Clays and Clay Minerals, Vol. 36, No. 3, 284–288, 1988.

INTERACTION OF PHENAMIPHOS WITH MONTMORILLONITE

J. MAZA RODRÍGUEZ, A. JIMÉNEZ LÓPEZ, AND SEBASTIÁN BRUQUE
Departamento de Química Inorgánica, Universidad de Málaga
Apartado 59, 29071 Málaga, Spain

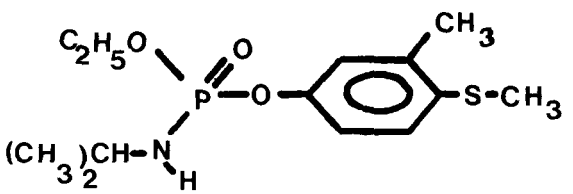
Abstract—Phenamiphos interacted with homoionic montmorillonites of Ca^{2+}, Mn^{2+}, Co^{2+}, and Ni^{2+} to form interlayer complexes having basal spacings of about 16.5 Å. In the infrared spectra, the ν-PO bands were displaced towards lower frequencies suggesting that this group interacted with the exchange cations. Moreover, a small shoulder at 1600 cm^{-1} indicated the partial protonation of the phenamiphos. After heating the complexes to 110°, 160°, and 200°C, however, the bands corresponding to δ-NH_2^+ and ν-NH intensified because of increased protonation, whereas the ν-PO bands had the same intensity as in pure phenamiphos. The fundamental implication of these observations is that phenamiphos interacts with exchange cations through molecules of coordinated water, possibly by means of the P=O group.

Key Words—Infrared spectroscopy, Montmorillonite, Organophosphorus compound, Pesticide, Phenamiphos, Protonation.

INTRODUCTION

Because of the increasing use of pesticides in agriculture it is essential to understand the interactions of such compounds with different crops and the soils in which they are grown. According to Bailey and White (1970), soil-pesticide interaction studies should embrace four aspects: (1) adsorption of the pesticide by soil components, (2) diffusion of the pesticide through the soil, (3) chemical and photochemical breakdown, and (4) microbiological breakdown. Adsorption of the pesticide by soil components affects all the other phenomena and is one of the commonest mechanisms of non-biological inactivation of pesticides in soils. In addition to providing information about the type of interaction involved, the results of pesticide adsorption studies suggest that silicates could serve as a retention matrix to permit a more controlled, sustained slow release of this class of substances.

Organophosphorus chemicals are widely used in agriculture; they are the pesticides most commonly inactivated by soils (Harris, 1972). The literature contains many studies of the interaction of organophosphorus compounds with montmorillonite. For example, Bowman *et al.* (1970) studied malathion; Saltzman and Yariv (1976), parathion; Sanchez Martin and Sanchez Camazano (1978), sumithion; Sanchez Camazano and Sanchez Martin (1980a), phosmet; Sanchez Martin and Sanchez Camazano (1980), phosdrin; and Sanchez Camazano and Sanchez Martin (1980b), dimethoate. The present work investigated the reactions of another organophosphorus compound, phenamiphos, the common name of O-ethyl-O-(3-methyl-4-methylthiophenyl)-isopropylamide phosphate, having the structural formula:



Because phenamiphos is a very toxic, solid compound, soluble in organic solvents and water, its application to soils may later produce surface and groundwater contamination. It is a persistent pesticide, and Homeyer (1971) reported activity in soils three or four months after application. This present report describes the interaction between the phenamiphos and montmorillonite in an organic medium.

EXPERIMENTAL

The montmorillonite employed in this study was from Tidinit, Morocco (Gutierrez Rios *et al.*, 1949). Homoionic forms of five cations, K^+, Ca^{2+}, Mn^{2+}, Co^{2+}, and Ni^{2+}, were prepared (fractions <5 μm). The samples containing the transition elements were prepared from homoionic Na-clay and 0.5 M solutions of the corresponding chlorides. The pH was maintained at 4 to avoid the formation of hydroxy cations or hydroxides. The resulting suspensions were then washed by centrifugation with deionized water until Cl^- was eliminated and the conductivity of the wash liquid was <15 μS. The cationic-exchange capacity of montmorillonite was 106 meq/100 g. The phenamiphos (99% purity) was supplied by Bayer-Hispania.

The complexes were prepared by immersing for 20 days 50 mg of each sample, previously dried for one week at 110°C, in one of a series of cyclohexane so-

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https://doi.org/10.1346/CCMN.1988.0360311 Published online by Cambridge University Press

Table 1. Basal X-ray powder diffraction spacings of homoionic smectites at 110°C and treated with phenamiphos.

Sample	110°C d(001) (Å)	Phenamiphos-treated d(001) (Å)	Δ (Å)
Mont-K	12.3	12.3	2.7
Mont-Ca	13.7	16.7	7.1
Mont-Mn	14.6	16.7	7.1
Mont-Co	15.3	16.3	6.7
Mont-Ni	14.6	16.2	6.6

Δ = d(001) − 9.6, for phenamiphos-treated samples.

lutions of phenamiphos (50 ml); the concentrations ranged from 1.5×10^{-4} to 3.0×10^{-3} M. Self-supporting films of the samples were prepared for the infrared (IR) studies and subsequently submerged for 20 days in 1×10^{-3} M cyclohexane-phenamiphos solution, washed with cyclohexane, and air dried.

The X-ray powder diffraction (XRD) studies were carried out on a Siemens D-501 instrument equipped with a DACO-MP microprocessor; the radiation was CuKα, monocromatized by a curved graphite crystal. The IR spectra were obtained with a Beckman 4620 spectrophotometer. Differential thermal analysis diagrams were obtained with a Rigaku-Thermoflex high-temperature apparatus using calcinated Al_2O_3 as the reference and a heating rate of 10 K/min.

RESULTS AND DISCUSSION

X-ray powder diffraction results

The XRD patterns of the homoionic samples treated with phenamiphos showed net increases in the basal spacings of the original clays; at least three orders of 00*l* reflections were seen in the patterns of all samples except those exchanged with potassium; here the basal spacings were smaller and the reflections were broad and weak. The basal spacings of the montmorillonite samples treated with pesticide solutions at the highest concentration indicated above were about 16.5 Å (Table 1) for the divalent cations, which suggests that the phenamiphos molecule was intercalated. The observed anomalous behavior of K-exchanged montmorillonite may have been due to the resistance to expansion of the partially dehydrated interlayer space, which was caused by the initial drying treatment at 110°C. After heating, the basal spacing of the K-clay was the lowest of the group (Table 1). In such a situation, the energy required to separate the layers represents a barrier which was only overcome if the final intercalate was more stable than the original. This increased stability of the final intercalate was unlikely because the affinity of an alkaline ion for a ligand such as phenamiphos must have been very weak; hence, only a partial intercalation resulted.

To investigate the effect of different concentrations of phenamiphos on interlayer complex formation, XRD patterns of the cation-exchanged smectites, which had previously been kept in contact with one of several different concentrations of the pesticide in cyclohexane, were obtained. The results (Table 2) indicate that above a certain concentration, fixed-space interlaminar complexes were formed. The smectite exchanged with the most polarizing cations (Mn^{2+}, Co^{2+}, and Ni^{2+}) needed concentrations close to 2×10^{-3} M, whereas for Ca^{2+}, the concentration was 1×10^{-3} M.

Table 2. Influence of concentrations (Ci) of phenamiphos on basal spacings of the interlayer complexes with montmorillonite.

Sample	$C_i \cdot 10^4$ (mole/liter)	d(001) (Å)
Mont-Ca	1.46	15.2
	4.37	15.9
	>11.65	16.5
Mont-Mn	1.46	15.0
	4.37	15.8
	>17.48	16.6
Mont-Co	1.46	14.7
	4.37	15.9
	>17.48	16.2
Mont-Ni	1.46	14.8
	4.37	15.2
	>23.30	16.2

Infrared spectra

The phenamiphos molecule contains two functional groups having pairs of free electrons, the P=O group and the secondary amine group, by which it interacts with interlayer cations to form intercalates having expanded basal spacings of about 7 Å. The IR spectra of pure phenamiphos and of the air-dried phenamiphos-smectite complexes are shown in Figure 1. A comparison of the spectra reveals a significant change in the stretching frequencies of the P=O groups. Table 3 lists the stretching frequencies of these groups in the phenamiphos and in the interlayer complexes. In the complexes, the band at 1235 cm^{-1} corresponding to ν-PO in the pure phenamiphos is shifted towards lower frequencies, the displacement magnitudes being between 10 and 12 cm^{-1}. No correlation was found between the polarizing power of the exchange cations and the observed displacements; however, the displacements suggest a decrease of the bond order in the P=O group and hence an interaction with the exchange cation,

Table 3. P=O stretching frequencies in the infrared spectra of phenamiphos adsorbed by homoionic montmorillonites.

Sample	P=O stretching (cm^{-1})
Pure phenamiphos	1235
Mont-K	1225
Mont-Ca	1225
Mont-Mn	1225
Mont-Co	1223
Mont-Ni	1225

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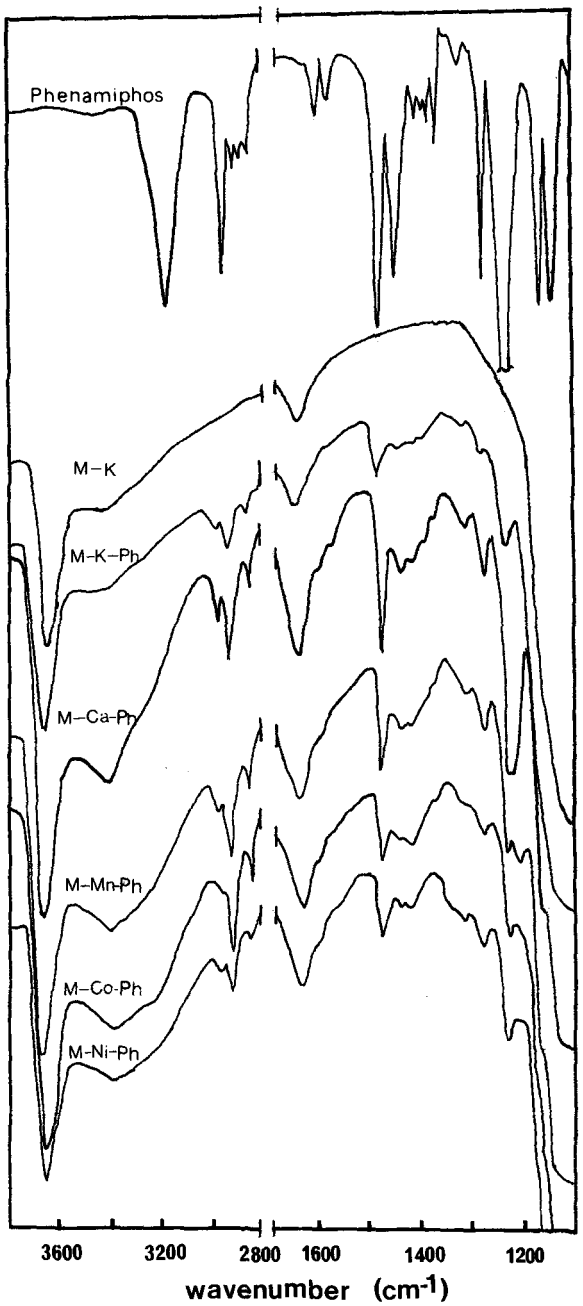


Figure 1. Infrared spectra of phenamiphos and montmorillonite-phenamiphos complexes (M-K-Ph = phenamiphos-K-smectite complex).

most probably through the water molecule coordinated with the cation. To test this hypothesis, films of the different complexes were heated for 24 hr to 110°, 160°, and 200°C (Figure 2). For all samples the ν-PO stretching band also showed a shift towards higher wavelengths in such a way that, at 160°C, it had the same value as for pure phenamiphos. These results confirm that the interaction between the exchange cations and

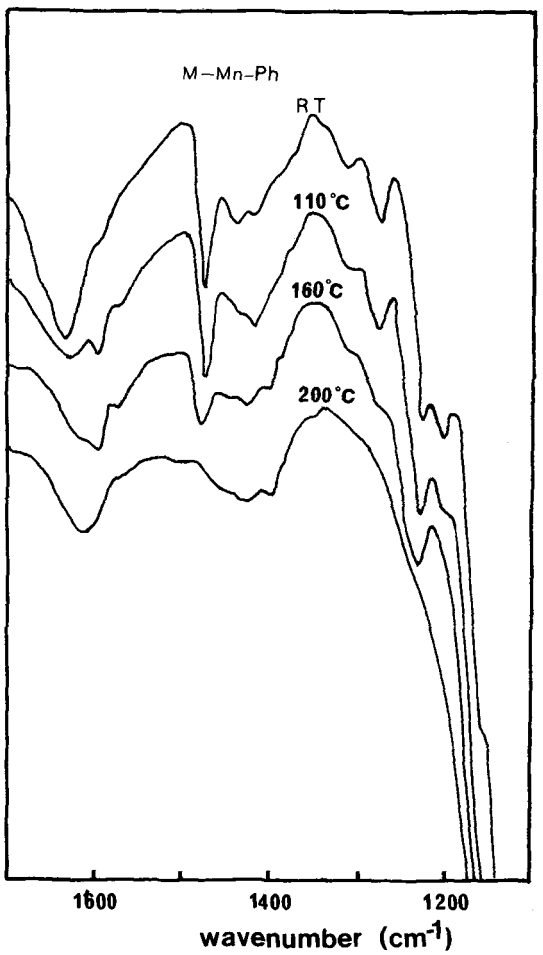


Figure 2. Evolution of infrared spectra of manganese montmorillonite-phenamiphos complexes (M-Mn-Ph) with temperature, in the 1000–2000-cm^{-1} region.

the phenamiphos molecules in the interlaminar complexes was through the coordinated water molecules. In the IR spectra of the Mn^{2+} and Ca^{2+} samples, however, another band was present next to the band at 1225 cm^{-1} (at 1205 and 1215 cm^{-1}, respectively), which persisted during the heating process. This band was probably due to a direct interaction between the exchange cation and the P=O group.

Another possible interaction between the phenamiphos molecule and the exchange cations is derived from the acid-base properties of both species. Phenamiphos has an amine group which can accept a proton; consequently, the exchange cations can behave as Brønsted acids according to the mechanism:

$$M(H_2O)^{2+}_n \leftrightharpoons [M(H_2O)_{n-1}OH]^+ + H^+.$$

This property is enhanced if the system is dehydrated, because the residual water on the cations is more polarized (Mortland and Raman, 1968). In the 1000–2000-cm^{-1} region of the IR spectra, a small

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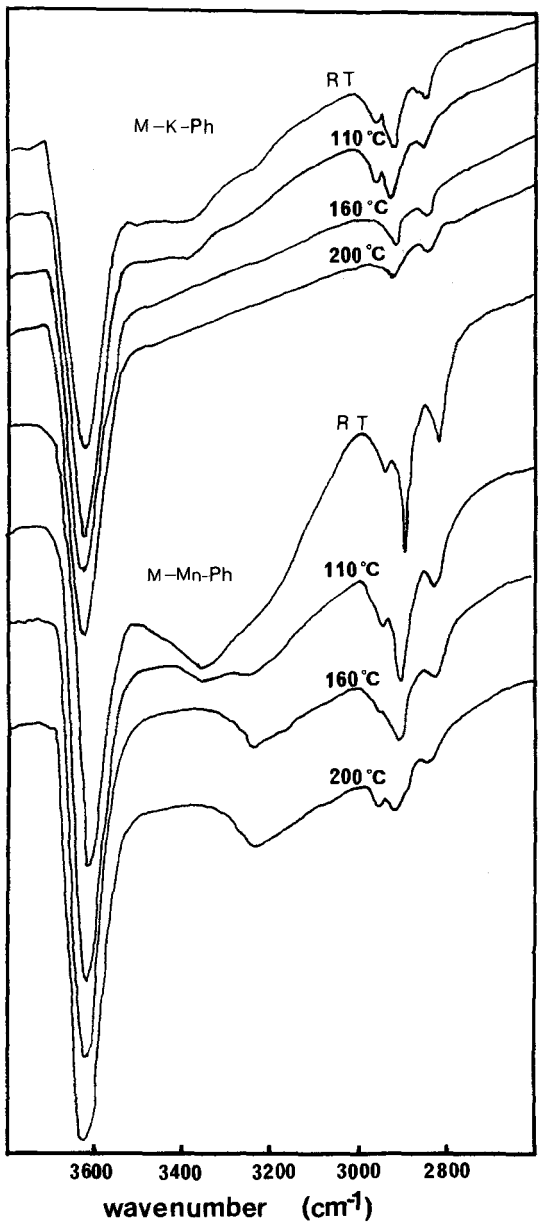


Figure 3. Evolution of infrared spectra of the K-montmorillonite (M-K-Ph) and Mn-montmorillonite-phenamiphos (M-Mn-Ph) complexes with temperature, in the 3000–4000-cm^{-1} region.

shoulder was observed at ambient temperature at about 1600 cm^{-1} which was attributed by Bellamy (1975) to δ-NH_2^+. This band might have been a consequence of restricted phenamiphos protonation. If the films were heated to 110° and 160°C, the intensity of the shoulder band increased because the acidic properties of the cations had been accentuated. Samples containing K^+ were the exception; no increase was noted because this cation has a less acid character.

The spectra in the region 3000–4000 cm^{-1} confirmed

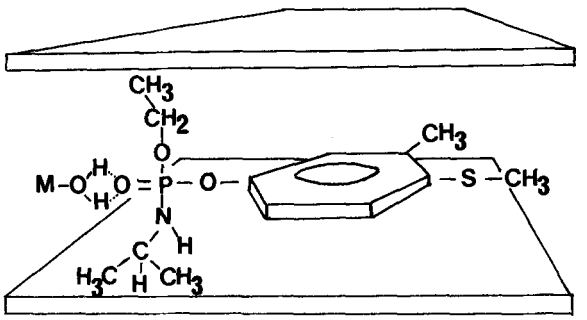


Figure 4. Schematic arrangement of phenamiphos molecules in the interlayer space of montmorillonite.

the hydrolysis of the exchange cations and the protonation of the phenamiphos (Figure 3). As the dehydration progressed, the intensity of the 3380 cm^{-1} band, which corresponds to ν-OH of the interlamellar water, decreased, whereas that of the 3260-cm^{-1} band, corresponding to ν-NH, increased. In the K^+-exchanged samples, however, although the 3380 cm^{-1} band almost completely disappeared, the 3260 cm^{-1} band did not intensify because no protonation had occurred.

The IR data indicate that the interaction between the phenamiphos molecules and the exchange cations at ambient temperatures took place principally by means of the P=O group and the molecules of water coordinated to the cations. A limited protonation was probably involved as well.

Phenamiphos molecule interlayer arrangement

The molecular configuration of the phenamiphos-smectite complexes shown in Figure 4 was arrived at from: (1) the dimensions of the phenamiphos molecule, obtained from molecular models (Interatomic Distances Supplement, 1965); (2) the observed increase of basal spacings (~7 Å); and (3) the IR data. These data may be reconciled by an arrangement in which the phenamiphos molecule is orientated within the interlayer space with the P=O group pointing towards the interlamellar cations and the aromatic ring plane almost parallel to the silicate layers. The theoretical increment of the basal spacing that would permit the suggested orientation of the phenamiphos molecule is 6.8 Å, a value close to the experimental values obtained for the interlaminar complexes.

Thermal stability of the interlaminar complexes

IR data established that phenamiphos remained in the interlayer space until at least 200°C and underwent protonation on heating. Differential thermal analysis (DTA) diagrams (Figure 5) showed an initial endothermic effect between 70° and 80°C that was assigned to weakly retained interlayer water. At temperatures of about 200°C, a shoulder was present which was assigned to the loss of the water coordinated to the cations.

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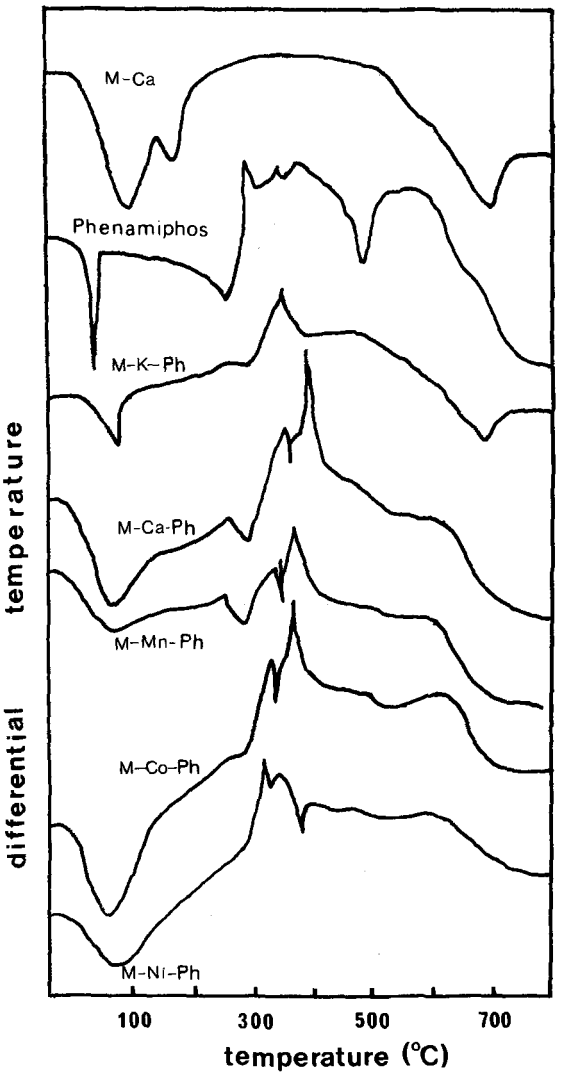


Figure 5. Differential thermal analysis curves of montmorillonite-phenamiphos complexes (M-K-Ph = phenamiphos-K-smectite complex).

The DTA diagram of phenamiphos shows a marked endothermic peak at 224°C which is followed by several exothermal peaks assignable to pyrolysis and combustion of the compound. This endothermal peak was recorded between 275° and 330°C for the sample complexes of K^+, Ca^{2+}, and Mn^{2+}. This retardation of phenamiphos decomposition in the complexes suggests that the silicate layers shielded the pesticide; however, for complexes of the samples containing Co^{2+} and Ni^{2+}, no endothermic effects were noted, perhaps because these cations catalyzed the direct oxidation of phenamiphos. All the complexes obtained were stable in air at normal temperatures; no decomposition was observed until about 275°C, although, at >110°C, the phenamiphos molecule in the interlayer space was protonated.

ACKNOWLEDGMENTS

The authors thank Bentonitas "El Ancla" (Málaga, Spain) for supplying the montmorillonite. They also express their gratitude to David W. Schofield for his translation of the Spanish text.

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(Received 14 July 1987; accepted 12 October 1987; Ms. 1688)

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