbonyl frequency shifted down to  $1714\text{ cm}^{-1}$  indicating hydrogen bonding. One must conclude from these data that a certain minimal amount of water must be present in the system before malathion can enter the interlayer region. Probably the water molecules tend to wedge open the interlayers of the montmorillonite because of their tendency to hydrate the saturating cation, calcium. This process then allows the malathion molecules to follow. Since this hydrogen bonding reaction has been observed to initiate immediately after exposure to water vapor (100 percent relative humidity), it is probable that the malathion molecules were transported into the interlayer region by the mass flow of the water molecules. It is doubtful that any significant hydrogen bonding occurred between the carbonyl groups and the bulk water before or during the penetration into the interlayer area because of the insufficient acidity of the bulk water. The interaction would occur as soon as the bulk water became part of the hydration shell of the cation and became polarized by the cationic charge.

Upon drying the hydrated Ca-montmorillonite-malathion system, the water deformation frequency decreased from  $1633\text{ cm}^{-1}$  to the  $1622$  to  $1625\text{ cm}^{-1}$  region. (Spectrum D, Figure 5). It is possible that this frequency shift was only an apparent one and that the hydration water involved in the hydrogen bonding ( $1633\text{ cm}^{-1}$ ) had been largely removed by evacuation. The

less intense 1622 to 1625  $\text{cm}^{-1}$  band may represent some entrapped bulk water. If, on the other hand, the 1633  $\text{cm}^{-1}$  band has shifted down to 1625  $\text{cm}^{-1}$ , this would seem to suggest a weaker hydrogen bonding interaction with the carbonyl groups.

When the dry calcium-montmorillonite-malathion system (Spectrum D, Figure 5) was re-exposed to water vapor, the spectrum was very similar to Spectrum C. As observed in the sodium system, there seemed to be a slight hysteresis effect in the shifting of the carbonyl band, probably attributable to a slow rehydration of water molecules in certain interlayer regions. The reference spectrum of malathion (Figure 11 and Table 13) has a band at 1375  $\text{cm}^{-1}$ , attributed to the symmetric  $\text{CH}_3$  deformation ( $\text{CH}_3\text{-C-}$ ) of the ethyl group. This band shifted up to 1382  $\text{cm}^{-1}$  upon exposure to water vapor (Spectrum C, Figure 5), and to 1385  $\text{cm}^{-1}$  upon evacuation (Spectrum D). This upward frequency shift may be attributable to the slight interaction between the hydrogen atoms of the methyl group and the electrical fields associated with the oxygen atoms comprising the interlayer surface. The extent of this shift may have been reduced in Spectrum C because of the shielding effect of the surface-adsorbed water molecules. Bellamy (1968) suggested that the  $\text{CH}_3\text{X}$  deformation frequencies were controlled by the electronegativity of X and by the repulsive, non-bonded force which came into play when all the hydrogen atoms bent simultaneously towards X. Although the atom X was not bonded directly to the  $\text{CH}_3$  group, as in Bellamy's illustration, but rather was an oxygen sheet in close proximity, it seems possible that the end result might be somewhat similar, although of lesser magnitude.

Upon initial exposure of the Ca-montmorillonite-malathion system to 100 percent relative humidity (Spectrum C, Figure 5), the  $1328\text{ cm}^{-1}$  band disappeared, as it did in the Na-montmorillonite-malathion system. In addition, an intense band appeared at  $1310\text{ cm}^{-1}$ . One can not be certain whether the  $1300\text{ cm}^{-1}$  band shifted, or whether the  $1310\text{ cm}^{-1}$  band was a different one that masked the  $1300\text{ cm}^{-1}$  band. After evacuation with the oil diffusion pump for several hours, this intense  $1310\text{ cm}^{-1}$  band became weak and much broader, extending from  $1300$  to  $1320\text{ cm}^{-1}$  (Spectrum D, Figure 5). Simultaneously, a relatively intense band formed in the  $1215$  to  $1220\text{ cm}^{-1}$  region and gradually shifted up to  $1225$  to  $1227\text{ cm}^{-1}$  with prolonged pumping. Calcium was the only cation that resulted in the development of the  $1225$  to  $1227\text{ cm}^{-1}$  band when malathion was adsorbed onto montmorillonite.

At first glance, such marked changes in the spectrum would suggest an alteration in the malathion molecule. However there are several facts that seem to diminish this possibility;

1. There are three main sites in malathion that could be cleaved; the two ethyl ester linkages and the thiol ester (P-S-C) linkage. If the ethyl groups were cleaved from the molecule, there would be noticeable changes in the C-H stretching region ( $2850$  to  $3000\text{ cm}^{-1}$ ). Although the C-H stretching bands weakened somewhat in the experiment, they did so in proportion to the other spectral bands. Furthermore, no changes in the C-H stretching region occurred as in the  $1310\text{ cm}^{-1}$  band developed. This would not have been the case if hydrolysis had occurred.

2. It is more difficult to detect a P-S-C cleavage since the phosphorus end sulfur vibrations mainly occur in the 700 to 1000  $\text{cm}^{-1}$  region where the clay also absorbs strongly. However in a later portion of this discussion, it will be shown that the spectrum of diethyl succinate adsorbed on montmorillonite had a 1310  $\text{cm}^{-1}$  band although the reference spectrum did not have this band (Spectrum 12, Table 10). Therefore the formation of the 1310  $\text{cm}^{-1}$  band could not have been associated with the P-S-C linkage.
  
3. Malathion, diethyl mercaptosuccinate and diethyl succinate each had a weak band at 1210, 1215 and 1212  $\text{cm}^{-1}$  respectively (Figures 11, 13 and 12). As mentioned above, a band in the 1215 to 1227  $\text{cm}^{-1}$  region developed only in the Ca-montmorillonite system and not in the other four cation-saturated montmorillonite systems. The reason for this is unknown and upon first inspection it would suggest that the malathion molecule had been altered. One can not be at all certain that the band observed in the reference spectrum was the same one that developed and intensified after adsorption and partial dehydration. Since there is good evidence that the ethyl ester linkages were unaltered, then the P-S-C linkage was the only other point of possible cleavage. However under identical conditions, what appeared to be the same band developed in diethyl succinate which does not have the thiol ester linkage. Therefore this band could not be indicative of a P-S-C cleavage in malathion.

Since it appears that the spectral changes were not due to an alteration in the malathion molecule, then they must be attributed to an interaction involving water and the interlayer surfaces of the montmorillonite. There was no interaction between the exterior surfaces of the montmorillonite and the malathion because the  $1310\text{ cm}^{-1}$  band did not form until after the water vapor was introduced and after that time, the band was never completely removed by evacuation. The  $1225\text{ cm}^{-1}$  band also always intensified upon evacuation. This band may be due to an orientation effect peculiar to the Ca-montmorillonite system.

There exists the possibility that in the presence of water molecules, there was a mixing of C-O stretching and water deformation frequencies giving rise to a new absorption band at  $1310\text{ cm}^{-1}$ . This would explain the change in intensity with changes with water content of the clay. However in a similar experiment where  $\text{D}_2\text{O}$  was used in lieu of  $\text{H}_2\text{O}$ , the  $1310\text{ cm}^{-1}$  band appeared upon adding  $\text{D}_2\text{O}$  vapor and the  $1225\text{ cm}^{-1}$  band appeared and intensified upon dehydrating the system by evacuation. These bands should not have been at the same frequency for both  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  if they were due to mixing of frequencies.

One other possibility seems to fit the data. This involves the interaction of the succinate portion of the malathion molecule with the interlayer surface of the montmorillonite. No interaction with the interlayer surface occurred until water had forced apart the interlayer surfaces allowing malathion to enter. The saturating cation appeared to have some effect upon the degree to which the  $1310\text{ cm}^{-1}$  band developed, with the effect increasing as follows;  $\text{Na}^+ < \text{Ca}^{+2} = \text{Fe}^{+3}$

=  $\text{Cu}^{+2} < \text{Al}^{+3}$ . This order somewhat paralleled the magnitude of the shift of the hydrogen bonded carbonyl group, suggesting that perhaps the hydration water was involved in the development of the  $1310 \text{ cm}^{-1}$  band, although not by mixing frequencies.

c) Cu-Montmorillonite-Malathion System.

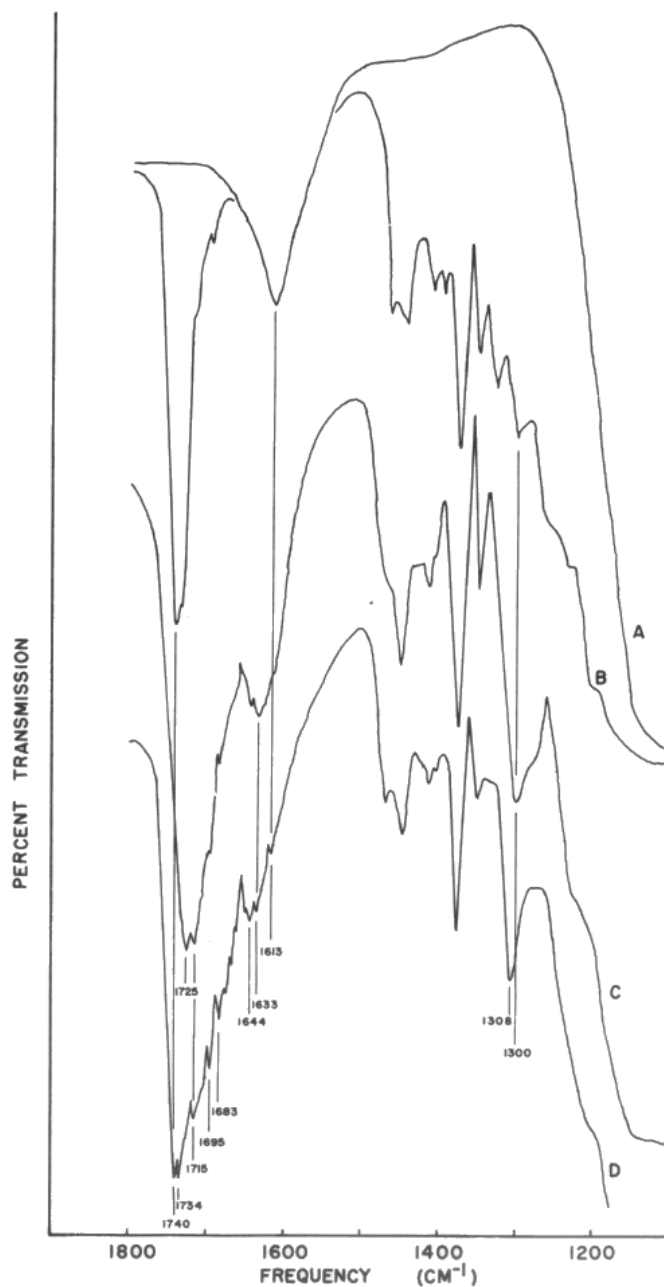
Malathion was applied to the surface of a Cu-montmorillonite film (partially dried by evacuation, Spectrum A, Figure 6), evacuated to approximately  $1000 \mu$  for five minutes and then scanned (Spectrum B, Figure 6). There had been no interaction between the malathion and the clay surface. Spectrum C, Figure 6, shows the same system after exposure to 100 percent relative humidity for 260 hours, followed by a brief evacuation to remove surface adsorbed water droplets. The carbonyl group frequency split into two main bands at  $1725 \text{ cm}^{-1}$  and  $1715 \text{ cm}^{-1}$ , and into two smaller spike shoulder bands at  $1695$  and  $1683 \text{ cm}^{-1}$ .

There are several possible explanations for the existence of two bands ( $1725, 1715 \text{ cm}^{-1}$ ) which presumably were due to hydrogen bonding, rather than just one band as exhibited in the calcium and sodium systems.

1. Perhaps the amount of malathion on the clay exceeded the capacity of the clay surfaces to completely interact with it. If this were the situation then one would have expected a band at  $1740 \text{ cm}^{-1}$  attributable to the unreacted carbonyl groups. This was not the case. Thus all the malathion carbonyl groups did undergo an interaction with the clay surface.

**Figure 6. IR Spectra of the Cu--Montmorillonite-Malathion System.**

- A. Spectrum of Cu-Montmorillonite evacuated to  $100\mu$  for 15 minutes.
- B. Spectrum of adsorbed malathion after surface-application followed by evacuation to  $1000\mu$  for five minutes.
- C. Spectrum of adsorbed malathion after equilibrating at 100 percent relative humidity for 260 hours, followed by a brief evacuation to remove surface-adsorbed water droplets.
- D. Spectrum of adsorbed malathion after evacuating for 46.5 hours.



2. The next question to be considered is whether both carbonyl groups on each malathion molecule underwent an identical hydrogen bonding interaction. There is a possibility that the phosphorodithioate portion of the molecule might have sterically hindered the alpha-carbonyl group in a hydrogen bonding interaction. There are three reasons to doubt this: (i) other clay systems studied showed essentially one main band attributable to hydrogen bonding, saying in effect that steric hindrance was not an important factor, (ii) the most likely configuration of malathion places the carbonyl oxygen atoms on the opposite side of the succinate moiety to that of the phosphorodithioate entity (Figure 29a), (iii) the most plausible explanation for the double bands is that the clay film was not uniformly hydrated and as a result the 1725 and 1715  $\text{cm}^{-1}$  bands represented carbonyl- $\text{H}_2\text{O}$ -cation interactions of varying energies.

Upon evacuating the Cu-montmorillonite-malathion system for 46.5 hours, the carbonyl group frequency (Spectrum D, Figure 6) split into five distinct bands and several weaker shoulder bands. It appeared that the 1725  $\text{cm}^{-1}$  band shifted upward, splitting into two bands at 1740 and 1734  $\text{cm}^{-1}$ , and that the bands at 1715  $\text{cm}^{-1}$  and below, which were very weak in Spectrum C, intensified. At least 50 percent of the integrated intensity of the entire multi-peak band was accounted for by the 1740 and 1734  $\text{cm}^{-1}$  bands, suggesting that a considerable proportion of the carbonyl groups that were hydrogen bonded in Spectrum C, were either weakly interacting or not interacting at all with the clay surface. During the 46.5 hour evacuation period, periodic scans of the clay-malathion system indicated that the 1740  $\text{cm}^{-1}$  band progressively intensified while the 1734  $\text{cm}^{-1}$  band weakened. Perhaps with extended

evacuation, the  $1734\text{ cm}^{-1}$  band might have completely disappeared and the  $1740\text{ cm}^{-1}$  band further intensified.

There appears to have been two different mechanisms operating to have shifted part of the carbonyl band upward from  $1725\text{ cm}^{-1}$  while the remainder of the band shifted downward. The bands in the  $1715$  to  $1662\text{ cm}^{-1}$  region probably represented an increasing ion-dipole interaction between the copper cation and the carbonyl group. Why there were so many bands is unclear. Perhaps the exceptional coordinating abilities of copper were involved in addition to the effect of different hydration states of the copper cation.

The Cu-montmorillonite system lost some of its capacity to interact with the carbonyl groups of malathion upon dehydration. Spectrum C, Figure 6, indicated that all carbonyl groups were interacting with the clay surface, but upon dehydration (Spectrum D), a considerable proportion of the carbonyl groups did not interact, producing the  $1740\text{ cm}^{-1}$  band. Perhaps several carbonyl groups were simultaneously hydrogen bonded to the hydration water shell of a single copper cation. Upon partial removal of the shell by evacuation, some carbonyl groups were excluded from the interaction. One might further speculate that the  $1734\text{ cm}^{-1}$  band represented an intermediate stage of weaker interaction during the removal of some of the hydration water molecules. There is another possibility that the hydrated copper ions were close enough so that both carbonyl groups of malathion could hydrogen bond equally, but during dehydration, the increased distance between the dehydrated copper ions might have made it impossible for both carbonyl groups to equally interact. The end result of this process would

be one carbonyl group undergoing an ion-dipole interaction ( $< 1715 \text{ cm}^{-1}$ ), and one "free" carbonyl group ( $1740 \text{ cm}^{-1}$ ).

The introduction of water vapor into the Cu-montmorillonite -malathion system resulted in the disappearance of the  $1327 \text{ cm}^{-1}$  band as previously discussed for the calcium system. Dehydration of the system (Spectrum D, Figure 6) caused the  $1300 \text{ cm}^{-1}$  band to shift up to  $1308 \text{ cm}^{-1}$ . Water vapor seemed to cause these two changes, in addition to causing the hydrogen bonding of the carbonyl groups. An experiment was conducted, using the Cu--montmorillonite system, to investigate these phenomena at various relative humidities (between 20 and 100 percent) using suitable sulfuric acid-water mixtures,  $\text{CaCl}_2$  and potassium acetate solutions (See Table 5) .

The  $1328 \text{ cm}^{-1}$  band disappeared very quickly in relative humidities exceeding approximately 30 percent. At 23 percent relative humidity, the  $1328 \text{ cm}^{-1}$  band disappeared over a period of 30 hours. The  $1300 \text{ cm}^{-1}$  band developed more quickly with relative humidities exceeding 45 percent. Only slight development occurred at lower humidities over a 24 hour period. Therefore, the disappearance of the  $1328 \text{ cm}^{-1}$  band was not associated with the intensification of the  $1300 \text{ cm}^{-1}$  band.

The effect of relative humidity upon the hydrogen bonding of the carbonyl group was mainly one of reaction rate. At 23 percent relative humidity (over KOAc) and 32 percent

**Table 5. Relative Humidity Mixtures.\***

<b>H<sub>2</sub>SO<sub>4</sub> (98%)(ml.)</b>	<b>H<sub>2</sub>O (ml.)</b>	<b>Density (gm/cc)</b>	<b>R.H.(25°C)</b>
500	0	1.835	0
255.5	244.5	1.552	10
219.2	280.8	1.478	20
192.2	307.8	1.425	30
170.1	329.9	1.377	40
149.4	350.6	1.335	50
129.1	370.9	1.293	60
108.5	391.3	1.248	70
84.1	415.9	1.197	80
54.5	445.5	1.127	90
0	500	1.000	100
<u>Saturated Salt Solution</u>		<u>R.H.</u>	
KOAc		22.9 (22.8°C)	
CaCl <sub>2</sub> ·6H <sub>2</sub> O		32.3 (20°C)	

\* Taken from: Lange's Handbook of Chemistry, Revised 10th Edition, McGraw-Hill, New York.  
P. 1432. 1967.

relative humidity (over  $\text{CaCl}_2$ ), 135 hours and 125 hours respectively were required to produce any significant degree of hydrogen bonding. At relative humidities exceeding 40 percent, the hydrogen bonding interaction occurred within two hours. As the relative humidity approached 100 percent, the interaction occurred within a few minutes. The slower reaction at lower relative humidities was probably because of the reduced rate of expansion of the lattice by the water molecules and the subsequent hydration process that necessarily preceded the hydrogen bonding interaction.

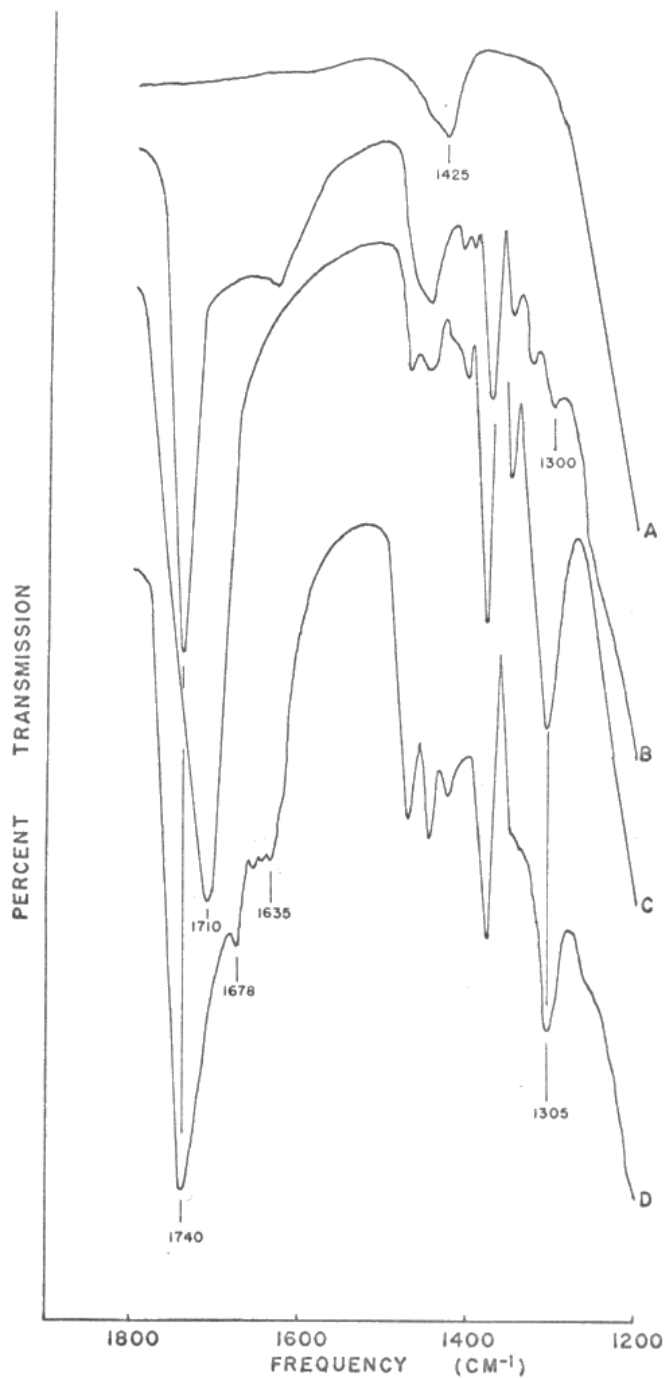
d) Al-Montmorillonite-Malathion System.

In this experiment, the  $\text{H}_2\text{O}$  on the clay was replaced by  $\text{D}_2\text{O}$  in order to remove the broad  $\text{H}_2\text{O}$  water deformation band in the  $1600$  to  $1750\text{ cm}^{-1}$  region which masks perturbations of the carbonyl band. The  $\text{D}_2\text{O}$  deformation band occurred at  $1425\text{ cm}^{-1}$  (Spectrum A, Figure 7), a considerably higher frequency than might have been expected for the D-O-D bending vibration. It is likely that there was an exchange between the  $\text{H}_2\text{O}$  and  $\text{D}_2\text{O}$  molecules, producing HDO, and that the  $1425\text{ cm}^{-1}$  band was actually a H-O-D bending vibration. Spectrum B, Figure 7, shows the system just after malathion application to the surface of the film. The film was partially dried by evacuation so that the malathion underwent no interaction with the clay. There was still a small amount of water left on the film as indicated by the  $1630\text{ cm}^{-1}$  and therefore the system was exposed to  $\text{D}_2\text{O}$  vapor a second time.

After exposure to  $\text{D}_2\text{O}$  vapor for 13 minutes (Spectrum C, Figure '7) the entire carbonyl band had shifted down to  $1710\text{ cm}^{-1}$  a result of deuterium bonding.

**Figure 7. IR Spectra of the Al-Montmorillonite-Malathion Systems.**

- A. Spectrum of Al-Montmorillonite in which D<sub>2</sub>O has replaced H<sub>2</sub>O (may actually be HDO).
- B. Spectrum of adsorbed malathion after surface-application followed by a five minute evacuation to 15  $\mu$ .
- C. Spectrum of adsorbed malathion after equilibrating at 100 percent humidity for 13 minutes, followed by a brief evacuation to remove surface-adsorbed D<sub>2</sub>O droplets.
- D. Spectrum of adsorbed malathion following evacuation for 180 hours.



This was the greatest frequency shift of all the clay-malathion systems studied, a consequence of the greater acidity of the hydration water. (The perturbation of the carbonyl group frequency due to deuterium bonding was the same as for hydrogen bonding.)

The  $1328\text{ cm}^{-1}$  band disappeared and the intense  $1309\text{ cm}^{-1}$  band developed upon the addition of  $\text{D}_2\text{O}$  vapor to the system, following malathion application. As discussed previously for the copper system,  $\text{D}_2\text{O}$  produced no different effects than water did, thereby proving that the  $1309\text{ cm}^{-1}$  band was not due to mixing of OH or OD bending frequencies with C-O stretching frequencies.

The extent to which the  $1309\text{ cm}^{-1}$  band developed was greatest for the aluminum system. One can't help but notice the fact that the degree to which the carbonyl frequency was perturbed somewhat paralleled the degree of development of the  $1309\text{ cm}^{-1}$  band. The Na-montmorillonite-malathion system exhibited the least shift in the carbonyl frequency due to hydrogen bonding (about  $10\text{ cm}^{-1}$ ) and least development of the  $1300\text{ cm}^{-1}$  region band, whereas the Al-montmorillonite-malathion system produced the greatest carbonyl shift ( $30\text{ cm}^{-1}$ ) and the greatest development of the  $1309\text{ cm}^{-1}$  band. Perhaps the development of the  $1300\text{ cm}^{-1}$  band was in some way related to the hydrogen bonding interaction.

It is interesting to note that Parfitt and Mortland (1968) found that 2,5-hexanedione, a compound somewhat related to the succinate portion of malathion, also had an absorption band at  $1313\text{ cm}^{-1}$  whose intensity and position seemed to be affected by its environment. Tensmeyer et al. (1960) studied the adsorption of 2,5-hexanedione by montmorillonite and found that one

or two monomolecular layers of the compound could be adsorbed. They attributed changes in the infrared spectrum between one and two layer coverage to partial replacement of a clay-organic contact by an organic-organic contact, and also to changes in orientation of the molecules. Parfitt and Mortland (1968) stated that the  $1313\text{ cm}^{-1}$  band noticeably changed on going from two layers to one layer and believed that it was an orientation effect and a different interaction with water. These results then raise the question as to whether malathion was adsorbed by montmorillonite as a single layer, or as a double layer, one monolayer on each interlayer surface. This point will be more fully explored in the section on x-ray diffraction.

The Al-montmorillonite-malathion system was evacuated for 18 hours and then scanned. The single carbonyl frequency band at  $1710\text{ cm}^{-1}$  (Spectrum C, Figure 6) had split into two bands at  $1735$  and  $1695\text{ cm}^{-1}$ , and a band at  $1634\text{ cm}^{-1}$  had also developed. At first glance this band would be attributed to the water deformation band. But infrared scans at the beginning of the evacuation period showed that the band did not exist. It had developed during the dehydration process. To be certain, the system was once more exposed to  $\text{D}_2\text{O}$  vapors and again the  $1634\text{ cm}^{-1}$  band disappeared and the carbonyl group frequency shifted down to the  $1710$  to  $1715\text{ cm}^{-1}$  region. The system was then evacuated for 180 hours with the oil diffusion pump and scanned (Spectrum D, Figure 7). The carbonyl group band split again into three components at  $1740$ ,  $1678$ , and  $1635\text{ cm}^{-1}$ . The low frequency band that appeared to be in the water deformation region developed with increasing dehydration. Since there was no water in the system and the cell was never opened to the atmosphere, this band must have been a result of an energetic interaction between the carbonyl group and the aluminum ion.

There are several explanations for the existence of the  $1740\text{ cm}^{-1}$  after dehydration. Obviously the capacity of the clay to interact with the carbonyl group was greatly reduced during the evacuation process, since initially the entire carbonyl band was hydrogen bonded at  $1710\text{ cm}^{-1}$ . As proposed for the copper system, several carbonyl groups might simultaneously hydrogen bond to the hydration water shell of the aluminum cation. Upon dehydration, the reduced number of water molecules might have made it physically impossible for all the carbonyl groups to simultaneously interact with the cation, thus producing the  $1740\text{ cm}^{-1}$  band. The  $1678\text{ cm}^{-1}$  band would represent the carbonyl groups that either hydrogen bonded to the residual hydration shell, or underwent a weak ion-dipole interaction with the aluminum ion. The  $1635\text{ cm}^{-1}$  band would be attributed to a stronger ion-dipole interaction where most or perhaps all the hydration water molecules had been stripped from the aluminum ion. It is very doubtful that more than one carbonyl group could simultaneously hydrogen bond to a hydration water shell. This would necessitate the existence of more than one labile proton per water shell, or else force the sharing of a single proton by two or more carbonyl groups. One would expect that the latter situation would result in a rather weak hydrogen bond and furthermore one could expect that carbonyl oxygens in such close proximity might create a considerable repulsive force between them.

The interlayer surface density of aluminum ions may be a determining factor in the development of the  $1740\text{ cm}^{-1}$  band upon dehydration. It is possible that the aluminum ions were spaced far enough apart so that when their water shells were removed (or partially so) by evacuation, the two carbonyl groups of malathion were not able to simultaneously electrostatically interact with the cations. As a result, the malathion molecule would shift toward

one aluminum, allowing one carbonyl group to bond electrostatically with the aluminum (1678 or 1635  $\text{cm}^{-1}$ ) while the other carbonyl group returned to its unperturbed state (1740  $\text{cm}^{-1}$ ).

There is a third possibility that during the evacuation process, substantial amounts of malathion migrated to the exterior surfaces with the water being removed and therefore would not undergo any significant interaction with the exterior clay surfaces. This is probably an unlikely mechanism since 1) the surface of the film did not appear "wet" as should be the case if there was a considerable amount of malathion on it, and 2) the lattice layers would tend to collapse onto the malathion layer as dehydration proceeded, thus making it difficult for molecules in the interlayer region to migrate.

After the system in Spectrum D, Figure 7, was rehydrated at 100 percent relative humidity, the spectrum was almost the same as before dehydration (Spectrum C, Figure 7). As noted in the other montmorillonite-malathion systems, there was a slight hysteresis effect exhibited by the carbonyl group band in returning to 1710  $\text{cm}^{-1}$ , the hydrogen bonded state. This reflects the slow diffusion of water molecules into certain interlayer areas because of slight structural imperfections in the clay, or by obstructions created by the malathion molecules.

e) Fe-Montmorillonite-Malathion Systems.

Spectrum A, Figure 8, shows the water deformation band of Fe-montmorillonite (air-dried) to be at 1630  $\text{cm}^{-1}$ . Before applying malathion, the clay film was dehydrated by evacuation for a few minutes, There was no apparent interaction between the malathion and the

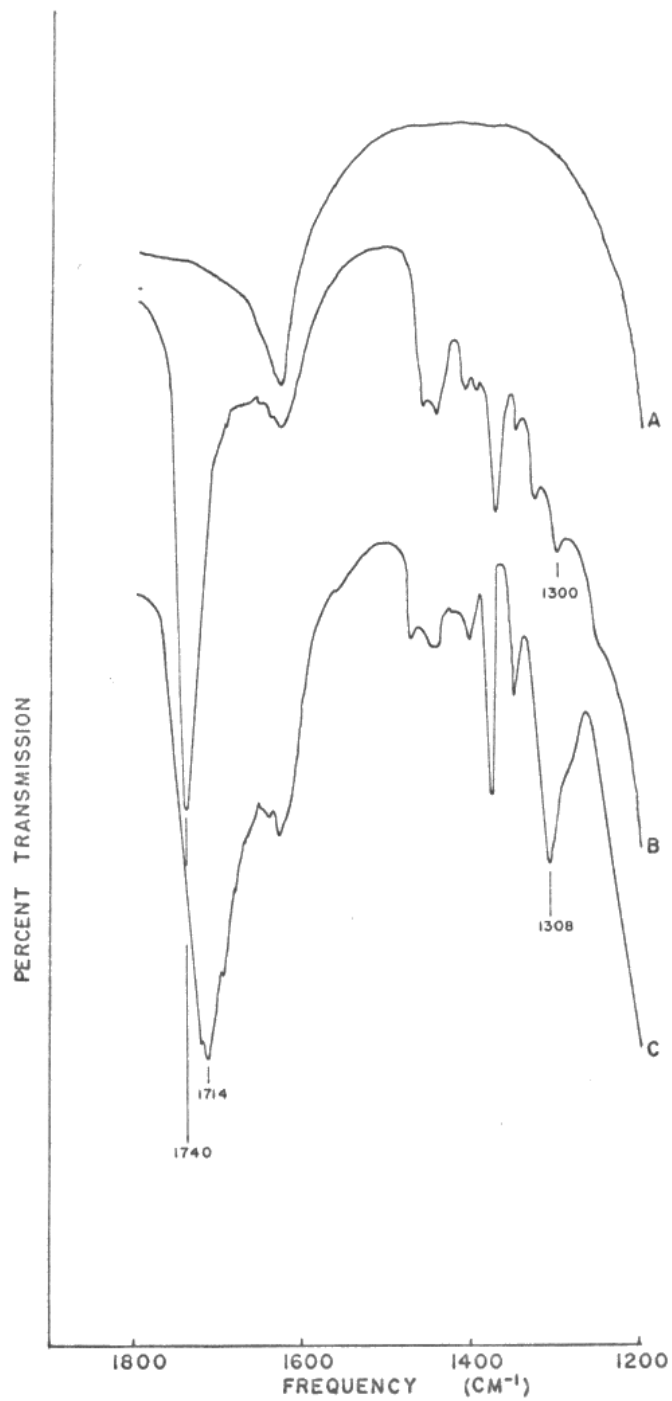
clay surface immediately following application, since all absorption bands were in their normal position (Spectrum B, Figure 8).

After equilibrating at 100 percent relative humidity for one hour, the main carbonyl group absorption band shifted to  $1714\text{ cm}^{-1}$ , accompanied by small shoulders at  $1723$ ,  $1695$  and  $1684\text{ cm}^{-1}$  (Spectrum C, Figure 8). The  $1714\text{ cm}^{-1}$  band represented a hydrogen bonding interaction between the carbonyl groups and the hydration water shells of the iron cations. The  $1723\text{ cm}^{-1}$  band was also due to a hydrogen bonding interaction that may have involved a small number of more highly hydrated cations. The  $1695$  and  $1684\text{ cm}^{-1}$  bands may be ascribed to an ion-dipole or a more energetic hydrogen bonding interaction between the carbonyl groups and iron cations that had lost most of their hydration shells. The  $1308\text{ cm}^{-1}$  band developed under the same circumstances as reported for the other montmorillonite-malathion systems.

Upon evacuating the system for 21 hours, the carbonyl group frequency split into many sharp bands between  $1650$  and  $1710\text{ cm}^{-1}$  (Spectrum D, Figure 9).

**Figure 8. IR Spectra of the Fe-Montmorillonite-Malathion System.**

- A. Spectrum of air-dried Fe-Montmorillonite.
- B. Spectrum of adsorbed malathion after surface-application, followed by a one minute evacuation to  $1000 \mu$ .
- C. Spectrum of adsorbed malathion after equilibrating at 100 percent relative humidity for one hour.

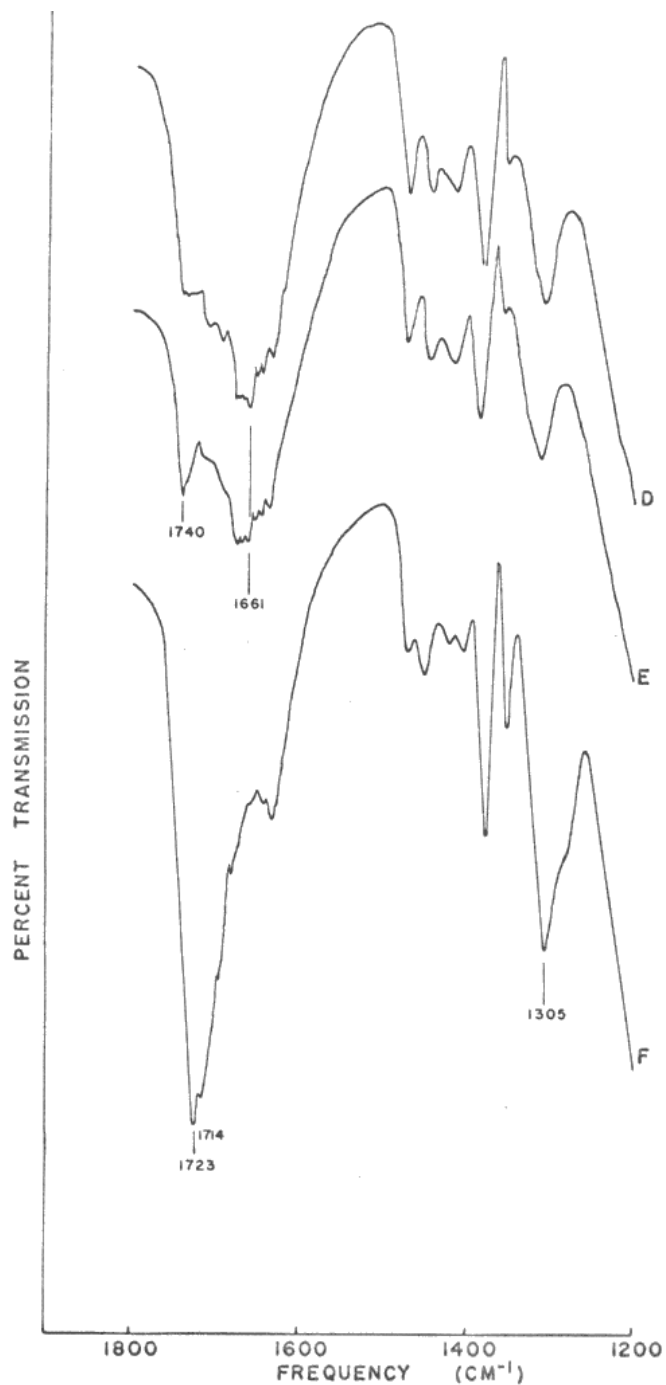


The main carbonyl band shifted from the 1714 to the 1661  $\text{cm}^{-1}$  region, indicating a more energetic interaction. In addition, a broad band started to develop in the 1730 to 1740  $\text{cm}^{-1}$  region indicating that a small proportion of the carbonyl groups were undergoing little or no interaction with the iron cations. After a total evacuation period of 47 hours, the carbonyl band had essentially split into two bands; one centered at 1740  $\text{cm}^{-1}$  and the second, a multipeak band in the 1660 to 1678  $\text{cm}^{-1}$  region. This frequency splitting was probably analogous to that reported for the Al-montmorillonite-malathion system, although not quite as well developed. It is postulated that the density of iron cations was low enough on the interlayer surface so that only one of the carbonyl oxygen atoms of malathion could energetically interact with a neighbouring iron cation at any given instant. The other carbonyl group underwent no interaction and therefore vibrated at 1740  $\text{cm}^{-1}$ .

Following the evacuation period, the clay film was equilibrated at 100 percent relative humidity for 4.5 hours. Spectrum F, Figure 9, shows that the iron cations rehydrated, once more initiating the hydrogen bonding interaction. The main band occurred at 1723  $\text{cm}^{-1}$  with smaller shoulders at 1714, 1695 and 1683  $\text{cm}^{-1}$ . It is possible that the 1740 and 1660  $\text{cm}^{-1}$  shifted to 1723 and 1714  $\text{cm}^{-1}$  respectively. During dehydration, it was postulated that the trivalent cations were far enough apart to cause the malathion molecule to move laterally, allowing one of the carbonyl groups to undergo a more energetic interaction. If the malathion molecule maintained this position during rehydration, then two bands due to hydrogen bonding (i.e. 1723, 1740  $\text{cm}^{-1}$ ) could be observed.

**Figure 9. IR Spectra of the Fe-Montmorillonite-Malathion System.**

- A. Spectrum of adsorbed malathion after evacuating for 21 hours.
- B. Spectrum of adsorbed malathion after evacuating for 47 hours.
- C. Spectrum of adsorbed malathion after equilibrating at 100 percent relative humidity for 4.5 hours, followed by a brief evacuation to remove surface-adsorbed water droplets.



In other words, the malathion molecules did not tend to return to their original orientation upon rehydration. A longer equilibrium period may be required to produce only one absorption band due to hydrogen bonding. There is a second explanation for the 1723 and 1714  $\text{cm}^{-1}$  bands. It is possible that many of the cations were more highly hydrated than in the original state, resulting in a weaker hydrogen bonding interaction thereby creating the 1723  $\text{cm}^{-1}$  band. The 1714  $\text{cm}^{-1}$  band would be associated with those cations hydrated to the same extent as in the original state. There appeared to be a possible change in orientation during the dehydration process. The band at 1472  $\text{cm}^{-1}$  in Spectrum C greatly intensified upon dehydration (Spectrum E), Also the bands at 1350 and 1378  $\text{cm}^{-1}$  (Spectrum C) shifted up to 1357 and 1383  $\text{cm}^{-1}$  respectively. These band alterations may also be indicative of changes in the degree of interaction between malathion layers, or between the malathion and the oxygen atoms on the interlayer surfaces of the montmorillonite lattice.

f) Montmorillonite-Diethyl Succinate Systems.

During the investigation of the various montmorillonite-malathion systems, several significant alterations were noted in the spectrum of adsorbed malathion. At that point, it was not known whether these changes represented clay-malathion interactions or whether an alteration in the malathion molecule had occurred.

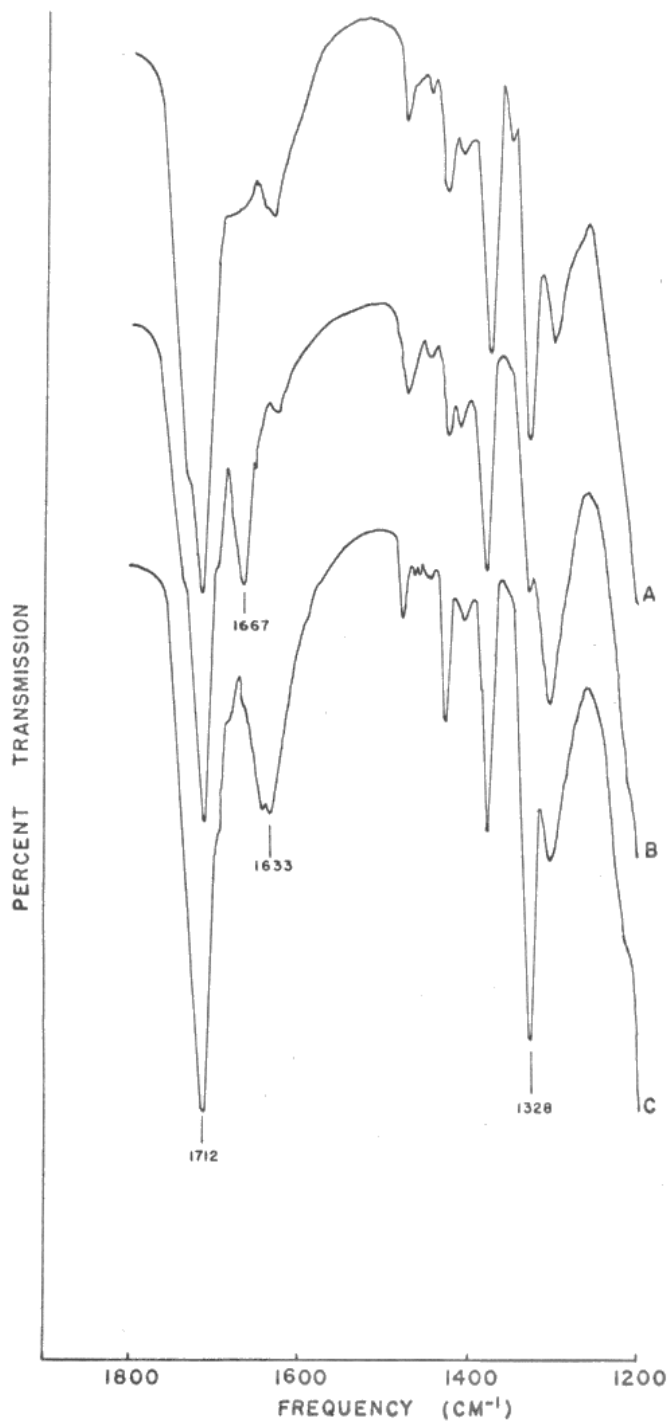
An extensive program was then initiated to investigate the observed spectral changes of adsorbed malathion. Infrared spectra of ten related compounds were obtained for comparison purposes (Figures 11 through 18). In addition, the behavior of two of the most closely related compounds (diethyl succinate and diethyl mercaptosuccinate) on montmorillonite was studied.

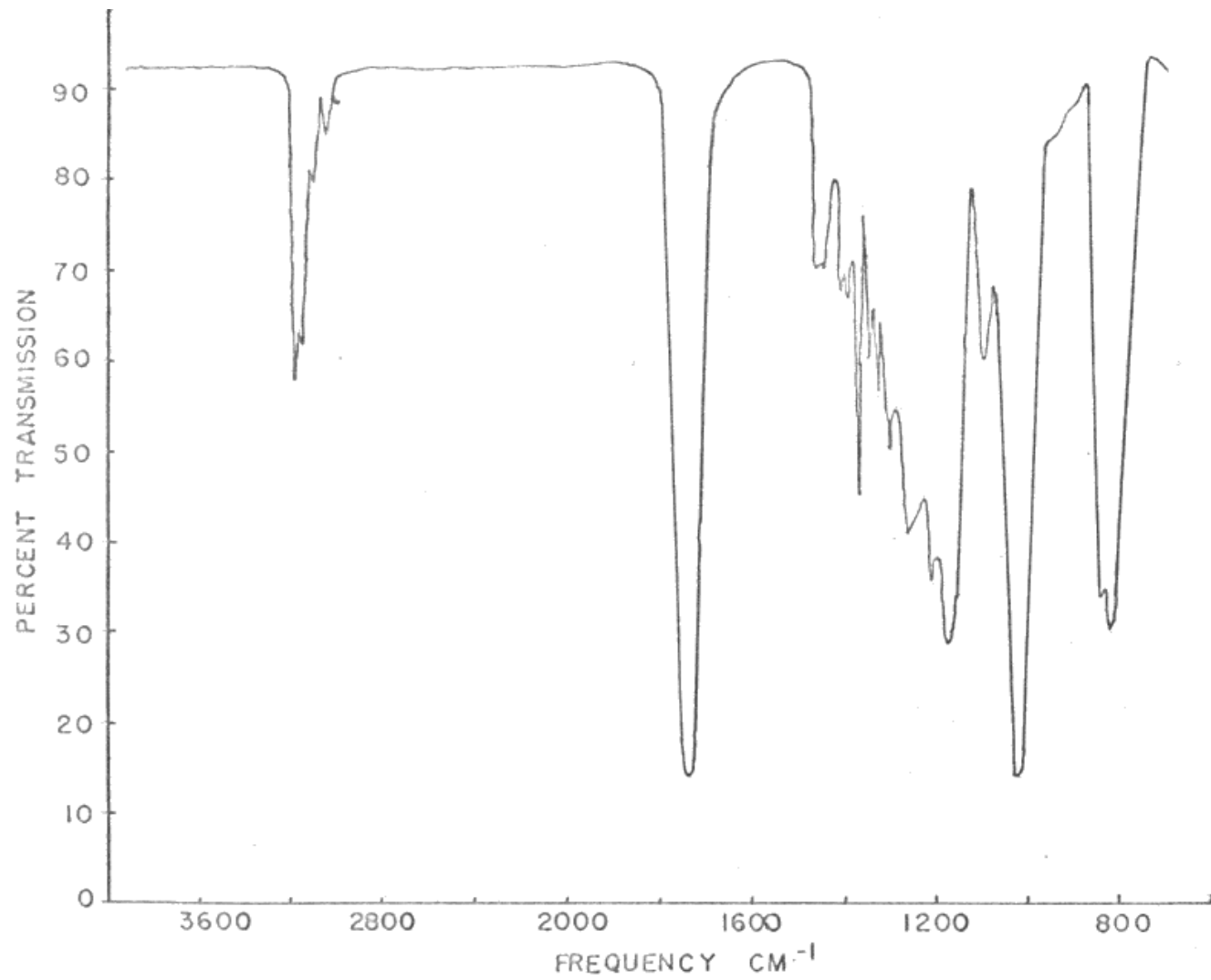
Spectrum A, Figure 10, shows the spectrum of diethyl succinate following its application onto a Na-montmorillonite film. The carbonyl groups have apparently undergone a hydrogen bonding and an electrostatic interaction with the sodium cation. It would appear that the 1730 to 1735  $\text{cm}^{-1}$  shoulder was due to the carbonyl groups hydrogen bonding to some slightly hydrated sodium cations. The 1712  $\text{cm}^{-1}$  band, which represented the majority of the carbonyl groups in the system, suggested an electrostatic interaction with the sodium cation. When the system was evacuated for 22 hours (Spectrum B, Figure 10), the 1712  $\text{cm}^{-1}$  band was still the most intense, further supporting the fact that the sodium cations had little or no hydration water associated with them. There was a lower frequency band at 1667  $\text{cm}^{-1}$  that developed with continued evacuation. This band represented a stronger ion-dipole interaction than the 1712  $\text{cm}^{-1}$  band. There are a couple of possibilities that might account for this band;

1. Perhaps more than one sodium cation was in close proximity to some of the carbonyl groups, resulting in a much more energetic ion-dipole interaction, and/or
2. Perhaps the dehydration process caused a reorientation of the diethyl succinate molecules that in turn rendered some carbonyl groups more susceptible to a more energetic interaction with neighbouring sodium cations.

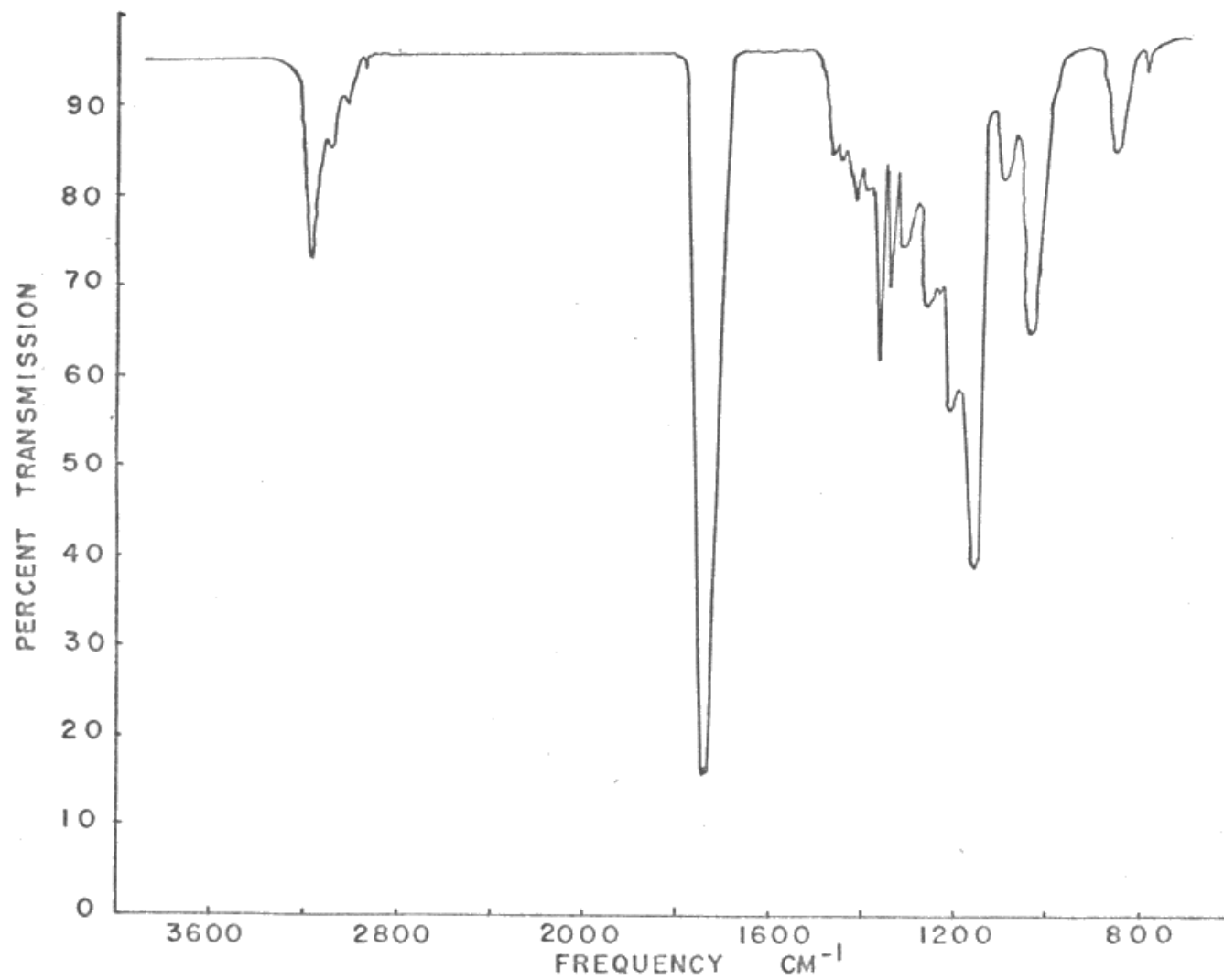
**Figure 10. IR Spectra of the Na-Montmorillonite-Diethyl Succinate System.**

- A. Spectrum of adsorbed diethyl succinate after surface-application.
- B. Spectrum of adsorbed diethyl succinate after evacuation for 22 hours.
- C. Spectrum of adsorbed diethyl succinate after equilibrating at 100 percent relative humidity for 0.5 hours, followed by a brief evacuation to remove surface-adsorbed water droplets.

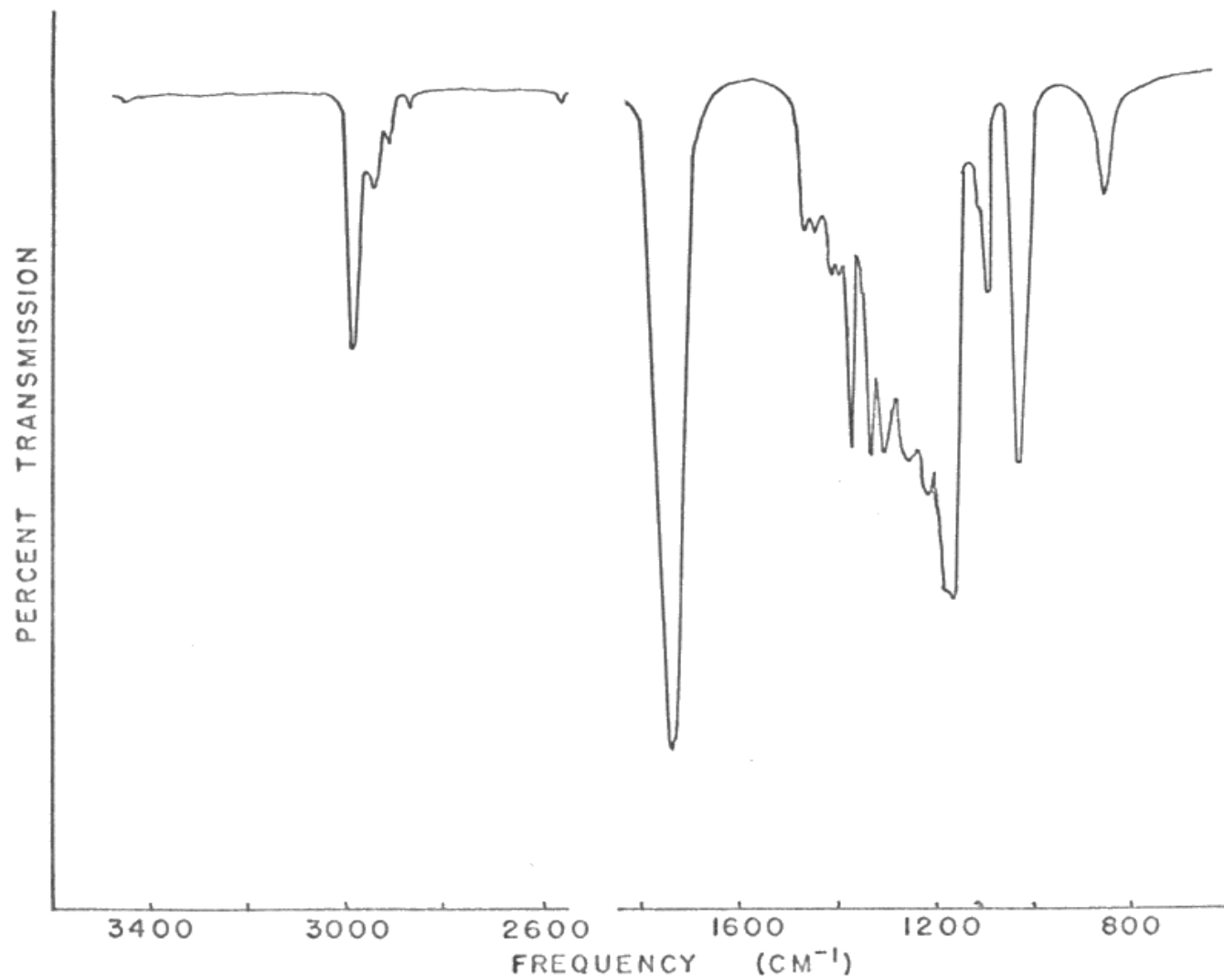




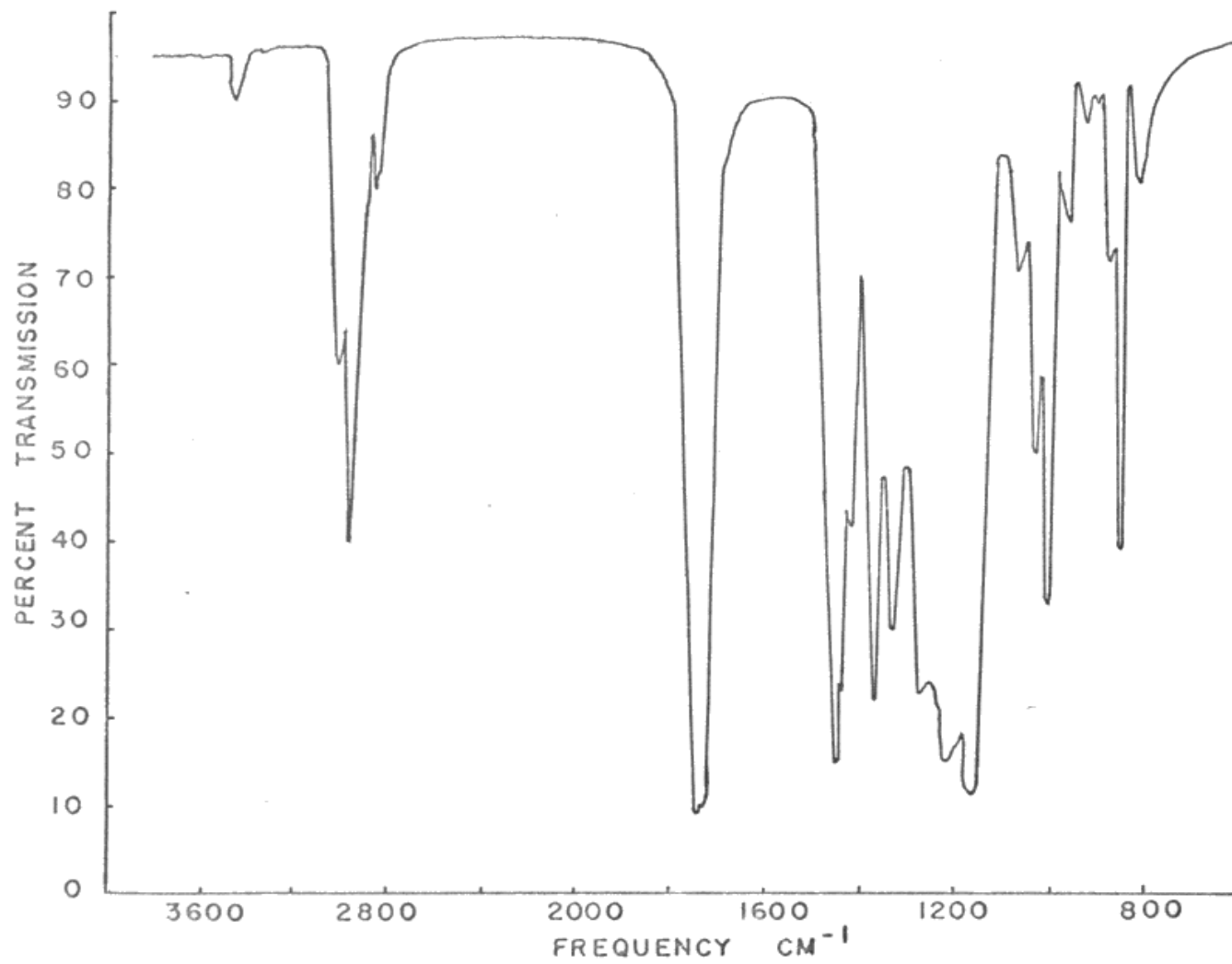
**FIGURE 11. INFRARED SPECTRUM OF MALATHION (Capillary Film)**



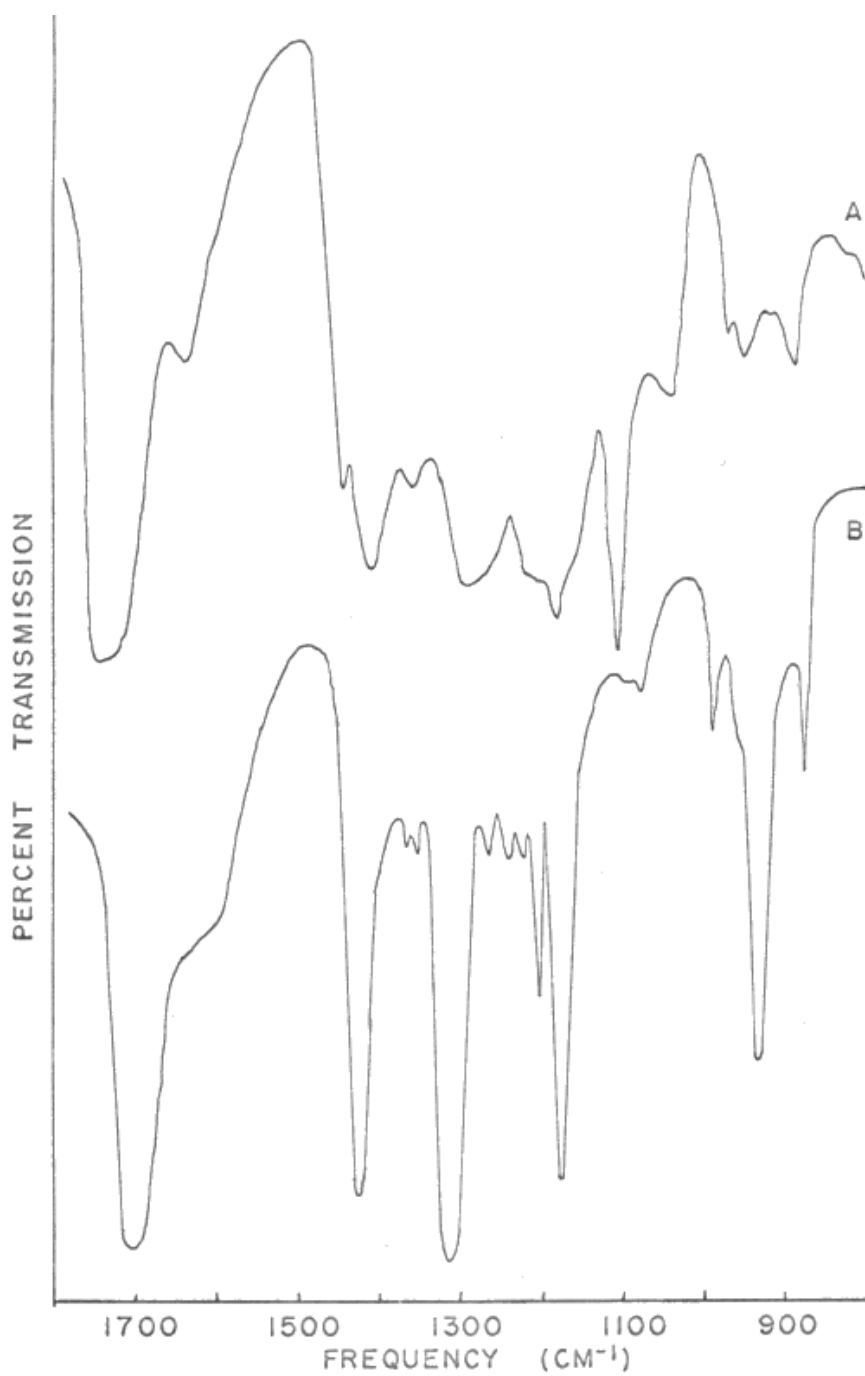
**FIGURE 12. INFRARED SPECTRUM OF DIETHYL SUCCINATE. (Capillary Film)**



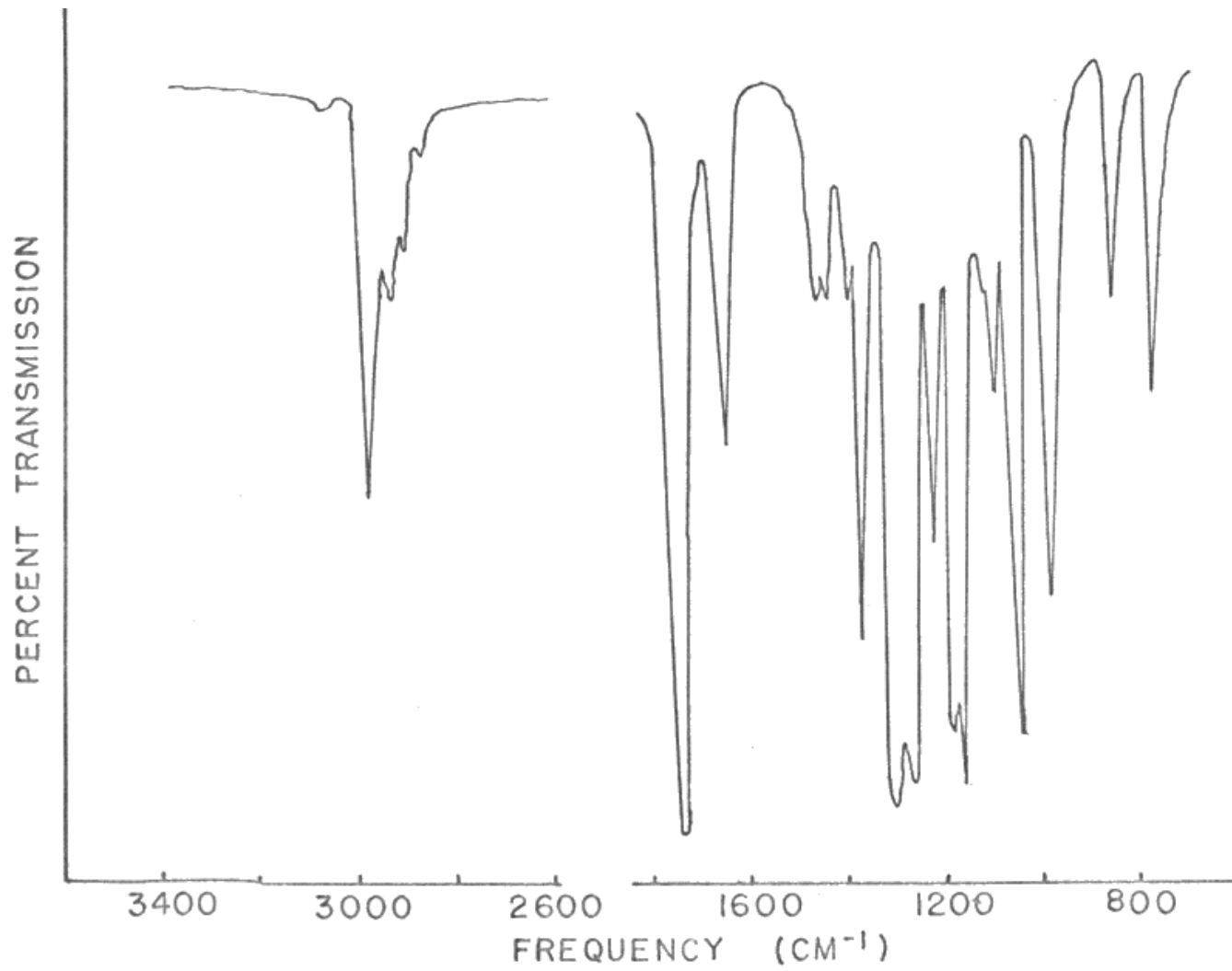
**FIGURE 13. INFRARED SPECTRUM OF DIETHYL MERCAPTOSUCCINATE (Capillary Film)**



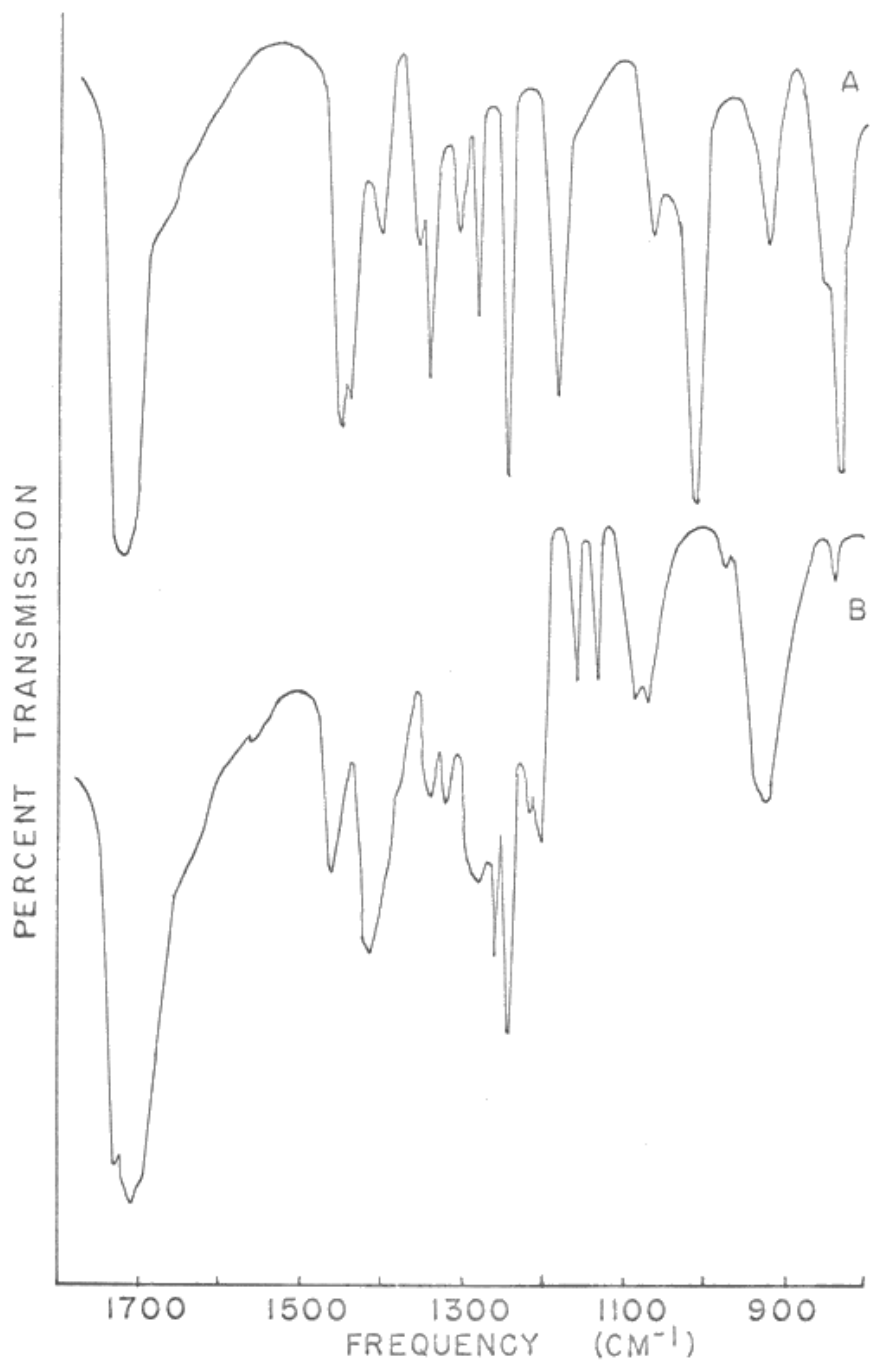
**FIGURE 14. INFRARED SPECTRUM OF DIMETHYL SUCCINATE (Capillary Film)**



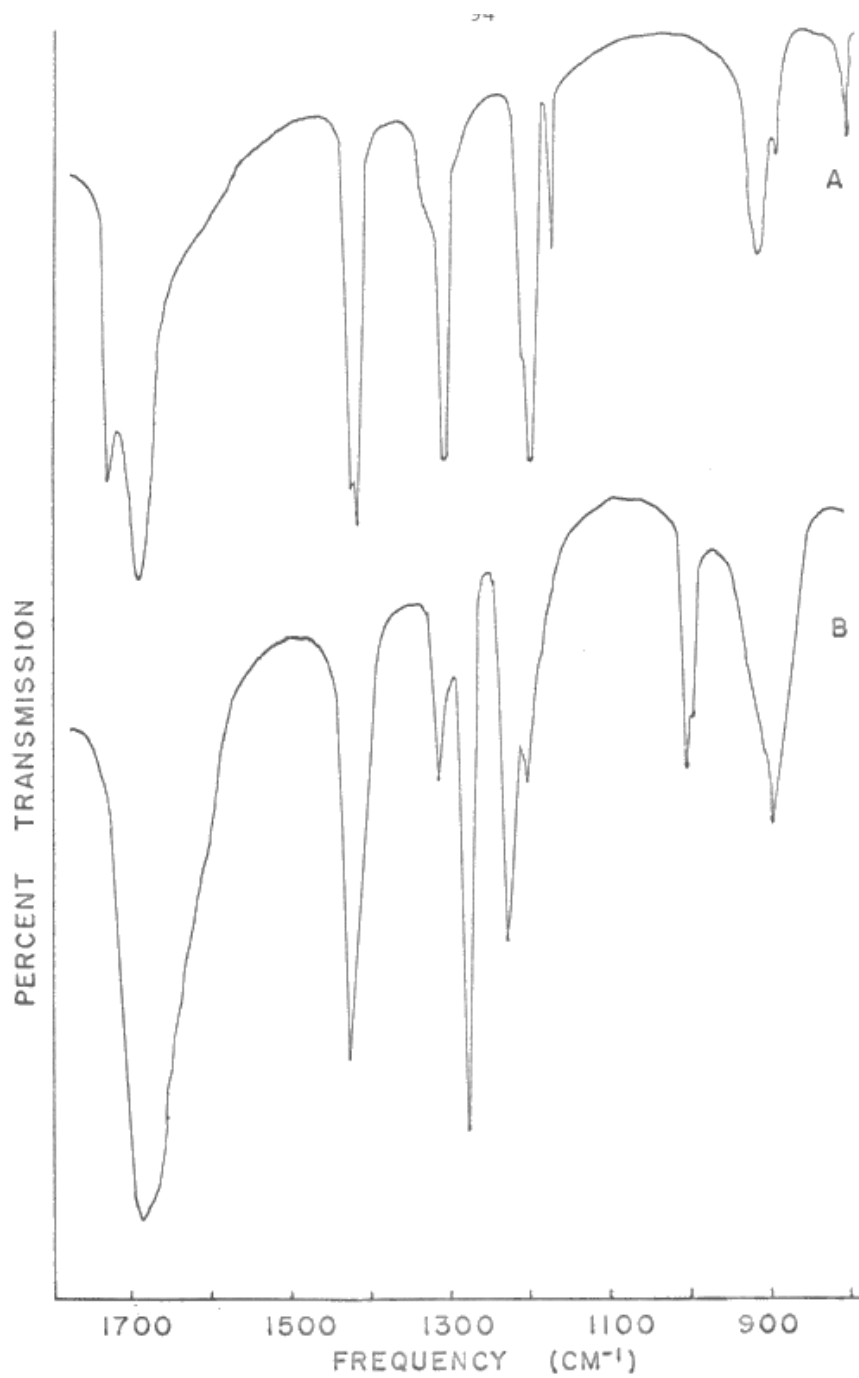
**FIGURE 15. INFRARED SPECTRUM OF;**  
**A. HYDROXYSUCCINIC ACID**  
*(KBr Pellet)*  
**B. MERCAPTOSUCCINIC ACID**



**FIGURE 16. INFRARED SPECTRUM OF DIETHYL FUMARATE.(Capillary Film).**

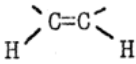

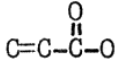
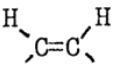


**FIGURE 17. INFRARED SPECTRUM OF ;**  
**A. MALATHION DI-ACID** (KBr Pellet)  
**B. 2,3-DIMETHYL SUCCINIC ACID**

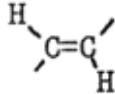
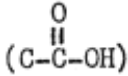


**FIGURE 18. INFRARED SPECTRUM OF;**  
**A. SUCCINIC ACID**  
**B. FUMARIC ACID** (KBr Pellet)


**Table 6. Assignments of Infrared Absorption Frequencies of Diethyl Fumarate and Diethyl Mercaptosuccinate.**

Diethyl Fumarate		Diethyl Mercaptosuccinate	
Frequency(cm <sup>-1</sup> )	Assignment	Frequency(cm <sup>-1</sup> )	Assignment
775		795	
860		860	
980	out of plane 	1030	C-O stretch
1035	C-O stretch	1098	
1095		1165	
1155		1215	
1180		1240	
1225		1260	
1265		1305	
1298		1333	
1370	CH <sub>3</sub> sym. def.	1352	
1395		1375	CH <sub>3</sub> sym. stretch (CH <sub>3</sub> -C)
1450		1397	
1470		1410	
1650		1448	CH <sub>3</sub> asym. stretch
1730	C=O	1468	CH <sub>2</sub> scissors
2880	CH <sub>3</sub> or CH <sub>2</sub> asym. stretch	1740	C=O
2910	CH <sub>2</sub> asym. stretch	2560	
2940	CH <sub>3</sub> asym. stretch	2875	CH <sub>2</sub> asym. stretch
2985	CH <sub>3</sub> asym. stretch	2910	" " "
3080	C-H stretch (-C=C-H)	2940	CH <sub>3</sub> asym. stretch
		2985	" " "
		3450	overtone of C=O

**Table 7. Assignments of Infrared Absorption Frequencies of Succinic Acid and Fumaric Acid.**

Succinic Acid		Fumaric Acid	
Frequency (cm <sup>-1</sup> )	Assignment	Frequency (cm <sup>-1</sup> )	Assignment
805		905	out of plane 
895		1010	
920	C-C stretch	1217	
1178		1233	
1207		1280	C-C stretch 
1312		1432	dimer
1422	dimer	1690	C=O
1428	CH <sub>2</sub> def.		
1695	C=O		
1732			

**Table 8. Assignments of Infrared Absorption Frequencies of Dimethyl Succinate.**

Frequency (cm <sup>-1</sup> )	Assignment
808	
848	
867	
898	
922	
958	
1002	
1030	C-O stretch (  )
1070	
1164	
1220	
1270	
1328	
1365	
1417	
1438	
1442	CH <sub>3</sub> sym. deformation
1745	C=O
2880	CH <sub>3</sub> sym. stretch
2910	CH <sub>2</sub> asym. stretch
2960	CH <sub>3</sub> sym. stretch
3000	
3465	C=O overtone

**Table 9. Assignments of Infrared Absorption frequencies of Malathion Di-acid and 2,3-Dimethyl Succinic Acid.**

Malathion Di-acid		2,3- Dimethyl Succinic Acid	
Frequency (cm <sup>-1</sup> )	Assignment	Frequency (cm <sup>-1</sup> )	Assignment
835		845	
920		931	
1022	C-O Stretch	978	
1062		1070	
1182		1085	
1245		1130	
1278		1156	
1302		1203	
1337		1216	
1350		1243	
1402	OH Deformation (dimer) ?	1258	
1440		1278	
1448		1318	
1720	C=O	1.34	
2660		1415	dimer (OH Def.) ?
2767		1463	
2855	CH <sub>3</sub> sym. stretch (CH <sub>3</sub> -O)	1708	C=O
2955	CH <sub>3</sub> asym. stretch	1729	
3035			

**Table 10. Assignments of Infrared Absorption Frequencies of Malathion and Diethyl Succinate.**

Malathion		Diethyl Succinate	
Frequency (cm <sup>-1</sup> )	Assignment	Frequency	Assignment
820	P-S stretch	795	
838		860	
1015	C-O stretch	1032	C-O stretch
1030	C-O stretch	1098	
1098	$\begin{array}{c} \text{O} \\ \parallel \\ \text{R}-\text{C}-\text{OR} \end{array}$	1160	
1165		1212	
1178		1240	
1210		1265	
1240		1300	
1260		1315	
1303		1349	
1328		1375	CH <sub>3</sub> sym. def.
1350		1395	
1375	CH <sub>3</sub> sym. def. (CH <sub>3</sub> -C)	1415	
1397		1448	CH <sub>3</sub> asym. def. .
1410		1468	CH <sub>2</sub> scissors
1448	CH <sub>3</sub> asym. def.	1480	
1460	CH <sub>2</sub> scissors ?	1740	C=O
1740	C=O	2880	CH <sub>2</sub> asym.stretch
2850	CH <sub>3</sub> sym. stretch (CH <sub>3</sub> -O)	2910	CH <sub>2</sub> " " "
		2940	CH <sub>3</sub> " " "
2880	CH <sub>2</sub> or CH <sub>3</sub> asym. stretch	2985	CH <sub>3</sub> " " "
2910	CH <sub>2</sub> asym. stretch	3460	C=O overtone
2955	CH <sub>3</sub> asym. stretch		
2985	" " "		
3460	C=O overtone		

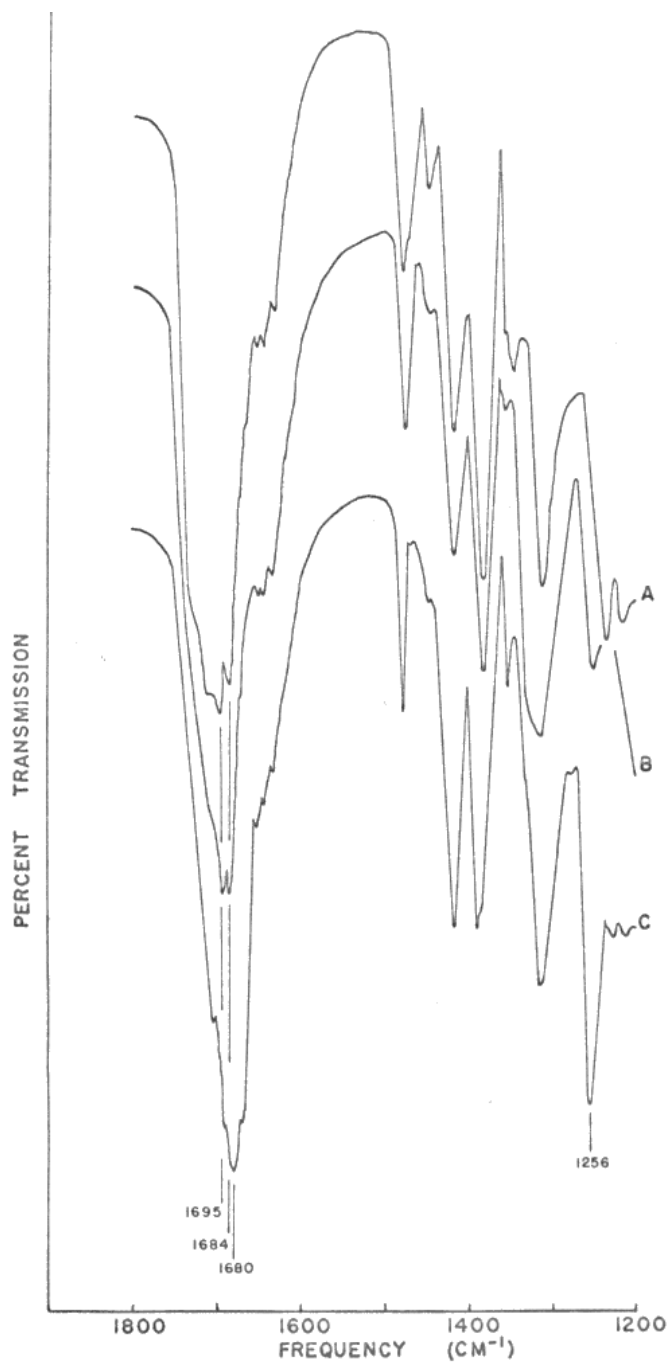
There were two significant changes in the 1300 to 1330  $\text{cm}^{-1}$  region of the spectrum upon adsorption and subsequent dehydration. Upon initial adsorption, the 1300  $\text{cm}^{-1}$  band developed as it did with malathion, but in this case the band was more intense. It appears that diethyl succinate can penetrate the interlayer regions of montmorillonite under drier conditions than was the case for malathion.

The band at 1315  $\text{cm}^{-1}$  (Figure 14, Table 10) disappeared and an intense band at 1328  $\text{cm}^{-1}$  developed (Spectrum A, Figure 10). Upon evacuation for 22 hours, the intensity of the 1328  $\text{cm}^{-1}$  band was greatly reduced (Spectrum B, Figure 10), but upon rehydration (at 100 percent relative humidity for 1/2 hour) the band became very intense (Spectrum C, Figure 10). The assignment of this band is unknown. Perhaps only coincidentally, the band at 1328  $\text{cm}^{-1}$  in malathion always disappeared upon the entry into the interlayer region of montmorillonite. In malathion, the 1300  $\text{cm}^{-1}$  band seemed to be more sensitive to changes in hydration status than the corresponding band of diethyl succinate. It seems apparent that malathion did not break down into diethyl succinate on the Na-montmorillonite because of these bands that seem unique to diethyl succinate.

Spectrum A, Figure 19, is of the Ca-montmorillonite-diethyl succinate system immediately following the application of the diethyl succinate. The position of the hydrogen bonded carbonyl group band at 1695  $\text{cm}^{-1}$  indicated that the diethyl succinate had entered the interlayer region.

**Figure 19. IR Spectra of the Ca-Montmorillonite-Diethyl Succinate System.**

- A. Spectrum following surface application of diethyl succinate.
- B. Spectrum following exposure of the system to 100 percent relative humidity for 10 minutes and a brief evacuation to remove surface-adsorbed water droplets.
- C. Spectrum following evacuation for 1300 minutes.



A 10 minute exposure to water vapor produced a double peaked carbonyl band at 1684 and 1695  $\text{cm}^{-1}$  (Spectrum B, Figure 19). Since the two peaks were of equal intensity, one wonders whether the two carbonyl groups of diethyl succinate were interacting differently, perhaps a result of an orientation effect.

During the hydration process, the two bands that occurred at 1215 and 1242  $\text{cm}^{-1}$  (Spectrum A) gave way to only one band at 1250  $\text{cm}^{-1}$  (Spectrum B). Simultaneously the 1312  $\text{cm}^{-1}$  band became very broad suggesting the presence of another band in the 1330  $\text{cm}^{-1}$  region. After the evacuation and subsequent rehydration periods, a strong band did develop at 1326  $\text{cm}^{-1}$  similar to the 1328  $\text{cm}^{-1}$  band that appeared in the sodium system. No assignment has been suggested for this band.

Upon evacuation of the system for 1300 minutes, the carbonyl group frequency shifted down to 1680  $\text{cm}^{-1}$ , indicative of an ion-dipole interaction (Spectrum C, Figure 19). A very intense band also developed at 1256  $\text{cm}^{-1}$ . A similar band developed in the Ca-montmorillonite-malathion system as 1225  $\text{cm}^{-1}$ , again suggesting that malathion did not break down into diethyl succinate, and furthermore that this peak was not associated with the P-S-C linkage.

The Cu-montmorillonite-diethyl succinate system was studied using the IRTRAN -2 window as a support for the clay film. Spectrum A, Figure 20, shows that a partial hydrogen bonding interaction has occurred. A 25 minute exposure to 100 percent humidity shifted the carbonyl group frequency down to 1695  $\text{cm}^{-1}$ , the same as for the calcium system (Spectrum B,

**Figure 20. IR Spectra of the Cu-Montmorillonite-Diethyl Succinate System.**

- A. Spectrum following surface application of diethyl succinate onto film deposited on IRTRAN- 2 window.
- B. Spectrum following exposure to 100 percent relative humidity for 25 minutes.
- C. Spectrum following evacuation for 1240 minutes.

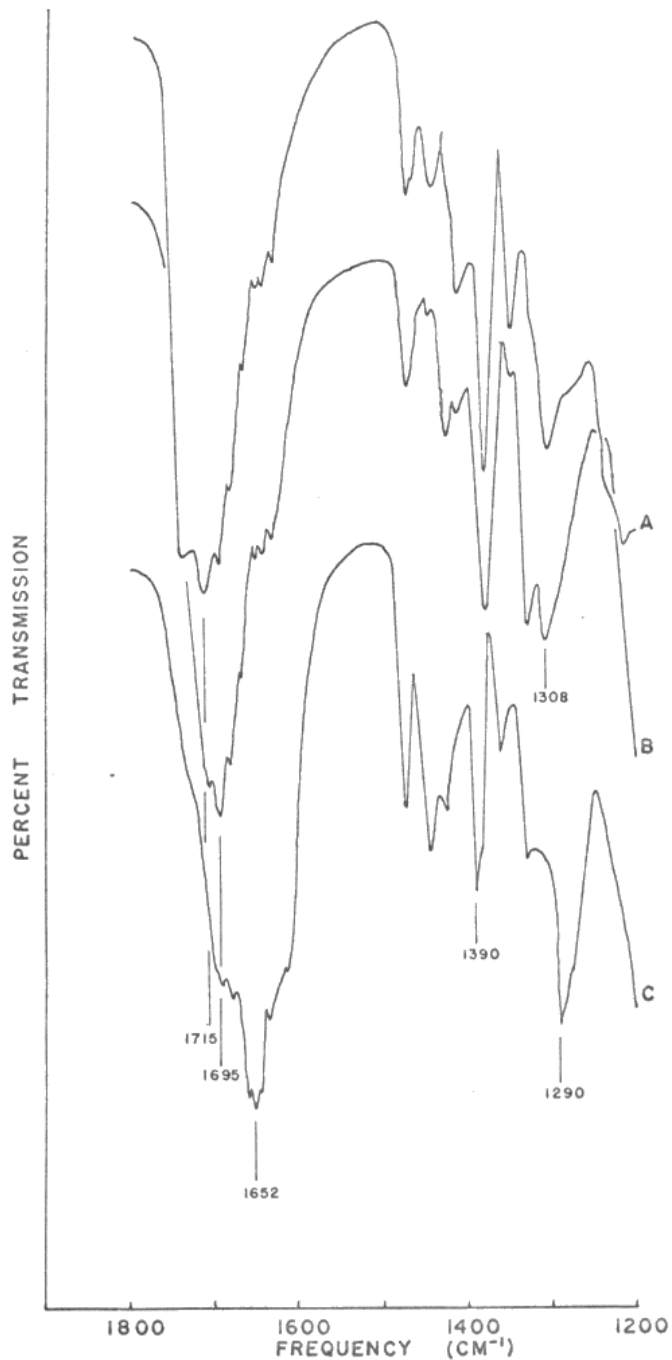


Figure 20). A  $1330\text{ cm}^{-1}$  band developed as a result of the exposure to water vapor. As in the calcium system, this band almost disappeared after evacuating for 1240 minutes (Spectrum C, Figure 20). In addition, the  $1308\text{ cm}^{-1}$  band in Spectrum B, shifted down to  $1290\text{ cm}^{-1}$  in Spectrum C. This is the first system in which the  $1300\text{ cm}^{-1}$  band ever shifted below the  $1300\text{ cm}^{-1}$  position. However upon rehydration, it shifted up to  $1314\text{ cm}^{-1}$ . During the evacuation, the  $\text{CH}_3$  symmetric band at  $1380\text{ cm}^{-1}$ , shifted up to  $1390\text{ cm}^{-1}$ .

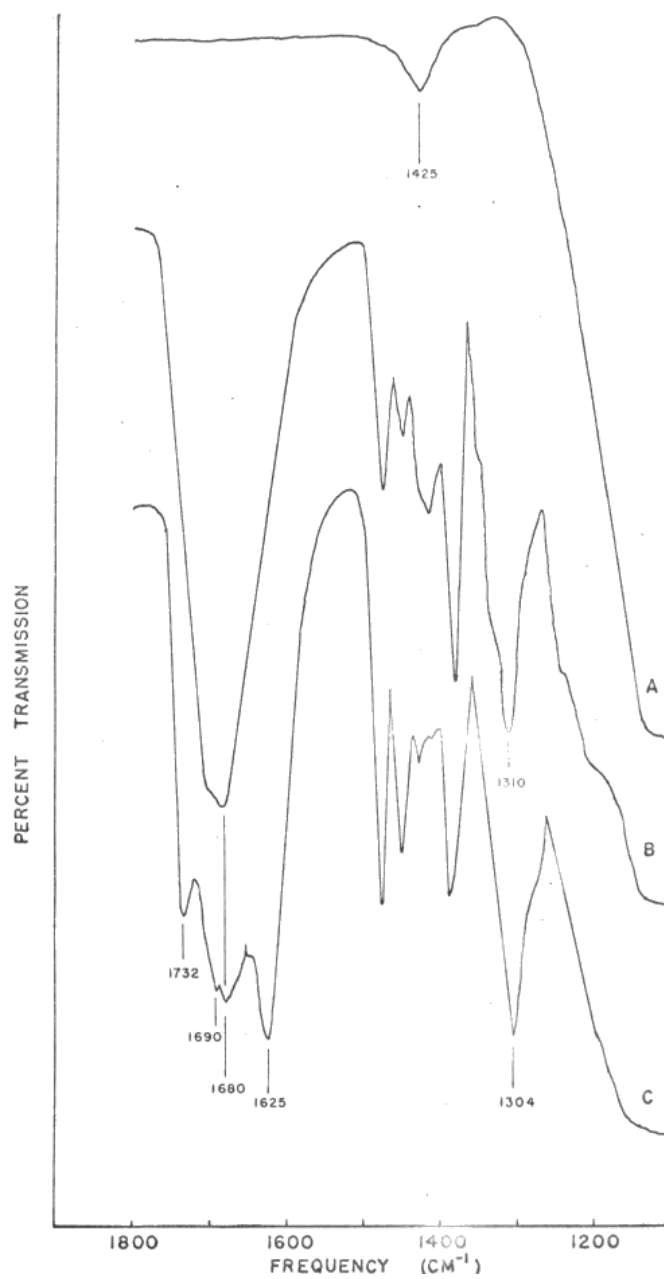
Dehydration for 1240 minutes caused the carbonyl band to shift down to  $1652\text{ cm}^{-1}$  (Spectrum C, Figure 20), about  $28\text{ cm}^{-1}$  more than in the calcium system. In some ways it seems a little unexpected that the hydrogen bonding interactions were of the same energy in both the calcium and copper systems while the ion-dipole interaction in the copper system was more energetic than in the calcium system. Rehydration resulted in the carbonyl band shifting back to  $1695\text{ cm}^{-1}$ .

$\text{D}_2\text{O}$  replaced  $\text{H}_2\text{O}$  for hydrating the Al-montmorillonite-diethyl succinate system in order to avoid the broad  $\text{H}_2\text{O}$  bending deformation band in the  $1600$  to  $1750\text{ cm}^{-1}$  region that would interfere with observations of carbonyl group frequency shifts. Exposure to  $\text{D}_2\text{O}$  vapor for 15 minutes caused the carbonyl band to shift down to  $1680\text{ cm}^{-1}$ , the largest due to hydrogen bonding (in this case deuterium bonding)(Spectrum B, Figure 21).

As in the calcium and copper systems, the  $1310\text{ cm}^{-1}$  band developed and also a weak band at  $1215\text{ cm}^{-1}$ . Evacuation for 120 hours caused the same carbonyl group frequency splitting as previously reported for the Fe- and Al-montmorillonite-malathion systems.

**Figure 21. IR Spectra of the Al-Montmorillonite-Diethyl Succinate System.**

- A. Spectrum of Al-Montmorillonite exposed to D<sub>2</sub>O vapor to remove adsorbed water.
- B. Spectrum following diethyl succinate application, a 15 minute exposure to D<sub>2</sub>O vapor and a slight evacuation to remove surface-adsorbed D<sub>2</sub>O droplets.
- C. Spectrum following evacuation for 120 hours.



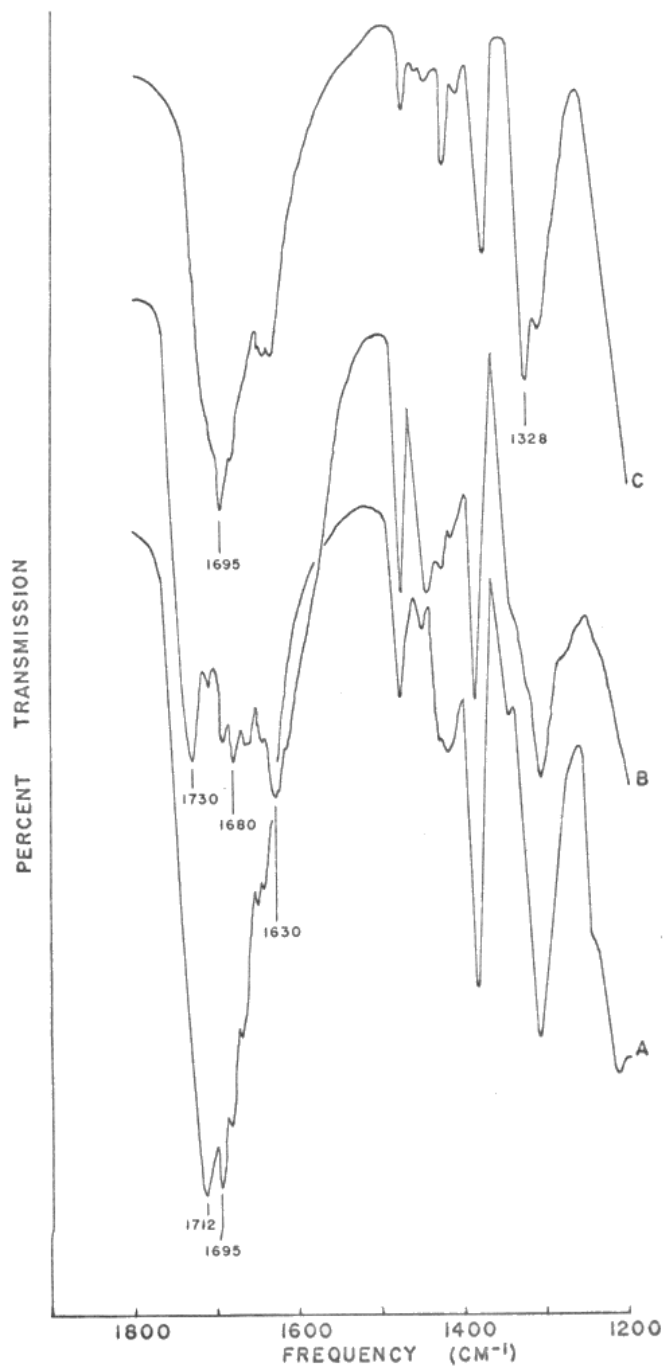
As the evacuation progressed, 1732 and the 1625  $\text{cm}^{-1}$  bands developed at the expense of the 1680  $\text{cm}^{-1}$  band (Spectrum C, Figure 21). This 1625  $\text{cm}^{-1}$  band represented a downward shift of 115  $\text{cm}^{-1}$ , the largest perturbation observed in this study. Such a large perturbation suggests that the carbon-oxygen bond assumed a considerable amount of single bond character. Perhaps if a great deal more time was allowed for evacuation, the 1680  $\text{cm}^{-1}$  band might have further decreased in intensity while the 1625  $\text{cm}^{-1}$  band intensified. The 1732  $\text{cm}^{-1}$  seemed to reach its maximum intensity rather early in the evacuation and then remained constant for the duration of the 120 hour period. It is interesting to note that a 10 minute exposure to  $\text{D}_2\text{O}$  vapor was sufficient to return the carbonyl group frequency to almost the same position as it was in Spectrum B, prior to evacuation.

In the Fe-montmorillonite-diethyl succinate system, an initial exposure to water vapor for 10 minutes shifted the carbonyl band down to 1695 and 1712  $\text{cm}^{-1}$  (Spectrum A, Figure 22). An evacuation period of 23 hours followed by a re-exposure to water vapor succeeded in producing a single carbonyl band at 1695  $\text{cm}^{-1}$ .

The evacuation period (Spectrum B) succeeded in splitting the carbonyl band as reported for the other trivalent systems studied. Again, 1730 and 1630  $\text{cm}^{-1}$  bands were developed at the expense of the 1680  $\text{cm}^{-1}$  region bands (Spectrum B). The many intermediate bands probably occurred because the system was still in the process of being dehydrated. A longer evacuation period would probably have resulted in these bands either shifting to higher or lower frequencies.

**Figure 22. IR Spectra of the Fe-Montmorillonite-Diethyl Succinate System.**

- A. Spectrum following surface application of diethyl succinate and a 10 minute exposure to 100 percent relative humidity. There was a slight evacuation to remove surface-adsorbed water droplets.
- B. Spectrum following an 1190 minute evacuation period.
- C. Spectrum following a 3.5 hour exposure to 100 percent relative humidity and a slight evacuation to remove surface-adsorbed water droplets.



In summary, the following facts were revealed in the study of the montmorillonite-diethyl succinate systems;

1. The hydrogen bonding interaction between the carbonyl oxygens of diethyl succinate and hydration water was always more energetic than for the corresponding montmorillonite-malathion systems. The magnitude of the perturbation increased in the following order;  $\text{Na} < \text{Cu} = \text{Ca} = \text{Fe} < \text{Al}$ . It is believed that the smaller physical size of the diethyl succinate molecule allowed it to more intimately interact with hydration water molecules. Furthermore, it was noted that upon dehydration, the perturbation was generally greater for the diethyl succinate than it was for malathion.
2. A comparison of the intensity of the water deformation band in the  $1630 \text{ cm}^{-1}$  region before and after adsorption of diethyl succinate showed that it was markedly less following adsorption of the diethyl succinate. This would suggest that water had been displaced during the adsorption process, Presumably this would be bulk water physically adsorbed to the interlayer surfaces. Although not previously discussed, the same phenomenon was noted following malathion adsorption onto the various montmorillonite systems.
3. Hydration and dehydration caused some very startling reversible changes in both intensity and in position of several bands in the  $1200$  to  $1475 \text{ cm}^{-1}$  region. The total effect is probably a combination of a four-way interaction between diethyl succinate molecules, water, saturating cations and the interlayer surfaces that result in altering the

configuration and/or orientation of adsorbed diethyl succinate molecules. These changes seemed to be greater than those observed for malathion under similar conditions.

4. Although the  $1310\text{ cm}^{-1}$  region band developed in both adsorbed malathion and adsorbed diethyl succinate systems, its intensity seemed more sensitive to hydration changes in the malathion systems. Another absorption band was believed to occur in the  $1270$  to  $1290\text{ cm}^{-1}$  region and when it shifted up and down, it caused apparent intensity changes in the  $1300\text{ cm}^{-1}$  band.
5. Since the intensity of the C-H stretching bands of diethyl succinate remained relatively constant during the course of the experiments, it was concluded that hydrolysis of the ethyl ester linkages were insignificant. There are essentially no other points of cleavage in the diethyl succinate molecule. One must conclude that all of the band perturbations noted were not due to degradation but only to orientation and interaction effects. Since several of these perturbations were common to the adsorbed malathion systems, it seems to follow that the band perturbations of adsorbed malathion were also a result of orientation and interactions, not degradation.

g) Montmorillonite-Diethyl Mercaptosuccinate Systems.

The main objective of studying diethyl mercaptosuccinate adsorption was to discover whether the changes in the spectrum of adsorbed malathion could be ascribed to its degradation into diethyl mercaptosuccinate.

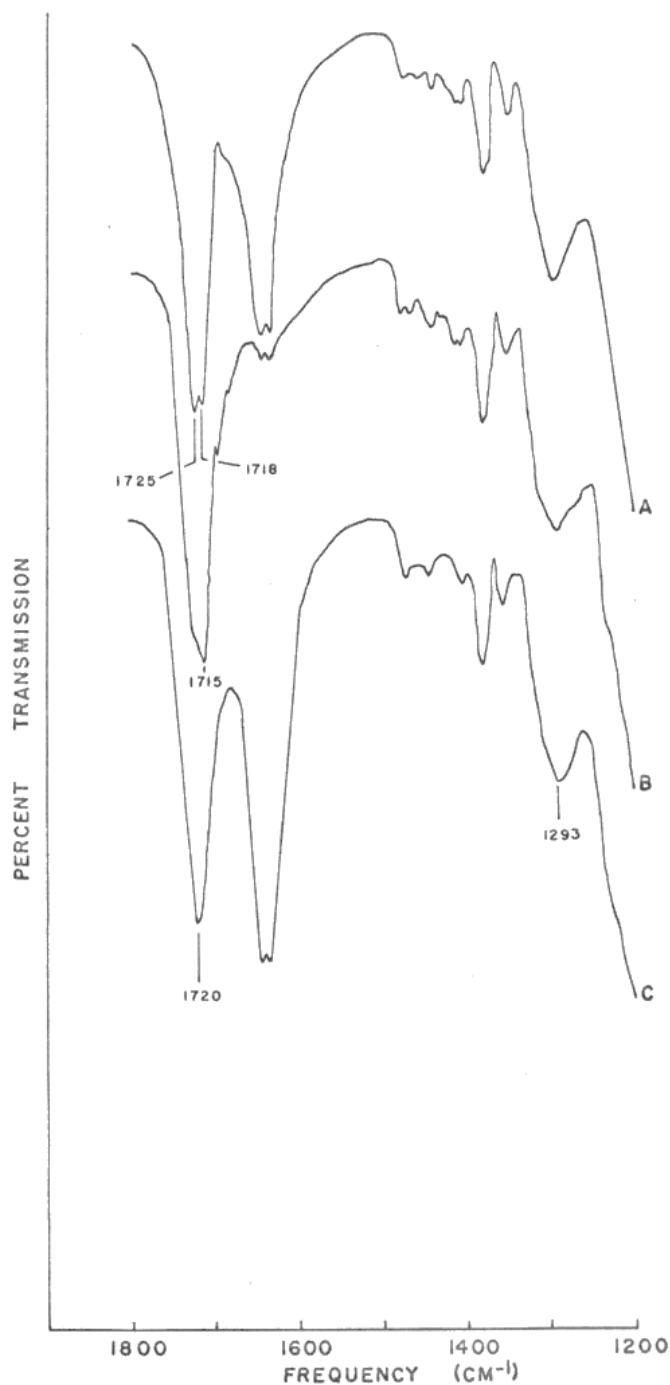
Spectrum A, Figure 23, shows the spectrum of diethyl mercaptosuccinate adsorbed onto Na-montmorillonite after a 10 minute exposure to 100 percent relative humidity. The carbonyl group frequency had shifted down to form a doublet at 1725 and 1718  $\text{cm}^{-1}$ , ascribed to hydrogen bonding interactions. One might speculate that the 1718  $\text{cm}^{-1}$  was a result of displacement of the limited amount of hydration water from some of the sodium cations during the adsorption of diethyl mercaptosuccinate molecules. Spectrum B showed that upon evacuation for 870 minutes, the doublet consolidated into a single band at 1715  $\text{cm}^{-1}$ . The band would be ascribed to an ion-dipole interaction between the carbonyl oxygens and sodium cations. It is interesting to note that upon rehydration for two hours, the carbonyl band shifted up to form a single band at 1720  $\text{cm}^{-1}$  (Spectrum C, Figure 23) .

It is possible that the doublet observed in Spectrum A could have been a result of a somewhat unstable orientation pattern established upon initial entry of the water vapor. Upon dehydration, this orientation pattern may have been forced into a more stable pattern, which upon rehydration provided the usual single band due to hydrogen bonding.

The band at 1300  $\text{cm}^{-1}$  apparently disappeared and a more intense band at 1293  $\text{cm}^{-1}$  developed as soon as water vapor was introduced (Spectrum A, Figure 23). The band similar to this in the montmorillonite-malathion systems never occurred below 1300  $\text{cm}^{-1}$ , perhaps another fact against malathion degradation on the interlayer surfaces.

Figure 23. IR Spectra of the Na-Montmorillonite-Diethyl Mercaptosuccinate System.

- A. Spectrum following surface application of diethyl mercaptosuccinate and a 10 minute exposure to 100 percent relative humidity. (Slight evacuation to remove surface-adsorbed water droplets.)
- B. Spectrum following an 870 minute evacuation period.
- C. Spectrum following a 2 hour exposure to 100 percent relative humidity and a slight evacuation to remove surface-adsorbed water droplets.



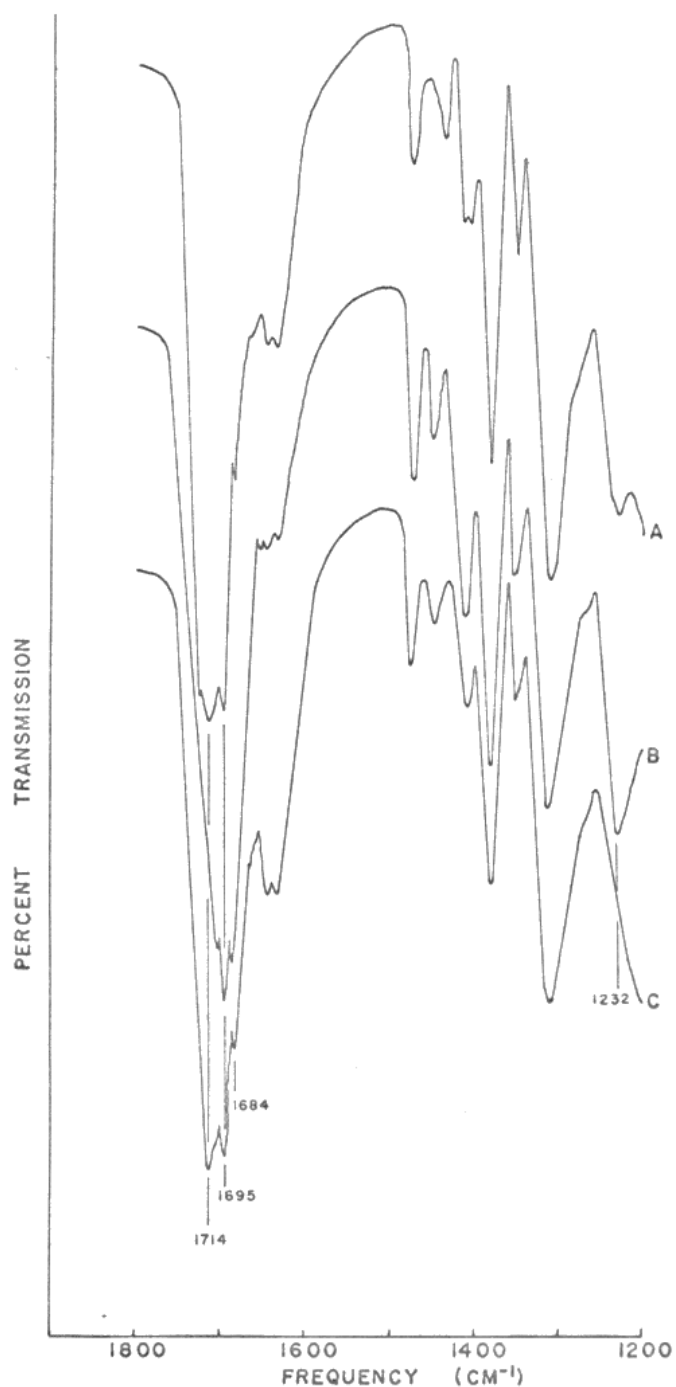
As previously noted, during malathion and diethyl succinate adsorption onto montmorillonite, the water deformation band decreased considerably in intensity upon adsorption of diethyl mercaptosuccinate. Interlayer bulk water was probably displaced during the entry of the diethyl mercaptosuccinate molecules.

Spectrum A, Figure 24, is of diethyl mercaptosuccinate adsorbed onto Ca-montmorillonite after a 40 minute exposure to 100 percent relative humidity. As in the sodium system, the hydrogen bonded carbonyl group frequency split into more than one band at 1714 and 1695  $\text{cm}^{-1}$  with a small spike shoulder at 1725  $\text{cm}^{-1}$ . Evacuation for 1350 minutes (Spectrum B) centered the band at 1695  $\text{cm}^{-1}$ , with small shoulders at 1707 and 1684  $\text{cm}^{-1}$ . Rehydration of the system shifted the bands back to 1714 and 1695  $\text{cm}^{-1}$ . At this point, these multiplex bands could be ascribed to 1) the carbonyl groups of diethyl mercaptosuccinate interacting to different extents, or 2) different cation hydration states existing simultaneously allowing for different degrees of interaction between the carbonyl oxygens and the saturating cations.

There was a band at 1230  $\text{cm}^{-1}$  in Spectrum A which upon evacuation shifted to 1232  $\text{cm}^{-1}$  (Spectrum B) and intensified considerably. Upon rehydration (Spectrum C), the band disappeared. A subsequent evacuation (not shown herein) resulted in the development of two small bands at 1220 and 1250  $\text{cm}^{-1}$ . Such behavior suggests changes in orientation of the adsorbed diethyl mercaptosuccinate. The spectrum of malathion adsorbed onto Ca-montmorillonite (Figure 5) had an absorption band at approximately 1215  $\text{cm}^{-1}$  which shifted up to 1227  $\text{cm}^{-1}$  upon evacuation. The calcium system was the only one of the five systems where adsorbed

Figure 24. IR Spectra of the Ca-Montmorillonite-Diethyl Mercaptosuccinate System.

- A. Spectrum following surface application of diethyl mercaptosuccinate and a 35 minute exposure to 100 percent relative humidity (slight evacuation to remove surface-adsorbed water droplets),
- B. Spectrum following a 1350 minute evacuation period.
- C. Spectrum following a 30 minute exposure to 100 percent relative humidity and a slight evacuation to remove surface-adsorbed water droplets.



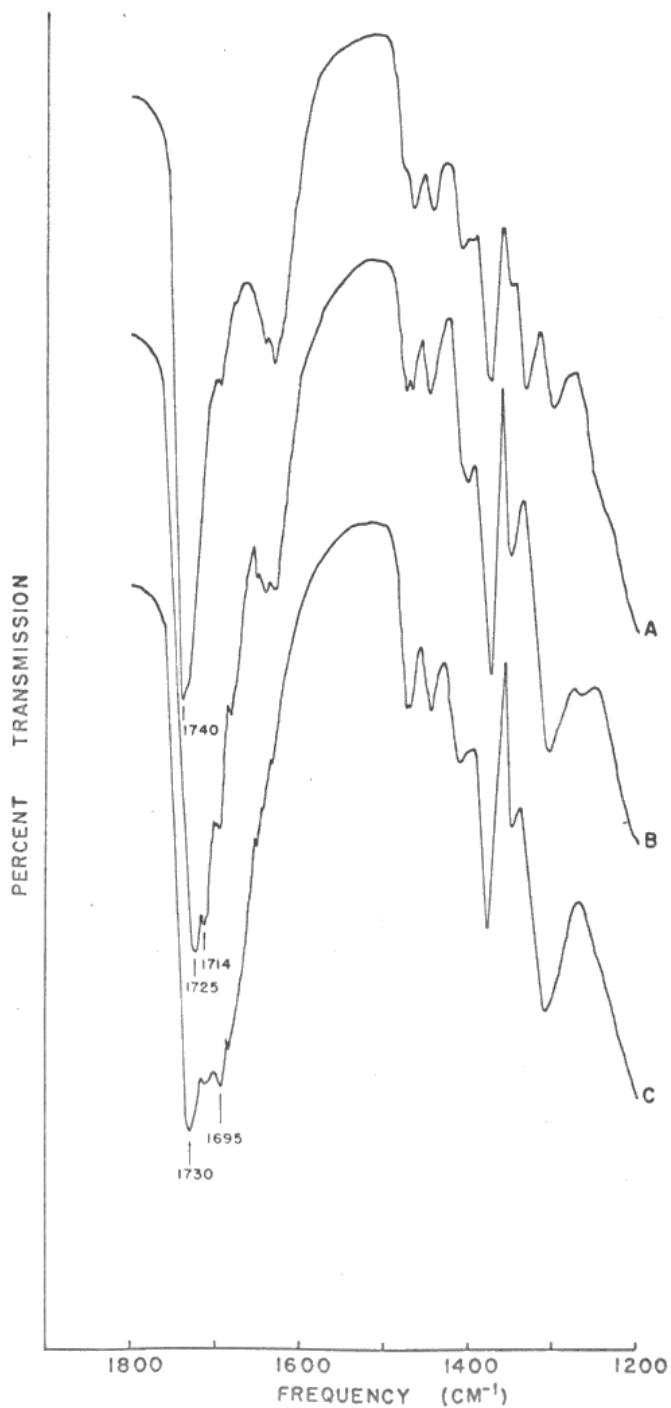
malathion produced this band. The band for adsorbed malathion was different than that for adsorbed diethyl mercaptosuccinate, suggesting that malathion was not degraded into diethyl mercaptosuccinate.

Spectrum A, Figure 25, is of diethyl mercaptosuccinate adsorbed onto Cu-montmorillonite sedimented on a IRTRAN -2 window. Since the film *was* dry, there was no interaction between the clay and the diethyl mercaptosuccinate. After a 2.5 hour exposure to 100 percent relative humidity (Spectrum B), the carbonyl group hydrogen bonded to the hydration water producing a doublet at 1725 and 1714  $\text{cm}^{-1}$ . This was very similar to that of adsorbed malathion. Evacuation for 19 hours resulted in the formation of a multipeak band (1730, 1695, 1683  $\text{cm}^{-1}$ )(Spectrum C), somewhat resembling that of adsorbed malathion (Spectrum D, Figure 6). Although there seemed to be quite a bit in common between the carbonyl absorption bands of malathion and diethyl mercaptosuccinate adsorbed on Cu-montmorillonite, there were marked differences in the relative intensities of the bands in the 1400 and 1475  $\text{cm}^{-1}$  region.

Spectrum A, Figure 26, is of diethyl mercaptosuccinate adsorbed onto Al-montmorillonite and equilibrated at 100 percent relative humidity for one hour. The main carbonyl band shifted down to 1710  $\text{cm}^{-1}$ , the same position assumed by the hydrogen bonded carbonyl groups of malathion. There was also a secondary band at 1695  $\text{cm}^{-1}$ . Upon evacuation for approximately 24 hours, a small band at 1725 and several bands in the 1635 and 1660  $\text{cm}^{-1}$  region developed.

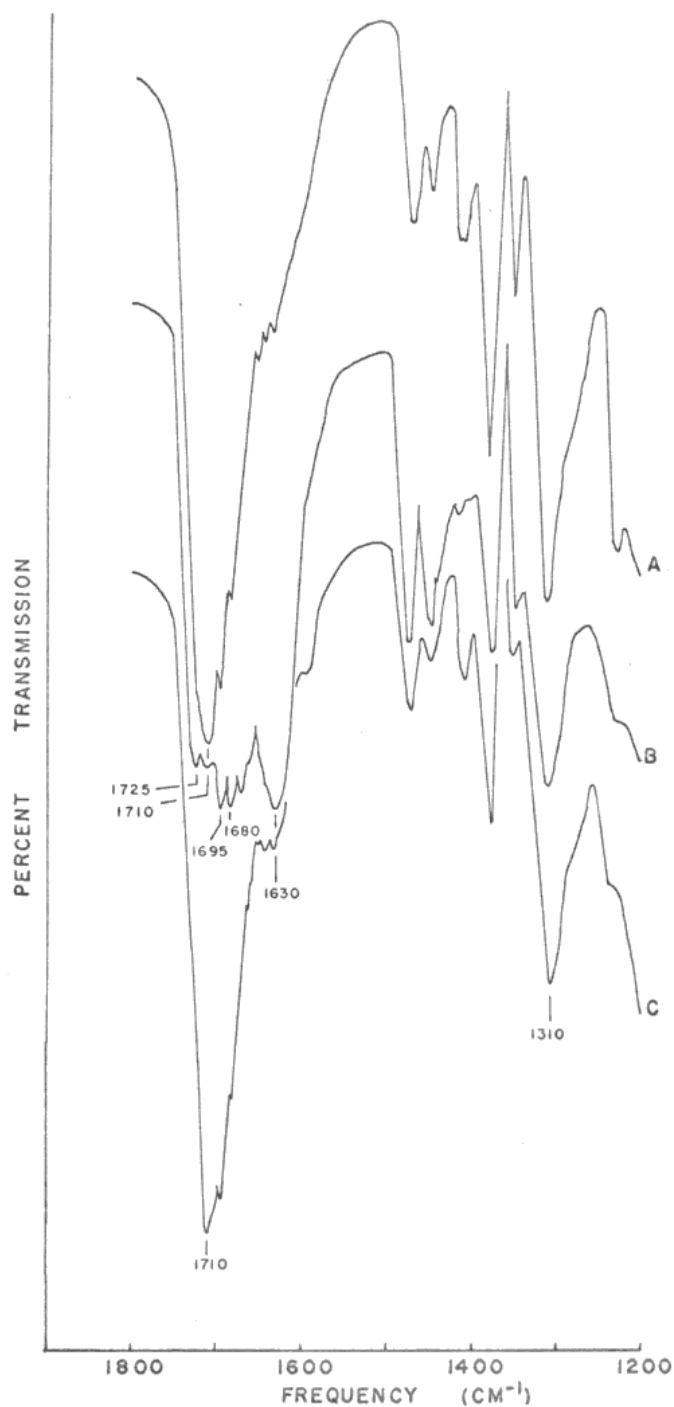
**Figure 25. IR Spectra of the Cu-Montmorillonite-Diethyl Mercaptosuccinate System.**

- A. Spectrum following surface application of diethyl mercaptosuccinate onto the clay film deposited on an IRTRAN-2 window.
- B. Spectrum following a 2.5 hour exposure to 100 percent relative humidity and a slight evacuation to remove surface-adsorbed water droplets.
- C. Spectrum following a 19 hour evacuation period.



**Figure 26. IR Spectra of the Al-Montmorillonite-Diethyl Mercaptosuccinate System.**

- A. Spectrum of adsorbed diethyl mercaptosuccinate after equilibrating at 100 percent relative humidity for one hour, followed by a brief evacuation to remove surface-adsorbed water droplets.
- B. Spectrum of adsorbed diethyl mercaptosuccinate after evacuating for 110 hours.
- C. Spectrum of adsorbed diethyl mercaptosuccinate after re-exposure to 100 percent relative humidity for 0.5 hours, followed by a brief evacuation to remove surface-adsorbed water droplets.



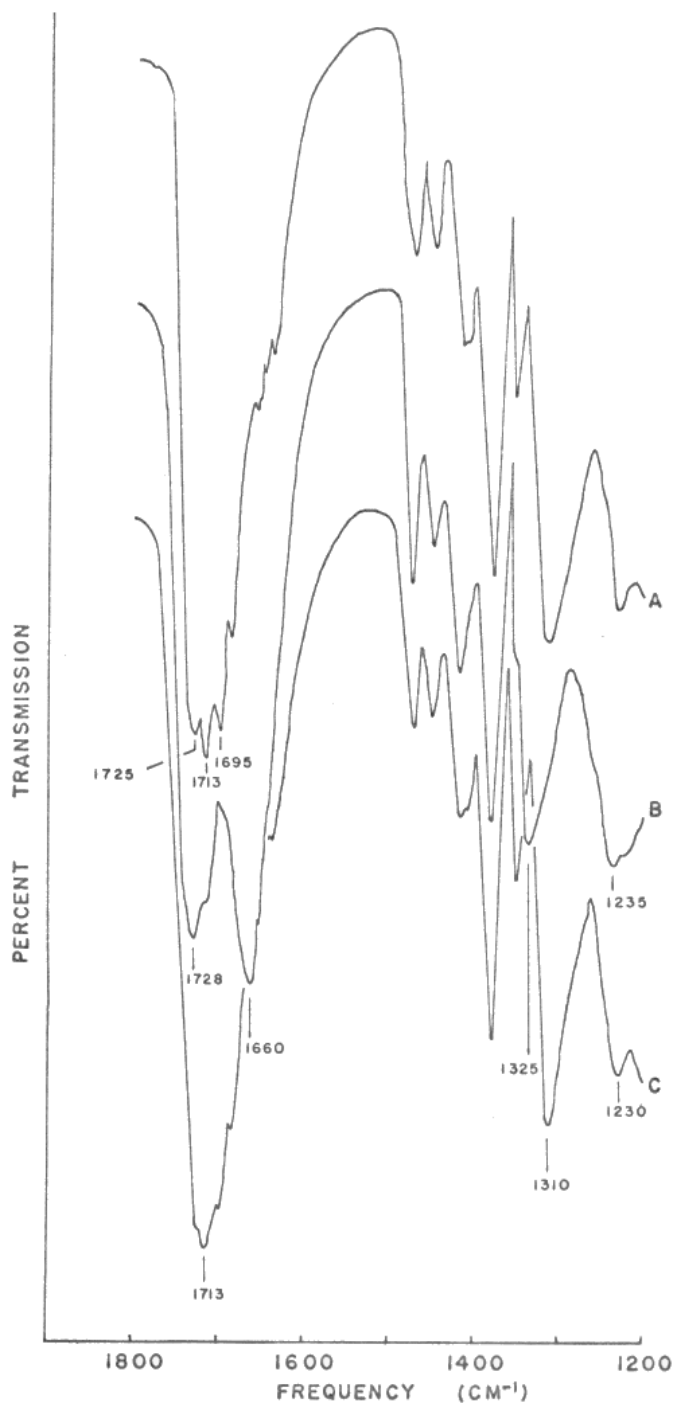
Therefore an extended evacuation of 110 hours was carried out and then scanned (Spectrum B, Figure 26). During this time the  $1725\text{ cm}^{-1}$  band intensified slightly while the  $1630\text{ cm}^{-1}$  band greatly intensified at the expense of the  $1695\text{ cm}^{-1}$  band. This splitting was similar to that reported for both the Al- and Fe-montmorillonite-malathion and Al- and Fe-montmorillonite-diethyl succinate systems. In the Al-montmorillonite-malathion system, the high frequency ( $1740\text{ cm}^{-1}$ ) band became relatively more intense than for the analogous situation for diethyl mercaptosuccinate. There is no apparent reason for this difference. Upon rehydration (Spectrum C, Figure 26) the carbonyl group frequency returned to the same position as it had in Spectrum A.

As in the copper system, there were differences in relative intensity of the 1400 to 1475  $\text{cm}^{-1}$  absorption bands between adsorbed malathion and diethyl mercaptosuccinate. The  $1230\text{ cm}^{-1}$  band (same as for Ca-montmorillonite) was also present in this system but not in the Al-montmorillonite-malathion system.

Spectrum A, Figure 27, is of diethyl mercaptosuccinate adsorbed on Fe-montmorillonite and equilibrated at 100 percent relative humidity for 25 minutes. The hydrogen bonded carbonyl occurred at  $1713\text{ cm}^{-1}$  with secondary bands at  $1725$  and  $1695\text{ cm}^{-1}$ . Upon evacuation for 1130 minutes (Spectrum B), the carbonyl band split into two intense bands at  $1728$  and  $1660\text{ cm}^{-1}$ . This splitting was more quickly achieved and was more distinct than that in the Fe-montmorillonite-malathion system. A 15 minute exposure to 100 percent relative humidity (Spectrum C, Figure 27) essentially returned the carbonyl band to the same position as

**Figure 27. IR Spectra of the Fe-Montmorillonite-Diethyl Mercaptosuccinate System.**

- A. Spectrum following surface application of diethyl mercaptosuccinate, a 25 minute exposure to 100 percent relative humidity and a slight evacuation to remove surface-adsorbed water droplets.
- B. Spectrum following an 1130 minute evacuation period.
- C. Spectrum following a 15 minute exposure to 100 percent relative humidity, and a slight evacuation to remove surface-adsorbed water droplets.



in Spectrum A.

In summary, there were definite similarities between the spectra of adsorbed diethyl mercaptosuccinate and adsorbed malathion on the various montmorillonite systems. However, with each of the five clay systems, there were some distinct differences between the spectra of the two compounds, especially in the relative intensity of bands in the 1400 to 1475  $\text{cm}^{-1}$  region, and in the calcium system, differences in the intensity of the band in the 1215 to 1230  $\text{cm}^{-1}$ . Because of the very marked shifts in the absorption bands of both adsorbed compounds, it was difficult to positively state that no malathion degradation occurred. However most of the shifts were easily reversed by changing the hydration status of the system. These types of frequency shifts were more typical of orientation and interaction effects than they were of degradation reactions.

h) Kaolinite-Malathion Systems.

The five cation-kaolinite-malathion systems were studied in two ways; 1) by sedimenting 10 mg. of kaolinite onto an IRTRAN-2 window and then surface-applying malathion with a syringe needle, or 2) by adding 2 or 10  $\mu\text{l}$ . of malathion to a 10 mg. clay-water suspension and subsequently sedimenting it on an IRTRAN-2 window.

Results from the five systems were quite similar and will be discussed together. Because of the very much lower capacity of kaolinite to interact with malathion (as compared to the montmorillonite system), surface application of malathion was an unsatisfactory technique owing to the relatively large amounts applied. In all cases where malathion was surface applied, there were no significant changes in the spectrum.

Even the 10  $\mu\text{l}$ . additions of malathion to the clay suspension exceeded the capacity of the kaolinite to interact with the carbonyl groups. With the 2  $\mu\text{l}$ . addition of malathion it became apparent that there was a weak interaction between the carbonyl groups and the kaolinite exterior surfaces. A small shoulder developed in the 1710 to 1730  $\text{cm}^{-1}$  region, indicating a hydrogen bonding interaction with hydrated cations on the edge of the lattice, Exposure to water vapor tended to slightly intensify this shoulder in relation to the main carbonyl peak that occurred in the 1730 to 1740  $\text{cm}^{-1}$ . It was difficult to accurately observe the exact band positions because of the poor resolution at such low intensities.

It was observed that the intense 1300  $\text{cm}^{-1}$  band did not develop and that the 1325  $\text{cm}^{-1}$  band did not disappear upon the introduction of water vapor as was the case in the montmorillonite systems. This would suggest that these changes in the montmorillonite-malathion systems were not a result of a direct interaction between the bulk water molecules and the carbonyl groups of malathion, but instead must have been associated with the entry of malathion into the interlayer region of montmorillonite.

#### B. X-ray Diffraction Studies.

The primary objective of the x-ray diffraction studies was to determine whether malathion could penetrate the interlayer region of montmorillonite at low relative humidities. The infrared spectroscopy studies suggested that the relative humidity must exceed 30 to 40 percent before

malathion would enter since very little hydrogen bonding of the carbonyl group occurred below this relative humidity range.

With all five clay systems that were kept dry before and after the surface application of malathion, the d spacing remained constant at a value very near that of the dry clay alone (Tables 11, 12 and 13). Therefore malathion did not penetrate the interlayer region of the clay. Unfortunately the x-ray diffraction apparatus was not designed to easily regulate the relative humidity of the slide and therefore no data (other than the infrared data for the Cu system) is available on the minimum relative humidity at which penetration occurred.

In all five systems, there was a difference in d spacing depending on whether malathion was added to a clay suspension and dried or applied to the dry clay, followed by exposure to 100 percent relative humidity, then dried. There are several possible explanations for these different results;

- 1) In the system where malathion was added to the dried clay, perhaps insufficient water vapor entered the interlayer space with the malathion to completely hydrate the saturating cation and separate the lattice sheets. In the clay suspension system, the expansion of the lattice layers would have been somewhat greater, thus possibly permitting a different spatial arrangement of the malathion that did not allow the lattice to collapse as much as the drier system.

**Table 11. X-ray Diffraction Data for the Na- and Ca-Montmorillonite-Malathion Systems.**

System	Treatment*	d Spacing (Å)
Na-Mont.	dried over P <sub>2</sub> O <sub>5</sub> + N <sub>2</sub>	9.81
Na-Mont.+Malathion <sup>1</sup>	" " " "	9.81
	@ 100% R.H. for 22 hr.	16.35 (weak) 12.6 (strong)
	dried over P <sub>2</sub> O <sub>5</sub> + N	15.77 (strong) 1015 (weak)
	@ 100% R.H. for 1/2 hr.	16.35 (strong) 12.6 (weak)
	dried over P <sub>2</sub> O <sub>5</sub> + N for 3 hr.	16.05 (strong) 10.15 (weak)
Na-Mont.-Malathion <sup>2</sup>	air dried	16.51
	dried over P <sub>2</sub> O <sub>5</sub> + N	16.3
Ca-Mont.	dried over P <sub>2</sub> O <sub>5</sub> + N <sub>2</sub>	11.78
Ca-Mont.+ Malathion <sup>1</sup>	" " " "	11.78
	@ 50% R.H. for 12 hr.	15.91
Ca-Mont.-Malathion <sup>2</sup>	air dried	16.66
	dried over P <sub>2</sub> O <sub>5</sub> + N	16.05

<sup>1</sup> Malathion was surface applied to dried montmorillonite slide.

<sup>2</sup> Malathion (10 µl.) was added to the montmorillonite suspension (10 mg.) and then dried.

\* Treatments listed under each system were carried out successively.

**Table 12. X-ray Diffraction Data for the Cu- and Fe-Montmorillonite-Malathion Systems.**

System	Treatment*	d Spacing (Å)
Cu-Mont.	dried over P <sub>2</sub> O <sub>5</sub> + N <sub>2</sub>	12.0
Cu-Mont.+ Malathion <sup>1</sup>	" " " "	12.0
	100% R.H. for 1 hr.	16.5
	over P <sub>2</sub> O <sub>5</sub> + N <sub>2</sub> for 5 hr.	16.0 (strong) 12.2 (weak)
Cu-Mont.-Malathion <sup>2</sup>	air-dried	16.8
	dried over P <sub>2</sub> O <sub>5</sub> + N	16.35
Fe-Mont.	dried over P <sub>2</sub> O <sub>5</sub> + N <sub>2</sub>	11.0
Fe-Mont.+ Malathion <sup>1</sup>	" " " "	10.8
	@ 100% R.H. for 1 hr.	16.35
	over P <sub>2</sub> O <sub>5</sub> + N <sub>2</sub> for 22 hr.	15.5
Fe-Mont.-Malathion <sup>2</sup>	air-dried	16.5
	dried over P <sub>2</sub> O <sub>5</sub> + N	16.35

<sup>1</sup> Malathion was surface applied to dried montmorillonite slide.

<sup>2</sup> Malathion (10 µl.) was added to the montmorillonite suspension (10 mg.) and then dried.

\* Treatments listed under each system were carried out successively.

**Table 13. X-ray Diffraction Data for the Al-Montmorillonite-Malathion system.**

System	Treatment*	d Spacing (Å)
Al-Mont.	dried over P <sub>2</sub> O <sub>5</sub> + N <sub>2</sub>	12.6
Al-Mont.+Malathion <sup>1</sup>	" " " "	12.6
	100% R.H. for 1 hr.	16.5
	dried over P <sub>2</sub> O <sub>5</sub> + N <sub>2</sub> for 5 hr.	16.0
Al-Mont.-Malathion <sup>2</sup>	air-dried	16.5
	dried over P <sub>2</sub> O <sub>5</sub> + N <sub>2</sub> for 24. hr.	16.2

<sup>1</sup> Malathion was surface applied to dried montmorillonite slide.

<sup>2</sup> Malathion (10 µl.) was added to the montmorillonite suspension (10 mg.) and then dried.

\* Treatments listed under each system were carried out successively.

- 2) Perhaps these differences in d spacing between the two systems only reflect differences in rates of attaining the same equilibrium position. For example, the system in which malathion was added to the suspension was more highly hydrated and may have required a much longer time to attain an equilibrium d spacing over  $P_2O_5$  than did the drier system. In most cases the systems were dried less than 24 hours. The drier system was more likely to displace much of the bulk or free water during the penetration process. With the clay suspension, the penetration of malathion molecules may have surrounded some bulk water molecules which later became entrapped as the lattice collapsed during dehydration.

After reviewing the recent literature on the adsorption of malathion onto montmorillonite (Berigari, 1967; Meyers, 1968) and comparing it with the work of Tensmeyer et al. (1960) and Parfitt and Mortland (1968), there is some doubt as to whether malathion exists as a single or double layer in the interlayer region of montmorillonite. Tensmeyer et al. (1960) and Parfitt and Mortland (1968) both reported that 2,5-hexanedione, a compound bearing considerable similarity to malathion, existed in both single and double layers in the interlayer region. Berigari (1967) claimed that a single layer of malathion on the interlayer surface gave a d spacing of 16.7 Å, whereas Meyers (1968) reported that a single layer coverage of malathion gave a d spacing of only 13.8 Å.

The x-ray diffraction data shown in Tables 11, 12 and 13, tend to agree more closely with Berigari's reported d spacing value of 16.7 Å. Several of the montmorillonite-malathion systems

investigated gave d spacings in the 16.5 to 16.8 Å region before drying over P<sub>2</sub>O<sub>5</sub> and dry N<sub>2</sub> gas. However there are two exceptions to this found in the sodium and copper systems (Tables 11 and 12). For some reason the Na-montmorillonite+ malathion system gave d spacings of 16.35 (weak) and 12.6 Å (strong) after exposure to 100 percent relative humidity which upon drying, quickly changed to d spacings of 15.77 (strong) and 10.15 Å (weak). Re-exposure to water vapor and subsequent drying intensified the 16 Å spacing. The question arises as to whether the strong 12.6 Å peak observed initially after hydration represented a single monolayer of malathion, or whether it was just interlayer water. The fact that re-exposure to water vapor quickly decreased the peak intensity, reduced the d spacing to 10.16 Å and also broadened the peak, tends to suggest that it was only interlayer water. For some reason malathion did not completely penetrate the interlayer region on the first exposure to water vapor.

Tensmeyer et al. (1960) believed that the 13.05 Å spacing they obtained for 2,5-hexanedione was a result of its adsorption as a monolayer, the plane of the molecule lying in the ab plane of the clay lattice. For some unknown reason Parfitt and Mortland (1968) have misinterpreted Tensmeyer's statement, stating that the plane of the 2,5-hexanedione molecule was parallel to the c-axis of the clay. This meant that the molecule either lay on its side, or stood on end in the interlayer space to give the 13.05 Å spacing, a very unlikely possibility. Tensmeyer et al. (1960) demonstrated that 2,5-hexanedione also formed a monolayer on each of the interlayer surfaces giving a d spacing of 16.85 Å.

At the present time it is somewhat a matter of speculation whether the 16.5 Å spacing represented one malathion monolayer between two partial monolayers of water, or a double layer of malathion with partially hydrated cations. A partial water mono-layer might be thought of as a limited amount of bulk or free water loosely associated with the hydration shells of the cations on opposite interplanar surfaces. A complete water layer would consist of a complete layer of bulk water molecules--in other words the depressions between hydrated cations would be completely occupied by free water.

The data in Tables 11, 12 and 13 suggest that malathion and/or water molecules must have expanded the lattice layers by 6.0 to 7.0 Å depending on the system and its hydration state. Meyers' values for the d spacing for a monolayer suggests a thickness of about 4 Å. Since he used a H-clay, P<sub>2</sub>O<sub>5</sub> may not have completely dehydrated the system and therefore the 4 Å dimension would include some interlayer water. Probably the thickness of a malathion monolayer would be closer to 2.5 to 3.5 Å. There is another possibility that for single layer coverage, malathion might assume a different orientation giving a greater monolayer thickness than is the case for a double mono-layer coverage.

The x-ray diffraction data for the sodium system (Table 11) is probably the most significant because sodium does not tend to hydrate on the interlayer surfaces. (The d spacing of Na-montmorillonite over P<sub>2</sub>O<sub>5</sub> was 9.81 Å within 0.3 Å of the theoretical minimum of 9.5 Å for montmorillonite.) Consequently, drying over P<sub>2</sub>O<sub>5</sub> and flushing with dry N<sub>2</sub> gas over the

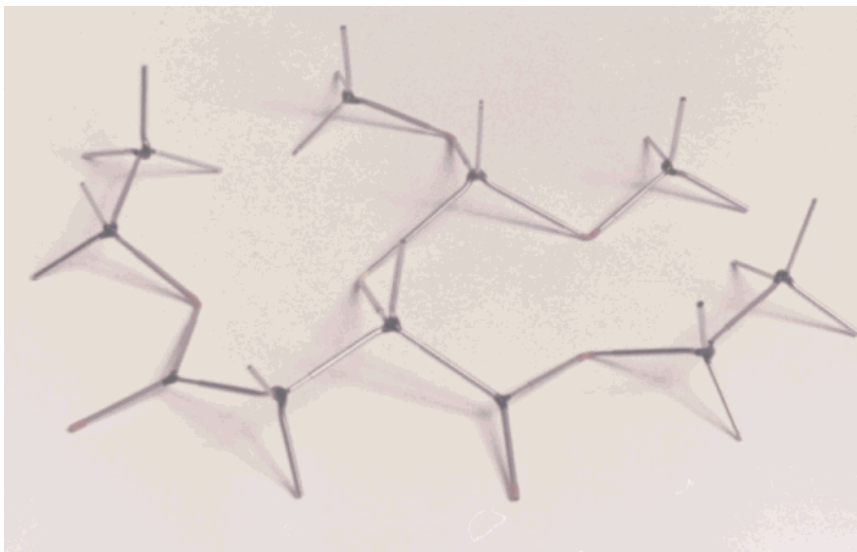
clay-malathion slide should have removed most of the interlayer water. Upon this assumption, the thickness of the malathion layer in the interlayer region of Na-montmorillonite would be 6.0 to 7.0 Å depending on the manner of preparation (Table 11). This would seem to suggest two planar layers, each approximately 3.0 to 3.4 Å in thickness. The thickness of a malathion monolayer probably could be 3.5 Å and still give a double layer expansion of only 6.5 Å because of intermeshing of the two layers. It has been observed that the distance between two non-bonded atoms is less than the sum of their atomic radii by 0.5 Å due to interpenetration of their electron clouds. (Green-Kelley, 1953).

A comparison of the d spacings of the sodium system with the other four systems indicates that at 100 percent relative humidity all five systems had almost the same d spacing (16.5 to 16.8 Å). Thus it would seem that there was very little water on the interlayer surfaces of any of the systems after adsorbing malathion and equilibrating over P<sub>2</sub>O<sub>5</sub>. During the adsorption process, malathion must have displaced most of the interlayer water while hydrogen bonding to the hydration water shell of the saturating cation. This displacement of water by malathion may have occurred because 1) malathion is relatively insoluble in water (only 145 ppm) making the two liquids almost immiscible, and 2) the hydrogen bonding of malathion carbonyl groups to the hydration water shell of the cation decreased the free energy of the system more than the very weak physical bonding of the bulk water to the tetrahedral oxygen layers.

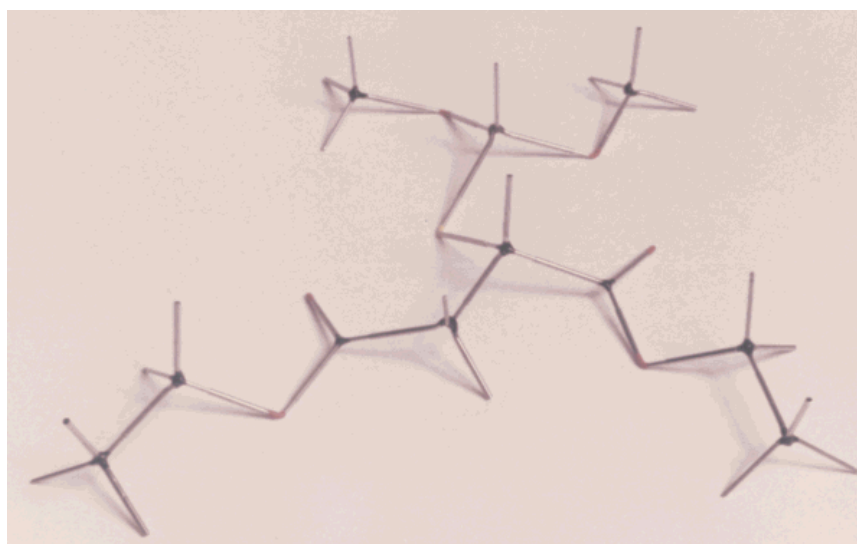
C. Configuration and Orientation of Malathion on the Interlayer Surfaces of Montmorillonite.

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. Figure 28 shows four possible planar configurations using a stereomodel (0.4 Å/cm.) (Dreiding Stereomodels, Rinco Instrument Co., 503 S. Prairie, P.O. Box 167, Greenville Ill., 62246). The carbonyl groups were in the plane of the molecule and by measurement were 4.7 to 5.8 Å apart depending on the configuration in question. Figure 29 shows the 2-dimensional representation of the Stereomodel configurations shown in Figure 28. It is believed that Figure 29a may represent the most probable configuration because (1) it is the most compact model, (2) the carbonyl oxygens are easily accessible for interactions, and (3) there appears to be little or no steric hindrance in this configuration. Therefore only this configuration will be referred to in this discussion, realizing the possibility that the other configurations are not entirely improbable.

Such a configuration would necessitate the interaction of the carbonyl oxygens with only the cations that are on the same interlayer surface, rather than on the opposite surfaces. The molecule in this configuration is approximately 2.5 Å in thickness and thus could not cause a 6.0 to 7.0 Å expansion of the lattice without being adsorbed as a monolayer on each interlayer surface. It does not seem reasonable that only the cations on one interlayer surface would interact with the malathion while those on the opposite surface interacted with water.

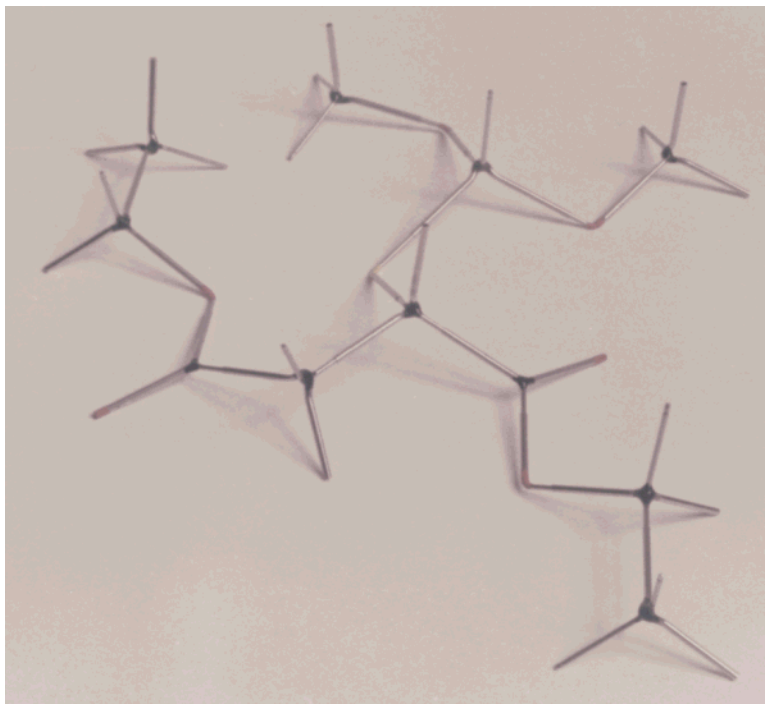


**FIGURE 28a.**

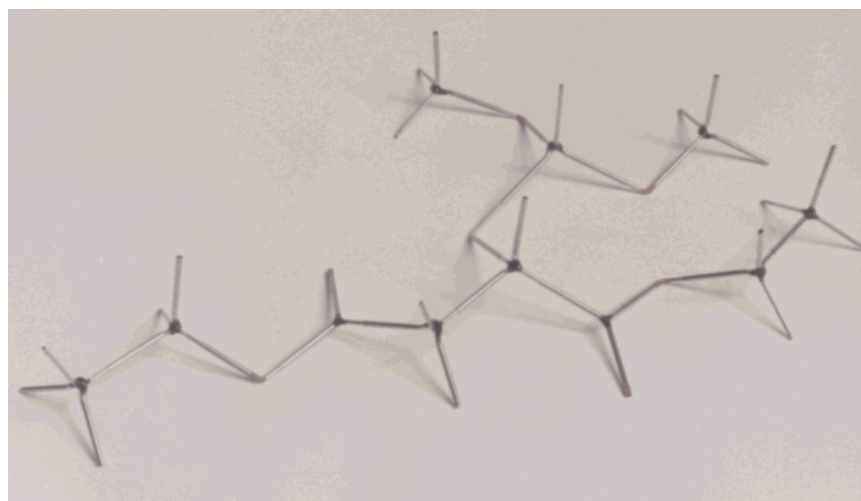


**FIGURE 29b.**

**PHOTOGRAPHS OF POSSIBLE 3-DIMENSIONAL  
CONFIGURATIONS OF MALATHION USING  
THE DREIDING STEREO MODEL.**

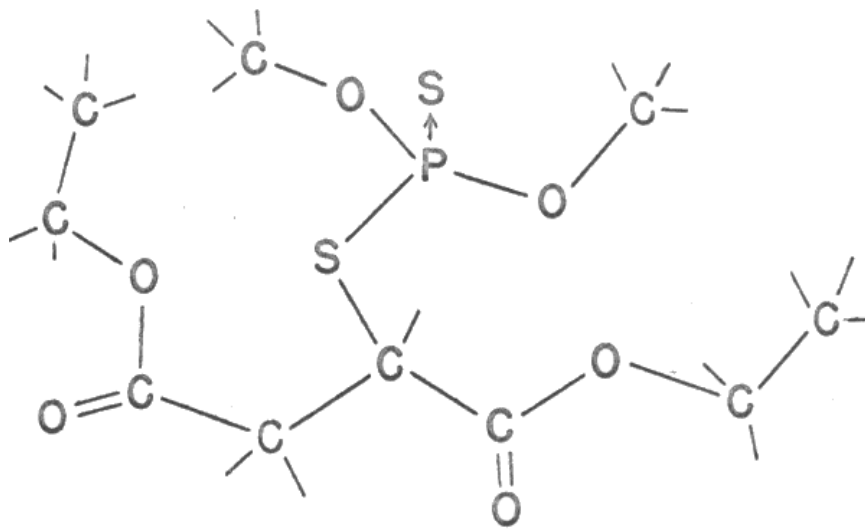


**FIGURE 28c.**



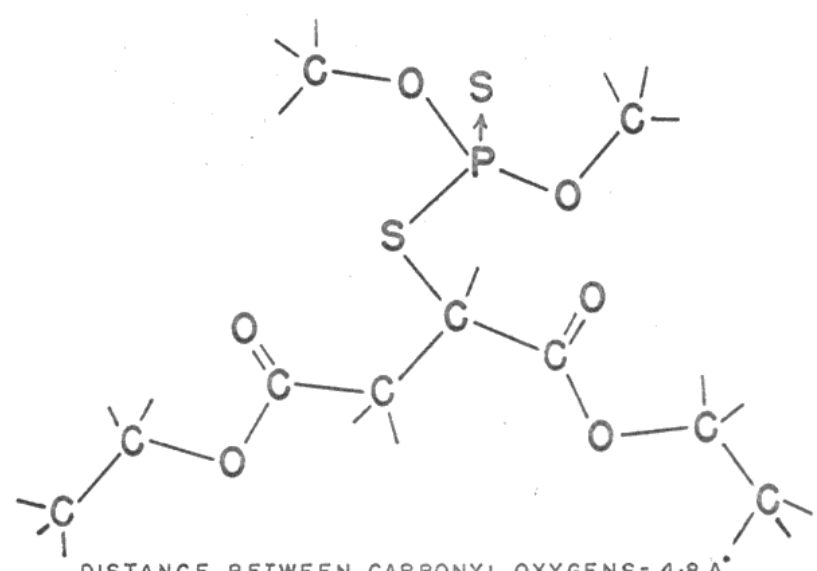
**FIGURE 28d**

**PHOTOGRAPHS OF POSSIBLE 3-DIMENSIONAL CONFIGURATIONS OF MALATHION USING THE DREIDING STEREO MODEL.**



DISTANCE BETWEEN CARBONYL OXYGENS = 4.9 Å

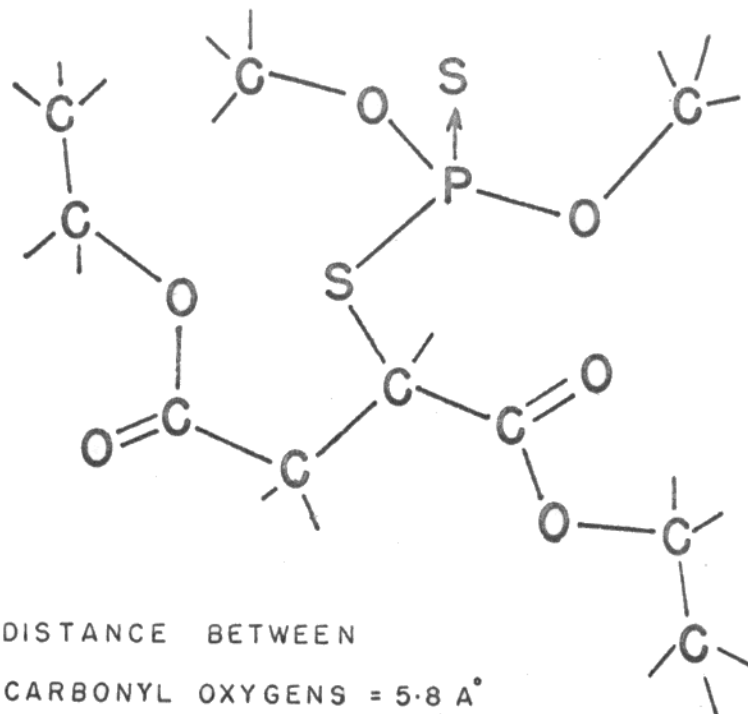
FIGURE 29 a



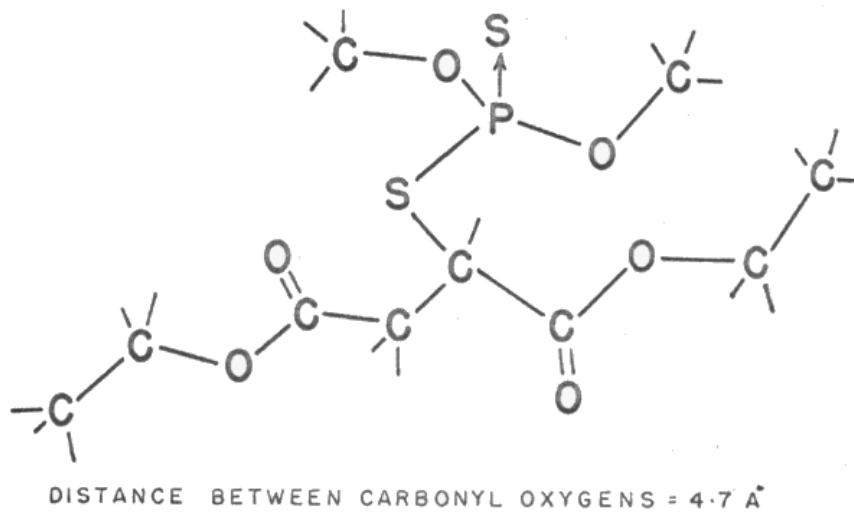
DISTANCE BETWEEN CARBONYL OXYGENS = 4.8 Å

FIGURE 29 b.

POSSIBLE CONFIGURATIONS OF MALATHION.



**FIGURE 29 c.**



**FIGURE 29 d.**

**POSSIBLE CONFIGURATIONS OF MALATHION.**

By virtue of the fact that the hydrogen bonding would lower the free energy more than the physical adsorption of a bulk water layer, the adsorption of malathion should be preferred over that of a bulk water monolayer. If the carbonyl groups of malathion interacted with opposite interlayer surfaces, it is likely that only one monolayer would exist in the interlayer region.

It is interesting to note that the carbonyl oxygen atoms, in this configuration have little freedom to move independently of each other without causing considerable strains and/or changes in the configuration of the entire molecule. This particular point becomes very important when considering the hydrogen bonding interaction and especially the electrostatic (ion-dipole) interaction with the saturating cation. The strength of these interactions will depend on (1) how well the positioning of the interlayer cations coincides with the spacing between carbonyl groups, and (2) the ease with which these cations can migrate on the interlayer surface to coincide with the 4.9 Å spacing of the carbonyl oxygens.

Another point that merits noting is that the surface density of cations decreases as the valence of the cation increases. The number of monovalent sodium ions would be expected to be triple that of the trivalent aluminum ions. Therefore there is a greater probability of the monovalent cations being in position for maximum interaction with the carbonyl groups than there is for the divalent or trivalent cations. This probability increases because the cations are not free to move on the interlayer surfaces, but are restricted by small potential energy barriers created as a result of isomorphous substitution within the body of the lattice. This fact may explain why the

carbonyl group frequency was observed to split upon dehydration in the trivalent systems, but not in the monovalent or divalent systems. It was consistently noted that in the Al-montmorillonite-malathion system the  $1710\text{ cm}^{-1}$  infrared absorption band (due to hydrogen bonding) split into a  $1740\text{ cm}^{-1}$  band and into several bands below  $1700\text{ cm}^{-1}$ , whereas in the Na-montmorillonite-malathion system, the entire band due to hydrogen bonding at  $1730\text{ cm}^{-1}$ , shifted down to the  $1714$  to  $1722\text{ cm}^{-1}$  region. The high frequency ( $1740\text{ cm}^{-1}$ ) band would occur because one carbonyl group did not interact and the low frequency band would be a result of the interaction of the other carbonyl group with the aluminum cation.

In the hydrated system there was no frequency splitting for the hydrogen bonding interaction in the aluminum system because of the relatively larger size of the hydration shell that made it possible for all carbonyl groups to interact in spite of the fact that the cations themselves might have been too far apart.

Perhaps it would be useful at this point to recall a few seemingly unrelated facts from the infrared spectroscopy studies. First of all, the  $1328\text{ cm}^{-1}$  band irreversibly disappeared as soon as there was sufficient water present to force apart the lattice layers and allow the malathion to enter. One might speculate that a slight change in the configuration of the molecule upon adsorption might have been responsible for this disappearance. It had previously been intimated that the association of the malathion with water might have caused the  $1328\text{ cm}^{-1}$  band to disappear, but in the kaolinite system in which the malathion remained on the exterior surfaces, the  $1328\text{ cm}^{-1}$

band did not disappear upon the addition of water vapor. Likewise the  $1300\text{ cm}^{-1}$  band never developed in the kaolinite system but it did in the montmorillonite system. However its existence seemed related to both the hydration state of the system and the saturating cation. It seemed to be more intense with the higher valence, more highly hydrated cations and/or with more highly hydrated systems.

Although it was not discussed in the section on infrared spectroscopy studies, it was observed that the bands in the  $1445$  to  $1470\text{ cm}^{-1}$  region of the montmorillonite-malathion system became more intense and better resolved during dehydration, suggesting an orientation effect or pleochroism. In order that an infrared vibration be detected, three conditions must be fulfilled;

- 1) The incident radiation must be of the same frequency as that of the band being observed,
- 2) A dipole moment change must accompany the bond vibration,
- 3) Only the component of the dipole moment change of the vibration perpendicular to the direction of the incident infrared beam will interact with it. Thus if a bond vibration satisfies the first two conditions, but is oriented parallel to the beam direction, no absorption can be observed. As soon as its orientation shifts, a component of the dipole moment change will be observed.

During sedimentation of the self-supporting films (as for x-ray slides) the sheet-like layers of the montmorillonite orient themselves so that the surface of the film is essentially in the ab plane of the clay and therefore the infrared beam travels parallel to the c-axis of the clay. Any molecule on the interlayer surfaces having infrared active bonds lying flat on the surface will be observed, whereas those bonds in the plane of the c-axis will not be observed. However, tilting the film at some angle to the infrared beam would then allow a perpendicular component of these bond vibrations to be observed. Since tilting the film would increase the path length of the beam, most bands become slightly more intense and therefore it is necessary to measure the relative peak heights when studying pleochroism.

No real attempt was made to investigate the possibility of pleochroism during this study because of physical limitations in the design of the infrared cell. In order to effectively study pleochroism, it is necessary to change the orientation of the clay film in the cell without releasing the vacuum. The present cell could probably be modified by placing a small magnet in the top of the sample holder and then using an electromagnet to raise and re-position the holder. It should be possible to study orientation effects as a function of moisture content by regulating the vacuum and scanning the clay film at  $0^{\circ}$  and at  $45^{\circ}$  angles.

One of the functions of the interlayer water is to expand the lattice layers of montmorillonite. When a monolayer of malathion is adsorbed on each interlayer surface of a hydrated clay system, there probably is not much interaction between the two monolayers. But as

the system is dehydrated, the lattice collapses, forcing the two monolayers to mesh together, resulting in some interactions not previously observed. It is during dehydration that strains develop in the molecules resulting in a slightly different orientation of some of the functional groups. The most susceptible of these groups may be the methylene --CH<sub>2</sub>- groups, and as was previously mentioned, the 1468 cm<sup>-1</sup> band tentatively assigned to CH<sub>2</sub> scissoring did change both in intensity and in position upon dehydration.

One might also speculate that the P—S vibrations might be altered during dehydration since the sulfur atom appears to project above the plane of the molecule. This would be rather difficult to investigate because there are bands ascribed to the clay lattice in this region.

## V. SUMMARY AND CONCLUSIONS

One of the primary objectives of this research project was to investigate the environmental conditions that promote the degradation of malathion adsorbed on montmorillonite clay and if possible, to identify some of the degradation products.

Upon initial inspection of the infrared spectra of the various montmorillonite-malathion systems, it appeared that a possible reaction had occurred when the systems were hydrated. The  $1328\text{ cm}^{-1}$  band always irreversibly disappeared (not due to association with bulk water) and an intense band in the  $1300\text{ cm}^{-1}$  region developed. As mentioned earlier in this dissertation, malathion is susceptible to cleavage in only three positions, the two ethyl ester linkage ( $-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{C}$ ) and the thiol ester linkage (P-S-C). Since the C-H stretching bands remained constant in position and also in relative intensity throughout the experiments, it was very unlikely that there was any significant amount of cleavage of the ethyl ester linkages.

Unfortunately a somewhat indirect method had to be used to decide whether the P-S-C linkage was cleaved following malathion adsorption onto montmorillonite. The majority of the phosphorus- sulfur absorption bands occur in the  $700\text{ to }1000\text{ cm}^{-1}$  region, somewhat coincident with the strong absorption bands of the clay lattice. Therefore it was necessary to obtain the spectra of many related compounds, in an attempt to see whether any of the altered absorption bands of adsorbed malathion coincided with absorption bands of these compounds.

It was soon discovered that the adsorption and subsequent hydration processes could produce some rather startling changes in the infrared adsorption spectrum of malathion. Therefore the spectra of adsorbed diethyl succinate and diethyl mercaptosuccinate were studied, these two compounds being the most likely degradation products.

Upon adsorption onto montmorillonite followed by hydration, the spectrum of diethyl mercaptosuccinate had a  $1300\text{ cm}^{-1}$  region band, somewhat similar to that observed in the montmorillonite-malathion system. Immediately one might speculate that upon exposure to water, the adsorbed malathion cleaved at the P-S position, thereby producing the spectrum of diethyl mercaptosuccinate. However, a similar  $1300\text{ cm}^{-1}$  band developed in the montmorillonite-diethyl succinate system where there was no -C-S-H band. Therefore it is very probably that the development of the  $1300\text{ cm}^{-1}$  band was not associated with the P-S-C linkage, but was an orientation effect of some sort. Thus the formation of this band was not indicative of malathion degradation.

Several other bands in the spectrum of adsorbed malathion changed both in intensity and position during the hydration and dehydration processes. However, these changes were reversible and therefore could not be the result of a degradation reaction. For example the bands at  $1445$  and  $1468\text{ cm}^{-1}$  always intensified and shifted to higher wave numbers upon dehydration, but returned to their original positions upon rehydration. Often the  $\text{CH}_3$  symmetric deformation band at  $1375\text{ cm}^{-1}$  shifted up to the  $1380$  to  $1385\text{ cm}^{-1}$  region upon dehydration, but returned to its original

position upon rehydration. These changes are likely a result of 1) orientation changes during the collapse of the lattice on the malathion layers, 2) a more intense interaction between the malathion molecules and the interlayer surfaces as a result of the removal of adsorbed water, 3) an increased interaction between the two malathion layers during the collapse of the lattice, or 4) any combination of these three factors.

Results from the x-ray diffraction studies of the montmorillonite-malathion systems suggest the following points;

1. Malathion can not penetrate the interlayer region of montmorillonite when the system has been dried over  $P_2O_5$ . Infrared spectroscopy studies indicated that the rate of malathion penetration into the interlayer regions became very slow at relative humidities less than 30 percent. When exposed to high relative humidities, the x-ray diffraction data showed that malathion entered the interlayer region within a few minutes. Quite possibly the strong tendency of the saturation cations to hydrate resulted in water molecules forcing apart the lattice layers, allowing malathion molecules to enter.
2. The adsorption of malathion by montmorillonite produced d spacings in the 15.5 to 16.8 Å region, approximately the same as those reported by Berigari (1967), who attributed a 16.7 Å spacing to a monolayer. In view of the fact that Meyers obtained a d spacing of 13.8 Å for a single monolayer of adsorbed malathion, it appears likely that d spacings of 15.5 to 16.8 Å represent a double monolayer, one monolayer on each interlayer surface.

The Stereomodel of malathion (Figure 28) suggested four possible planar configurations, the most probable one having its carbonyl oxygen atoms separated by approximately 4.9 Å. The height (in the direction perpendicular to the plane of the molecule) of the molecule would appear to be approximately 2.5 Å. Thus a double monolayer would require about a 5 Å lattice expansion. The other 1.0 to 1.5 Å expansion could be accounted for by the saturating cation and its partial hydration shell, or to imperfections in the clay lattice. Because malathion is adsorbed as a planar molecule, the carbonyl groups of one molecule could hydrogen bond with only the cationic hydration shells on one interlayer surface. It seems unreasonable that only one interlayer surface should react with the carbonyl groups of malathion, resulting in the conclusion that malathion is adsorbed as a double monolayer. At very low malathion concentrations, it might be expected that molecules would be alternately adsorbed on opposite interlayer surfaces in a staggered fashion, giving the d spacing of only one monolayer, as perhaps Meyers obtained.

The infrared spectroscopy studies have shown an interesting relationship between the carbonyl groups of malathion and the saturating cation with its hydration shell. The positive charge of the saturating cation polarizes the hydration water, effectively increasing its acidity, or extent of dissociation. This acidity increases with increasing cationic charge. By the same token, the strength of the hydrogen bond increases as the proton on the water shell becomes more labile. Thus, the higher the cationic valence, the greater the perturbation of the carbonyl frequency towards lower wavenumbers (Table 14).

During the dehydration process, the hydration water molecules are progressively removed allowing the cations and the carbonyl oxygens to come into closer proximity. Two results follow from this;

1. Partial removal of the hydration water shell should increase the acidity of the remaining coordination water molecules. This should produce a stronger hydrogen bond (ie. a greater carbonyl group frequency shift to lower wavenumbers) than the complete hydration shell would produce.
2. As the carbonyl oxygen approaches the cation, an ion-dipole interaction will occur. This interaction should be the strongest possible interaction resulting in the greatest shift in the carbonyl group frequency. The data in Table 14 tend to confirm these proposals.

The carbonyl frequency splitting in the trivalent systems during dehydration was attributed to the inability of the two carbonyl groups of malathion to equally interact with neighboring cations because of their separation distances. The increased density of cations in the monovalent and divalent montmorillonite systems apparently circumvented this phenomenon and allowed all carbonyl oxygens to interact equally with neighboring cations.

In summary, this study suggests the following points;

1. Malathion does not appear to break down on the interlayer surfaces of Na, Ca, Cu, Fe or Al-montmorillonite films over the three to five day periods of the experiments,

**Table 14. Carbonyl Group Absorption Frequencies of Malathion as Affected by the Saturating Cation and Hydration State of the Montmorillonite.**

Treatment	Na <sup>+</sup>	Ca <sup>+2</sup>	Cu <sup>+2</sup>	Fe <sup>+3</sup>	Al <sup>+3</sup>
	Wavenumbers, cm <sup>-1</sup>				
Hydrated System	1730	1714	1725	1723 (sh)	1710
		1695 (sh)	1715	1714	
				1695 (sh) 1684 (sh)	
Dehydrated System	1722	1695	1740	1740	1740
	1714	1683 (sh)	1734	1660-	1678
			1715 (ah)	1678	1635
			1695 (sh)		
			1683 (sh)		

sh = shoulder band

2. Although water tends to produce some drastic changes in the infrared spectrum of adsorbed malathion, these changes can be attributed to interaction and orientation effects and not to degradation reactions. Water was also shown to be a necessary factor for the entry of malathion into the interlayer region of montmorillonite (> 30 percent relative humidity).
3. Infrared spectroscopy data on the water deformation band of the various clay systems indicated that some interlayer water was displaced upon the adsorption of malathion. This water was believed to be bulk water and not hydration water.
4. Malathion appeared to be adsorbed as a double monolayer on the interlayer surfaces of montmorillonite clay, giving d spacings ranging from 15.5 to 16.3 Å depending on the saturating cation and the hydration status of the system.
5. Kaolinite clay has a very low capacity to interact with the carbonyl groups of malathion.
6. The valence of the saturating cation determines the strength of the hydrogen bond between the carbonyl group of malathion and the hydration water shell. The greater the valence, the more acidic the hydration water, the stronger the hydrogen bond and therefore the greater the downward shift of the carbonyl group frequency.
7. A direct ion-dipole interaction between the carbonyl oxygens and the saturating cation is more energetic than that for the hydrogen bonding interaction, resulting in a greater perturbation of the carbonyl group (as much as 115 cm<sup>-1</sup> in the Al-montmorillonite-diethyl succinate system). Such a large perturbation suggests that the carbonyl group has assumed a considerable amount of single bond character .

8. The Stereomodel suggests four possible planar configurations for malathion, the most probable configuration having its carbonyl oxygen atoms being separated by approximately 4.9 Å. It is assumed that malathion is adsorbed on the interlayer surfaces of montmorillonite with the plane of the molecule lying in the ab plane of the clay lattice.

There are several areas that require further investigation;

1. Although no degradation of adsorbed malathion was observed in this study over a period of a few days, it is possible that over a longer period, some degradation might occur.
2. In this study, particular care was taken to remove organic matter from the clay before studying malathion adsorption. The role of organic matter in malathion degradation should also be investigated. Perhaps the combination of organic matter, clay and moisture operate collectively to degrade malathion.
3. Further study on orientation of malathion on the interlayer surfaces of montmorillonite is warranted. It would be necessary to be able to rotate the clay film at some angle to the incident infrared beam without releasing the vacuum in the cell.
4. With a vacuum x-ray diffraction unit, the d spacing of various montmorillonite-malathion systems could be more thoroughly examined. It would be interesting to see if only one monolayer of malathion might be adsorbed by montmorillonite at very low malathion concentrations.

## BIBLIOGRAPHY

- Arthur, B.W. and J.E. Casida. 1959. Biological activity and metabolism of Hercules AC-528 components in rats and cockroaches. *J. Econ. Entomol.* 52: 20-27.
- Bellamy, L.J. 1968. *Advances in Infrared Group Frequencies*. Methuen and Co. Ltd., London.
- Berigari, M.S. 1967. Adsorption of malathion by montmorillonite. *Agronomy Abstracts*: P73. Washington, D.C.
- Blinn, R.C. 1968. Abate insecticide. Fate of O,O,O',O'-tetramethyl O,O'-thiodi-p-phenylene phosphorothioate on bean leaves. *J. Agric. Food Chem.* 16(3): 441-445.
- Bowman, B.T., R.L. Thomas and D.E. Elrick. 1967. The movement of phytic acid in soil cores. *Soil Sci. Soc. Proc.* 31(4): 477-481.
- Bowman, J.S. and J.E. Casida. 1958. Further studies on the metabolism of Thimet by plants, insects and mammals. *J. Econ. Entomol.* 51: 838-843.
- Brett, Charles H. and T.G. Bowery. 1958. Insecticide residues on vegetables. *J. Econ. Entomol.* 51(6): 818-821.
- Camp, H.B., T.R. Fukuto and R.L. Metcalf. 1969a. Selective toxicity of isopropyl parathion. Effect of structure on toxicity and anticholinesterase activity. *J. Agric. Food Chem.* 17(2): 243-248.
- Camp, H.B., T.R. Fukuto and R.L. Metcalf. 1969b. Selective toxicity of isopropyl parathion. Metabolism in the housefly, honey bee and white mouse. *J. Agric. Food Chem.* 17(2): 249-254.
- Casida, John E., Morifusa Eto and Ronald L. Baron. 1961. Biological activity of a tri-o-cresyl phosphate metabolite. *Nature* 191: 1396-1397.
- Chen, P.R., W.P. Tucker and W.C. Dauterman. 1969. Structure of biologically produced malathion monoacid. *J. Agric. Food Chem.* 17(1): 86-90.
- Coffin, D.E. 1966. Oxidative metabolism and persistence of parathion and malathion on field-sprayed lettuce. *J. Assoc. Offic. An. Chem.* 49(5): 1018-1021.
- Edwards, C.A. 1966. Insecticide residues in soils. *Residue Reviews* 13: 83-132.
- Faust, Samuel D. and Irwin H. Suffet. 1966. Recovery, separation and identification of organic pesticides from natural and potable waters. *Residue Reviews* 15: 44--116.

- Fox, Austin, Theodore Eichers, Paul Andrienas, Robert Jenkins and Helen Blake. 1966. Extent of Farm Pesticide Use on Crops in 1966. Agric. Economic Report No. 147, U.S.D.A. Economic Research Service, Washington, D.C.
- Getzin, L.W. and Irving Rosefield. 1968. Organophosphorus insecticide degradation by heat-labile substances in soil. *J. Agric. Food Chem.* 16(4): 598-601.
- Greene-Kelley, R. 1953. Sorption of aromatic compounds by montmorillonite. Part 1. Orientation studies. Part 2. Packing studies with pyridine. *Trans. Faraday Soc.* 51: 412-424, 425-430.
- Harris, C.R. 1964. Influence of soil type and soil moisture on the toxicity of insecticides in soils to insects. *Nature* 202: 724.
- Heath, D.F., D.W.J. Lane and P.O. Park. 1955. The decomposition of some organophosphorus insecticides and related compounds in plants. *Phil. Trans. Roy. London B239*, 191-214,
- Hopkins, T.L. 1967. Humidity effects on the persistence of malathion leaf-surface residues. *J. Econ. Entomol.* 60(4): 1167-1168.
- Ibrahim, Payez B., Jack M. Gilbert, R. Thomas Evans and Jerry C. Cavagnol. 1969. Decomposition of Di-Syston {O,O-diethyl S-[2-(ethylthio)ethyl phosphorodithioate]} on fertilizers by infrared, gas-liquid chromatography and thin-layer chromatography. *J. Agric. Food Chem.* 17(2): 300-305.
- Jackson, M.L. 1956. *Soil Chemical Analysis. Advanced Course.* (Fourth Printing, 1968. Published by the author, Dept. of Soil Science, Univ. of Wisc., Madison, Wisc. 53706.
- Kansouh, A.S.H. and T.L. Hopkins. 1968. Diazinon absorption, translocation and metabolism in bean plants. *J. Agric. Food Chem.* 16(3): 446-450.
- Kohl, R.A. and Sterling A. Taylor. 1961. Hydrogen bonding between the carbonyl group and Wyoming bentonite. *Soil Science* 91: 223-227.
- Konrad, J.G., G. Chesters and D.E. Armstrong. 1969. Soil degradation of malathion, a phosphorodithioate insecticide. *Soil Sci. Soc. Proc.* 33: 259-262.
- Larson, G. Olof and Larry R. Sherman. 1964. Infrared spectrophotometric analysis of some carbonyl compounds adsorbed on bentonite clay. *Soil Science* 98: 328-331.
- Lichtenstein, E.P. 1958. Movement of insecticides in soils under leaching and non-leaching conditions. *J. Econ. Entomol.* 51(3): 380-383.

- Lichtenstein, E.P., T.W. Fuhremann and K.R. Schulz. 1968. Effect of sterilizing agents on persistence of parathion and diazinon in soils and water. *J. Agric. Food Chem.* 16(5): 870-873.
- MacNamara, George Malcolm. 1968. Adsorption of some pesticides in soils, clay minerals and humic acid. Ph.D. Thesis, Rutgers Univ.
- Mahan, John N., D. Lee Fowler, and Harold H. Shepard. 1968. *The Pesticide Review*. Agricultural Stabilization and Conservation Service. Washington, D.C., U.S. Dept. of Agric.
- Main, A.R. 1964. Affinity and phosphorylation constants for the inhibition of esterases by organophosphates. *Science* 144: 992-993.
- Malina, Marshall A., Arthur Goldman, Leo Trademan and Percy B. Polen. 1956. Deactivation of mineral carriers for stable Heptachlor-dust formulations. *J. Agric, Food Chemistry* 4(12): 1038-1042.
- Matsumura, F. and G.M. Bousch. 1966. Malathion degradation by *Trichoderma viride* and *Pseudomonas* species. *Science* 153: 1278-1280.
- Meyers, Norman Larry. 1968. Adsorption of selected organic insecticides on well characterized watershed soils and their corresponding pond sediments. M.S. Thesis, Purdue University.
- Mortland, M.M. 1966. Urea complexes with montmorillonite: an infrared adsorption study. *Clay Minerals* 6: 143-156.
- O'Brien, R.D. 1960. *Toxic Phosphorus Esters. Chemistry, Metabolism and Biological Effects*. Academic Press. New York.
- O'Brien, R.D. 1967. *Insecticides. Action and Metabolism*. P. 262. Academic Press. New York and London.
- Parfitt, R.L. and M.M. Mortland. 1968. Ketone adsorption on montmorillonite. *Soil Sci. Soc. Proc.* 32: 355-363.
- Polon, J.A. and E.W. Sawyer, Jr. 1962. The use of stabilizing agents to decrease decomposition of malathion on high-sorptive carriers. *J. Agric. Food Chem.* 10(3): 244-248.
- Roberts, John D. and Marjorie E. Caserio. 1964. *Basic Principles of Organic Chemistry*. P. 1194. W.A. Benjamin, Inc., New York.
- Rowlands, D.G. 1964. The degradation of malathion on stored maize and wheat grains. *J. Sci. Food Agric.* 15: 824-829.

- Salonius, P.O., J.B. Robinson and F.E. Chase. 1967. A comparison of autoclaved and gamma-irradiated soils as media for microbial colonization experiments. *Plant and Soil* 27: 239-248.
- Shipp, O.E., D.A. Lindquist and J.R. Brazzel. 1963. Characteristics of residues of methyl parathion applied to field cotton. *J. Econ. Entomol.* 56(6): 793--798.
- Spencer, E.Y., R.D. O'Brien and Robert W. White. 1957. Permanganate oxidation products of schradan. *J. Agr. Food Chem.* 5: 123-127.
- Spiller, D.A. 1961. A digest of available information on the insecticide malathion. *Adv. in Pest Control Res.* 4: 249-335.
- Swoboda, Allen R. and Grant W. Thomas. 1968. Movement of parathion in soil columns. *J. Agric. Food Chem.* 16(6): 923-927.
- Tahoun, Salah A. and M.M. Mortland. 1966. Complexes of montmorillonite with primary, secondary and tertiary amides: II. Coordination of amides on the surface of montmorillonite. *Soil. Sci.* 102: 314-321.
- Tensmeyer, Lowell G., Reinhard Hoffmann and G.W. Brindley. 2960. Infrared studies of some complexes between ketones and calcium montmorillonite. *Clay-organic studies, Part III. J. Phys. Chem.* 64: 1655-1662.
- Walling, Chaves. 1950. The acid strength of surfaces. *J. Amer. Chem. Soc.* 72: 1164-1168.
- Yost, J.F., I.B. Frederick and V. Migrdichian. 1955. Malathion and its formulations. *Agricultural Chemicals* 10(9): 43-45, 137-139; 10(10): 42-44, 105, 107.