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# Montmorillonite Surface-Catalyzed Hydrolysis of Fenoxaprop-ethyl

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The degradation of the herbicide fenoxaprop-ethyl [ethyl 2-[4-[(6-chloro-2-benzoxazolyl)oxy]phenoxy]-propanoate] on homoionic $Fe^{3+}$, $Al^{3+}$, $Ca^{2+}$, and $Na^+$ montmorillonite in aqueous medium was studied. The results show that the hydrolysis of the pesticide may involve two different mechanisms, both depending on the nature of the exchangeable cations. The herbicide hydrolyzes to 6-chlorobenzox-azolinone and ethyl 2-(4-hydroxyphenoxy)propanoate on $Fe^{3+}$ and $Al^{3+}$ clays, whereas the fenoxaprop acid [2-4-[(6-chloro-2-benzoxazolyl)oxy]phenoxy]propanoic acid] is the main hydrolysis product on $Ca^{2+}$ and $Na^+$ clays with minor amounts of 6-chlorobenzoxazolinone and 2-(4-hydroxyphenoxy)-propanoic acid. The protonation of the benzoxazole ring nitrogen of the herbicide can be responsible for the cleavage of the ether bridge of fenoxaprop-ethyl in the $Fe^{3+}$ and $Al^{3+}$ systems. Instead, the hydrolysis of the ester bond appears to be favored by the coordination of the carbonyl oxygen of fenoxaprop-ethyl with the hydrated exchangeable metal ions in the $Ca^{2+}$ and $Na^+$ systems.

## INTRODUCTION

Studies of herbicide fate in soil systems are complicated because of the complex chemical nature of the components that may take part in such processes. Attention has been focused on the role of natural organic matter (Perdue and Wolfe, 1983) and of the oxide surfaces (Torrents and Stone, 1994) and clays (Pusino et al., 1988; Pusino and Gessa, 1990; Sánchez-Camazano and Sánchez-Martín, 1991) in pesticide hydrolysis.

Clay surfaces are rather effective in catalyzing hydrolysis of organic pollutants. For instance, the herbicide phosmet is reported to hydrolyze 500 times faster in Ca montmorillonite suspensions than in homogeneous solutions (Sánchez-Camazano and Sánchez-Martín, 1983). The identity of the saturating cation is critical to the catalytic effect; in fact, when the nature of the cation associated with the clay is changed, different hydrolysis pathways may be observed (Pusino and Gessa, 1990; Pusino et al., 1988, 1993).

In this work, we examined the effect of a montmorillonite, saturated by different exchangeable cations, on the hydrolysis of fenoxaprop-ethyl, a herbicide used for postemergence control of a broad spectrum of grass weeds in broadleaf crops (Bieringer et al., 1982). The study could allow evaluation of the widespread importance of surface-catalyzed reactions in pollutant fate in soils.

## MATERIALS AND METHODS

**Materials.** Fenoxaprop-ethyl [ethyl 2-[4-[(6-chloro-2-benz-oxazolyl)oxy]phenoxy]propanoate] (**1**) with a chemical purity of 98.9% was provided by Roussel-Hoechst Agrovet, Italy. The product was recrystallized from ethanol and its purity checked by HPLC.

The clay used was a montmorillonite no. 25 (bentonite) from Upton, WY, supplied by Ward's Natural Science Establishment, Rochester, NY. The <2 $\mu$m fraction was obtained by sedimentation. The cation-exchange capacity (CEC) of the clay

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**Table 1. TLC and HPLC Data for Fenoxaprop-ethyl and Its Metabolites**

| compound | $R_f$ | retention time (min) |
|---|---|---|
| **1** | 0.69 | 10.9 |
| **2** | 0.33 | 3.9 |
| **3** | 0.58 | 6.2 |
| **4** | 0 | 5.8 |
| **5** | 0 | 3.1 |

(sodium form), determined following literature methods (Hendershot and Duquette, 1986), was 90.2 mequiv/100 g. $Al^{3+}$-, $Fe^{3+}$-, $Ca^{2+}$-, and $Na^+$-exchanged samples were prepared by repeated treatments of the clay with 1 N solutions of metal chlorides. The samples were centrifuged, washed repeatedly with deionized water until $Cl^-$-free, and dried at room temperature.

**Hydrolysis.** Hydrolysis of fenoxaprop-ethyl was performed in aqueous clay-containing suspensions. In general, 50 mg of $Al^{3+}$, $Fe^{3+}$, $Ca^{2+}$, and $Na^+$ air-dried clay was suspended in 25 mL of 39.86 $\mu$M aqueous solution of fenoxaprop-ethyl in glass vials sealed with Teflon/silicon rubber septa. The suspensions were continuously stirred in a 25 °C constant-temperature bath using Teflon-coated magnetic stir bars. The hydrolysis was followed by removing 3-mL aliquots at different times. After ultracentrifuging, fenoxaprop-ethyl and hydrolysis products were analyzed in supernatant solutions by high-performance liquid chromatography (HPLC). The experiments were run in duplicate. The pH of suspensions did not vary significantly in the hydrolysis experiments (4.5, 3.9, 6.2, and 7.0, for $Al^{3+}$, $Fe^{3+}$, $Ca^{2+}$, and $Na^+$ clays, respectively). Clay-free blanks were conducted in distilled water at pH values of 3.1, 6.2, and 8.0

**HPLC.** A Waters 510 liquid chromatograph equipped with a 250 × 4 mm i.d. $\mu$Bondapack $C_{18}$ (10 $\mu$m) analytical column, a multiwavelength Waters 490 programmable detector operating at 238 nm, and a Waters Baseline 810 chromatography workstation were used. The mobile phase (1 mL $min^{-1}$) was composed of acetonitrile plus water (65 + 35 by volume, pH 3). The retention times for fenoxaprop-ethyl and its metabolites, under the chromatographic conditions described previously, are listed in Table 1. The molar extinction coefficients in the chromatographic eluant mixture at 238 nm were 23 930, 10 792, 2 542, 24 940, and 2 451 $M^{-1}$ $cm^{-1}$ for fenoxaprop-ethyl (**1**), 6-chlorobenzoxazolinone (**2**), ethyl 2-(4-hydroxyphenoxy)-propanoate (**3**), fenoxaprop acid (**4**), and 2-(4-hydroxyphenoxy)-

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**Table 2. $^1H$ NMR Chemical Shifts for Fenoxaprop-ethyl and Its Degradation Products in $CD_3CN^{a,b}$**

| assignment | $\delta_H$ (ppm) | | | |
|---|---|---|---|---|
| | **1** | **2** | **3** | **4** |
| benzoxazolyl ring | 7.56 (1H, d, $J = 1.8$) | 7.23 (1H, d, $J = 1.8$) | | 7.58 (1H, d, $J = 2.1$) |
| | 7.41 (1H, d, $J = 8.4$) | 7.14 (1H, dd, $J = 1.8$ and 8.4) | | 7.42 (1H, d, $J = 8.8$) |
| | 7.30 (1H, dd, $J = 8.4$ and 1.8) | 7.02 (1H, d, $J = 8.4$) | | 7.31 (1H, dd, $J = 8.8$ and 2.1) |
| phenyl | 7.36–6.95 (4H, m) | | 6.78–6.76 (4H, m) | 7.38–6.95 (4H, m) |
| **CH**(CH$_3$) | 4.85 (1H, q, $J = 6.9$) | | 4.70 (1H, q, $J = 6.9$) | 4.86 (1H, q, $J = 6.8$) |
| **CH$_2$**(CH$_3$) | 4.20 (2H, q, $J = 7.2$) | | 4.17 (2H, q, $J = 7.2$) | |
| **CH$_3$**(CH) | 1.58 (3H, d, $J = 6.9$) | | 1.52 (3H, d, $J = 6.9$) | 1.59 (3H, d, $J = 6.8$) |
| **CH$_3$**(CH$_2$) | 1.24 (3H, t, $J = 7.2$) | | 1.22 (3H, t, $J = 7.2$) | |

[a] $J$ values in Hz. [b] The NMR spectrum of metabolite **5** is reported in the literature (Pouchert and Behnke, 1993).

propanoic acid (**5**), respectively. Therefore, the quantitation of fenoxaprop-ethyl and its degradation products was based on an external standard. The detector response was calibrated with reference standards of fenoxaprop-ethyl and its metabolites **2**–**5** obtained as described below. Calculations were based on the average peak areas of the external standards.

**Metabolite Isolation.** Hydrolysis reactions were carried out on fenoxaprop-ethyl to isolate and identify the degradation products. In a first experiment, 250 mg of fenoxaprop-ethyl was dissolved in 100 mL of a solution of acetonitrile plus water (50 + 50 by volume, pH 2.5). After 48 h, the crude reaction mixture was concentrated and extracted three times with dichloromethane. The combined organic phase was dried over anhydrous sodium sulfate and concentrated under vacuum. The residue was separated by column chromatography on silica gel using diethyl ether plus ethyl acetate (3 + 1 by volume) as eluant. Under these experimental conditions, compounds **2** and **3** were isolated. Metabolite **4** was obtained, as a major product, by hydrolysis of **1** (250 mg) in distilled water at pH 11 (NaOH). In this case, after about 10 h of reaction, the crude mixture was filtered off, acidified to pH 5, and then extracted with dichloromethane. The organic phase, after drying over anhydrous sodium sulfate, concentration under vacuum and crystallization from ethanol, gave the product **4**. The identity of metabolite **5** was checked by comparison of its spectral and chromatographic features with those of a standard purchased from Aldrich Chemical Co. (Milwaukee, WI). The purity of all degradation products was tested by TLC and NMR. TLC was performed on Merck silica gel F$_{254}$ plates, the developing solvent system being chloroform plus diethyl ether (1 + 1 by volume). $R_f$ values are listed in Table 1.

**NMR Analysis.** $^1H$ nuclear magnetic resonance spectra (NMR) were obtained on a Varian VXR 300 spectrometer. Proton shifts of fenoxaprop-ethyl (**1**) and degradation products **2**–**4**, measured in CD$_3$CN, are reported in Table 2. Tetramethylsilane was the internal standard.

**Infrared Analysis.** Fourier transform infrared (FT-IR) spectra were recorded with a FT-IR Nicolet 205 spectrophotometer over the range 4000–600 cm$^{-1}$ (optical resolution, 2 cm$^{-1}$). IR spectra of fenoxaprop-ethyl and its metabolites were obtained in KBr disks except those of clays, which were recorded using self-supporting films. The latter ones were prepared by evaporating a few milliliters of clay suspension on a polyethylene sheet. These air-dried films were divided in two parts. One was immersed in a 2% herbicide CHCl$_3$ solution for 24 h, then removed from solution and rinsed several times with the pure solvent, and finally air-dried. The remaining part was treated in a similar way with pure solvent. Differential spectra were obtained for herbicide–bentonite complexes by subtracting the spectra of the corresponding blank clay film from those of clay–organic complexes.

## RESULTS

**Hydrolysis.** Figures 1 and 2 show the amount of fenoxaprop-ethyl remaining in solution with elapsing time. In the clay suspensions, the observed trends may be the result of concomitant processes, namely adsorption on the surface, particularly in the first stages of contact, and degradation both in solution or on the
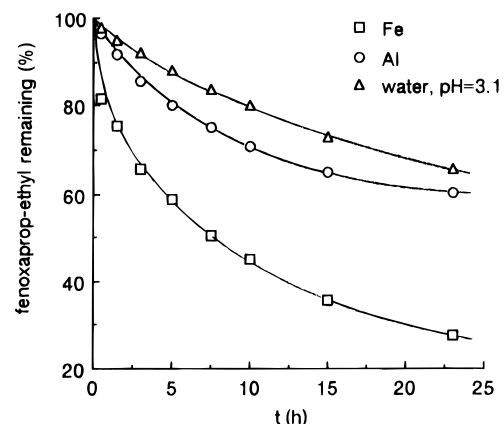


**Figure 1.** Amount of fenoxaprop-ethyl remaining in solution upon contact with $Fe^{3+}$ and $Al^{3+}$ clays and a comparison with clay-free blank in distilled water at pH 3.1.
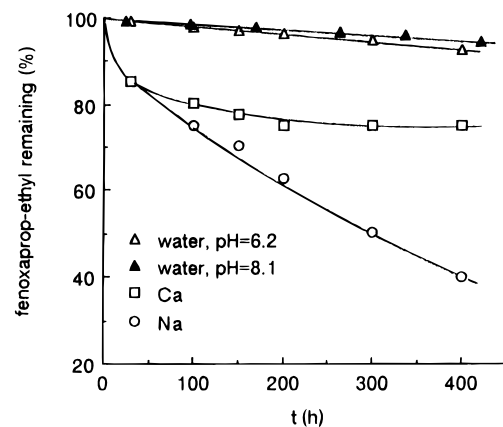


**Figure 2.** Amount of fenoxaprop-ethyl remaining in solution upon contact with $Ca^{2+}$ and $Na^+$ clays and comparison with clay-free blanks in distilled water at pH 6.2 and 8.1.

surfaces. Actually, no simple kinetic law can interpret satisfactorily the time dependence of the herbicide profile. Particularly in the case of the $Ca^{2+}$ sample, the shape of the curve suggests that adsorption predominates at short reaction times and, after equilibrium is reached, the herbicide concentration in solution does not undergo further significant changes because of a very slow decomposition rate.

Depending on the nature of the exchangeable cations, the product distribution was different both quantitatively and qualitatively (Table 3). In the presence of $Al^{3+}$ and $Fe^{3+}$ montmorillonite (pH 4.5 and 3.9, respectively), the hydrolysis was quite rapid and metabolites **2** and **3** were identified as the only products. On the contrary, in the $Ca^{2+}$ and $Na^+$ clay systems (pH 6.2 and 7.0, respectively), the hydrolysis was significantly slower and compound **4** appeared as a major metabolite with

**Table 3. Percentage Distribution (Mole Percent) of Fenoxaprop-ethyl and Its Decomposition Products in the Solvolysis Mixture in the Presence of Clays or in Clay-Free Blanks (B)**

|  | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| $B_{pH6.2}{}^a$ | 99.2 |  |  |  |  |
| $B_{pH3.1}{}^a$ | 65.5 | 18.2 | 16.3 |  |  |
| Fe clay$^a$ | 27.5 | 38.1 | 34.4 |  |  |
| Al clay$^a$ | 60.2 | 20.1 | 19.7 |  |  |
| $B_{pH6.2}{}^b$ | 92.8 | <2 |  | 3.6 | <2 |
| $B_{pH8.1}{}^b$ | 94.7 |  |  |  |  |
| Ca clay$^b$ | 75.3 | 3.2 |  | 18.7 | 2.8 |
| Na clay$^b$ | 40.1 | 6.0 |  | 48.2 | 5.7 |

$^a$ Distribution referred to 23 h. $^b$ Distribution referred to 400 h.

**Table 4. Principal Infrared Absorption Frequencies ($cm^{-1}$) for Fenoxaprop-ethyl and Its Degradation Compounds**

| assignment | 1 | 2 | 3 | 4 | 5 |
|---|---|---|---|---|---|
| $\nu_{C=O}$ | 1737 | 1781 | 1731 | 1710 | 1708 |
|  |  | 1732 |  |  |  |
| $\nu_{C=N}$ | 1628 | 1623w$^a$ |  | 1625 |  |
| ring stretches | 1573 | 1479 | 1509 | 1571 | 1509 |
|  | 1505 |  | 1447 | 1505 | 1453 |

$^a$ w, weak.

only minor amounts of **2** and **5**. This trend may indicate that the pH of the suspension is a determining factor in the hydrolysis of the herbicide.

Experiments performed in clay-free blank solution showed negligible hydrolysis at pH 6.2 and 8.0. On the other hand, at pH 3.0 (HCl) only 34% hydrolysis of fenoxaprop-ethyl occurred in water solution after 24 h, as compared with a yield of about 72% in the acidic $Fe^{3+}$ clay system (Table 3). In this case, too, the acidic medium afforded metabolites **2** and **3**.

The results rule out a homogeneous catalytic effect due to the external solution as the only factor responsible for the hydrolysis pathways observed and substantiate the clay participation in the degradation of fenoxaprop-ethyl. Actually, the pH change in the interlayer, which e.g. for $Fe^{3+}$ and $Al^{3+}$ is more acidic than the external solution, may play a major role in the overall extent and product distribution of the reaction. However, the behavior of $Ca^{2+}$ and $Na^+$ clay systems indicates a specific catalytic effect due to the surface also. This catalytic effect implies that adsorption of the herbicide on the clay is a necessary prerequisite for hydrolysis of fenoxaprop-ethyl. Evaluating the mechanisms involved in the adsorption from aqueous solutions is a rather difficult task. Herbicide molecules compete with solvent for binding to surfaces; therefore, because of the low adsorption level of the pesticide from water solution, FT-IR spectra were not defined enough to provide pertinent information. This problem was overcome by a FT-IR study of clay samples after adsorption of fenoxaprop-ethyl from organic solutions ($CHCl_3$).

**Adsorption from Organic Solvent**. The main IR bands of fenoxaprop-ethyl and its metabolites are listed in Table 4. The neat herbicide exhibits an absorption at 1737 $cm^{-1}$ due to the carbonyl group of the ester linkage and a band 1628 $cm^{-1}$ due to $-C=N-$ stretch. Usually, the frequency of the $-C=N-$ bond lies between 1665 and 1645 $cm^{-1}$, but the band shifts to about 1630 $cm^{-1}$ as an effect of aromatic conjugation when the ring is attached to the nitrogen atom (Bellamy, 1975). The carbonyl absorption of benzoxazolone **2** is split into two bands at 1781 and 1732 $cm^{-1}$. Most likely, the lower
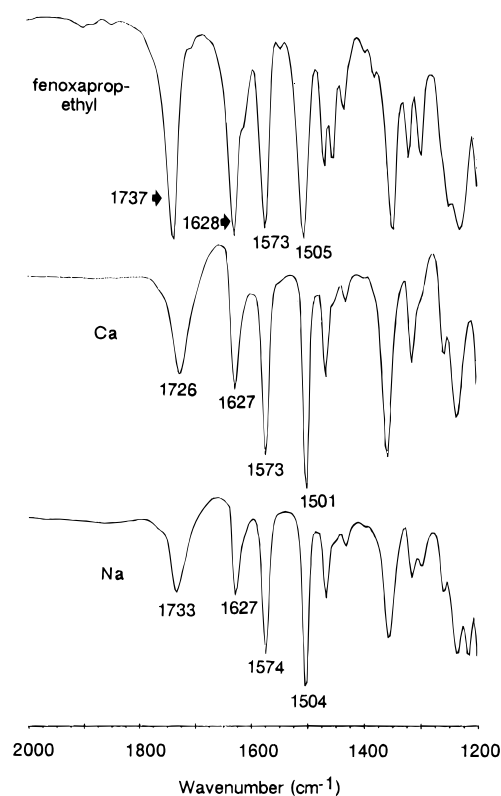


**Figure 3.** FT-IR spectra of fenoxaprop-ethyl (KBr disk) and $Ca^{2+}$ and $Na^+$ clay treated with fenoxaprop-ethyl.

**Table 5. Principal Infrared Absorption Frequencies ($cm^{-1}$) of Fenoxaprop-ethyl on Homoionic Clays and of 2 and 3 on Fe and Al Clays**

| assignment | Fe | Al | Ca | Na | Fe-**2** | Al-**2** | Fe-**3** | Al-**3** |
|---|---|---|---|---|---|---|---|---|
| $\nu_{C=O}$ | 1735 | 1731 | 1726 | 1733 | 1748 | 1747 | 1722 | 1720 |
| $\nu_{C=N}$ | 1670 | 1670 | 1627 | 1627 |  |  |  |  |
|  | 1509 | 1509 | 1573 | 1574 |  |  | 1509 | 1509 |
| ring stretches | 1482 | 1482 | 1501 | 1504 | 1482 | 1482 |  |  |

frequency band is due to vibration of the C=O group involved in intermolecular hydrogen bonding. The FT-IR spectra of fenoxaprop-ethyl $Ca^{2+}$ and $Na^+$ montmorillonite complexes (Table 5 and Figure 3) showed bands at 1726 and 1733 $cm^{-1}$, respectively. This indicates a perturbation of the CO ester group by the metal ions through direct bonds or, more probably, via hydrogen bonding to residual water molecules linked to the cations. Such an interaction is expected to lower the force constant of the CO group and to decrease the frequency value to a greater extent the higher the polarizing force of the metal ion is. A similar behavior has been observed for the adsorption of a number of pesticides on clays (Micera et al., 1988; Bosetto et al., 1993). FT-IR data reported in Table 5 suggest that a different mechanism takes place on $Fe^{3+}$ and $Al^{3+}$ montmorillonite surfaces. In particular, the spectra of $Fe^{3+}$ and $Al^{3+}$ complexes are very similar to each other and significantly different from those of the corresponding $Ca^{2+}$ and $Na^+$ samples and fenoxaprop-ethyl itself, the main distinguishing feature being the presence of a new common band at about 1670 $cm^{-1}$. These findings suggest that, in the $Fe^{3+}$ and $Al^{3+}$ clay interlayer, fenoxaprop-ethyl could be partially decomposed into metabolites **2** and **3**, as observed in water suspension. Therefore, the FT-IR spectra of herbicide$-Fe^{3+}$ and $Al^{3+}$ clay complexes are not easy to explain because of the simultaneous presence of fenoxaprop-ethyl and its
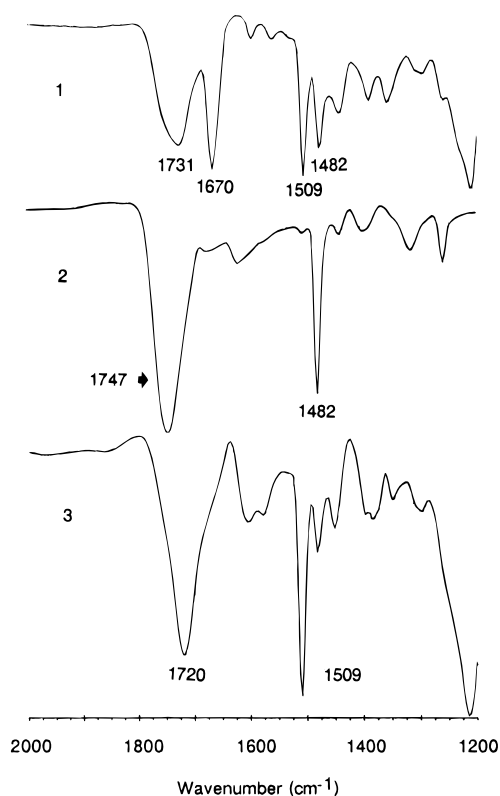
**Figure 4.** FT-IR spectra of $Al^{3+}$ clay treated with fenoxaprop-ethyl (**1**), 6-chlorobenzoxazolinone (**2**), and ethyl 2-(4-hydroxyphenoxy)propanoate (**3**), respectively.

degradation products. The comparison of the spectra of each metabolite separately adsorbed on the clay was of help in overcoming the problem (Table 5). The spectra of the fenoxaprop-ethyl and two metabolites, individually adsorbed on $Al^{3+}$ clay, are reported in Figure 4. The degradation product **2** is characterized by the presence of a strong band at about 1747 cm$^{-1}$ that could be assigned to the C=O group coordinated to the exchangeable cation and by a weaker band at 1482 cm$^{-1}$ attributable to benzoxazolone ring stretch. On the other hand, compound **3** shows the C=O ester group at 1720 cm$^{-1}$ and a phenol ring stretch at 1509 cm$^{-1}$. The fenoxaprop-ethyl$-Al^{3+}$ clay complex exhibits a very broad band at 1731 cm$^{-1}$, which could be due to different carbonyl groups, and two absorptions at 1509 and 1482 cm$^{-1}$ analogous to those observed for compounds **2** and **3** adsorbed onto Al clay. A further feature of the FT-IR spectra of the herbicide$-Al^{3+}$ clay complex is a strong absorption at 1670 cm$^{-1}$, the value being typical of protonated aromatic heterocyclic compounds (Cook, 1961; Pouchert and Behnke, 1975). The protonation very likely occurs at the nitrogen atom of the benzoxazole ring, which is the most basic site of the molecule. This band disappears, and no new band shows up, when the pellet of the fenoxaprop-ethyl$-Al^{3+}$ clay complex is left at room temperature for about 10 h. Therefore, we can reasonably conclude that the spectrum of the fenoxaprop-ethyl$-Al$ clay complex is composed of absorptions due to metabolites **2** and **3** and to protonated herbicide.

## DISCUSSION

The results indicate that, depending on the nature of the metal ions, the fenoxaprop-ethyl clay-catalyzed hydrolysis may cleave two bonds in the herbicide molecule consistent with two different mechanisms.

The first one, acting on Fe and Al clays, involves the protonation of the benzoxazole ring nitrogen of the herbicide owing to a proton transfer from the acidic
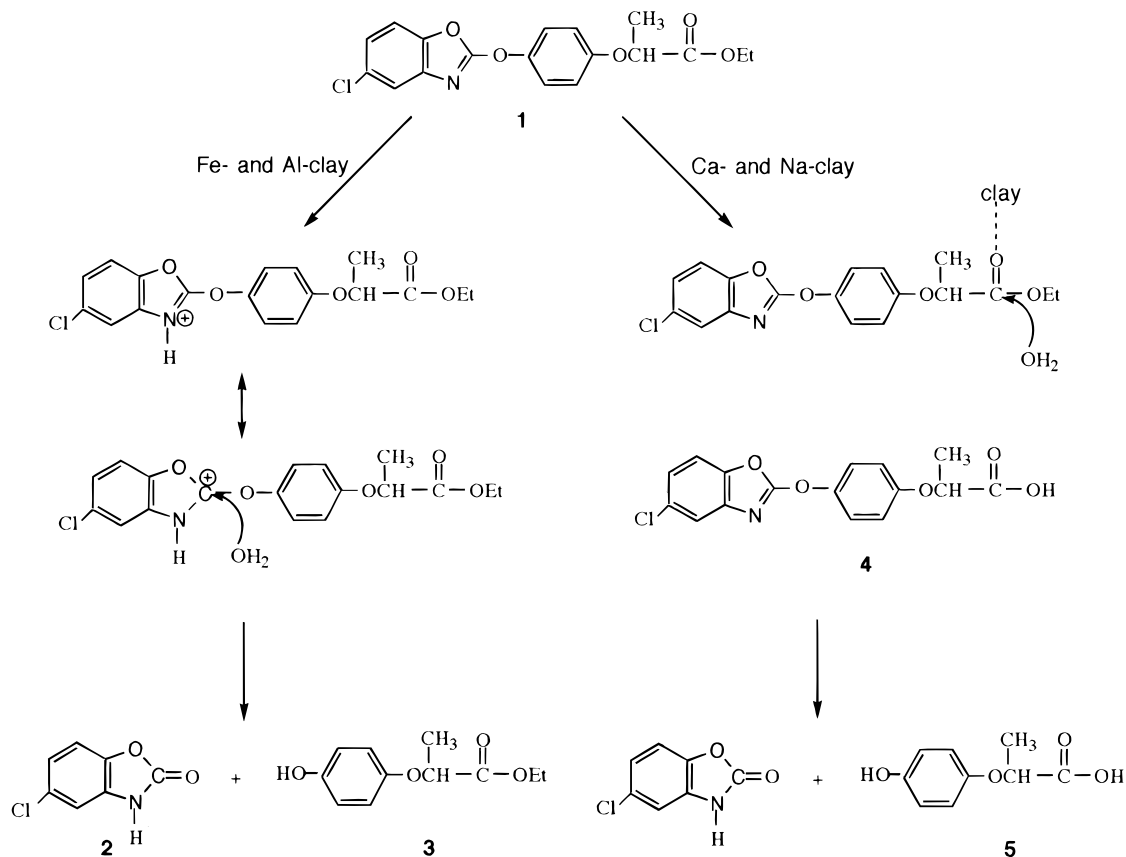


**Figure 5.** Proposed hydrolysis mechanism of fenoxaprop-ethyl on clays.

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water of metal ions. Supporting evidence is the appearance of a stretch at 1670 cm$^{-1}$ in the spectra of fenoxaprop-ethyl–Fe and Al clay complexes. According to the mechanism shown in Figure 5, the positive charge of the benzoxazole ring can be delocalized onto the adjacent carbon of the ether bridge. Such a carbocation is greatly stabilized by resonance because of the presence of a heteroatom bearing an unshared pair, e.g., oxygen, next to the cationic center (March, 1985). As a consequence, this carbon is well suited for nucleophilic attack by water, affording compounds **2** and **3**. This reaction is made possible by the greater acidic properties of Fe$^{3+}$ and Al$^{3+}$ ions compared with Ca$^{2+}$ and Na$^+$ ions. In fact, the fenoxaprop-ethyl ether bridge, likewise in related enol ethers, can be easily hydrolyzed by acids, but it is more resistant to hydrolysis by bases.

On Ca$^{2+}$ and Na$^+$ clays, a second mechanism takes place involving the coordination of the carbonyl oxygen of fenoxaprop-ethyl to the metal ions (hydrated or not). The assumption is in agreement with the observed low-frequency shift of the C=O stretch in the IR spectra of Ca$^{2+}$ and Na$^+$ samples. This interaction shifts electron density away from the carbonyl carbon, facilitating the cleavage of the ester bond by water to yield the corresponding acid **4**. In a second step, part of the metabolite **4** undergoes the same fate of fenoxaprop-ethyl, giving compounds **2** and **5**, but only at very long times, because of the failure of medium acidity. The possibility that the benzoxazolone **2** observed in the Ca$^{2+}$ and Na$^+$ systems could derive directly from fenoxaprop-ethyl is ruled out by the isolation of metabolites **4** and **5** and the lack of **3** in the reaction mixture. Na$^+$ clay is more effective in hydrolysis than is Ca$^{2+}$ clay, in spite of its less polarizing power. This behavior is a well-known process occurring in Na clays (Bar-on and Shainberg, 1970; Llorca and Cruz-Romero, 1977). In fact, Na montmorillonite is not stable over a prolonged time in aqueous suspension because of its tendency to hydrolyze. Consequently, as the medium becomes more basic, the hydrolysis rate becomes greater.

Previous studies (Smith, 1985; Toole and Crosby, 1989; Smith and Aubin, 1990) showed that, under laboratory and field conditions, fenoxaprop-ethyl undergoes hydrolysis to yield fenoxaprop acid and several minor products such as a phenetole, a phenol, and 6-chlorobenzoxazolone due to chemical and microbial degradation. Our results indicate the effectiveness of surface-catalyzed hydrolysis in affecting the fate of fenoxaprop-ethyl in soil. Due to the complexity of the system, further research may be needed to further understand the overall mechanisms.

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