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## HERBICIDE ABSORBANCE

# Interaction of Ethyl N,N-Di-n-propylthiolcarbamate (EPTC) with Montmorillonite

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Results of infrared studies of EPTC-montmorillonite complexes show a decrease in the CO stretching and an increase in the CN stretching frequencies indicating coordination of the EPTC to the exchangeable metal ion through the oxygen of the carbonyl group. The amount of shift was determined by the kind of metal ion on the exchange complex. The EPTC-montmorillonite complexes were stable against atmospheric humidity but, when immersed in water, the EPTC could be completely displaced. Bioassay showed that EPTC-montmorillonite complexes exerted herbicidal activity against germination and growth of rye grass.

THE LITERATURE concerned with the interaction of organic pesticides and soil colloids has been reviewed recently by Bailey and White (1). Considerable work has been done in investigating the various factors affecting adsorption of various pesticides such as pH, moisture content, kind of exchangeable ion, nature of clay mineral, and effect of organic matter. However, relatively little has been reported on the status of the adsorbed molecule concerning exactly what sort of interaction exists between the adsorbent and the adsorbate. Infrared absorption provides a tool which can often establish such interactions as hydrogen bonding, coordination, salt formation, and actual breakdown or conversion of the compound to other forms. The work reported here is concerned with the mechanism of adsorption of ethyl N,N-di-n-propylthiolcarbamate (EPTC) by montmorillonite, a clay mineral of high specific surface (800 sq. meters per gram), as revealed by infrared absorption.

The EPTC compound is a selective herbicide especially active against annual grasses and certain broadleaf weed species. The structural formula is:

$$CH_3CH_2-S-\overset{\overset{\displaystyle O}{\|}}{C}-N\overset{\displaystyle CH_2CH_2CH_3}{\underset{\displaystyle CH_2CH_2CH_3}{}}$$
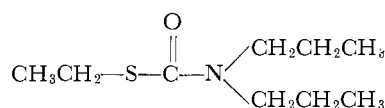
Its boiling point is 232° C. at 760 mm., and the vapor pressure is 0.15 mm. at 25° C. The solubility in water is 375 p.p.m., and it is miscible in such organic solvents as benzene, toluene, xylene, acetone, methanol, and 2-propanol.

### Methods

The montmorillonite used in this study was H-25 from Upton, Wyo., supplied by Wards Natural Science Establishment. Homoionic clays were prepared by treating the <0.5-micron fraction with chloride salts of the various cations in excess of the exchange capacity. After flocculation had occurred, the supernatant liquid was siphoned off, distilled water was added to bring it to the original volume, and the chloride salts were added again. This process was repeated three times at the end of which no more salts were added, but the clays were allowed to settle and were redispersed with distilled water until the clays showed signs of not reflocculating, at which time they were placed in dialysis bags and dialyzed against distilled water until the conductivity of the dialyzate approached that of distilled water.

Thin films (2 to 5 mg. per sq. cm.) of montmorillonite were prepared by evaporating in dishes of aluminum foil. The films, which could be readily stripped from these surfaces, were placed in a vacuum desiccator containing a dish of liquid EPTC. The desiccator was evacuated with a rotary pump for an hour, the stopcock to the vacuum line closed off, and the samples were allowed to adsorb EPTC from the gaseous state provided by the vapor pressure of the liquid EPTC. Five days were apparently sufficient to give maximum adsorption since liquid as well as complexed EPTC was noted in the infrared spectra after this period. Infrared spectra were obtained by mounting the films at right angles to the beam in a Beckman IR-7 spectrophotometer.

### Infrared Spectra of EPTC-Montmorillonite Complexes

Figure 1 shows the infrared spectra of EPTC complexed with montmorillonite of varying cation saturation in the region 1150 to 1750 cm.$^{-1}$ The top spectrum is that of pure liquid EPTC. Great changes in the spectra of the compound are indicated. The intense peak at 1655 cm.$^{-1}$ in the liquid is the carbonyl stretching band which shifts to much lower frequencies upon complexation with montmorillonite. The peak at about 1630 cm.$^{-1}$ is the deformation band for water. This figure shows that the amount of shift is a function of the kind of metal ion on the clay exchange sites. There is a relationship between the amount of shift of the carbonyl stretching band and the known complexing abilities of the various ions; copper, aluminum, and cobalt cause a greater shift than the alkali metal and alkaline earth cations represented. The band at 1222 cm.$^{-1}$ is allocated mostly to C—N stretching in accordance with the observations of Nyquist and Potts (6) in their work on thiocarbamates where they reported this strong band in the 1152 to 1275 cm.$^{-1}$ region. The
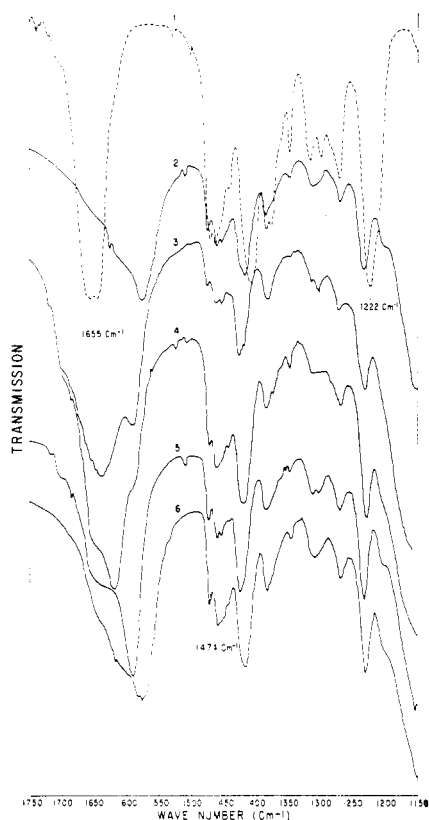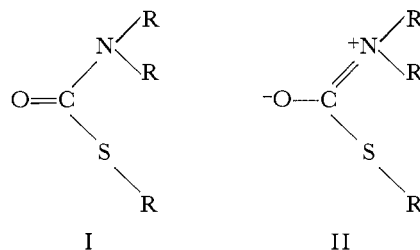
Figure 1. Infrared spectra of EPTC and its complexes with montmorillonite in the region 1150–1750 cm.$^{-1}$

1. Liquid EPTC
2. Al-clay
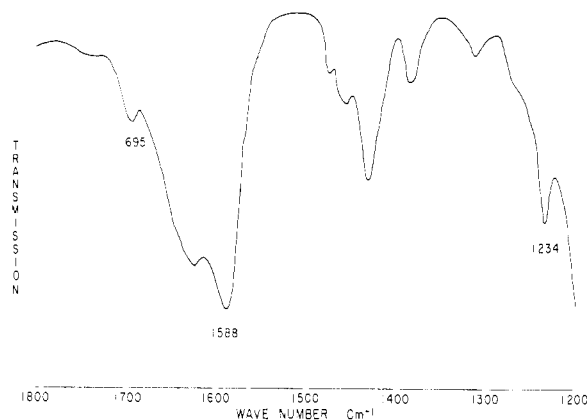3. Mg-clay
4. Li-clay
5. Ca-clay
6. Cu-clay



Figure 2. Infrared spectrum of an EPTC-Mg montmorillonite complex subjected to desiccation by evacuation and heating at 70° C. for one hour

## Table I. Infrared Absorption Bands of EPTC Complexes with Montmorillonite

| Exchangeable Cation on Clay | C—O Stretching, Cm.$^{-1}$ | C—N Stretching, Cm.$^{-1}$ |
|---|---|---|
| Li$^+$ | 1593 | 1227 |
| Na$^+$ | 1590 | 1222 |
| Ca$^{+2}$ | 1594 | 1232 |
| Mg$^{+2}$ | 1587 | 1232 |
| Al$^{+3}$ | 1570 | 1234 |
| Cu$^{+2}$ | 1566 | 1232 |
| Co$^{+2}$ | 1583 | 1231 |
| EPTC (liquid) | 1655 | 1222 |



spectra and, more precisely, in Table I show that this band is shifted to a higher wave number when the EPTC is complexed with the montmorillonite. These results strongly suggest that the coordination of the EPTC with the metal ion is through the carbonyl group. Nakamoto (5) points out that in the case of urea, thiourea, and related compounds, the CO stretching frequency is reduced when coordination occurs through this group and concurrently the CN stretching frequency increases. Both of these changes were observed in the EPTC-clay complexes as shown in Table I. These results agree with work done in the senior author's laboratory on complexes of tertiary amides with montmorillonite where it was observed that coordination to the metal was through the oxygen. Apparently the two unshared electrons on the nitrogen atom are not very accessible for coordination probably because of steric factors brought about by relatively large groups on the nitrogen atom—propyl groups, in the case of EPTC. There may be a resonance hybrid of the form:

Coordination through the oxygen would enhance the resonance and structure II, thus lowering the CO and increasing the CN stretch frequencies. The CS stretching frequency might also be affected but this band could not be identified in the EPTC-clay complex.

An attempt was made to obtain some information on the orientation of the EPTC molecule in the clay complex. X-ray diffraction results showed that the stable EPTC-clay systems had 001 reflections at 14 A. (10 A. of this is the silicate structure) regardless of the kind of metal cation on the exchange complex. Since there was relatively little water in these systems, as indicated by the low intensity of the H$_2$O deformation band at 1620 cm.$^{-1}$ and the OH stretching in the 3000 to 3500 cm.$^{-1}$ region, the above spacing can reasonably be as-

sumed to result from the bulk of the EPTC rather than water of hydration. Noting the relative length of the molecule compared with the small distance between successive silicate sheets (about 4 A.), it must be concluded that the molecules are lying approximately flat between the sheets and not in a perpendicular position.
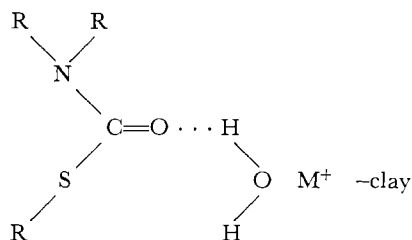
The method of preparation of the EPTC-clay films leads to a well-oriented sample with the 001 planes of the clay mineral predominantly in the plane of the film. Absorption bands whose component is perpendicular to the clay sheets could be enhanced if the film is positioned at an angle to the infrared beam. The only band enhanced in intensity was at 1474 cm.$^{-1}$ This was true on all the clay-EPTC complexes. The absorbance of the 1474 cm.$^{-1}$ band was increased about 38% when the film was positioned at 45° with respect to the beam. The assignment of this particular band is not certain but in this region of the spectra is likely to be a CH$_2$ or CH$_3$ deformation of some kind. It may be a CH$_2$ scissoring vibration which Farmer and Mortland (2) found (at 1472 cm.$^{-1}$) to be enhanced in the case of ethylamine complexes of montmorillonite. Considering their reasoning in the case of the ethylamine clay complexes, and the observed x-ray and infrared data here, the EPTC molecule is oriented with its long axis approximately parallel to the silicate sheets, and one or more methylene groups are oriented with the bisector of the H—C—H angle pointed to some extent in the C direction. Since the dipole change is along this bisector, enhancement should be observed with the film at an angle to the beam. It may be that the hydrogens of the methylene groups are attracted to some extent by the oxygen atoms of the silicate sheet (hydrogen bonding), thus accounting for the observed orientation.

The band at 1460 cm.$^{-1}$ (unaffected by film angle) may be the antisymmetric vibration of CH₃.

It is impossible to account for all the changes in the spectrum of EPTC when it is adsorbed on montmorillonite. Some of the changes have been described above, but major shifts in methyl and methylene bands and skeletal vibrations may result from changes in molecular symmetry and force field effects of the silicate sheets on the electron distribution in the molecular structure.

A relatively weak but discrete band appeared at 1695 cm.$^{-1}$ in fresh preparations of Mg and Al-clay-EPTC complexes that were highly dehydrated is shown in Figure 2. This is attributed to CO stretching of some EPTC which is coordinated through the nitrogen rather than the oxygen. This would tend to enhance structure I and to increase the frequency of the CO bond. The authors believe that, while the EPTC tends to coordinate through the carbonyl group and most of its does, some of the EPTC molecules are sterically hindered by crowding of adjacent molecules and limitations imposed by the clay structure so that a small proportion may coordinate through the nitrogen to the metal ion.

There is the possibility that some of the EPTC is associated with the metal ions through a bridging effect of coordinated water as has been suggested by Farmer and Mortland (2) for certain pyridine-metal-clay complexes:

$$
\begin{array}{c}
R \quad\quad R \\
\diagdown \,\diagup \\
N \\
\diagdown \\
C\!=\!O \cdots H \\
\diagup \quad\quad\quad \diagdown \\
S \quad\quad\quad\quad O \quad M^{+} \;\; -clay \\
\diagup \quad\quad\quad\quad \diagup \\
R \quad\quad\quad\quad H
\end{array}
$$

It is felt, however, with the possible exception of the Al-clay system, that relatively little of this takes place because the OH stretching bands of H₂O have not been displaced to lower frequencies nor has the deformation band increased much in frequency as is the case in hydrogen bonding. In the EPTC Al-clay system, OH stretching bands were somewhat displaced downward (a broad band with its peak near 3250 cm.$^{-1}$) compared with the other EPTC-metal-clay systems but not to the extent observed by Farmer and Mortland (2) in some pyridine-metal-clay complexes.

### Stability of EPTC-Montmorillonite Complexes

Table II shows the EPTC content of clay films exposed to the atmosphere and warmed, as a function of time after formation of the complexes. These complexes were stable during the 35-day period, as there was no significant

**Table II.   EPTC Content[a] of Montmorillonite after Initial Treatment[b]**

| Time after Treatment, Days | Exchangeable Cation | | | |
| --- | --- | --- | --- | --- |
| | Cu$^{+2}$ | Mg$^{+2}$ | Ca$^{+2}$ | Al$^{+3}$ |
| 10 | 72 | 62 | … | 93 |
| 18 | 62 | … | 79 | 82 |
| 35 | 79 | 62 | 76 | 100 |

[a] Millimoles of EPTC per 100 grams of clay.
[b] Analyses of very small samples for nitrogen by microkjeldahl. Samples were exposed to atmosphere and heated on a steam radiator during this period.

change in the EPTC content. Under these conditions, the water vapor was not able to displace the organic compound. Farmer and Mortland (3) and James and Harward (4) have noted that ethylamine and ammonia, respectively, may be displaced from certain clay complexes by water in that they all compete for coordinating sites with the metal ion. In some copper-montmorillonite systems, coordinated ethylamine was stable and could not be displaced by water vapor.

However, when the EPTC-clay complexes were immersed in distilled water, the EPTC was readily displaced as shown in Figure 3. The clay films retained their form during immersion after which they were dried in the air and scanned with the spectrophotometer. In both Ca$^{+2}$ and Al$^{+3}$ systems, the EPTC could be completely displaced as indicated by the disappearance of the EPTC bands. These results suggest that, as far as the clay mineral fraction of soil is concerned, residues of EPTC will not remain on the clay surfaces in the presence of liquid water, yet under dried conditions, a stable EPTC-clay complex may exist. In the latter condition, the compound would not be expected to be very active biologically if it were in the interlamellar regions of swelling clay minerals since it would be removed from the proximity of plant roots. An influx of water would be expected, then, to displace the material again into the soil solution where it would exert its influence on growing plants. Apparently, water and EPTC compete for coordination position with the metal ions. Water is successful in displacing coordinated EPTC, however, mainly in an aqueous medium where the clay will expand to its limit, allowing easier entrance of water and egress of EPTC, and where the concentration of water is very great compared with that of EPTC.

### Quantitative Estimation of EPTC Complexed with Montmorillonite by Infrared Absorption

An attempt was made to utilize infrared absorption to determine quantita-
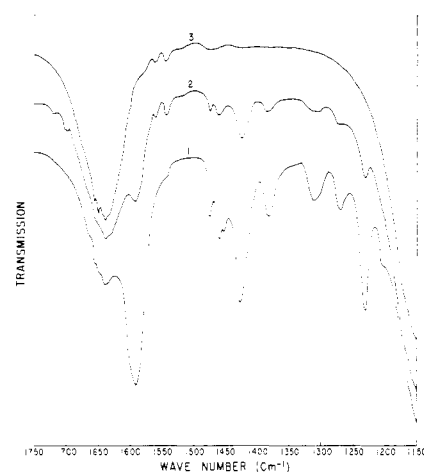


Figure 3.   Infrared spectra of EPTC-Ca-montmorillonite complex in 1150 to 1750 cm.$^{-1}$ region

1. Stable complex in air
2. After immersion in water for 16 hours
3. After immersion in water for 32 hours

tively the amount of EPTC complexed with montmorillonite. Freeze-dried Ca-montmorillonite was placed in thin layers in Petri dishes and then positioned in a vacuum desiccator containing a dish of liquid EPTC. The system was evacuated for 30 minutes, then maintained at about 40° C. for 3 days. The Petri dishes were then removed from the desiccator and exposed to the atmosphere at a temperature of 40° C. for 40 days to remove all free EPTC as indicated by the infrared spectrum. The EPTC-clay complex was then mixed with KBr in a Wig-L-Bug dental amalgam mixer at a concentration of 4 mg. per 600 mg. KBr. Then, 400 mg. of this mixture was made into standard circular KBr pellets. This pellet represented the highest EPTC concentration which was found by microkjeldahl analysis of the complex to be 0.76 mmole of EPTC per gram of clay. Lower concentrations were made by using less than 4 mg. of the EPTC-clay complex and making up the differences with the original freeze-dried Ca-montmorillonite containing no EPTC. All mixtures then contained a total of 4 mg. of clay.

Figure 4 shows the plot of the absorbance of the band at 1420 cm.$^{-1}$ vs. concentration of complexed EPTC in the clay. Apparently this technique can be used to obtain quantitative information on amount of EPTC complexed in clay minerals. A plot of the absorbance of the carbonyl band near 1590 cm.$^{-1}$ vs. concentration also gave a relatively good linear plot; however, the deformation band of H₂O at 1620 cm.$^{-1}$ interfered to some degree with the determination of the absorbance.
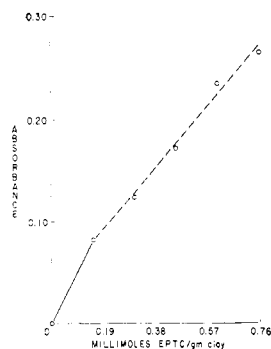
Figure 4. Plot of absorbance of the 1420 cm.$^{-1}$ band of EPTC-Ca-montmorillonite vs. m-mole of EPTC in the clay

## Table III. Biological Activity of EPTC on Ryegrass Seedlings in a Bioassay

| Treatment | Concentration of EPTC, P.P.M. | Germination, per 20 Seeds | | Mean Shoot Length per Plant, Mm. | |
|---|---|---|---|---|---|
| | | Sand | Filter paper | Sand | Filter paper |
| | | Test I | | | |
| EPTC | 0 | 12 | 10 | 10.6 | 12.7 |
| (technical) | 1 | 15 | 10 | 10.3 | 10.4 |
| | 2.5 | 10 | 8 | 8.5 | 6.4 |
| | 5 | 9 | 1 | 6.2 | 1.0 |
| EPTC-clay | 0 | 14 | 11 | 11.1 | 9.6 |
| complex | 10 | 15 | 6 | 12.5 | 7.4 |
| | 25 | 6 | 9 | 4.3 | 5.5 |
| | 50 | 6 | 7 | 5.1 | 4.5 |
| | | Test II | | | |
| EPTC | 0 | 16 | 16 | 6.6 | 6.7 |
| (technical) | 5 | 0 | 0 | 0 | 0 |
| | 10 | 0 | 0 | 0 | 0 |
| | 25 | 0 | 0 | 0 | 0 |
| EPTC-clay | 0 | 17 | 14 | 7.2 | 8.2 |
| complex | 50 | 14 | 13 | 2.1 | 3.0 |
| | 100 | 15 | 12 | 2.0 | 2.4 |
| | 250 | 8 | 11 | 1.5 | 1.8 |

## Biological Activity of Clay-Adsorbed EPTC

A bioassay of EPTC-montmorillonite complex that was stable in the atmosphere was conducted and compared directly with a standard using technical EPTC. The bioassay was carried out in Petri dishes using annual ryegrass (*Lolium multiflorum*) as a test plant. Twenty seeds of ryegrass were put in the Petri dish on both filter paper and sand media. Clay that contained EPTC at 0.76 mmole per gram was added to provide 10, 25, and 50 p.p.m. of EPTC in 10 cc. of water. In another series, technical EPTC was included at 1, 2.5, and 5 p.p.m. in 10 cc. of water. In a second experiment, the EPTC-clay complex was increased to 50, 100, 250 p.p.m., and the pure EPTC series was 0, 5, 10 and 25 p.p.m. The seeds were germinated in controlled environment incubators for 7 days at 80° F. in the first experiment and for 5 days in the second. Readings were also taken in the second experiment at the end of 11 days. The number germinated and the shoot length in millimeters were recorded.

The data shown in Table III show little biological activity from the EPTC-clay complex at concentrations below 25 p.p.m. The range of activity from this complex is approximately 10% of the technical EPTC used as a standard. Table III shows the data at higher concentrations of both the EPTC-clay complex and the technical EPTC. At 5 p.p.m., the technical EPTC inhibited germination of ryegrass seeds. At 50 p.p.m. of the complex, some seeds germinated; however, a high degree of biological activity was noted indicating a substantial release of active EPTC from the EPTC-clay complex in the presence of water used in the bioassay. These results are in accord with those obtained above in the study of the stability of the EPTC-clay complex where it was shown that liquid water could displace EPTC from the clay system.

## Conclusions

The results presented above suggest the mode of adsorption of EPTC on the clay mineral montmorillonite may involve at least three mechanisms: coordination of the EPTC to exchangeable metal cations through the carbonyl group; coordination of the EPTC to the metal cations through the nitrogen if the molecule is sterically hindered; and hydrogen bonding of hydrogen on methylene groups to surface oxygen atoms on the clay mineral surface. Complexes of EPTC with montmorillonite were stable in the atmosphere, yet when immersed in water, the EPTC could be quantitatively displaced from the clay. Bioassay results indicated that the EPTC-clay complex, which was stable in the air, exerted bioactivity when placed in the assay medium. Quantitative estimation of EPTC complexed with clay was accomplished utilizing infrared absorption techniques.

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