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INTERACTION OF RIMSULFURON WITH SMECTITES

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Abstract—The adsorption of the sulfonylurea herbicide rimsulfuron, [N-((4,6-dimethoxypyrimidin-2-yl)aminocarbonyl)-3-(ethylsulfonyl)-2-pyridinesulfonamide], on clay minerals with different saturating cations was studied. Three smectites with different lattice charge distribution (hectorite, montmorillonite and nontronite) were selected and made homoionic to Ca^{2+}, Cu^{2+} and Al^{3+}. Because of the instability of rimsulfuron in water, the experiments were carried out in chloroform solution. The interaction mechanism depends on the nature of the saturating cation and the tetrahedral layer charge of the silicate. Among the exchangeable ions studied, only Al^{3+} is able to produce degradation of the herbicide to N-(4,6-dimethoxypyrimidin-2-yl)-N-[(3-(ethylsulfonyl)-2-pyridinyl]urea. In this case, the lower the tetrahedral charge, the more active the degradation. The Ca^{2+}-saturated clays are ineffective in the degradation. In contrast, the formation of a stable chelate complex with the saturating ion permits rimsulfuron to be adsorbed to a rather high extent into Cu(II)-clays and to be stable against degradation.

Key Words—Adsorption, Infrared Spectroscopy, Pesticides, Rimsulfuron, Smectites.

INTRODUCTION

Rimsulfuron is a new postemergence sulfonylurea herbicide characterized by a broad-spectrum weed control at very low use rates (5–15 g ha^{-1}) (Palm et al. 1989) and a low acute and chronic toxicity for mammalians (Beyer et al. 1988). Various reviews emphasize the role played by the clay surfaces in catalyzing the hydrolysis of organic pollutants (Ortego et al. 1991; Kowalska et al. 1994). The saturating cation is critical to the catalytic effect, since upon changing the nature of the cation associated with the clay, different hydrolysis rates and pathways are observed (Saltzman et al. 1974; Pusino et al. 1988; Pusino and Gessa 1990; Pusino et al. 1993). Sulfonylureas are also strongly adsorbed (Ukrainczyk and Rashid 1995) and degraded on smectites (Pantani et al. 1994). Furthermore, the catalytic activity of clay surfaces is often critically influenced by the charge localization arising from isomorphous substitution, even when the active site (i.e., the exchangeable ion) is the same (Ristori et al. 1982; Franci et al. 1990). Pantani et al. (1996) showed that rimsulfuron is adsorbed on Al-hectorite surfaces from an organic medium and degraded. Based on these findings, it was thought of interest to investigate the effect of the lattice charge and exchangeable cations on the adsorption mechanisms of this herbicide. Three clays with different lattice charge distribution (hectorite, montmorillonite and nontronite) saturated with Ca^{2+}, Cu^{2+} and Al^{3+} were chosen. Rimsulfuron degrades rather rapidly in water above pH 5, primarily through the contraction of the sulfonylurea bridge (Schneiders et al. 1993). Most probably, this reaction is favored by the electron-withdrawing sulfone substituent. Due to this instability, the experiments were carried out in chloroform solution.

EXPERIMENTAL METHODS

Materials

Rimsulfuron (aqueous solubility <10 mg L^{-1}) was supplied by Du Pont de Nemours & Co., Italy. The purity (98.8%) was checked by both high-pressure liquid chromatography (HPLC) and flash combustion microanalysis.

The clays examined, along with their sources, charge distribution (Jaynes and Bigham 1987) and cation exchange capacities (CEC) (Jaynes and Bigham 1986), are listed in Table 1: hectorite (SHCa-1), a trioctahedral smectite substituted in the octahedron layer (Li^+ for Mg^{2+}); montmorillonite (SWy-1), dioctahedral, with tetrahedral (Al^{3+} for Si^{4+}) and octahedral (Mg^{2+} for Al^{3+}) substitution; and nontronite (NG-1), dioctahedral, exhibiting tetrahedral (Al^{3+} for Si^{4+}) substitution. The clays were obtained from the Source Clays Repository of the Clay Minerals Society. The source material for nontronite was a sandstone; previous grinding, sonication and suspension in water were necessary to separate the clay fraction.

The <2-μm fraction of all clay samples was separated and made homoionic by treating 3 times with a 1 *N* solution of Ca^{2+}, Cu^{2+} and Al^{3+} chlorides. The clays were washed with distilled water and centrifuged until the supernatant gave a negative test for Cl^-.

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Table 1. Clay samples.

Sample	Source	CEC (meq/100 g)	Charge distribution (mole/unit cell) Tetrahedral	Octahedral	Total
SWy-1	Crook County, Wyoming	87	0.16	0.52	0.68
NG-1	Hohen Hagen, Germany	97	0.60	0.02	0.62
SHCa-1	San Bernardino County, California	89	0.00	0.62	0.62

Aqueous suspensions of homoionic clays were freeze-dried and stored under vacuum at 7 °C until used.

Degradation Studies and HPLC Analyses

To study the kinetics of rimsulfuron degradation, 500 mg each of air-dried clay were treated with 100 mL of a $1.16 \cdot 10^{-3}$ *M* chloroform solution of rimsulfuron in glass vials and kept in an end-over-end shaker at 20 °C. At different times (from 1 to 1000 h), 150-μL aliquots of the suspension were removed and centrifuged. After evaporation of chloroform, the residue was redissolved in 1 mL of eluant mixture and then analyzed by HPLC. The amount of herbicide was calculated by a linear calibration curve. Only 1 degradation product was found and identified as [N-(4,6-dimethoxy-pirimidinyl)-N-[3-(ethylsulfonyl)-2-pyridinyl]urea] by comparison of the chromatographic and spectral features with those of a pure compound supplied by Du Pont de Nemours & Co. (Wilmington, Delaware).

The HPLC system (Perkin Elmer, Norwalk, Connecticut) consisted of: an LC410 pump, an LC235C diode array detector, an Omega 2 software system and a Rheodyne (Cotati, California) Model 7125 injection valve with a 20-μL sampling loop. The samples were eluted through a 25 × 0.8 cm Kromasil 5C8, 5-μm column supplied by Technicol (England). A solvent gradient was used. Flux was 1.7 mL/min. Total elution time was 13 min: 2 min 62% H_2O and 38% CH_3CN, 5 min 35% H_2O and 65% CH_3CN (concave gradient), 2 min 35% H_2O and 65% CH_3CN, 2 min 62% H_2O and 38% CH_3CN (concave gradient) and, finally, 2 min 62% H_2O and 38% CH_3CN. The detector was tuned at 250 nm. All of the experiments were carried out in triplicate.

Infrared Analysis

Fourier transform infrared (FTIR) spectra were recorded at room temperature over the 4000–600 cm^{-1} range using an FTIR Perkin Elmer Model 1710 spectrophotometer interfaced to a computer. The spectra of the herbicide-clay complexes were recorded using self-supporting films prepared by evaporating 5 mL of aqueous clay suspension (2% w/v) on a polyethylene sheet at room temperature, which was subsequently removed. The air-dried films were divided into 2 parts. One of these was immersed in a herbicide-saturated $CHCl_3$ solution at room temperature. After 3 d, the film was removed from the solution and rinsed several times with the pure solvent. After air-drying, the film was examined by IR spectroscopy and the equilibrium solution tested by HPLC. The second part of the film was treated with $CHCl_3$ only. To obtain the spectra of adsorbed compounds, the corresponding blank clay films were accurately subtracted by software from those of the herbicide-clay complexes. Only the IR absorptions between 2000 and 1200 cm^{-1} are discussed here, because this region is the most appropriate for the adsorption mechanisms in clays.

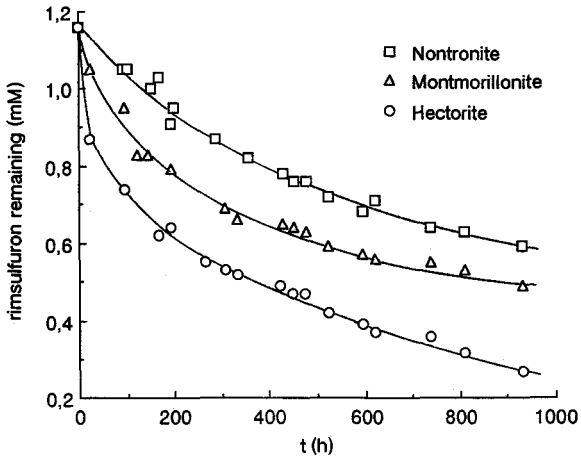


Figure 1. Amount of rimsulfuron remaining in solution upon contact with Al^{3+}-saturated clays.

EPR and Electronic Absorption Spectra

X-band (9.15 GHz) electron paramagnetic resonance (EPR) spectra were recorded using a Varian E-9 spectrometer. Spectra of powdered Cu(II)-clay samples after treatment with rimsulfuron were obtained at 298 K, and they did not change significantly on cooling to 140 K, indicating a complex immobilized in the clay interlayer in the experiment time-scale. Spectra of frozen aqueous solutions of rimsulfuron and $CuSO_4$, at metal-to-ligand molar ratio of 1:2, were recorded at 140 K with varying pH. No significant decomposition of rimsulfuron was observed below pH 5.5 ($t_{1/2}$ = 4.7 d at pH 5, according to Schneiders et al. 1993). Ethylene glycol was added to solutions in order to obtain good glasses. Axial anisotropic spectra were obtained in all cases, indicating a tetragonally elongated geometry at the Cu(II) ion. As usual, approximate values for the *g*-factors ($g_\parallel$ and $g_\perp$) and hyperfine Cu coupling constants ($A_\parallel$) along the principal molecular directions may be extracted from such spectra. The symbols $\parallel$ and $\perp$ refer to the tetragonal *z* axis and to the *xy* plane of the complex, respectively. Electronic absorption spectra were also recorded on the aqueous solutions

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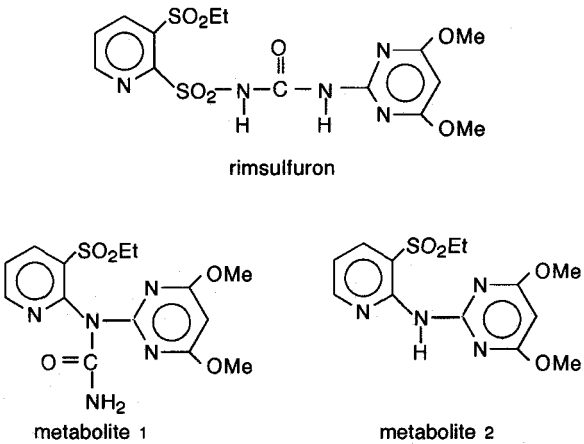


Figure 2. Rimsulfuron and its metabolites.

of rimsulfuron and $CuSO_4$ using a Beckman Acta MIV spectrophotometer and 1-cm quartz cells over the range 300–900 nm.

RESULTS AND DISCUSSION

Rimsulfuron is stable in chloroform solution over a long period. A significant degradation was observed only in the presence of aluminium-saturated clays. Figure 1 shows the amount of herbicide remaining in suspension after different times of contact with 3 Al-clay-systems. The observed trend may be the combined result of concomitant processes taking place on the surfaces: namely, adsorption and degradation.

Al-hectorite is the most effective in promoting rimsulfuron degradation, followed by Al-montmorillonite and Al-nontronite. The only metabolite detected in Al-clay suspensions was N-(4,6-dimethoxypyrimidin-2-yl)-N-((3-(ethylsulfonyl)-2-pyridinyl)urea (metabolite 1), though traces of N-((3-ethylsulfonyl)-2-pyridinyl)-4,6-dimethoxy-2-pyrimidineamine (metabolite 2) were extracted by washing the Al-hectorite-herbicide complex with an aqueous $BaCl_2$ solution (Figure 2). The degradation of rimsulfuron to metabolite 1 depends on the ability of the clay to establish H-bonds with the carbonyl group of rimsulfuron (Pantani et al. 1996). Different conclusions have been reached by studies of the effect of isomorphous substitutions of the clay lattice on the acidity of the water coordinated to the exchangeable cation. In a study on the degradation of Asulam (Ristori et al. 1982), it was found that, for a given saturating cation, the acidity of the hydration water is higher if the isomorphous substitution is located in the octahedral sheet. Similar results were obtained by Franci et al. (1990) for the adsorption of Linuron and by Mortland and Raman (1968) in a specific study on smectite acidity. In contrast, Swoboda and Kunze (1968) demonstrated that smectites are more effective in protonating aromatic amines when the isomorphous substitution is located in the tetrahedral sheet. In our case, the greatest acidity appears to be associated

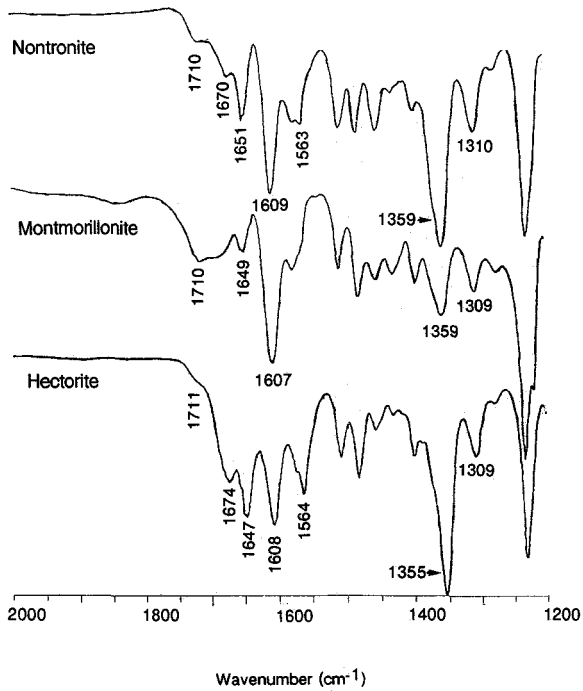


Figure 3. FTIR spectra of Al^{3+}-saturated clays treated with rimsulfuron.

with the octahedral substitution. However, the accessibility of the interlayer region (that is, the interlayer expandability) can affect the extent of adsorption-degradation. The interlayer expandability in clays is determined by the saturating ions–layers attractive forces, which are particularly important when the charges are localized in the tetrahedral sheet (Farmer 1978). Therefore, clays with a lower tetrahedral charge (such as hectorite) are more favorable for the adsorption of the herbicide, which is a requisite for degradation (Sanchez Camazano and Sanchez Martin 1983).

All 3 Ca-saturated clays were poorly effective both in the adsorption and the degradation of the herbicide in $1 \cdot 10^{-3}$ *M* chloroform suspensions. This is probably due to the lower acidity of the hydration shells of Ca^{2+} (as compared to Al^{3+}), which hinders an efficient coordination of the carbonyl group.

Cu-clays showed a higher affinity for rimsulfuron. In fact, upon treating a Cu-montmorillonite sample with a chloroform solution containing an amount of rimsulfuron equivalent to the CEC value, the herbicide was totally adsorbed. No metabolite was observed in solution, indicating an interaction mechanism involving the undecomposed herbicide molecule.

To obtain evidence of the adsorption-degradation mechanisms, FTIR spectra were recorded on clays treated with chloroformic solutions at a rather high herbicide concentration (see EXPERIMENTAL METHODS). The FTIR spectra of Al^{3+}-nontronite-, montmorillonite- and hectorite-rimsulfuron complexes are compared in Figure

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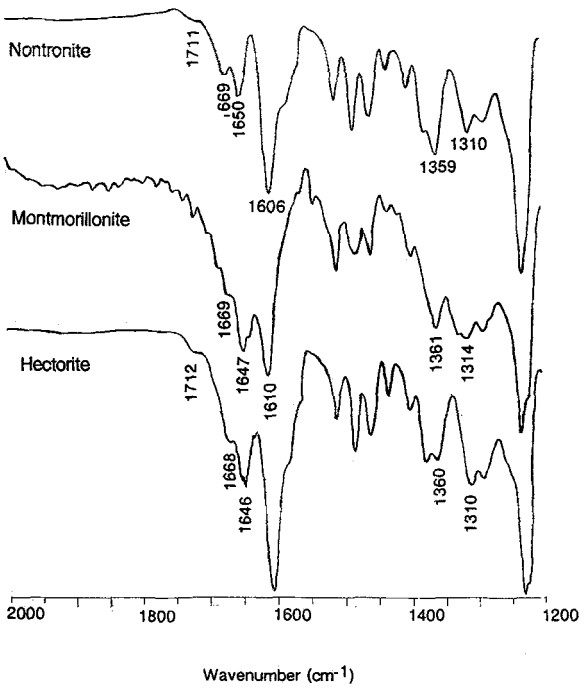


Figure 4. FTIR spectra of Ca^{2+}-saturated clays treated with rimsulfuron.

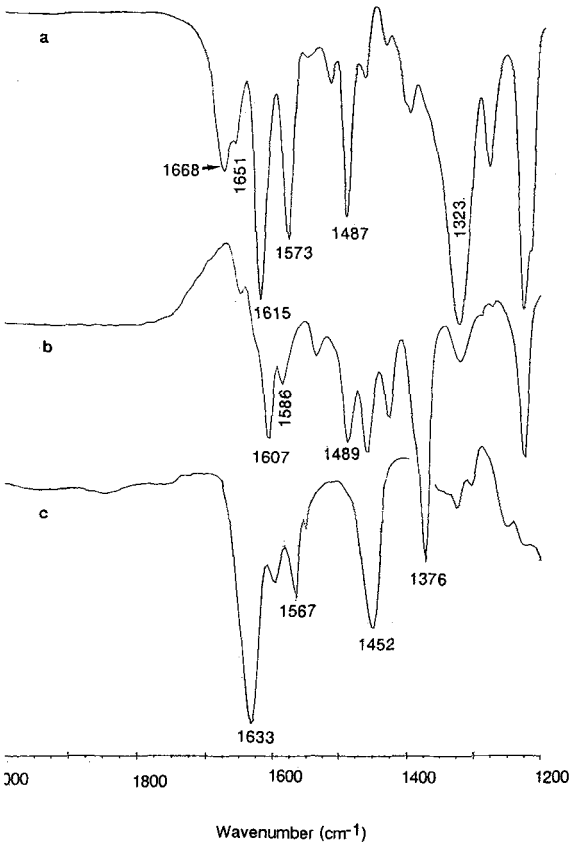


Figure 5. FTIR spectra of Cu^{2+}-montmorillonite treated with: a) rimsulfuron, b) metabolite 2 and c) metabolite 1.

3. A weak absorption at about 1710 cm^{-1} and a band at 1650 cm^{-1}, both indicative of rimsulfuron protonated at the pyrimidine ring (Pantani et al. 1996), show up in all the spectra. Moreover, bands around 1670 cm^{-1} are assigned to the stretching mode of the carbonyl group of the neutral herbicide molecule coordinated to the saturating cation. Besides these common features, the spectrum of the Al-hectorite-herbicide complex exhibits a strong band at 1564 cm^{-1}, that is weak in the nontronite system and absent in the montmorillonite system. The absorption, most probably due to skeletal vibrations of aromatic rings, was also observed when the metabolite 1 was separately adsorbed on the clay. This finding suggests that, within 3 days, rimsulfuron is partly degraded to metabolite 1, but only on Al-hectorite. The FTIR spectra of all Ca^{2+}-saturated clays, shown in Figure 4, exhibit the peculiar frequencies of the herbicide in either the free or protonated form. Moreover, the band at 1564 cm^{-1} is always absent, supporting the absence of metabolite 1. The spectra of 3 Cu^{2+}-saturated clay-rimsulfuron complexes are very similar to each other; therefore, only the spectrum of Cu^{2+}-montmorillonite herbicide complex is reported in Figure 5. This is quite different from the spectra of corresponding Al- and Ca-clay complexes, the main distinguishing features being: 1) weak bands (appearing as shoulders) at 1651 cm^{-1}, indicating a low extent of protonation for the pyrimidine ring, despite the greater acidity of Cu- as compared to Ca-clay; 2) asymmetric stretches of the SO_2 groups overlapping each other into a single band centered at 1323 cm^{-1}. By contrast,

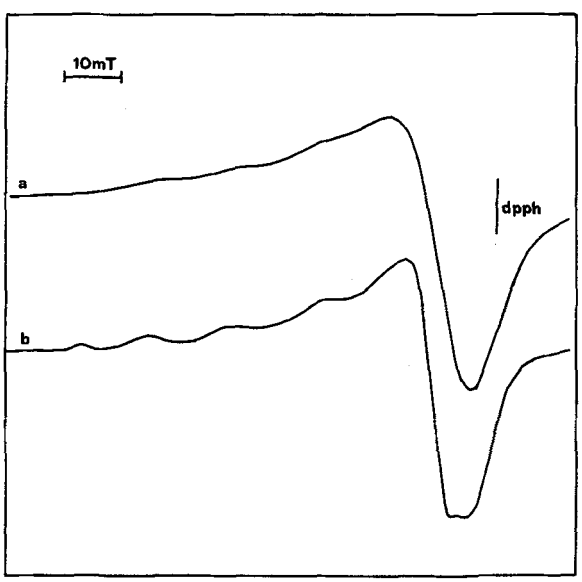


Figure 6. EPR spectra of a) Cu^{2+}-montmorillonite treated with rimsulfuron (T = 298 K) and b) Cu^{2+}-rimsulfuron aqueous solution (metal-to-ligand molar ratio = 1:2, pH = 5.5, T = 140 K).

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values of 1359 cm^{-1} and 1310 cm^{-1} are observed for the bridge and external SO_2 groups in the herbicide Ca- and Al-clay complexes. The results suggest that the interaction of rimsulfuron in Cu(II)-saturated clays is different from that in Al- and Ca-clays. To support this hypothesis, each potential metabolite was separately adsorbed on Cu-clays. The comparison of IR spectra in Figure 5 excludes the presence of these metabolites in the Cu-clay complexes of rimsulfuron. Distinct evidence was provided by EPR spectroscopy, which indicated that, upon adsorption of rimsulfuron, most Cu^{2+} ions yield a complex immobilized in the clay interlayer. Noticeably, the EPR parameters of this complex ($g_{\|} = 2.27$, $g_{\perp} = 2.07$, $A_{\|} = 166 \times 10^{-4}$ cm^{-1}) are quite the same as those measured for the species in equilibrium with the aquaion in aqueous solutions of rimsulfuron and Cu^{2+} below pH 6 (Figure 6). This is a good indication that the complex involves a 1:1 Cu(II):rimsulfuron molar composition. In addition, the EPR parameters and the *d-d* electronic absorption maximum ($\lambda_{max} = 710$ nm, $\epsilon_{max} = 80$ M^{-1} cm^{-1} in aqueous solution) indicate a Cu(II) ion coordinated to 2 N atoms of rimsulfuron. The stronger donor site of rimsulfuron is the N atom of the deprotonated sulfonamide group in the ureic bridge ($pK_a = 4.1$ in the free molecule) which is an effective target for metal coordination. In rimsulfuron, this N atom is suitable for 6-membered ring chelation through the assistance of a pyrimidine ring N, which is a further basic site. This binding mode explains also the peculiar IR features of the Cu(II)-rimsulfuron-clay complex. In fact, according to Menabue and Saladini (1993), the metal coordination to the sulfonamide group shifts both the SO_2 stretches, particularly the asymmetric one, to lower wavenumbers, owing to the electron-withdrawing effect of the coordinated N atom.

CONCLUSIONS

In conclusion, the formation of a stable chelate complex with the saturating ion permits rimsulfuron to be adsorbed to a rather high extent into Cu(II)-clays and be stable against degradation. This feature, which is unique for Cu ions, at least among the saturating ions examined in this study, may be ascribed to the greater tendency of the cation to form stable complexes with nitrogenous ligands. Although it cannot be proved that the results may be extrapolated to soil water medium, rimsulfuron interactions similar to those observed in an organic medium may be important factors in dry soil conditions.

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