

HYDROLYSIS OF AZINPHOSMETHYL INDUCED BY THE SURFACE OF SMECTITES

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Abstract—The effect of layer charge and of the interlayer cations of smectites on the hydrolysis of azinphosmethyl (0,0-dimethyl S-((4-oxo-1,2,3-benzotriazine-3(4H)-yl)methyl) phosphorodithioate) in an aqueous medium was investigated. Ultraviolet spectroscopy was used for monitoring the hydrolysis process. Hydrolysis of the pesticide is catalyzed by Ca-hectorite (layer charge 0.216) but is not catalyzed by Ca-nontronite nor by Ca-montmorillonites with a layer charge above 0.216. The Mg- and Cu-hectorites and Cu-montmorillonite with a layer charge of 0.264 also show catalytic activity. The catalytic activities of the Ca^{2+} and Cu^{2+} cations as exchange cations of the smectite and as salts are compared. In agreement with previously reported work, the results show that the hydrolysis of azinphosmethyl may involve the adsorption of the pesticide into the interlayer space of the smectites, forming a bidentate complex with the interlayer cations. This interaction must enhance the electrophilic nature of the phosphorus atom, thereby facilitating its nucleophilic attack by the OH^- ion and producing rupture of the P–S bond.

Key Words—Hydrolysis, Adsorption, Azinphosmethyl, Smectite, Organophosphorus pesticides.

INTRODUCTION

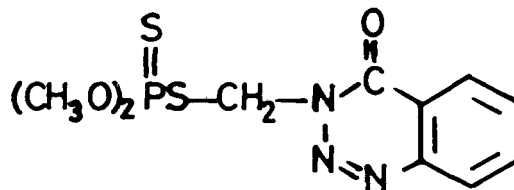
Clay minerals are able to inactivate adsorbed pesticides by catalyzing their decomposition. In most cases, this degradation occurs through hydrolysis (Hance, 1970; Mortland, 1970; Theng, 1974). This ability of clays to convert toxic organic compounds into their corresponding nontoxic forms may be of great importance if it is taken into account that these minerals are a common component of the colloidal fraction of soils, and also that they are used in the practical formulation of pesticides. Finely-divided clays are often used as inert diluting agents to reduce the concentration of pesticides to levels appropriate for their use in agriculture, and also for improving their handling properties.

The catalytic effect of kaolinite (Saltzman *et al.* 1976; Mingelgrin *et al.*, 1977), montmorillonite (Mortland and Raman, 1967; Sánchez-Camazano and Sánchez-Martín, 1983; Pusino *et al.*, 1988) and some soils (Konrad *et al.*, 1967, 1969; Konrad and Chester, 1969) in the hydrolysis of organophosphorus pesticides has been demonstrated.

A previous work by the authors on different aspects of the adsorption of azinphosmethyl by smectites (Sánchez-Martín and Sánchez-Camazano, 1984) included the study of the adsorption of this pesticide by different minerals from this group in an aqueous medium. In that study, occasional traces of azinphosmethyl hydrolysis were observed. Accordingly, it was thought of interest to investigate the effect of the layer charge and interlayer cations of smectite on the catalytic hydrolysis of this pesticide.

Azinphosmethyl is the common name of the organophosphorus insecticide (0,0-dimethyl S-((4-oxo-

1,2,3-benzotriazine-3(4H)-yl)methyl) phosphorodithioate). Its structural formula is:



MATERIALS AND EXPERIMENTAL METHODS

The clay samples employed in the present work are shown in Table 1. In all cases the $<2\text{-}\mu\text{m}$ fraction was used. Homoionic samples were prepared according to the method described by González-García and González-García (1953). The azinphosmethyl (98% purity), was supplied by Chem Service, West Chester, PA. It is a solid crystalline substance with a melting point of 73°C . Its solubility in water is $29\ \mu\text{g}/\text{ml}$ and it is soluble in most organic solvents (Worthing and Walker, 1987).

To study the influence of the interlayer cations and of the layer charge of the smectite on azinphosmethyl hydrolysis, 10 mg of the different samples ($=0.008$ meq of exchange cation) were treated with 10 ml of an aqueous solution containing $20\ \mu\text{g}/\text{ml}$ of the pesticide. The suspensions were kept for different periods of time with intermittent shaking in a chamber maintained at 30°C . The suspensions were centrifuged at 5500 rpm for 30 min. Hydrolysis was followed in the supernatant solution by UV spectrophotometry; absorption maximum of azinphosmethyl 228 nm, and absorption maximum of the hydrolysis product at 210 nm. The linear

Table 1. Smectites and exchange forms studied.

Smectite	Layer charge ¹	Cationic form
Tidinit montmorillonite ²	0.264	Ca, Mg, Cu
Hectorite-34, Hector, CA ³	0.216	Ca, Mg, Cu
Montmorillonite-24, Otay, CA ³	0.350	Ca
Nontronite-33b, Manito, WA ³	0.335	Ca

¹ Referred to an O₁₀(OH)₂ formula unit.

² Gutierrez-Ríos and González-García (1949).

³ American Petroleum Institute (1950).

range of concentrations for the measurement of azinphosmethyl was 2–20 µg/ml ($r = 0.99$; $p < .001$), and the linear range for the hydrolysis product was 2–10 µg/ml ($r = 0.98$, $p < .001$). The amount of azinphosmethyl adsorbed was calculated as the difference between the concentration of initial pesticide and that present at equilibrium. The amounts of azinphosmethyl adsorbed and hydrolyzed were expressed as percentages of the azinphosmethyl added initially.

To study the effect of Ca²⁺ and Cu²⁺ cations as salts on the hydrolysis of the azinphosmethyl, 0.008 meq of calcium chloride and copper sulfate were treated with 10 ml of the 20 µg/ml pesticide solution. The solutions were kept with intermittent shaking in a chamber maintained at 30°C for 10 days, thereafter recording their UV spectra. Distilled water was used generally. A few experiments were repeated using sterilized water in order to check for the possible existence of microbial degradation.

RESULTS AND DISCUSSION

Figure 1 shows the hydrolysis of azinphosmethyl by Mg-hectorite as followed by UV spectroscopy. It includes the spectrum of the 20 µg/ml solution of azinphosmethyl free of clay and the spectra corresponding to solutions of azinphosmethyl treated with clay over different periods of time. After 24 hr of treatment with the clay a decrease in absorbance of the maximum at 228 nm is observed due to the adsorption of the pesticide by the clay. At 48 hr, apart from the absorption at 228 nm, a shoulder appears at 210 nm that must correspond to a hydrolysis product. Subsequently, the absorbance of the maximum at 228 nm does not decrease, while that corresponding to the maximum at 210 nm increases progressively, showing that hydrolysis increases. It should be noted that after 20 days no hydrolysis is observed in the solution of azinphosmethyl free of clay kept under same conditions as the suspensions.

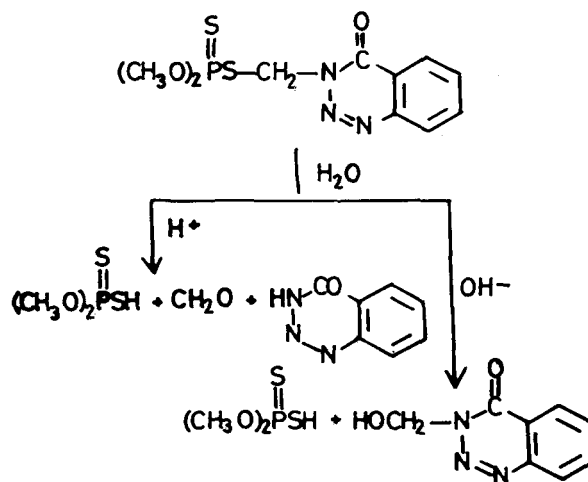
Figure 2 shows the process of azinphosmethyl hydrolysis by Cu-hectorite. The spectrum corresponding to the 20 µg/ml solution of pesticide is compared with spectra of the supernatant fluids after the solution has remained in contact with the Cu-hectorite for different

periods of time under the indicated experimental conditions.

Figure 3 shows the catalytic activity of the Ca²⁺ and Cu²⁺ cations as inorganic salts (CaCl₂, CuSO₄) in the hydrolysis of azinphosmethyl. In the presence of the Ca²⁺ cation, no modifications are seen in the spectrum of the compound in the 200–400 nm zone, indicating that the catalytic activity of Ca²⁺ as a salt is nil. In the presence of the Cu²⁺ cation, the maximum at 228 nm disappears completely and a maximum appears again at 210 nm, showing that the hydrolysis of the compound is 100%.

Although identification of the hydrolysis product that absorbed at 210 nm was not essential for the interpretation of the experimental results, attempts were made to determine it. To do so, we induced acid and alkaline hydrolysis of azinphosmethyl and hydrolysis products absorbing at 210 and 220 nm, respectively, were obtained.

The hydrolysis of azinphosmethyl in aqueous medium reported by Eto (1974) and by Melnikov (1971) is depicted below:



When azinphosmethyl is hydrolyzed in acid medium it yields 4-oxo, 3H-1,2,3-benzotriazine, but in alkaline medium it yields a hydroxymethyl derivative. Accordingly, it was considered that the product of the catalytic hydrolysis of azinphosmethyl by smectites and by CuSO₄ could be the benzotriazine.

The percentages of azinphosmethyl adsorbed after the different times of treatment and the percentages of the hydrolyzed compound were determined. As a reference for the hydrolysis product, that obtained by total hydrolysis of azinphosmethyl by CuSO₄ was employed. 4-oxo, 3H-1,2,3-benzotriazine was not found on the market when the study was being conducted. However, the later commercial availability of this product (Aldrich Chemical Co.) allowed us to confirm that, indeed, the benzotriazine absorbs at 210 nm under UV in an aqueous medium.

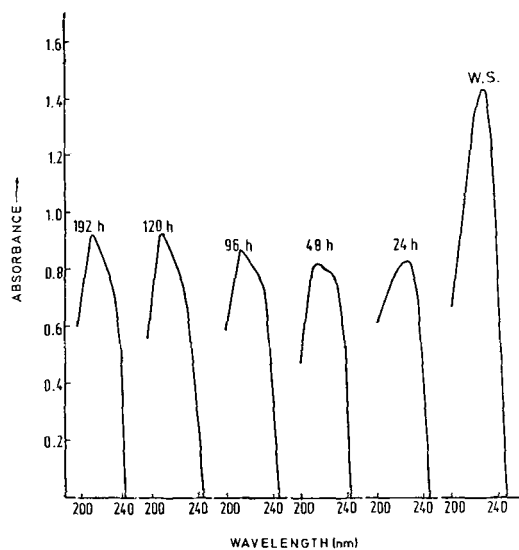


Figure 1. Hydrolysis of azinphosmethyl by Mg-hectorite as followed by UV spectroscopy: spectra of azinphosmethyl solution free of clay (W.S.) and of azinphosmethyl solution treated with clay over increasing periods of time.

Table 2 shows the results of the hydrolysis of azinphosmethyl in the presence of smectites and salts after 10 days. It should be noted that similar results are observed when using distilled or sterilized water in the experiments, which indicates that there is no microbial degradation. The chemical is hydrolyzed by the Ca-, Mg- and Cu- hectorites. The percentage of hydrolysis for the first two samples is similar. 20% of the hydrolysis produced by the Cu sample is apparent; the true

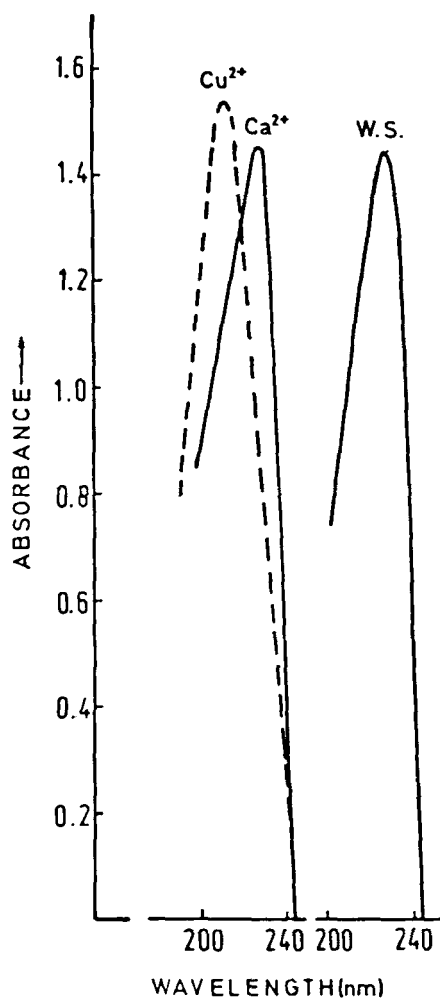


Figure 3. Hydrolysis of azinphosmethyl by Ca^{2+} and Cu^{2+} cations in solution as followed by UV spectroscopy: spectra of azinphosmethyl solution free of salts (W.S.) and of azinphosmethyl solution treated with CaCl_2 and with CuSO_4 for 10 days.

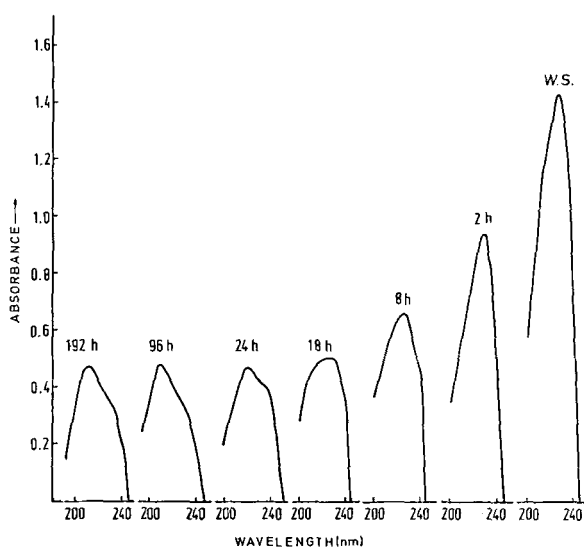


Figure 2. Hydrolysis of azinphosmethyl by Cu-hectorite as followed by UV spectroscopy: spectra of azinphosmethyl solution free of clay (W.S.) and of azinphosmethyl solution treated with clay over increasing periods of time.

percentage is possibly higher, as will be detailed below. It may be seen that the compound is not hydrolyzed by the Ca-smectites with a charge higher than that of hectorite. Neither is it hydrolyzed by the Tidinit Mg-montmorillonite, whereas it is hydrolyzed by the Cu sample of this mineral (charge 0.264). Additionally, the catalytic activity of Cu^{2+} is greater as a salt in solution than as an interlayer cation, unlike the situation with the Ca^{2+} ion. The results show that the catalytic activity of the smectites is related to the saturating cation and possibly to its layer charge, precisely the factors that generally govern the adsorption of organic molecules in the interlayer space of smectites and, in particular, that of azinphosmethyl (Sánchez-Martín and Sánchez-Camazano, 1984). The interlayer adsorption of the pesticide may therefore be involved in the cat-

Table 2. Hydrolysis of azinphosmethyl after 10 days contact with different homoionic samples and salts (% on initial chemical added).

Sample ¹	Layer charge	Hydrolysis ²
H-Ca	0.216	42
H-Mg	0.216	46
H-Cu	0.216	20
M-Ca	0.264	0
M-Mg	0.264	0
M-Cu	0.264	20
M-Ca	0.350	0
N-Ca	0.335	0
CuSO ₄	—	100
CaCl ₂	—	0
Water solution	—	0

¹ H, hectorite; M, montmorillonite; N, nontronite.

² Observed by UV spectroscopy. The true levels are possibly higher (see text).

alytic process of hydrolysis, in addition to the adsorption on the external planar surfaces of the clays.

Table 3 shows the influence of the interlayer cation of the hectorite on hydrolysis. It is seen that after adsorption equilibrium has been reached, at 24 or 48 hr and, although the percentage of hydrolyzed compound increases, the sample does not adsorb more azinphosmethyl. This suggests that the adsorption sites may continue to be occupied by hydrolysis products, although the product absorbing under UV partly passes into the solution. The Cu-hectorite, which owing to the characteristics of the Cu cation may adsorb more azinphosmethyl and produce a stronger degree of hydrolysis, apparently only hydrolyzes 20%. In a previous work (Sánchez-Martín and Sánchez-Camazano, 1984) on the mechanism of interaction of azinphosmethyl with homoionic samples of montmorillonite, IR spectroscopy findings suggested that the P-S and C-O groups of the pesticide molecule interact simultaneously with the interlayer cations of the phyllosilicate to form a bidentate complex. The Cu sample was an exception; interaction with the cation probably occurred through the P-S group and a nitrogen atom on the triazine ring, also forming a bidentate complex. The strong affinity of the Cu²⁺ cation for electrons, together with this different mechanism of interaction, may allow a greater proportion of hydrolysis products to remain in the interlayer space. The authors have observed that 4-oxo, 3H-1,2,3-benzotriazine is adsorbed into the interlayer space of Cu-hectorite. X-ray and IR results showed that the interaction occurs, like azinphosmethyl, between the Cu²⁺ cation and a nitrogen atom of the triazine ring.

From the foregoing, it may be inferred that the catalytic hydrolysis of azinphosmethyl by smectites must be the result of the formation of the aforementioned bidentate complex. The normal hydrolysis reaction is strongly mediated by the deficiency of electrons in the

Table 3. Adsorption and hydrolysis of azinphosmethyl (% on initial chemical added) by different homoionic hectorites.

Time (h)	Ca hectorite		Mg hectorite		Cu hectorite	
	Adsorption	Hydrolysis ¹	Adsorption	Hydrolysis ¹	Adsorption	Hydrolysis ¹
2	56	0	20	0	32	0
8	58	24	25	0	52	0
18	60	27	30	0	61	0
24	62	27	42	0	71	20
48	62	31	48	41	74	20
72	62	34	48	42	74	20
96	62	37	48	43	74	20
120	62	39	48	46	74	20
192	62	42	48	46	74	20

¹ Observed by UV spectroscopy. The true levels are possibly higher (see text).

phosphorus atom. The interaction in question increases the electrophilic nature of the phosphorus atom by facilitating its nucleophilic attack by the OH⁻ ion, thus leading to rupture of the P-S bond. The strong catalytic activity of the Cu²⁺ cation as a salt in solution may be due to the same easy accessibility for the pesticide. The null catalytic activity of the Ca²⁺ cation in solution is probably due to the fact that under these conditions this cation forms a monodentate rather than a bidentate complex. The bidentate complex would only be formed by the Ca²⁺ cation on the restricted internal surface of the hectorite, governed by the configuration that the molecules necessarily have to adopt owing to the negative surface of oxygen atoms of the phyllosilicate. Many reactions catalyzed by the surface of phyllosilicates involve the selective intercalation of compounds on the restricted surface of these minerals (Theng, 1974; Setton, 1986).

CONCLUSIONS

Hydrolysis of azinphosmethyl in an aqueous medium is catalyzed by different smectites. The catalytic activity of these silicates in the hydrolysis seems to be related to their layer charge and to the nature of the saturating cations. Adsorption of azinphosmethyl on clay surfaces, especially adsorption into the interlayer space, may be involved in the hydrolysis process. The formation of a bidentate interlayer complex between azinphosmethyl and the interlayer cations, in agreement with previously reported work, may strongly enhance the normal hydrolysis reaction of the pesticide in aqueous media.

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