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Adsorption of acetanilide herbicides on soil and its components Ⅱ. Adsorption and catalytic hydrolysis of diethatyl-ethyl on saturated Na^+-, K^+-, Ca^{2+}-, and Mg^{2+}- montmorillonite

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Abstract: Adsorption and catalytic hydrolysis of the herbicide diethatyl-ethyl [N-chloroacetyl-N-(2,6-diethylphenyl) glycine ethyl ester] on homoionic Na^+-, K^+-, Ca^{2+}-, and Mg^{2+}-montmorillonite clays were investigated in water solution. The Freundlich adsorption coefficient, K_f, got from isotherms on clay followed the order of $Na^+ \approx K^+ > Mg^{2+} \approx Ca^{2+}$. Analysis of FT-IR spectra of diethatyl-ethyl adsorbed 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 adsorption, indicating that adsorption may have preceded and thus caused hydrolysis. Preliminary product identification showed that hydrolysis occurred via nucleophilic substitution at the carboxyl carbon, causing the cleavage of the ester bond and formation of diethatyl and its dechlorinated derivative, and at the amide carbon, yielding an ethyl ester derivative and its acid. These pathways also suggest that hydrolysis of diethatyl-ethyl was catalyzed by adsorption on the clay surface.

Key words: adsorption; catalytic hydrolysis; diethatyl; diethatyl-ethyl; montmorillonite

Introduction

It is well known that in moist and organic matter-rich soils, adsorption of an organic compound is usually dominated by its partitioning into soil organic matter. In dry or organic matter-poor soils, however, adsorption onto mineral surfaces is often more important. Adsorption on clay minerals is important also because it can inactivate adsorbed pesticides by catalyzing their decomposition. Rapid and extensive transformations catalyzed by mineral surfaces have been reported for a variety of pesticides, including organophosphorus insecticides (Konrad, 1967; Saltzman, 1974; 1976; Mingelgrin, 1975; 1977; 1979; Camazano, 1983; Pusino, 1988; Torrents, 1994), *s*-triazine herbicides (Brown, 1969; Skipper, 1978), and other pesticides (Gessa, 1987; Pusino, 1990; 1993). For instance, it was noted that phosmet hydrolyzed 500 folds faster in the presence of montmorillonite than in a clay-free solution (Camazano, 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 the characteristics of exchangeable cations. In particular, the hydration water surrounding cations in clay interlayers was found to be active in catalyzing pesticide hydrolysis (Mingelgrin, 1977), while the nature of cations was found to affect both the route and rate of surface-catalyzed transformations through influencing the reactivity of hydration water (Saltzman, 1974; Skipper, 1978; Mingelgrin, 1979; Camazano, 1983; Pusino, 1988, 1993; 1990).

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 adsorption of non-ionic organic molecules in soil has been the subject of many studies (Chiou, 1979; Laird, 1994; Senesi, 1994; Cox, 1995; 1998). In this study, we determined clay-catalyzed hydrolysis of diethatyl-ethyl [N-(chloroacetyl)-N-(2,6-diethylphenyl) glycine ethyl ester], and investigated the probable correlation between hydrolysis and adsorption. Diethatyl-ethyl is used on beets, sugarbeets, spinach, grass, and peppers for annual grass and broad-leaved weed control. Relatively little has been reported about its degradation and adsorption in soil. Diethatyl-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, diethatyl-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.

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1 Materials and methods

1.1 Clay and chemicals

The clay used was a montmorillonite Swy-2 from Crook County, Wyoming, and was purchased from the Source Clay Minerals Repository at University of Missouri, Columbia, MO. The < 2 μm fraction was obtained by sedimentation. Na^+-, K^+-, Mg^{2+}- and Ca^{2+}-saturated clays were prepared by repetitive treatment of the clay with 0.5 mol/L NaCl, KCl, $MgCl_2$ and $CaCl_2$ solutions. The prepared clay samples were centrifuged, washed repeatedly with deionized water until Cl- free, and ground to a fine powder after dried at room temperature.

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

1.2 Batch adsorption experiment

Adsorption isotherms of diethatyl-ethyl on Na^+-, K^+-, Mg^{2+}- and Ca^{2+}- saturated clays were determined at 20 ± 1℃. 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 μmol/L. The use of 5% methanol in the herbicide solution was to overcome the solubility, and is allowed according to U.S. EPA's relevant guidelines for sorption studies. The sample flasks were shaken for 24h to achieve equilibrium. Preliminary kinetic studies using multiple sampling intervals showed that over 95% of the adsorption took place within the first 6h. No decomposition product was detected by HPLC analysis during the 24h equilibration. At equilibrium, the suspension was centrifuged at 10000 r/min 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 colour change after stirring the suspension for 20 min. Delayed colour 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.

1.3 FT-IR analysis of adsorbed herbicide

Adsorption mechanisms of diethatyl-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 24h, 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 diethatyl-ethyl were obtained by subtracting the spectra of the herbicide-treated film from that of herbicide-free film. The spectrum of the pure diethatyl-ethyl was obtained from a KBr disk containing 20 mg of the herbicide.

1.4 Hydrolysis experiment

Hydrolysis of diethatyl-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 μmol/L) 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 in a parallel experiment. Methyl or ethyl alcohol was also used in similar studies (Pusino, 1988; 1990). The suspension was continuously stirred using a Teflon-coated magnetic bar at room temperature (21 ± 1℃). Hydrolysis was followed by removing 1 ml aliquot at different times and analyzing the remaining 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 diethatyl-ethyl concentration was conducted using a HP 1090 HPLC (Hewlett-Packard, Wilmington, DE) equipped with an auto-injection system and a Diode-Array detector (DAD). The column was a 250 mm × 4.6 mm (i.d.) reverse phase adsorbosphere HS C_{18} 5μm(Alltech, Deerfield, IL), the injection volume 10 μl, and the wavelength of detection 230 nm. Mobile phase (1 ml/min) was made of acetonitrile-water (80:20, v/v) and acidified to pH 3 with phosphoric acid. The retention time of diethatyl-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 GC-MS using 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 0.5g. The GC column was a HP 5 MS capillary column (crosslinked 5% phenylmethyl silicone, 30 m × 0.25 mm × 0.25 μm). Analysis was performed using aliquots sampled 10d after treatment.

2 Results and discussion

2.1 Adsorption

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^+-clay was about one unit greater than that of Mg^{2+}- and Ca^{2+}-clay. The interlayer pH range estimated by the use of pH indicators was substantially higher than the external pH for the same clay. The increased alkalinity in clay interlayers is caused by the localized interaction of the hydrated cation and its surrounding water molecules. For instance, 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, 1973; Shainberg, 1973; Llorca, 1977):

$$H_2O + Na^+\text{-clay} \longrightarrow H^+\text{-clay} + Na^+ + OH^-.$$

Therefore, the pH at the locality in the interlayer of Na^+-montmorillonite could be extremely high because of the very small space between the layers and the presence of a high level of OH^-. A similar mechanism may also be expected for K^+-clay.

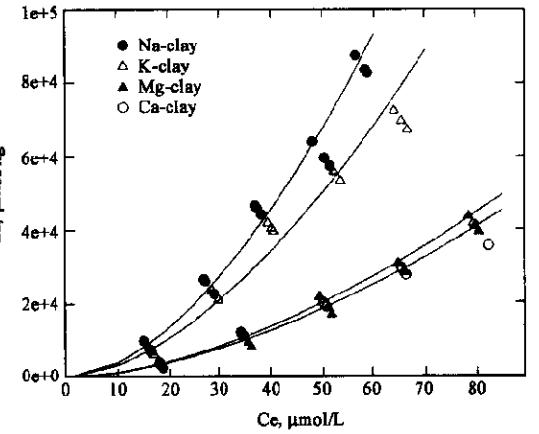

Fig.1 Adsorption isotherms of dietyatyl-ethyl on homoionic montmorillonites

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

Table 1 External and interlayer pH values of homoionic montmorillonite clays

Cationic montmorillonitea[a]	External pH	Interlayer pH
Na^+ -	7.9	10.5 > pH≥9.2
K^+ -	7.9	10.5 > pH≥9.2
Mg^{2+} -	6.9	9.2 > pH≥8.2
Ca^{2+} -	6.8	9.2 > pH≥8.2

a. Measured in clay suspensions made of 50 mg adsorbent in 50 ml deionized water

Table 2 Freundlich constants (K_f and n_f) and correlation coefficients (r^2) for adsorption of diethatyl-ethyl on homoionic clays

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

To gain information on possible bonds formed during adsorption of diethatyl-ethyl, FT-IR spectra of the herbicide adsorbed on clay were obtained. The differential spectra of sorption on Na^+- and Ca^{2+}- clay are shown in Fig.2. After adsorption, 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. Based on the characteristics of the herbicide and the clay surface, it may be suggested that H-bonds may have formed between the carboxyl or amide carbonyl oxygen and water molecules surrounding clay cations. Hydrogen bonding has been frequently observed in the interaction of pesticides with clay minerals and humic substances. For instance, H-bonding was found to play an important role in the adsorption of several acetanilide herbicides on clay minerals. Hydrogen bonding was also assumed to occur between the water

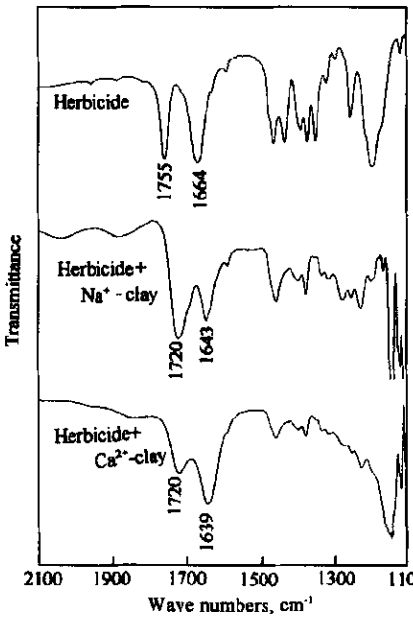

Fig. 2 Differential infrared spectra of diethatyl-ethyl and its complexes with Na^+- and Ca^{2+}-montmorillonite

molecules surrounding interlayer clay cations and the carbonyl oxygen of diclofop-methyl (Pusino, 1988) and fluazifop-butyl (Gessa, 1987).

2.2 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 in 50 ml of water in the current study to observe degradation kinetics. As shown in Fig. 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 adsorption and degradation. After the adsorption was completed, however, further concentration decrease may be assumed to be caused by herbicide degradation in the solution or on the surface of clay. It is clear that the degradation of diethatyl-ethyl was significantly faster in Na^+- and K^+-clay suspensions than in Mg^{2+}- and Ca^{2+}-clay suspensions (Fig. 3). Disappearance of diethatyl-ethyl in Ca^{2+}- and Mg^{2+}-clay suspensions followed the first-order kinetics, with $r > 0.97$. 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 cause for such a biphasic phenomenon was not understood from this study. Similar degradation kinetics was observed by Pusino *et al*. (Pusino, 1988) for hydrolysis of quinalphos on Na^+- and K^+-bentonite. The order of herbicide hydrolysis rate in clay suspensions coincided with that for herbicide adsorption, which suggests that there may be a correlation between herbicide hydrolysis and adsorption, or that adsorption may have preceded or caused the hydrolysis of diethatyl-ethyl.

Four metabolites were positively identified on GC-MS (Fig. 4). 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 $B_{AC}2$ hydrolysis mechanism (Larson, 1994). A $B_{AC}2$ 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. The rapid hydrolysis of diethatyl-ethyl in Na^+- and K^+-clay suspensions is a good evidence for this reaction mechanism. 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 S_N1 or S_N2 hydrolysis caused by a rearrangement inside compound Ⅱ, where the nucleophilic group was -COO- and leaving group was -Cl (Schwarzenbach, 1993). The molecular mass for compound 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)-imino-acetate ethyl ester and N-(2, 6-diethylphenyl)-imino-acetate methyl ester, respectively, where again, the methyl ester (V) was formed from the acid due to the presence of methanol.

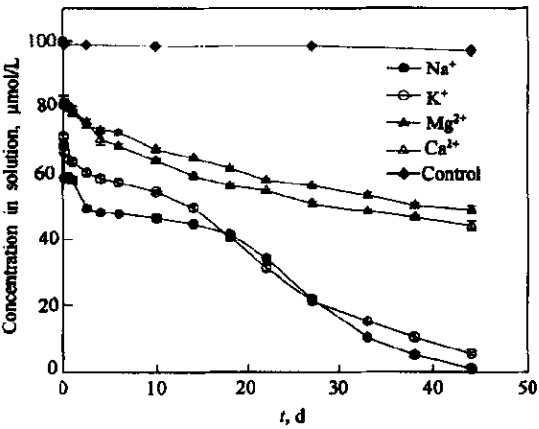

Fig. 3 Dissipation of diethatyl-ethyl in cationic clay suspension

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 ester bond and -C-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, route A and B, as shown in Fig. 5. In route A, diethatyl-ethyl hydrolyzed by nucleophilic attack at the carboxyl carbon, causing the displacement of $-OC_2H_5$. 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 compound Ⅱ and Ⅲ were formed in a greater amount than compound 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 initiate, i.e., the carboxyl group of the ester bond and the carbonyl group of the amide, are also the binding sites for herbicide adsorption. This further suggests that hydrolysis of diethatyl-ethyl in clay suspensions was caused first by adsorption and then by catalysis of herbicide by homoionic clays. The rate of this catalysis

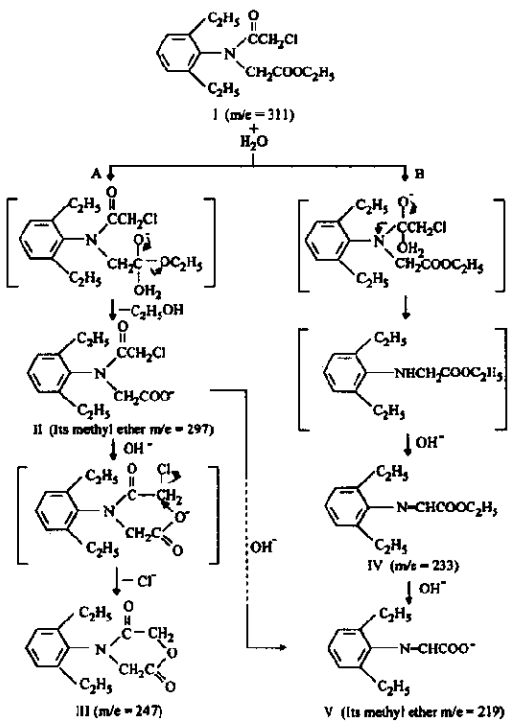

Fig. 5 Probable hydrolysis pathways of diethatyl-ethyl on homoionic clays

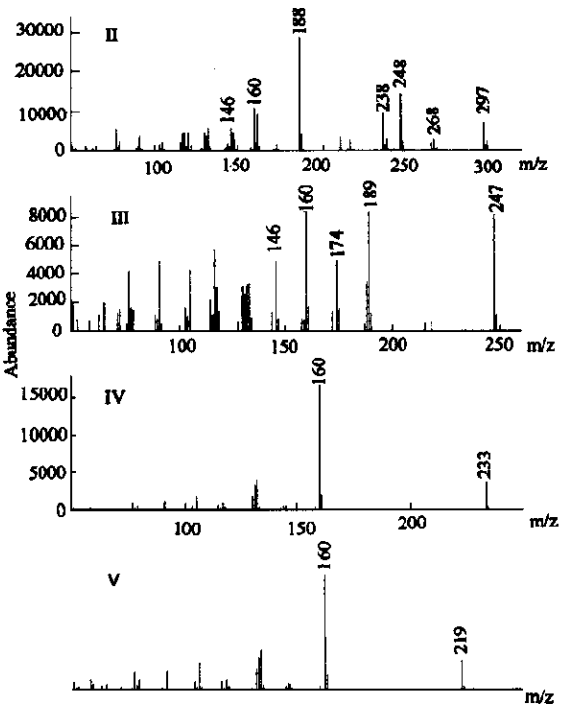

Fig. 4 Mass spectra of metabolites from clay-catalyzed hydrolysis of diethatyl-ethyl

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+} and Ca^{2+}. This dependence is in agreement with that found for other ester bonds (Saltzman, 1974; 1976; Mingelgrin, 1975; 1977; 1979; Camazano, 1983; Pusino, 1988), and may be explained from the nucleophilicity of the hydration water surrounding the cation. Especially, in K^+- and Na^+-clay, dissociation of the cations from clay could result in the production of OH^-, while OH^- is several orders of magnitude stronger in nucleophilicity than water (Schwarzenbach, 1993).

3 Conclusions

Diethatyl-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 suggest that the hydrolysis was catalyzed by clay surfaces following adsorption. First, similar dependence on cations was found for hydrolysis and adsorption, indicating that hydrolysis may have occurred in an adsorbed 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 or polarizing power of the hydrated cations, and by their influences on the hydrolytic pathways. These conclusions also indicate that

similar catalytic transformation may occur for diethatyl-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 diethatyl-ethyl.

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