Adsorption and Degradation of Rimsulfuron on Al Hectorite

Ottorino Pantani,*,† Alba Pusino,‡ Luca Calamai,§ Carlo Gessa,⊥ and Paolo Fusi§

Centro di Studio per i Colloidi del Suolo, CNR, Piazzale Cascine 28, 50144 Firenze, Italy,
Dipartimento di Agrochimica ed Agrobiologia, Università di Reggio Calabria, Piazza S. Francesco,
89061 Gallina di Reggio Calabria, Italy, Dipartimento di Scienza del Suolo e Nutrizione della Pianta,
Università di Firenze, Piazzale Cascine 28, 50144 Firenze, Italy, and Istituto di Chimica Agraria,
Università di Bologna, via Berti Pichat 11, 40127 Bologna, Italy

A study was carried out to examine the interactions between a smectite (hectorite) saturated with Al^{3+} and a sulfonylurea herbicide, rimsulfuron [*N*-((4,6-dimethoxypyrimidin-2-yl)aminocarbonyl)-3-(ethylsulfonyl)-2-pyridinesulfonamide]. As rimsulfuron is extremely unstable in water, to evaluate the role of the clay surface in decomposing the herbicide, the experiments were carried out in chloroform solution. The coordination of the C=O group is initially involved in the adsorption as revealed by FT-IR analysis. The adsorbed rimsulfuron decomposes initially into *N*-(4,6 dimethoxy-pyrimidin-2-yl)-*N*-((3-(ethylsulfonyl)-2-pyridinyl)urea (metabolite 367). This metabolite is adsorbed onto a clay surface by coordination of the C=O group and protonation of the pyrimidine ring. Successively, this metabolite decomposes on a clay surface to *N*-[(3-ethylsulfonyl)-2-pyridinyl]-4,6-dimethoxy-2-pyrimidineamine (metabolite 324). This second metabolite remains adsorbed by protonation of its pyrimidine ring.

INTRODUCTION

Sulfonylureas are a new class of herbicides characterized by a low acute and chronic toxicity for mammalians and an extremely high biological activity against weeds (Beyer *et al.*, 1988). These characteristics have promoted extensive efforts to synthesize new sulfonylureas that are more and more biologically active and easily degradable by microorganisms and by chemical hydrolysis. This latter characteristic has been particularly emphasized, as the latest sulfonylureas promptly decompose even in plain water, leading to various degradation products depending on pH value (Schneiders *et al.*, 1993). Generally, low values of pH enhance the degradation (Beyer *et al.*, 1988). The studies carried out on these molecules generally stress the role of organic matter and microbes on adsorption and degradation, whereas little attention has been paid to the role of inorganic constituents of soil. As the main goal of the new sulfonylureas is a relatively rapid chemical decomposition, information on adsorption and degradation mechanisms of such molecules by inorganic colloids is extremely important in determining their fate and environmental impact. The catalytic activity of clay minerals in decomposing pesticides has been widely demonstrated. Inasmuch, the degradation on inorganic materials sometimes follows different pathways from those observed in water solution (Ristori *et al.*, 1982; Franci *et al.*, 1990; Pantani *et al.*, 1993; Pusino *et al.*, 1993). Therefore, the aim of this paper is to investigate the mechanism of degradation of rimsulfuron on a homoionic clay (Al hectorite).

---

* Author to whom correspondence should be addressed.
† CNR Firenze, Italy.
‡ Università di Reggio Calabria.
§ Università di Firenze.
⊥ Università di Bologna.

MATERIALS AND METHODS

Materials. Rimsulfuron (Figure 1) was supplied by DuPont de Nemours & Co., Inc., Italy. Its purity (98.8%) was checked both by HPLC and by flash combustion microanalysis. Metabolites 367 and 324 (Figure 1) were obtained by hydrolysis of rimsulfuron in unbuffered aqueous solution at pH 5 and 9 (adjusted with NaOH and/or HCl), respectively. At pH 5, metabolite 367 was the main product; at pH 9, the reaction afforded almost solely metabolite 324. These hydrolysis products were isolated by semipreparative HPLC and identified on the basis of their LC−MS−MS, FT-IR, and NMR spectrometry data. In particular, the spectral features of metabolite 367 were consistent with those kindly furnished by DuPont, Agricultural Products, Wilmington, DE. Moreover, metabolite 324 showed a mass spectrum concordant with literature data (Shalaby *et al.*, 1992). Finally, the hydrochlorides of rimsulfuron and of its metabolites were prepared by bubbling anhydrous HCl into a chloroform solution of each chemical species. The precipitates were filtered and dried under vacuum.

The clay used was a hectorite (San Bernardino County, CA) i.e. a trioctahedral smectite with Al^{3+} for Si^{4+} substitution in the tetrahedral sheet (supplied by American Clay Mineral Society, New York). The <2 μm fraction of the source material was separated and made homoionic in Al^{3+} by treating it three times with a 1 N $AlCl_3$ solution. This clay was washed with distilled water and centrifuged until the supernatant gave a negative test for Cl^- and then stored at 7 °C in water suspension.

Infrared Analysis. Fourier transform IR spectra were recorded at room temperature within the range 4000−600 cm^{-1} using a FT-IR Perkin-Elmer Model 1710 spectrophotometer interfaced to a computer. The IR spectra of rimsulfuron and its metabolites in neutral and protonated form were obtained in KBr disks. The spectra of the herbicide−clay complexes were recorded using self-supporting films prepared by evaporating the water of 5 mL of clay suspension on a polyethylene sheet at room temperature. These air-dried films, about 50 mg in weight, 4.5 cm in diameter, 10 μm thick, and having a moisture content of 14.7% (obtained by calcination at 990 °C), were divided into two parts. One of these was immersed in a herbicide-saturated $CHCl_3$ solution (35 g/L) at room temperature. After 3 days, the film was removed from

618 *J. Agric. Food Chem.,* Vol. 44, No. 2, 1996

Pantani et al.
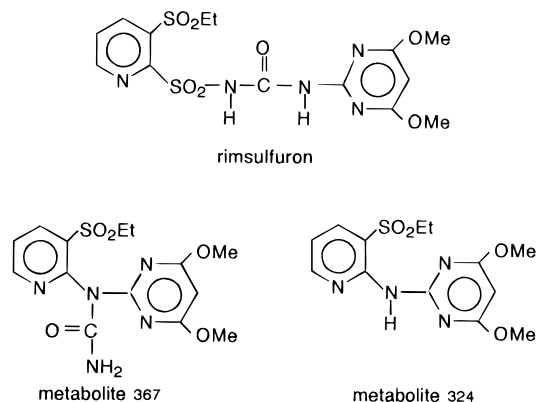
Figure 1. Structural formulas of rimsulfuron and its metabolites.

the solution and rinsed several times with the pure solvent. After air-drying, the film was examined by infrared spectroscopy, whereas the equilibrium solution was tested by HPLC. The remaining part of the film was treated with pure solvent. Metabolites 367 and 324 were also adsorbed on a clay film in the same way as described for rimsulfuron. To obtain the spectra of adsorbed compounds, those of the corresponding blank clay films were accurately subtracted by software from those of the herbicide— or metabolite—clay complexes. All FT-IR spectra of the pure and adsorbed compounds are reported between 2000 and 1200 cm^{-1} because this region is the most appropriate to provide evidence for the adsorption mechanisms. Each adsorption experiment was run in duplicate and repeated three times. All of the spectra recorded were the mean of at least 64 scansions at a resolution of 2 cm^{-1}: these conditions were enough to obtain a good signal to noise ratio.

Degradation Studies. Rimsulfuron and its metabolites were stable in chloroform solutions for at least 20 days at room temperature. The degradation on clays was followed by determining the amounts of rimsulfuron and its metabolites by HPLC. Typically, 0.5 g of air-dried powder of Al hectorite was treated with 100 mL of a 1.16 mM rimsulfuron solution. The suspension was kept in an end-over-end shaker at 20 °C for 3 days and then centrifuged. The supernatant was pipetted off and analyzed immediately by HPLC. The amount of remaining herbicide was calculated from the difference between the initial and final concentrations of rimsulfuron in solution. As rimsulfuron is easily decomposed (Shalaby *et al.*, 1992; Schneiders *et al.*, 1993), the spectrum obtained from the clay film was thought to have contributions from the adsorbed rimsulfuron and its possible metabolites. To identify any possible degradation product, the clay, after adsorption and FT-IR analysis, was sequentially washed with solvents of increasing polarity (CHCl$_3$, CH$_3$COCH$_3$, and BaCl$_2$ 10% water solution) to extract nonpolar and polar adsorbed species. Each washing supernatant was run on the HPLC system, and all washings were repeated until a chromatogram of the pure extracting solvent was obtained. The stability of rimsulfuron and its metabolites was tested both in CH$_3$COCH$_3$ and in BaCl$_2$ 10% water solution. All of the compounds are stable after 1 h in these solvents. In aqueous BaCl$_2$ solution the herbicide is only partly degraded (about 4%) to metabolite 367 after 14 h. In all cases, the time required for extraction, shaking, and centrifugation was about 30 min. The HPLC system (Perkin-Elmer, Norwalk, CT) consisted of a series LC410 pump, an LC235C diode array detector, an Omega 2 software system, and a Rheodyne (Cotati, CA) 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, 1.7 mL/min; total elution time, 13 min [2 min 62% H$_2$O−38% CH$_3$CN, 5 min 35% H$_2$O−65% CH$_3$CN (concave gradient), 2 min 35% H$_2$O−65% CH$_3$CN, 2 min 62% H$_2$O−38% CH$_3$CN (concave gradient), and, finally, 2 min 62% H$_2$O−38% CH$_3$CN]; the detector was tuned at 250 nm. The data obtained were the results of triplicate experiments.
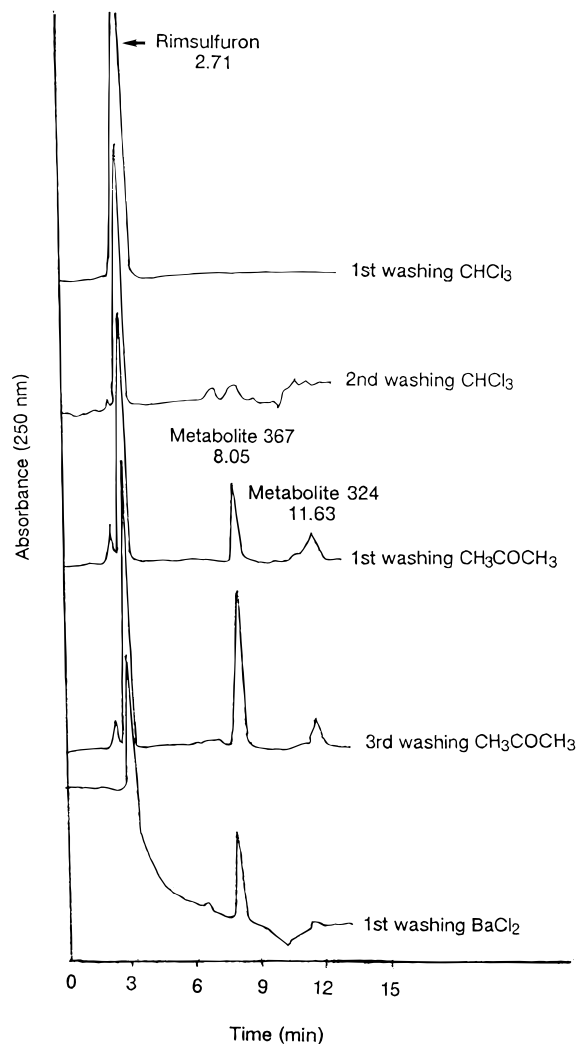

Figure 2. HPLC chromatograms of rimsulfuron and its metabolites extracted from Al hectorite with different solvents.

RESULTS AND DISCUSSION

Rimsulfuron was found to be stable when dissolved in CHCl$_3$, and no appreciable degradation was noted over a long period. Instead, it was not possible to establish the precise extent of degradation on the Al hectorite film by HPLC, because of the high concentration of herbicide remaining in the equilibrium solution after 3 days. However, in a separate test, using a more dilute solution of herbicide and a greater amount of clay (see Materials and Methods), about 30% of the rimsulfuron was missing after 3 days. Under these working conditions, only traces of metabolite 367 were found in the supernatant solution.

The chromatograms relative to the washings of clay—herbicide complex (Figure 2) show that chloroform was able to desorb only the undecomposed herbicide. With increasing solvent polarity (acetone), two new peaks appear in the chromatogram and demonstrate the presence of *N*-(4,6 dimethoxypyrimidin-2-yl)-*N*-[(3-(ethylsulfonyl)-2-pyridinyl]urea (metabolite 367) and *N*-[(3-ethylsulfonyl)-2-pyridinyl]-4,6-dimethoxy-2-pyrimidineamine (metabolite 324). These two metabolites have been also identified by Shalaby *et al.* (1992) and Schneiders *et al.* (1993) as the main hydrolysis products of rimsulfuron in soil. An aqueous BaCl$_2$ solution extracted the same metabolites, but only in very low amounts. The total recovery from clay after completion of the washing was 70% of undecomposed rimsulfuron,

Table 1. Assignments of the Main Vibration Bands of Rimsulfuron and Its Metabolites[a]

assignment	rimsulfuron			metabolite 367			metabolite 324		
	KBr	protonated	Hect[b]	KBr	protonated	Hect	KBr	protonated	Hect
ν_{CO}	1736	1712	1710sh 1680	1701					
ν_{NH^+} (pyrimidine ring)		1650	1647		1648	1652		1642	1651
$\nu_{SO_2\,asym}$									
bridge	1359	1382	1355						
external	1317	1359	nd	1341	1359	nd	1310		nd
$\nu_{SO_2\,sym}$									
bridge	1171	nd	nd	nd					
external	1131	nd	nd	1128	nd	nd	1133	nd	nd
	1612	1608	1608	1590	nd	1607	1603	1606	1610
ring breathing	1585	nd	nd	1567	nd	nd	1571	nd	nd

[a] Rao, 1963; Bellamy, 1975; Socrates, 1980. [b] Bands relative to rimsulfuron and degradation metabolites. sh, shoulder; nd, not detected.

24% of metabolite 367, and 6% of metabolite 324. A herbicide degradation due to extracting solvent can be excluded because of the stability of rimsulfuron and its metabolites in $CHCl_3$, CH_3COCH_3, and $BaCl_2$ within the time required for the extraction.

On the basis of these results, the FT-IR spectrum of the rimsulfuron–clay complex is not easy to explain because of the presence of the degradation products accompanying rimsulfuron. This problem was overcome by a cross comparison of the spectra of (i) each metabolite separately adsorbed on the clay, (ii) protonated compounds, and (iii) the rimsulfuron–clay complex.

Some of the main FT-IR bands of free, protonated, and clay complexes of rimsulfuron and its metabolites are listed in Table 1. The spectra of rimsulfuron and its metabolites are reported in Figure 3. The corresponding protonated species (Figure 4) share a common band at about 1650 cm^{-1} that could be assigned to a protonated nitrogenous aromatic heterocycle (Pouchert, 1975). The protonated site is, most likely, one of the pyrimidine nitrogens, which are assumed to be the most basic sites in the molecule. Such an assumption is based on simple argumentation. Pyridine (pK_a = 5.31, Martell and Smith, 1985, p 219) is more basic than pyrimidine (pK_a = 1.61, Martell and Smith, 1975); however, the presence of substituents may affect the basicity of the ring nitrogens. In aromatic rings the effect of a substituent may be evaluated by the σ_p and σ_m parameters (often additive) accounting of the total electrical effects (resonance plus field) of the group in the para and meta positions, respectively, a positive value being indicative of an electron-withdrawing group and a negative value of an electron-donating group (March, 1985). The value of σ_m = 0.64 for the SO_2CH_3 group indicates a strong electron-withdrawing effect quite comparable to that of the cyano substituent (σ_m = 0.62) in 3-cyanopyridine, which lowers the pK_a value to 1.64 (Martell and Smith, 1985, p 230). On the other hand, the σ_p value of −0.78 for OCH_3 group indicates a strong electron-releasing effect. Therefore, it is reasonable to assume that in rimsulfuron, due to the combined effect of two strong electron donors, the pyrimidine ring is more basic than the pyridine ring bearing two strong withdrawing groups. A further feature in the spectra of protonated species is the C=O group stretch of rimsulfuron, which moves from 1736 cm^{-1} in the free form to 1712 cm^{-1} in the protonated form, whereas for metabolite 367 the carbonyl group seems to be not affected by protonation, as its frequency does not shift significantly. The downward displacement of the rimsulfuron carbonyl group is likely due to a decreased double-bond character of the C=O group because of the
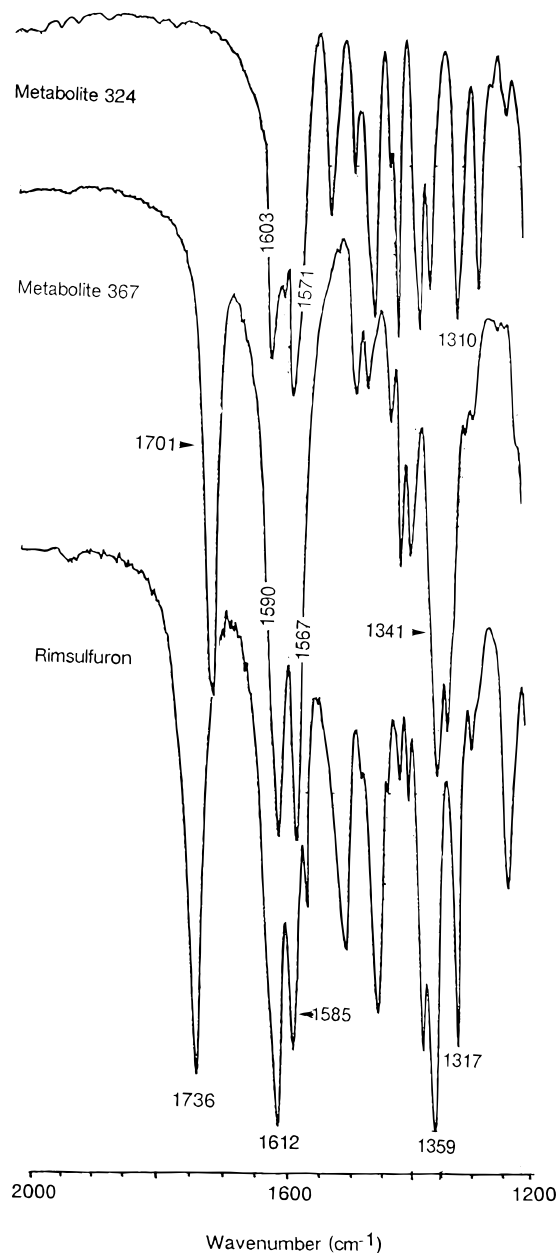
Figure 3. FT-IR spectra of rimsulfuron and its metabolites.

formation of an internal hydrogen bond between the carbonyl oxygen and protonated nitrogen of the pyrimidine ring, yielding a six-membered ring. In principle, a similar hydrogen bond could take place also in the protonated metabolite 367, but the steric hindrance
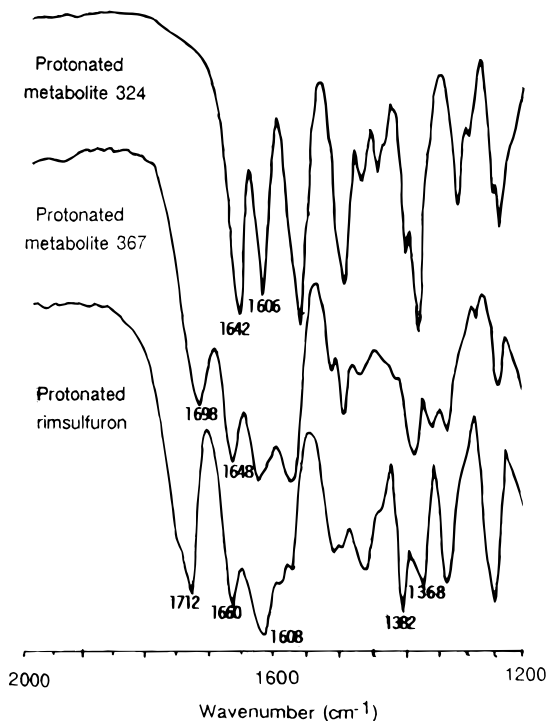
620 *J. Agric. Food Chem.,* Vol. 44, No. 2, 1996

Pantani et al.

Figure 4. FT-IR spectra of rimsulfuron and its metabolites in protonated form.
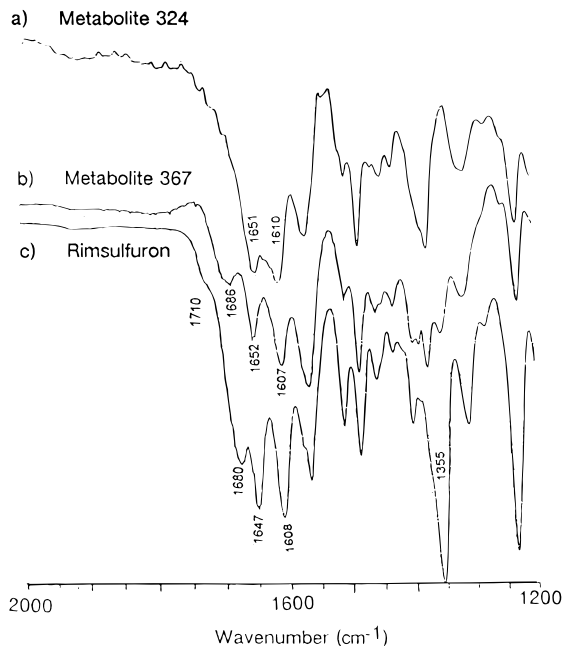
Figure 5. FT-IR spectra of rimsulfuron and its metabolites adsorbed on Al hectorite.

Figure 6. Proposed degradation mechanism of rimsulfuron adsorbed on Al hectorite.

arising from the large sulfone substituent makes it unlikely, as checked by examination of molecular models.

The spectra obtained after individual adsorption of rimsulfuron and its two metabolites on clay are shown in Figure 5. Both metabolites are characterized by a band at about 1650 cm^{-1} (Figure 5a,b), consistent with the protonated forms, but metabolite 367 shows also an absorption at about 1686 cm^{-1} (1701 cm^{-1} in KBr) that could be assigned to the C=O group coordinated to the exchangeable cation. The remaining parts of the spectra are so similar that it is difficult to distinguish the metabolites from each other. Spectrum 5c relative to interaction of rimsulfuron with Al hectorite exhibits a
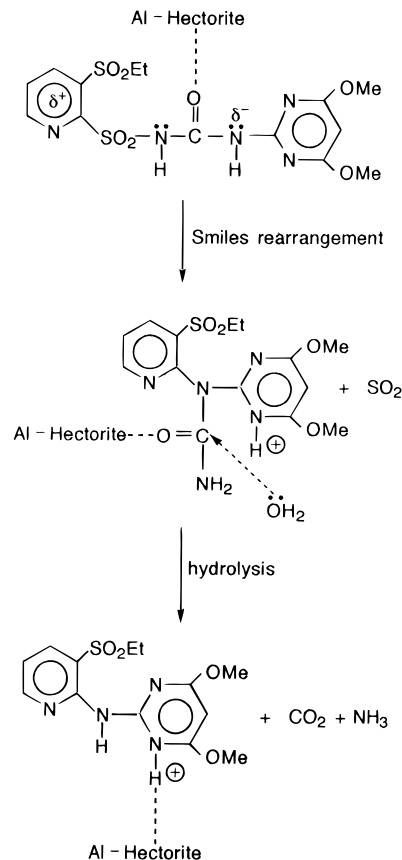
band at 1647 and a shoulder at 1710 cm^{-1} analogous to those observed for the herbicide protonated form. A further feature of spectrum 5c is a strong absorption at 1680 cm^{-1}, the wavenumber value being typical of a C=O group coordinated to the saturating cation. Furthermore, HPLC tracings revealed also the presence of the two metabolites 367 and 324 on the clay–rimsulfuron complex. Consequently, we can reasonably conclude that the spectrum is actually composed of bands due to neutral (1680 cm^{-1}) and protonated (1710 cm^{-1}) herbicide and protonated metabolites. It is not easy to establish the extent of protonated versus neutral form of rimsulfuron from FT-IR band intensities, also because of possible effects due to molecular orientation in clay. However, a protonated species is not expected to be easily desorbed by a nonpolar solvent, whereas a large amount of rimsulfuron is removed by CHCl$_3$ washings (Figure 2). So it is reasonable to think that a large part of rimsulfuron is coordinated to clay in the neutral form through the carbonyl group and a smaller amount in the charged form (extractable by acetone and BaCl$_2$). As usual in clays, the proton source of the protonated species is the acidic water of hydration of saturating ions. Actually, although the pH of an aqueous suspension of Al^{3+} hectorite is 4.0–4.5 (Sposito, 1985), in our system (clay in CHCl$_3$) the pH at the surfaces is extremely acid, being in the range of 0.5–1.0 (Mortland, 1968; Mortland and Raman; 1968; Frenkel, 1974).

On the basis of the above considerations, it is possible to propose a degradation mechanism on clay (Figure 6) involving two steps: (1) adsorption of rimsulfuron and degradation to metabolite 367; (2) hydrolysis of metabolite 367 to metabolite 324.

For metabolite 367 to be formed, it is necessary to assume a nucleophilic attack by the nitrogen close to

Adsorption and Degradation of Rimsulfuron

J. Agric. Food Chem., Vol. 44, No. 2, 1996 **621**

the pyrimidine ring. Actually, the rimsulfuron molecule is provided with a pyridine ring having a very low electron density (δ^+) (Figure 6), because of the presence of two electron-withdrawing sulfone and sulfonamide groups. As a consequence, the pyridine moiety is a well-suited substrate for aromatic nucleophilic substitution. However, such a type of reaction does not occur in neat chloroform, while it takes place in the presence of clay. This suggests that the coordination of the carbonyl group to the clay exchangeable cation enables the reaction. The coordination enhances the partial positive charge on the carbonyl carbon, allowing the dissociation of the NH group within the sulfonamide bridge, which becomes remarkably more acidic. This group already exhibits a pK_a value of 4.1 in water solution (Worthing and Hance, 1991). The negative charge following this deprotonation can be delocalized onto the carbonyl oxygen, which makes the lone electron pair of the nitrogen atom adjacent to the pyrimidine ring (δ^-) more prone to act as a nucleophile (Figure 6). The whole process leads to a nucleophilic migration, where sulfur dioxide is the leaving group, known as the Smiles rearrangement of arylsulfones (Cerfontain, 1968). In the second step, metabolite 324 is formed from metabolite 367 that is coordinated through the C=O group to the exchangeable cation. Similarly as in rimsulfuron, this coordination increases the partial positive charge of the C=O carbon. This allows a nucleophilic attack by the solvation water of the exchangeable clay cation, leading to the formation of carbamic acid and metabolite 324. This latter remains adsorbed on clay by protonation, while carbamic acid, being unstable, may decompose to NH_3 and CO_2.

The possibility that the hydrolysis observed could be due to water associated with hectorite without clay assistance is ruled out by the isolation of metabolite 324 on the clay. In fact, the water content of Al hectorite, determined by heating from room temperature to 990 °C, is 14.7%. This value includes also the structural OH (Si−OH), which disappears at high temperature. The actual free water content depends on temperature and external relative humidity. Since experiments were performed at room temperature, an average value of 5.5% can be reasonably assumed on the basis of literature data (Deer *et al.*, 1962). Upon contact of the clay with chloroform this small amount of water is strongly polarized by interlayer cation and the pH is in the range previously reported.

In aqueous solution, according to Schneiders *et al.* (1993), metabolite 324 is formed, at short times, from the intermediate 367 only at pH $\geq$7, probably because of the need of a strong nucleophilic water. The water of chloroformic clay suspension is a very poor nucleophile, and the hydrolysis reaction can take place only if assisted by C=O interaction with saturating ions. Therefore, the observed distribution of metabolites indicates that the different properties of the interlayer solution, as compared to normal aqueous solution, affect the degradation mechanism.

LITERATURE CITED

Bellamy, L. J. *The Infrared Spectra of Complex Molecules*; Chapman and Hall: London, 1975.

Beyer, E. M., Jr.; Duffy, M. J.; Hay, J. V.; Schlueter, D. D. Sulfonylurea herbicide. In *Herbicides: Chemistry, Degradation and Mode of Action*; Kearney, P. C., Kaufman, D. D., Eds.; Dekker: New York, 1988; Vol. 3, pp 117−190.

Cerfontain, H. *Mechanistic Aspects in Aromatic Sulfonation and Desulfonation*; Interscience: New York, 1968; pp 262−274.

Deer, W. A.; Howie, R. A.; Zussman, J. *Rock-Forming Minerals, Vol. 3, Sheet Silicates*; Longmans Canada: Toronto, 1962; pp 227−245.

Franci, M.; Fusi, P.; Ristori, G. G. The influence of structural characteristics of two smectites on linuron adsorption. *Agrochimica* **1990**, *34*, 405−410.

March, J. *Advanced Organic Chemistry,* 3rd ed.; Wiley: New York, 1985; pp 237−250.

Martell, A. E.; Smith, R. M. *Critical Stability Constants*, Vol. 2, Amines; Plenum Press: New York, 1975; p 264.

Martell, A. E.; Smith, R. M. *Critical Stability Constants, Vol. 5, First Supplement*; Plenum Press: New York, 1985; pp 219, 230.

Mortland, M. M. Protonation of compounds at clay mineral surface. *Trans. 9th Int. Congr. Soil Sci.* **1968**, *I*, 691−699.

Mortland, M. M.; Raman, K. V. Surface acidity of smectites in relation to hydration, exchangeable cation, structure. *Clays Clay Miner.* **1968**, *16*, 393−398.

Pantani, O.; Calamai, L.; Fusi P. Influence of clay minerals on adsorption and degradation of a sulfonylurea herbicide (cinosulfuron). *Appl. Clay Sci.* **1994**, *8*, 373−387.

Pouchert, C. J. *The Aldrich Library of Infrared Spectra*, 2nd ed.; Aldrich Chemical Co.: Milwaukee, WI, 1975; No. H5740-8, p 1178.

Pusino, A.; Liu, W.; Gessa, C. Dimepiperate adsorption and hydrolysis on Al^{3+}, Fe^{3+}, Ca^{2+} and Na^+-montmorillonite. *Clays Clay Miner.* **1993**, *41*, 335−340.

Rao, C. N. R. *Chemical Applications of Infrared Spectroscopy*; Academic Press: New York, 1963.

Ristori, G. G.; Fusi, P.; Cecconi, S. The influence of structural characteristics of smectites on catalytic decomposition of Asulam. In *International Clay Conference: Proceedings, 1981*; Van Olphen, H., Veniale, F., Eds.; Elsevier: Amsterdam, 1982; pp 267−272.

Schneiders, G. E.; Koeppe, M. K.; Naidu, M. V.; Horne, P.; Brown, A. M.; Mucha, C. F. Fate of rimsulfuron in the environment. *J. Agric. Food Chem.* **1993**, *41*, 2404−2410.

Shalaby, L. M.; Bramble, F. Q., Jr.; Lee, P. W. Application of thermospray LC/MS for residue analysis of sulfonylurea herbicides and their degradation products. *J. Agric. Food Chem.* **1992**, *40*, 513−517.

Socrates, G. *Infrared Characteristic Group Frequencies*; Wiley: Chichester, U.K., 1980.

Sposito, G. *The Surface Chemistry of Soils*; Oxford University Press: New York, 1984.

Worthing, C. R., Hance, R. J., Eds. *The Pesticide Manual*, 9th ed.; British Crop Council: Bracknell, U.K., 1991; p 297.