

Sorption and Catalytic Hydrolysis of Diethyl-Ethyl on Homoionic Clays

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Sorption and catalytic hydrolysis of the herbicide diethyl-ethyl [*N*-chloroacetyl-*N*-(2,6-diethylphenyl)glycine ethyl ester] on homoionic Na⁺, K⁺, Ca²⁺, and Mg²⁺-montmorillonite clays were studied in aqueous media. The Freundlich sorption coefficient, K_f , measured from isotherms on clay followed the order of Na⁺ \approx K⁺ > Mg²⁺ \approx Ca²⁺. Analysis of FT-IR spectra of diethyl-ethyl sorbed on clay suggests probable bonding at the carboxyl and amide carbonyl groups of the herbicide. The rate of herbicide hydrolysis in homoionic clay suspensions followed the same order as that for sorption, indicating that sorption may have preceded and thus caused hydrolysis. Preliminary product identification showed that hydrolysis occurred via nucleophilic substitution at the carboxyl carbon, causing cleavage of the ester bond and formation of diethyl-ethyl and its dechlorinated derivative, and at the amide carbon, yielding an ethyl ester derivative and its acid. These pathways also suggest that hydrolysis of diethyl-ethyl was catalyzed by sorption on the clay surface.

Keywords: Sorption; adsorption; diethyl-ethyl; diethyl-ethyl; hydrolysis; montmorillonite; clay; catalytic hydrolysis

INTRODUCTION

The environmental fate of pesticides depends greatly on the interactions between pesticides and the solid surface of soil or sediments. The contribution of organic and mineral fractions to the sorption of nonionic organic molecules in soil has been the subject of many studies (e.g., Chiou et al., 1979; Laird et al., 1994; Senesi, 1994; Cox et al., 1998). It is well-known that in moist and organic matter-rich soils, sorption of an organic compound is usually dominated by its partitioning into soil organic matter. In dry or organic matter-poor soils, however, sorption onto mineral surfaces is often more important. Sorption on clay minerals is important also because it can result in decomposition of certain pesticides. Rapid and extensive clay-catalyzed transformations have been reported for organophosphorus insecticides (e.g., Konrad et al., 1967; Mortland and Raman, 1967; Saltzman et al., 1974; Mingelgrin et al., 1975; Camazano and Martin, 1983; Pusino et al., 1988; Torrents and Stone, 1994), *s*-triazine herbicides (e.g., Brown and White, 1969; Skipper et al., 1978), and other pesticides (e.g., Gessa et al., 1987; Pusino and Gessa, 1990; Pusino et al., 1996). For instance, it was noted that phosmet hydrolyzed 500-fold faster in the presence of montmorillonite than in a clay-free solution (Camazano and Martin, 1983). In most cases, transformation occurs through hydrolysis and rearrangement reactions, and the rate of transformation is typically related to the pesticide structure as well as to the type of exchangeable cations. The hydration water surrounding cations in clay interlayers was found to be much more protonated than

the bulk water (Mortland, 1970; Frenkel, 1974; Solomon and Hawthorne, 1983). The polarized water molecules, typically in clay saturated with polyvalent cations such as Al³⁺ and Fe³⁺, could form hydrogen bonds or other covalent bonds, causing bond cleavage of pesticides (Saltzman et al., 1974; Skipper et al., 1978; Mingelgrin and Saltzman, 1979; Camazano and Martin, 1983; Pusino et al., 1988, 1996; Pusino and Gessa, 1990).

In this study, we determined clay-catalyzed hydrolysis of diethyl-ethyl [*N*-(chloroacetyl)-*N*-(2,6-diethylphenyl)glycine ethyl ester] and investigated the probable correlation between sorption and hydrolysis. Diethyl-ethyl is used on beets, sugarbeets, spinach, grass, and peppers for annual grass and broad-leaved weed control. Diethyl-ethyl was selected in this study because it is a member of the widely used chloroacetanilide herbicide family and thus contains the chloroacetanilide structure like herbicides such as alachlor and metolachlor. Unlike most chloroacetanilide herbicides, however, diethyl-ethyl also has an ethyl ester substitution, and the catalytic hydrolysis of the ester bond is of interest because the mechanisms may be applicable to many other pesticides that have similar structures.

MATERIALS AND METHODS

Clay and Chemicals. The clay used was a montmorillonite Swy-2 from Crook County, WY, and was purchased from the Source Clay Minerals Repository at University of Missouri, Columbia, MO. The <2- μ m fraction was obtained by sedimentation. Na⁺, K⁺, Mg²⁺, and Ca²⁺-saturated clays were prepared by repetitive treatment of the clay with 0.5 mol L⁻¹ NaCl, KCl, MgCl₂, and CaCl₂ solutions. The prepared clay samples were centrifuged, washed repeatedly with deionized water until Cl⁻ free (determined by titration with AgNO₃), and ground to a fine powder after dried at room temperature.

Diethyl-ethyl with a purity of 99% was purchased from Chem Service (West Chester, PA). Indicators used for measur-

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ing the internal pH of homoionic clays were purchased from Aldrich Chemical Co. (Milwaukee, WI) and included phenol red (pH 6.8–8.2), thymol blue (pH 8.0–9.2), and thymolphthalein (pH 8.8–10.5).

Batch Sorption Experiment. Sorption isotherms of diethyl-ethyl on Na^+ , K^+ , Mg^{2+} , and Ca^{2+} -saturated clays were determined at $20 \pm 1^\circ\text{C}$. Triplicate samples of 25 mg of air-dried homoionic clay were equilibrated with 50.0 mL of herbicide solution containing 5% methanol in 150-mL flasks. The initial concentration of herbicide ranged from 20 to 100 $\mu\text{mol L}^{-1}$. The use of 5% methanol in the herbicide solution was to overcome the solubility. The sample flasks were shaken for 24 h to achieve equilibrium. Preliminary kinetic studies using multiple sampling intervals showed that over 95% of the sorption took place within the first 6 h. No decomposition product was detected by HPLC analysis during the 24-h equilibration. At equilibrium, the suspension was centrifuged at 10 000 rpm for 15 min, and an aliquot was injected in HPLC after filtering through a 0.2- μm syringe filter. The amount adsorbed on clay was calculated from the difference between the initial and final concentration of herbicide in solution.

The external and internal pH values were measured for montmorillonite clays saturated with different cations. The external pH was measured directly in the suspension by using a glass pH electrode. The interlayer pH was estimated by adding different pH indicators in the suspension and observing color change after stirring the suspension for 20 min. Delayed color change after a few minutes of stirring was assumed to indicate pH in the clay interlayer, because any response in the bulk solution would have been instantaneous. Similar indicator methods were used in other studies for measuring surface acidity of clays (Frenkel, 1974; Solomon and Hawthorne, 1983).

FT-IR Analysis of Adsorbed Herbicide. Sorption mechanisms of diethyl-ethyl on clay were investigated by using FT-IR analysis of thin films of herbicide–clay complexes. Self-supporting films of clay were prepared by evaporating 5 mL of homoionic clay suspension in a 5-cm (i.d.) ring on a polyethylene sheet at room temperature. After air-drying, the thin film was lifted off the plastic sheet and divided into two halves. One half was immersed in 1% herbicide– CHCl_3 solution for 24 h and rinsed several times with clean CHCl_3 after removal. The other half of the film was not treated with herbicide but was similarly washed with CHCl_3 . FT-IR spectra of the treated and untreated films were recorded under the same conditions using a Galaxy 4020 series FT-IR spectrometer (Mattson Instrument Co., Madison, WI). Differential spectra of adsorbed diethyl-ethyl were obtained by subtracting the spectra of the herbicide-treated film from that of the herbicide-free film. The spectrum of the pure diethyl-ethyl was obtained from a KBr disk containing 20 mg of the herbicide.

Hydrolysis Experiment. Hydrolysis of diethyl-ethyl was measured in clay suspensions. In general, 25 mg of Ca^{2+} , Mg^{2+} , K^+ , or Na^+ -clay was suspended in 50 mL of herbicide solution (100 $\mu\text{mol L}^{-1}$) made of methanol (20%) and water (80%) in 150-mL flasks. The use of 20% methanol was to overcome the solubility and was also needed to methylate acidic metabolites to allow structure identification on GC–MS. Methyl or ethyl alcohol was also used in similar studies (Pusino et al., 1988; Pusino and Gessa, 1990). The suspension was continuously stirred using a Teflon-coated magnetic bar at room temperature ($21 \pm 1^\circ\text{C}$). Hydrolysis was followed by removing 1-mL aliquots at different times and analyzing herbicide concentration on HPLC after filtering the sample through a 0.2- μm syringe filter. The pH of the suspensions was periodically checked and was found to remain almost constant during the entire experiment (6.8, 6.9, 7.9, and 7.9 for Ca^{2+} , Mg^{2+} , K^+ , and Na^+ -clays, respectively). A clay-free control was included, and its pH was 5.5.

HPLC analysis for diethyl-ethyl concentration was conducted using a HP 1090 HPLC (Hewlett-Packard, Wilmington, DE) equipped with an autoinjection system and a diode-array detector (DAD). The column was a 250 mm \times 4.6 mm (i.d.) reverse-phase Adsorbosphere HS C_{18} 5 μm (Alltech, Deerfield,

Table 1. External and Interlayer pH Values of Homoionic Montmorillonite Clays

cationic montmorillonite ^a	external pH	interlayer pH
Na^+	7.9	10.5 > pH \geq 9.2
K^+	7.9	10.5 > pH \geq 9.2
Mg^{2+}	6.9	9.2 > pH \geq 8.2
Ca^{2+}	6.8	9.2 > pH \geq 8.2

^a Measured in clay suspensions made of 50 mg of adsorbent/50 mL of deionized water.

Table 2. Freundlich Constants (K_f and n_f) and Correlation Coefficients (r^2) for Sorption of Diethyl-Ethyl on Homoionic Clays

homoionic clay	K_f	n_f	r^2
Na^+	72.1 \pm 1.2	1.74 \pm 0.09	0.97
K^+	67.7 \pm 1.2	1.69 \pm 0.08	0.97
Mg^{2+}	28.4 \pm 1.2	1.65 \pm 0.08	0.97
Ca^{2+}	27.1 \pm 1.1	1.67 \pm 0.07	0.98

IL), the injection volume 10 μL , and the wavelength of detection 230 nm. Mobile phase (1 mL min^{-1}) was made of acetonitrile–water (80:20, v/v) and acidified to pH 3 with phosphoric acid. The retention time of diethyl-ethyl, under the used chromatographic conditions, is 5.8 min. External calibration was used for quantification.

Preliminary identification of metabolites from clay-catalyzed hydrolysis was conducted on a HP5890 GC in tandem with a HP 5971 MSD. To enrich metabolites, the initial herbicide concentration was increased to 0.1% (w/w) and the amount of clay (Na^+ -clay) was increased to 0.5 g. Ten days after treatment, clay suspension of pesticide was centrifuged, and the supernatant was partitioned with hexane. The hexane extract was scanned in the EI mode for the m/z range of 50–500. The GC column was a HP-5 MS capillary column (cross-linked 5% phenylmethyl silicone, 30 m \times 0.25 mm \times 0.25 μm). Oven temperature was held at 100 $^\circ\text{C}$ for 3.0 min and then ramped to 210 $^\circ\text{C}$ at 10 $^\circ\text{C}/\text{min}$ and held at 210 $^\circ\text{C}$ for 6.0 min.

RESULTS AND DISCUSSION

Sorption. The external and internal pH values of the clay suspensions are given in Table 1. The pH in the bulk suspension of Na^+ - and K^+ -clays was about 1 log unit greater than that of Mg^{2+} - and Ca^{2+} -clays. The interlayer pH range estimated by the use of pH indicators was substantially higher than the external pH for the same clay. It was previously found that the suspension of Na^+ -montmorillonite was not stable and could undergo hydrolysis according to the following schematic equation (Bar-on and Shainberg, 1973; Shainberg, 1973; Llorca and Cruz-Romero, 1977):



Therefore, the pH in the interlayer of Na^+ -montmorillonite could be extremely high because of the presence of OH^- . A similar mechanism may also be expected for K^+ -clay. The difference in basicity between clays saturated with Ca^{2+} or Mg^{2+} and Na^+ or K^+ was in agreement with the general trend of clay acidity established by either using Hammett indicators or titration with bases (Solomon and Hawthorne, 1983; Mortland and Raman, 1968). Acidity of homoionic clays was found to increase in the order of $\text{K}^+ = \text{Na}^+ > \text{Li}^+ > \text{Ca}^{2+} > \text{Mg}^{2+} > \text{Al}^{3+}$ (Mortland and Raman, 1968).

Figure 1 shows the sorption isotherms of diethyl-ethyl on K^+ , Na^+ , Ca^{2+} , and Mg^{2+} -montmorillonite. All of the isotherms appear to be the “S” type according to the general classification of sorption isotherms (Sparks,

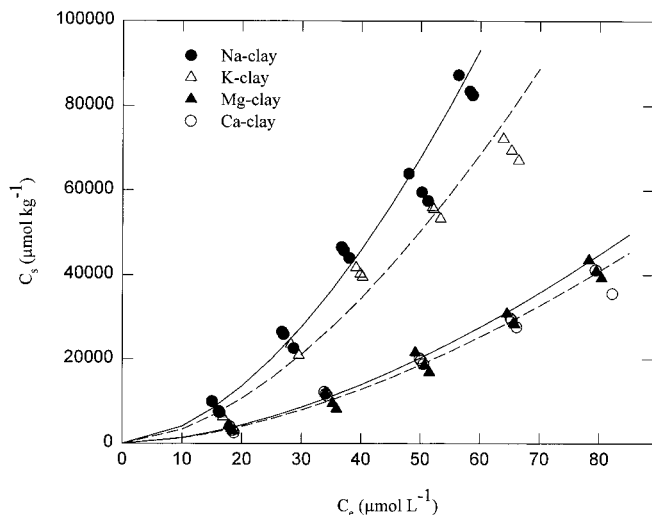


Figure 1. Sorption isotherms of diethatyl-ethyl on homoionic montmorillonites.

1995). The isotherms were all adequately described by the Freundlich equation, and the correlation coefficient, r , was >0.98 . The estimated Freundlich sorption coefficient, K_f , was significantly greater for Na^+ - and K^+ -clays (72.1 and 67.7, respectively) than for Mg^{2+} - and Ca^{2+} -clays (28.4 and 27.1, respectively). The overall order of sorption follows $\text{Na}^+ \approx \text{K}^+ > \text{Mg}^{2+} \approx \text{Ca}^{2+}$. This order coincided with the order of decreasing basicity in both the interlayer and the external solution of these homoionic clays (Table 1). The results suggest that the extent of sorption on clay may correlate with the pH in the interlayer of saturated clay or the type of the exchangeable cations.

To gain information on possible bonds formed during sorption of diethatyl-ethyl, FT-IR spectra of the herbicide adsorbed on clay were obtained. The differential spectra of sorption on Na^+ - and Ca^{2+} -clays are shown in Figure 2. After sorption, the vibration band of carboxyl was shifted from 1755 to 1720 cm^{-1} , while that of amide carbonyl was changed from 1664 to 1639–1643 cm^{-1} . These shifts in bond vibration indicate that these two groups were involved in bond interactions with clay surfaces. Based on the characteristics of the herbicide and the clay surface, it may be suggested that coordination bonds may have been formed between the carboxyl or amide carbonyl oxygen and saturation cations. Formation of coordination bonds was proposed to occur between $\text{C}=\text{O}$ of alachlor and hydrated cations of clay minerals by Bosetto et al. (1993). It was also proposed to contribute to the sorption of several acetanilide herbicides on clay minerals (Liu et al., 1999).

Hydrolysis. In a preliminary study, very rapid transformation of diethatyl-ethyl was observed in suspensions containing relatively high levels of clay. The clay-to-water ratio had to be reduced to 25 mg of adsorbent/50 mL of water in the current study to observe degradation kinetics. As shown in Figure 3, even at this very low clay level, hydrolysis of diethatyl-ethyl was still rather rapid compared to that in the clay-free control. In all cases, the initial dissipation of the herbicide was caused concomitantly by both sorption and degradation. From Figure 3, about 42% and 37% of diethatyl-ethyl was lost to sorption on Na^+ - and K^+ -clays, respectively, and 19% was lost to sorption on

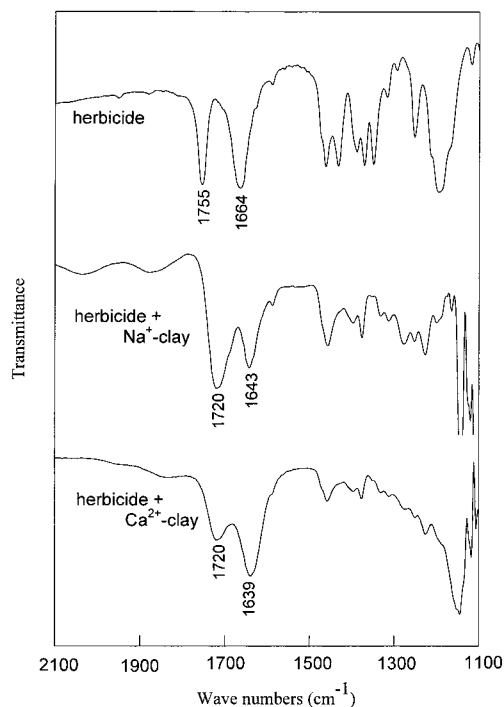


Figure 2. Differential infrared spectra of diethatyl-ethyl and its complexes with Na^+ - and Ca^{2+} -montmorillonite.

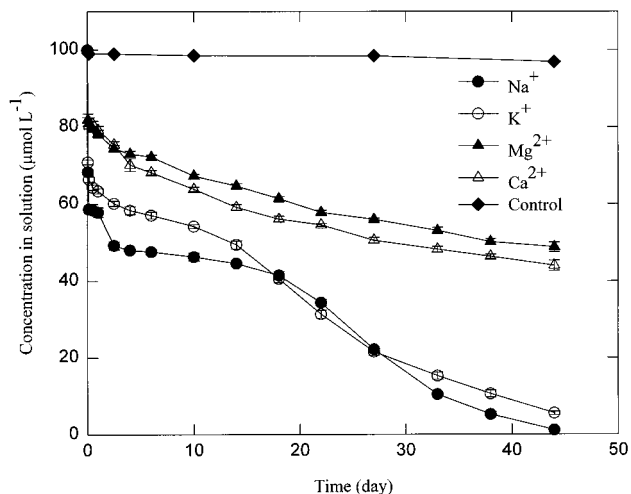


Figure 3. Dissipation of diethatyl-ethyl in cationic clay suspension.

Ca^{2+} - and Mg^{2+} -clays. After the sorption was completed, further concentration decrease may be attributed to herbicide decomposition in the solution or on the surface of the clay. Degradation of diethatyl-ethyl was significantly faster in Na^+ - and K^+ -clay suspensions than in Mg^{2+} - and Ca^{2+} -clay suspensions (Figure 3). Disappearance of diethatyl-ethyl in Ca^{2+} - and Mg^{2+} -clay suspensions followed first-order kinetics, and the half-life of dissipation was 50 days for Ca^{2+} -clay and 61 days for Mg^{2+} -clay. However, in Na^+ - and K^+ -clay suspensions, herbicide degradation appeared to have two phases, with a slow first phase followed by a fast second phase. The overall order of herbicide hydrolysis rate in clay suspensions coincided with that of herbicide sorption and further with that of basicity of homoionic clays. In a preliminary experiment, hydrolysis of diethatyl-ethyl was determined in water–methanol (80:20, v/v) mixtures that were adjusted to pH 5.5, 8.0, and 10.0. No

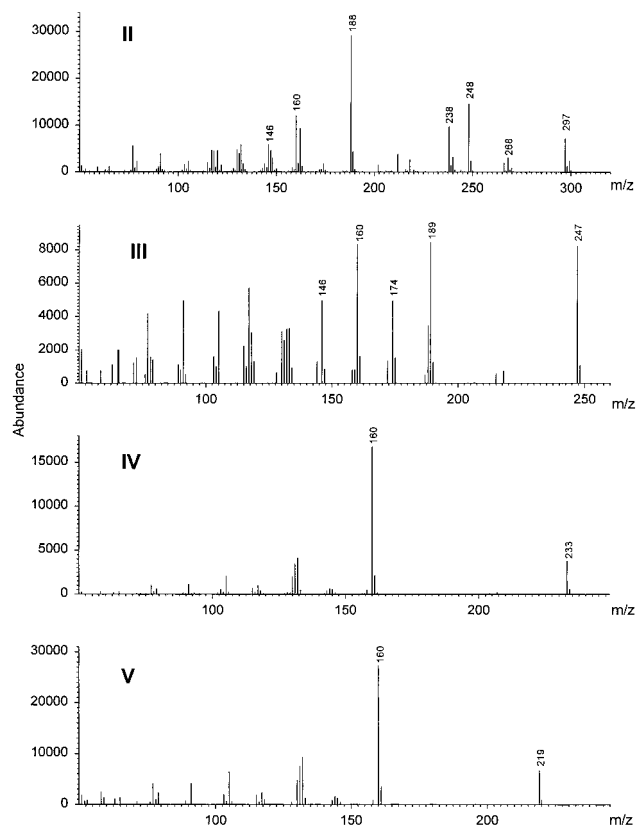


Figure 4. Mass spectra of metabolites from clay-catalyzed hydrolysis of diethatyl-ethyl.

hydrolysis was observed at pH 5.5 or 8.0, but rapid hydrolysis occurred at pH 10.0, with a first-order half-life of ~ 2.5 days. Therefore, hydrolysis of diethatyl-ethyl in clay suspensions would correspond better with the interlayer pH of these clays rather than their external pH. This would suggest that diethatyl-ethyl may have been first sorbed onto the interlayer clay surfaces where the high OH^- concentration in Na^+ - and K^+ -clays accelerated the hydrolysis.

Four metabolites were tentatively identified by interpreting mass spectra of unknown peaks (Figure 4). The retention times for compounds **II**, **III**, **IV**, and **V** were 14.1, 13.1, 9.5, and 8.8 min, respectively. Compound **II** had a molecular mass of 297, and its mass spectrum was consistent with the fragmentation pattern for diethatyl-methyl ester. Because methanol was used in the hydrolysis experiment, it is likely that diethatyl-methyl ester was formed from the acid diethatyl [*N*-chloroacetyl-*N*-(2,6-diethylphenyl)glycine, MW = 284]. This hydrolysis pathway resembled the $\text{B}_{\text{AC}2}$ hydrolysis mechanism (Larson and Weber, 1994). A $\text{B}_{\text{AC}2}$ reaction is known to be more effective when the environment is more alkaline, because OH^- serves as a more effective nucleophile than H_2O in the displacement reaction. This provides an explanation for the rapid hydrolysis of diethatyl-ethyl in Na^+ - and K^+ -clays, as these clays tend to dissociate, releasing OH^- . The delay observed in the first stage of diethatyl-ethyl hydrolysis on Na^+ - and K^+ -clays may have been caused by the time needed for the hydrolysis of the clay suspension to take place. A very similar decomposition pattern was observed by Pusino et al. (1988) for hydrolysis of quinalphos on Na^+ - and K^+ -bentonite. The same authors also observed faster hydrolysis of quinalphos on Na^+ - and K^+ -clays than on

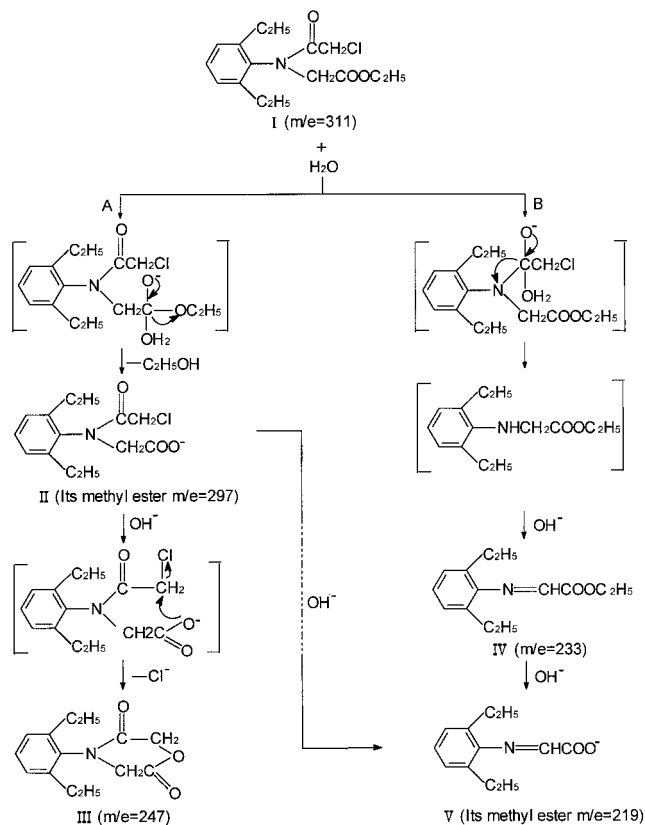
Ca^{2+} -clay. On the other hand, compound **II** could be also formed as a result of transesterification of diethatyl-ethyl with methanol in the reaction medium, where methanol served as a nucleophile. This pathway, however, may be insignificant in the Na^+ -clay suspension, as Na^+ - and K^+ -clays were known to be rather ineffective in catalyzing transesterification of diclofop-methyl in aqueous ethanol solution when compared to Ca^{2+} -clay (Pusino and Gessa, 1990).

Compound **III** had a mass of 247, and its mass spectrum was indicative of a stable six-atom ring because of the presence of a strong molecular ion (247). It was also noted that Cl of compound **II** was lost through this step, and thus compound **III** can be assumed to be *N*-(2',6'-diethylphenyl)-2,6-dione-morpholine. It seems that the transformation from **II** to **III** was a base-catalyzed $\text{S}_{\text{N}1}$ or $\text{S}_{\text{N}2}$ hydrolysis caused by a rearrangement inside compound **II**, where the nucleophilic group was $-\text{COO}^-$ and the leaving group was $-\text{Cl}$ (Schwarzenbach et al., 1993). This mechanism was likely again because of the presence of OH^- in the interlayer of Na^+ -clay. The molecular mass for compounds **IV** and **V** was respectively 233 and 219, and their mass spectra also showed that both compounds contained no Cl. Their mass spectra were consistent with the fragmentation pattern suggested for *N*-(2,6-diethylphenyl)iminoacetate ethyl ester and *N*-(2,6-diethylphenyl)iminoacetate methyl ester, respectively, where again the methyl ester (**V**) was formed from the acid due to the presence of methanol. In the conversion either from **II** to **V** or from **IV** to **V**, it appears that OH^- was involved, which again points to the role of Na^+ -clay in herbicide hydrolysis.

The formation of these metabolic products together suggests that hydrolysis of diethatyl-ethyl occurred through nucleophilic substitution at the carbon atom of the carboxyl and amide carbonyl groups, involving the cleavage of the ester bond and $-\text{C}-\text{N}$ of the acetamide. The fact that the molecule could be cleaved at both positions implies that the hydrolysis can take place via two different pathways, namely, routes A and B, as shown in Scheme 1. In route A, diethatyl-ethyl is hydrolyzed by nucleophilic attack at the carboxyl carbon, causing the displacement of $-\text{OC}_2\text{H}_5$. As OH^- is much better a nucleophile than H_2O , this reaction occurred rapidly in Na^+ -clay suspension. In route B, the first step is hydrolysis by nucleophilic attack at the carbon of the amide carbonyl group, followed by displacement of the entire chloroacetyl group, while the leaving group formed compound **IV** and subsequently **V**. Based on the relative peak size, it appears that compounds **II** and **III** were formed in a greater amount than compounds **IV** and **V**, indicating that route A may be faster than route B, likely because an ester is normally less stable than an amide.

The sites at which herbicide transformation initiates, i.e., the carboxyl group of the ester bond and the carbonyl group of the amide, are also the binding sites for herbicide sorption. This further suggests that hydrolysis of diethatyl-ethyl in clay suspensions was promoted by sorption to clay. The rate of this catalysis was closely dependent on the type of the exchangeable cation, with monovalent cations Na^+ and K^+ being substantially more reactive than bivalent cations Mg^{2+}

Scheme 1. Probable Hydrolysis Pathways of Diethyl-Ethyl on Homoionic Clays



and Ca²⁺. This dependence is in agreement with that found for other ester bonds (Saltzman et al., 1974; Mingelgrin et al., 1975; Mingelgrin and Saltzman, 1979; Camazano and Martin, 1983; Pusino et al., 1988). Especially, in K⁺- and Na⁺-clays, dissociation of the cations from clay could result in the production of OH⁻ that accelerates nucleophilic substitution (Schwarzenbach et al., 1993). Formation of a strong coordination bond between herbicide carboxyl and carbonyl groups and cations of Na⁺- and K⁺-clays may have also contributed to the rapid hydrolysis on these clays.

CONCLUSIONS

Diethyl-ethyl hydrolyzed in aqueous solution containing homoionic montmorillonite, and the rate of hydrolysis was closely dependent on the nature of the exchangeable cations. Several observations together suggested that the hydrolysis was catalyzed by clay surfaces following sorption. First, similar dependence on cations was found for hydrolysis and sorption, indicating that hydrolysis may have occurred in the sorbed state. Second, hydrolytic reactions occurred at the same sites where herbicide binding to clay surfaces was expected. And third, the effect of exchangeable cations on hydrolysis can be adequately explained by the pH of the hydrated cations and by their influences on the hydrolytic pathways. These conclusions also indicate that similar catalytic transformations may occur for diethyl-ethyl on other mineral surfaces having similar chemical-physical characteristics to that of montmorillonite and for other pesticides having similar molecular structures to that of diethyl-ethyl.

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