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Hydrolysis of Sulfonylurea Herbicides in Soils and Aqueous Solutions: a Review

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Sulfonylureas are a unique group of herbicides used for controlling a range of weeds and some grasses in a variety of crops and vegetables. They have been extremely popular worldwide because of their low mammalian toxicity, low use rate, and unprecedented herbicidal activity. Knowledge about the fate and behavior of sulfonylurea herbicides in the soil-water environment appears to be of utmost importance for agronomic systems and environmental protection. Because these herbicides are applied at a very low rate, and their mobility is greatly affected by the chemicals' anionic nature in alkaline soils, a thorough understanding of their degradation/hydrolysis processes and mechanisms under aqueous and soil systems is important. This review brings together published information on the hydrolysis of several sulfonylureas in aqueous and soil solutions that includes the effects of pH, temperature, functional relationship between pH vs hydrolysis rate constants, and hydrolysis behavior of sulfonylureas in the presence of minerals. In addition, the transformations of sulfonylureas in soil, under laboratory and field experiments, have been discussed in connection with the compounds' varied structural features, i.e., sulfonylueas that are with or without the pyridinic, pyrimidine, and triazinic ring.

Keywords: Sulfonylurea; hydrolysis; degradation pathways; pyridinic ring, triazinic ring

INTRODUCTION

Sulfonylureas are a unique group of herbicides used to control a range of weeds and some grasses in a variety of crops and vegetables including wheat, barley, oats, rice, maize, turf, soybeans, oilseed rap, flax, sugar beets, plantation crops, pastures, forestry, blueberries, potatoes, and tomatoes (*1−3*). Because of their low application rates (10−40 g ha⁻¹), low mammalian toxicity, and unprecedented herbicidal activity they have become very popular worldwide. The subsequent worldwide development effort has led to the commercialization of about 25 different active ingredients, and additional developmental products have been identified.

Sulfonylureas are based on a general structure where R_1 moiety can be either aliphatic, aromatic, or heterocyclic grouping connected by the sulfonylurea bridge to the R_2 moiety. This can be either a substituted triazine or pyrimidine system (*4, 5*) as shown in **Figure 1a**, **b**, and **c**. The chemistry, biology, biochemistry, degradation, and mode of action of sulfonylurea herbicides have been discussed in several reviews (*1, 6, 7*).

Knowledge about the fate and behavior of sulfonylurea herbicides in the soil-water environment appears to be of utmost importance for agronomic systems and environmental protection. Because the herbicides are applied at a very low rate, and their mobility is greatly affected by their anionic nature in alkaline soils, analysis of sulfonylurea herbicide residues in soil is a challenging task for analytical chemists (*8*). This has resulted in a number of diverse analytical techniques being developed worldwide involving three main methodologies: chromatographic analyses (*9−18*), bioassays (*19, 20*), and enzyme-linked immunosorbent assays (ELISA; *21, 22*).

Sulfonylureas are weak acids and have pK_a values generally ranging from 3 to 5. The herbicides in aqueous solution exist primarily in the neutral form at pH values below pK_a, and in the anionic form at pH levels above the pK_a. Therefore, the herbicides are predominantly anionic in most agricultural soils, and the relative concentrations of the neutral form are greatest in soils of low pH (*23*). This group of herbicides is subject to pH-dependent hydrolysis of the sulfonylurea linkage. The hydrolysis half-lives ($t_{1/2}$) for several sulfonylurea herbicides are summarized in **Table 1**. The two primary hydrolytic mechanisms are acid-catalyzed cleavage and base-catalyzed contraction/rearrangement of the sulfonylurea linkage. This bridge or the linkage is susceptible to attack by water on the

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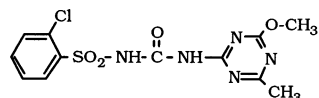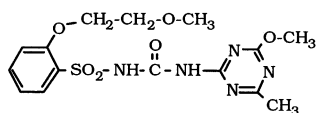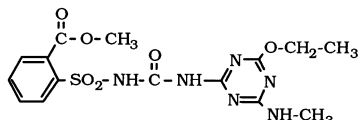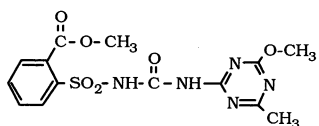† Purdue University.
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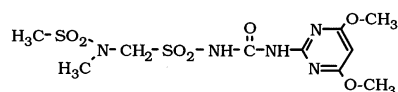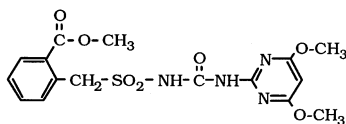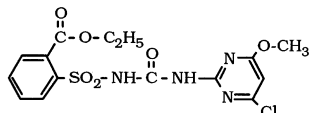
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(a)

(b)

(c)
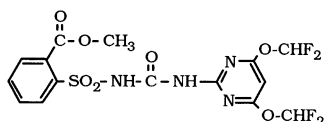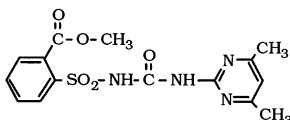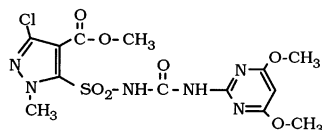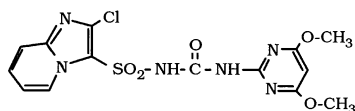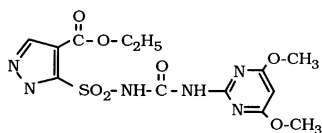
Figure 1. (a) Sulfonylurea herbicides without pyridinic ring [R_1] and triazinic ring [R_2]; (b) sulfonylurea herbicides with a triazinic ring [R_2]; (c) sulfonylurea herbicides with a pyridinic ring [R_1] and a pyrimidine ring [R_2].

carbonyl carbon of the bridge, and thus produces CO_2 and the corresponding aryl sulfonamide and amino-heterocyclic portions of the molecule. The rate of this reaction can often be hundreds of times faster under acidic conditions. For example, the hydrolysis half-lives ($t_{1/2}$) for chlorsulfuron at pH 3 and pH 7.5 at 25 °C are reported to be 1 day and >500 days, respectively (*24, 25*). Likewise, Sabadie (*26*) reported that bensulfuron-methyl at 30 °C hydrolyzes with $t_{1/2}$ of 7 and 460 days at pH 5 and 8, respectively.

Although the recovery of sulfonylurea herbicides from soils does not seem to present any difficulty (*8*), their degradation pathway in soil often remains complicated to investigate because most of the degradation products are difficult to extract, identify, and quantify. However, concomitant biotransformation and chemical hydrolysis appear to be significant for the breakdown of these herbicides in soil (*24, 27*). To assess the relative importance of these two processes, degradation in sterilized and nonsterilized soil has been extensively studied (*15, 23, 28, 29*). Observed differences in the rate of breakdown between the biotic

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Table 1. Hydrolysis Rate Constants (k, Day^{-1}) and First-Order Half-Lives ($t_{1/2}$, Days) for Some Sulfonylureas in Aqueous Buffer Solutions at pH 4 as a Function of Temperature (*39*)

temp (°C)	chlorsulfuron		prosulfuron		primisulfuron		rimsulfuron		thifensulfuron-methyl		metsulfuron-methyl		triasulfuron	
	k	$t_{1/2}$	k	$t_{1/2}$	k	$t_{1/2}$	k	$t_{1/2}$	k	$t_{1/2}$	k	$t_{1/2}$	k	$t_{1/2}$
15			0.08	8.78	0.29	2.34	0.33	2.09	1.05	0.66				
20	0.12	5.59	0.14	4.97	0.49	1.41	0.62	1.11	1.31	0.53	0.14	4.98	0.15	4.62
25	0.29	2.38	0.26	2.64	0.65	1.06	2.48	0.27	1.61	0.43	0.37	1.87	0.36	1.92
30			0.46	1.48	1.05	0.65	3.29	0.21	1.99	0.35				
35	1.19	0.58	0.88	0.79	1.47	0.47	6.25	0.11	2.46	0.28	1.07	0.64	0.95	0.73
45	2.76	0.25	2.52	0.27	3.20	0.21	21.81	0.03	3.52	0.19	3.09	0.22	3.37	0.21
55	8.11	0.08	5.85	0.12	5.7	0.12	31.22	0.02	6.48	0.11	7.95	0.08	7.95	0.09

and abiotic degradation can be used to estimate the contribution of chemical hydrolysis (*1*), but problems with regard to the extraction and identification of the daughter products have not been fully investigated, and whatever efforts have been made lately (*25*, *30*) are mostly directed at laboratory investigations using radio-labeled compounds.

Therefore, it is not surprising that many hydrolysis studies have been conducted in the past in an attempt to describe the behavior of sulfonylurea herbicides in aqueous buffer solutions as simplified models of soil solution (*31*−*34*). These studies provide useful information allowing a deeper understanding and proper evaluation of the hydrolysis of this group of compounds, as their role is a significant one in terms of evaluating their potential contamination of aquatic bodies such as groundwater and surface water. Besides hydrolysis studies, chemical degradation of several sulfonylureas on various dry minerals and on solid humic acid has also been investigated in the past (*35*, *36*). The purpose of this study is to bring together published information on hydrolysis of several sulfonylureas and present an overview of major results of chemical hydrolysis of sulfonylurea herbicides in aqueous buffer solutions/natural water, soils, and sediments. In addition, transformation of this group of herbicides in soil with regard to their structural composition is briefly discussed.

MECHANISMS OF DEGRADATION/HYDROLYSIS IN AQUEOUS ENVIRONMENT

A literature search on the degradation and metabolism of sulfonylurea herbicides in soil and water suggests that although there are quantitative differences in the degradation pathways, the most common primary degradation and metabolic pathways are the cleavage of the sulfonylurea bridge, *O*- and *N*-dealkylation, aryl and aliphatic hydroxylation, ester hydrolysis, and conjugation reactions with glutathione and carbohydrates (*2*, *7*). Cleavage of the sulfonylurea bridge can also occur through the base-catalyzed reaction of the linkage. For instance, pyridine-2-sulfonylureas such as flazasulfuron, rimsulfuron, and flupyrsulfuron methyl have been reported to undergo an interesting base-catalyzed contraction rearrangement of the sulfonylurea bridge, and their hydrolysis rates are faster in alkaline conditions than acidic conditions (*37*). It has been reported that these three sulfonylureas degrade in water 10−1000 times faster than many other sulfonylureas via an intramolecular nucleophilic addition and elimination reaction (*38*, *39*). The 2-position of the pyridine ring is readily attacked by the distal urea nitrogen of the linkage, eliminating SO$_2$ and producing a "bridge contracted" product. Under alkaline conditions, this product can be further hydrolyzed to a pyridinyl-pyrimidinylamine; however, the products formed upon bridge contraction have been found to be biologically inactive.

Furthermore, bridge hydrolysis can occur on the *N*-methyl group or due to the sterically induced intramolecular ester

Table 2. Model-Estimated Rate Constants (Day^{-1}) of Triasulfuron, Metsulfuron-methyl, and Chlorsulfuron in Buffer Solutions (pH 5.2–11.2) at 25 °C[a]

herbicide	rate constants (day^{-1})		
	k_1	k_2	k_3
triasulfuron	0.477 (± 0.015)	0.00479 (± 0.00109)	26.10 (± 1.96)
metsulfuron-methyl	5.471 (± 0.161)	0.00846 (± 0.00084)	43.34 (± 1.52)
chlorsulfuron	3.273 (± 0.100)	0.00853 (± 0.00103)	44.93 (± 1.87)

[a] Standard errors (±) of regressions are given in parentheses ($n = 3$).

hydrolysis of the herbicide molecule. An example of *N*-methyl sulfonylurea bridge hydrolysis is the tribenuron methyl, unique among the commercial sulfonylureas in that it has an *N*-methyl substituent on the linkage (**Figure 1b**). This linkage is much more susceptible to acid-catalyzed hydrolytic cleavage within the environmental pH regime (5−7), and at 25 °C the compound hydrolyzes nearly 15−110 times more rapidly than its *N*-demethylated product, metsulfuron-methyl (*26*). In addition, alcoholysis and ethanolyis can be other degradation pathways for these groups of herbicides (*26*, *40*).

Chemical Hydrolysis of Sulfonylurea Herbicides. Sulfonylurea herbicides undergo hydrolysis in aqueous media at a rate which is a function of both temperature and pH (**Tables 1** and **2**), and the hydrolysis rate seems to vary according to the structural feature of the molecule. This was well demonstrated in several studies involving a number of sulfonylureas which examined the effect of both pH and temperature in aqueous buffer and soil solutions (*1*, *26*, *31*−*34*, *40*−*44*).

Temperature Effect. Hydrolysis showed a marked effect with temperature, and a very acceptable description with first-order kinetics allowed determination of first-order half-lives (*1*, *39*, *31*). An Arrhenius diagram was described at pH 4 for chlorsulfuron (*40*), metsulfuron methyl (*41*), primisulfuron and rimsulfuron (*38*), and prosulfuron, primisulfuron methyl, rimsulfuron, and thifensulfuron methyl (*39*). The activation energy values from 83 to 135 kJ/mol, obtained from the slope of the line, were compared (*43*) according to diverse literature data (*1*, *45*), but it was impossible to draw any significant conclusion on hydrolysis of these compounds as affected by different temperatures due to other confounding factors such as pH and moisture content.

pH Effect. Because the aqueous solubility of sulfonylurea herbicides is pH-dependent, pH is expected to have a direct effect on the hydrolyis of sulfonylureas in aqueous buffer solution. Several studies in the past showed that these compounds hydrolyze more rapidly in water at acidic pH, but remained fairly stable in neutral solutions (*26*, *34*, *40*, *46*−*47*). This effect is illustrated in **Figure 2** for chlorimuron ethyl hydrolysis at 45 °C (*2*). When the available literature data on the observed rate constants for three most commonly used
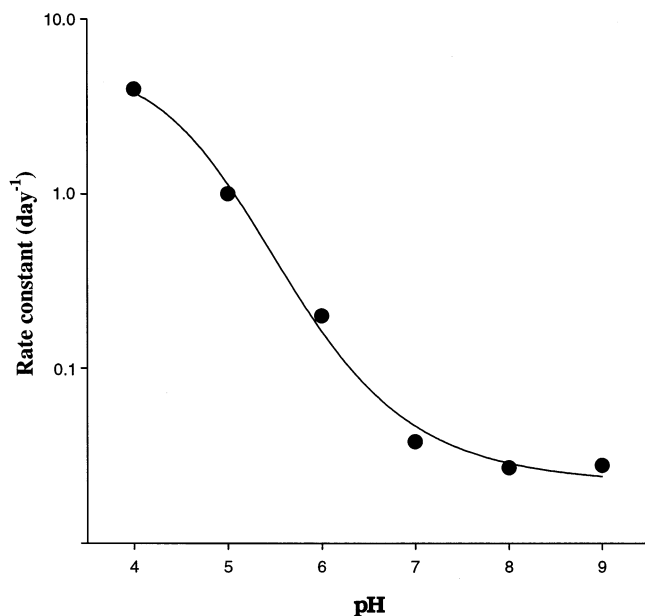
Figure 2. Chlorimuron-ethyl hydrolysis rate constants versus pH at 45 °C (*2*).

sulfonylureas (with distinct triazinic ring [R_2]) were plotted against the aqueous solution pH (at 25 °C), a similar trend was observed, as shown in **Figure 3**. Because sulfonylureas are weak acids, they exist as an equilibrium mixture of the neutral form and dissociated form much less subject to hydrolysis (*1*) as shown by the following equation:

$$R_1 - SO_2 - NH - CO - NH - R_2 \rightleftharpoons$$
$$[R_1 - SO_2 - N - CO - NH - R_2]^- + H^+$$
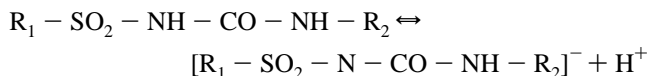
In that way, degradation rates were measured at different pH values for diverse sulfonylureas such as sulfometuron methyl (*48*), triasulfuron (*33*), chlorsulfuron (*40*), and metsulfuron methyl (*42*). In the same experimental conditions, hydrolysis rates were compared for several sulfonylureas (*31, 38, 43, 49*). Relationship between degradation constants (natural logarithm) and pH was established for chlorsulfuron (*40, 41*), metsulfuron methyl (*42*), prosulfuron, primisulfuron methyl, rimsulfuron, and thifensulfuron methyl (*39*). All sulfonylureas showed a linear but discontinuous dependence at different pH levels as illustrated in **Figure 4**. The slope variation occurred presumably as an effect of a different reactivity with respect to dissociated and neutral forms of these herbicides.

Alkaline hydrolysis for sulfonylureas was also reported in the literature, although the rate constants appeared to be discordant (*41, 27*). For example, Berger et al. (*27*) investigated 12 sulfonylurea herbicides and did not observe (except for thifensulfuron) an increase in degradation rates when pH values were increased from 7 to 10. However, an increase in degradation rates in alkaline buffers was described for some of the same herbicides such as rimsulfuron (*37*), chlorimuron ethyl (*44*), bensulfuron methyl (*26*), and more recently for triasulfuron, metsulfuron methyl, and chlorsulfuron (*34*). It is conceivable that a buffer effect could explain these opposed results reported in these studies. In another study, thifensulfuron, which was hydrolyzed at the ester moiety, appears as a special case (*32*).

Hydrolysis Pathways. Until the 1990s, it was believed that the predominant hydrolysis reaction of all sulfonylureas (under mildly acidic conditions) was the cleavage of the sulfonylurea
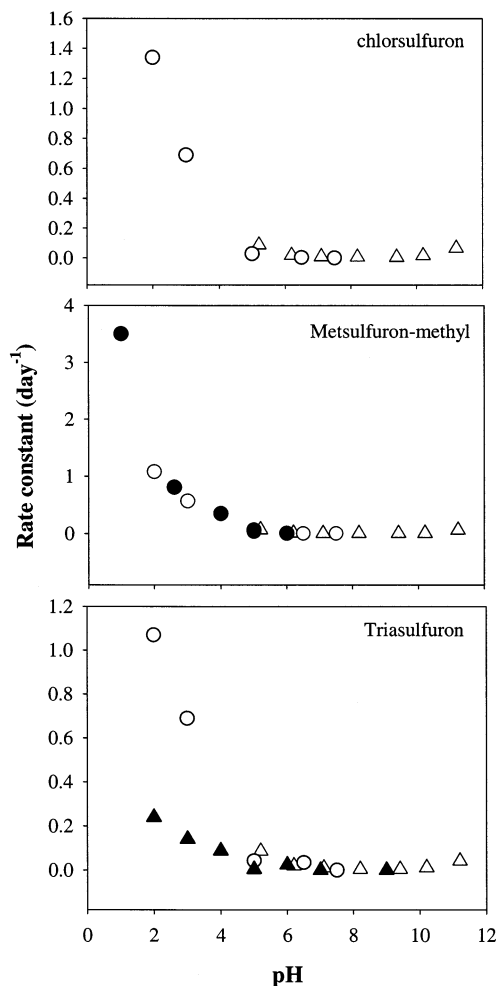
Figure 3. Comparison of rate constant (day^{-1}) for three sulfonylureas in aqueous buffer solutions against pH at 25 °C. Data are from ● (*46*); ○ (*47*); ▲ (*33*); and △ (*34*).

bridge (*1, 49*) as depicted by the equation below.

$$R_1 - SO_2 - NH - CO - NH - R_2 + H_2O \Rightarrow$$
$$R_1 - SO_2 - NH_2 + NH_2 - R_2 + CO_2$$
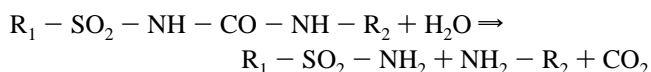
Hydrolysis proceeds through the attack of the neutral bridge carbonyl carbon by water, releasing carbon dioxide and the herbicidal-inactive sulfonamide and heterocyclic amine, which may sometimes undergo further hydrolytic degradation. However, Dinelli et al. (*11*) who evaluated the potential of capillary electrophoresis for the hydrolysis studies of nine sulfonylurea herbicides, observed an unexpected number of degradation products. If simple sulfonylurea bridge cleavage can explain the four degradation compounds obtained with chlorimuron or bensulfuron (hydrolysis of the formed sulfonamide then cyclization), the six compounds observed for chlorsulfuron or metsulfuron methyl (triazinic ring as R_2) probably implicated a more complex pathway. However, rimsulfuron led to only one (pyridinic ring as R_1). The number of daughter products that were produced during hydrolysis appeared to be related to the structure of the sulfonylurea. On the basis of their mechanisms of hydrolysis, three classes of sulfonylureas can be grouped as follows.

Sulfonylurea Herbicides Without Pyridinic (R$_1$) and Triazinic Ring (R$_2$). This class involves most of these herbicides in which chemical structures do not include triazinic (R_2) and a pyridinic ring (R_1) as shown in **Figure 1a**. The simple hydrolytic cleavage

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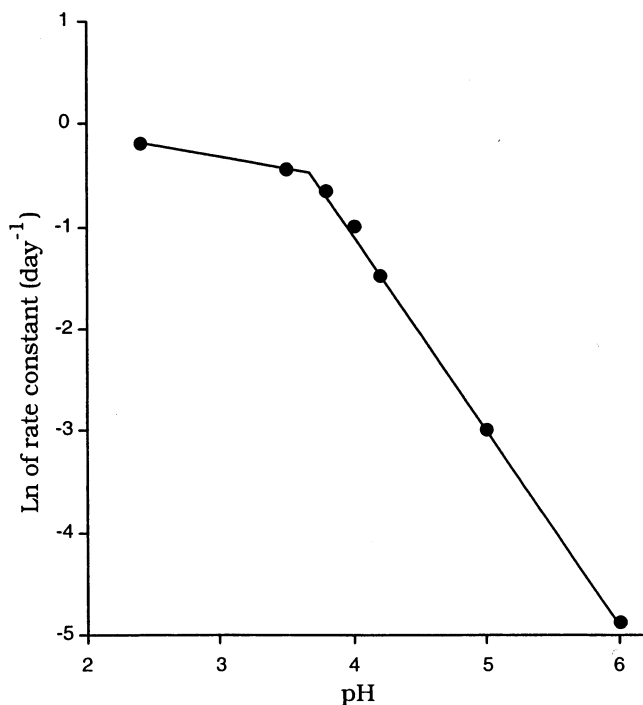
Figure 4. Hydrolysis of chlorsulfuron (25 °C); Ln of rate constant versus pH (*40*).

of sulfonylurea bridge is observed. The stable heteocyclic amine (R_2-NH_2) was identified as a major hydrolysis product of amidosulfuon in aqueous solutions (*43*), whereas the sulfona-

mide moiety ($R_1-SO_2-NH_2$) was detected when sulfometuron methyl was hydrolyzed at pH 5, 7, and 9 (*48, 50*). Further cyclization into saccharin was also observed.

The two moieties of sulfonylurea bridge cleavage were simultaneously observed with chlorimuron ethyl (*51, 52*), and an extensive hydrolysis study of this herbicide was described (*44*). The proposed degradation pathway suggested the breakdown of the urea bridge only at pH ≤ 8, however, under alkaline conditions (pH ≥ 10) the way of the saponification of ethyl ester appeared preponderant (**Figure 5**). Similar results were obtained for another sulfonylurea, bensulfuron methyl; however, significant saponification appeared to occur above pH 8 (*26*).

Sulfonylurea Herbicides With a Triazinic Ring (R₂). An unexpected degradation pathway for this class of sulfonylureas (**Figure 1b**) with R_2 as a methoxy-triazinic ring was first described for metsulfuron methyl (*42*). Most of the hydrolysis studies with regard to this class of herbicide were involved with chlorsulfuron (*25*), which was, incidently, the first sulfonylurea herbicide to be discovered and commercialized (*53*).

For this class of sulfonylureas, the major degradation products are the stable chlorobenzene sulfonamide and triazine amine resulting from the hydrolytic cleavage of the sulfonylurea bridge (*49, 54*), and it appears to be the major hydrolytic pathway especially at elevated temperature (**Figure 6**). However, a second concomitant hydrolysis pathway was described under acidic pH (*10, 40*). The product of the *O*-demethylation of the methoxy substitute fixed to the triazine ring was first formed, followed by hydrolytic cleavage of the triazine ring (**Figure 6**). Further studies confirmed these observations (*31*). Structure of the triazine ring cleavage compound has been a subject of

Figure 5. Simplified pathway of chemical hydrolysis of chlorimuron ethyl (*44, 71*).

Figure 6. Simplified hydrolysis pathway of chlorsulfuron at pH 5 (*25, 78*).

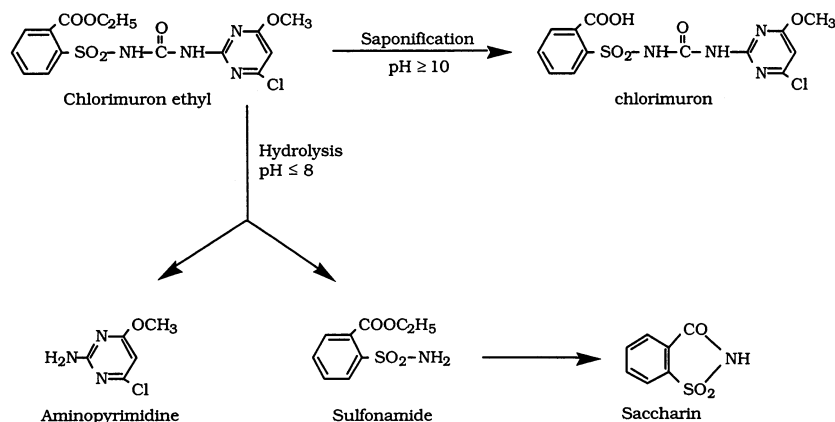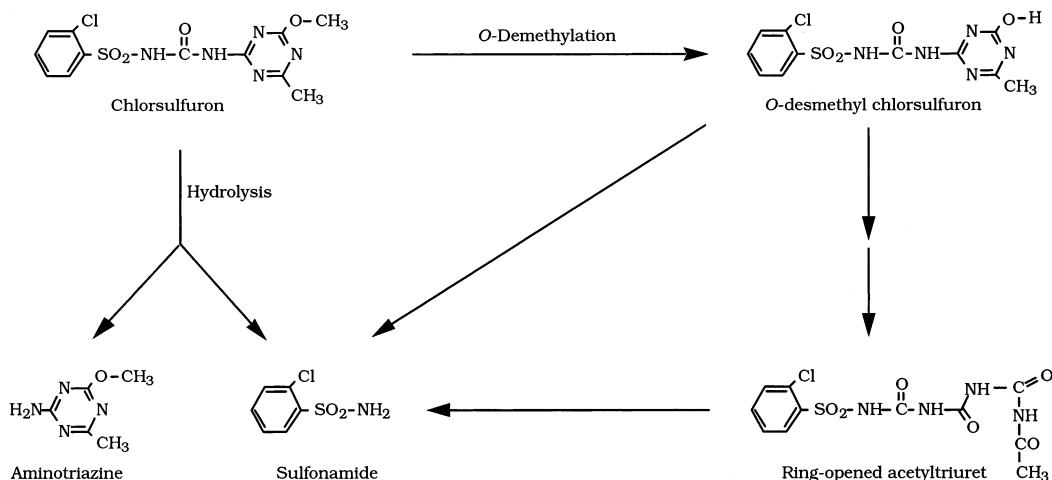considerable debate. From NMR studies, two possible structures were proposed (*55*). The acetyl triuret structure, initially suggested by Reiser et al. (*10*) seems more acceptable, and later a detailed hydrolytic degradation pathway for chlorsulfuron at pH 5 was proposed by Strek (*25*).

Other methoxy-triazine substituted sulfonylurea herbicides also presented a similar hydrolysis pathway with both sulfonylurea bridge breakdown and *O*-demethylation observed when metsulfuron methyl was hydrolyzed (*8*). The proposed degradation pathways with the structure of the acetyl triuret (triazine ring cleavage compound) appeared to be inconclusive (*42*), or incorrect (*31*). Others reported an unexpected cyclization of the sulfonamide moiety (*56*). More recently, under highly alkaline conditions (pH 11.2) the hydrolysis of the methyl ester group fixed to the aromatic ring and the *O*-demethylation were simultaneously observed by Sarmah et al. (*34*) with the correspondent acetyl triuret compound being formed upon hydrolysis.

Braschi et al. (*33*) described a complete hydrolysis pathway for triasulfuron, another methoxy-triazine substituted sulfonylurea, in aqueous buffer solutions at pH values ranging from from 2 to 9. The primary path of degradation was the cleavage of the sulfonylurea bridge, and a minor degradation path was also observed such as *O*-demethylation and opening of the methoxy-triazine ring. Similar pathways were described for hydrolysis of prosulfuron at pH 5 (*57*). The work of Braschi et al. (*33*) and Bray et al. (*57*) were analogous, with both groups proposing a two-step mechanism for the hydrolytic opening of the triazine ring.

Therefore, the type of reactions that are discussed above seem to be common to the new methoxy-triazine-substituted sulfonylurea herbicides such as tribenuron methyl, ethametsulfuron methyl, or triflusulfuron methyl (*7*). However, when their hydrolysis rates were measured in aqueous solutions under controlled laboratory conditions (*31*), their degradation products still remained unidentified (*56*).

Thifensulfuron methyl is also a member of this same class of herbicide, and the thiofene part of the molecule seems to induce a particular reactivity (*24, 1, 32*). The proposed acidic hydrolysis pathways for this compound in aqueous buffer solutions (pH 4 and 5) showed a concomitant cleavage of the sulfonylurea bridge and *O*-demethylation of the methoxy group according to the general scheme. However, hydrolysis in alkaline condition was observed to be specific to this herbicide leading to the saponification of the methyl ester substitute and formation of the metabolite, thifensulfuron (*32*). This metabolite was, however, also found to be rapidly produced in soil by biological degradation as reported earlier by Smith et al. (*58*) and later by Brown et al. (*59*) through laboratory studies.

Sulfonylurea Herbicides With a Pyridine Ring (R_1). The replacement of the aromatic ring (R_1) by a pyridine one affords a new class of sulfonylurea herbicide (R_2 = pyrimidine ring), rimsulfuron. This compound has been found to degrade rapidly in soil and water through a specific path attested by hydrolysis of rimsulfuron in water at 25 °C at pH 4, 7, or 9 (*60*), and gave only one product at 55 °C and pH 4 (*61*). For rimsulfuron, the breakdown of sulfonylurea bridge appeared as a minor degradation path as shown below, whereas sulfonylurea bridge contraction was preponderant (*37, 62−64*):

The primary hydrolysis product at pH 5 was compound **1**, resulting from the contraction of the sulfonylurea bridge, whereas amine **2** was the major hydrolysis product at pH 7 and 9. A reaction mechanism proceeding through a five-member transition state was suggested (*65*).
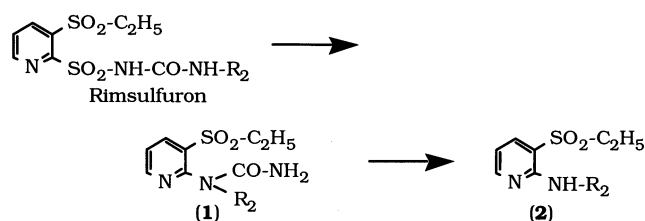
Studies conducted by Teaney et al. (*66*) and Rouchaud et al. (*67*) revealed that the hydrolysis pathway of flupyrsulfuron methyl seems comparable with that of other pyridylsulfonylurea herbicides, however, the formed product **1'** was allowed to cyclize into **3'** as shown below:
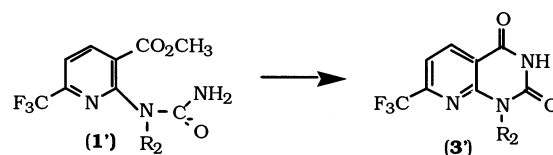
At pH 7 or 9 this latter product **3'** appeared in good yields, whereas at pH 5 there were four major degradation products: compound **1'** and its internal cyclization product **3'**, as well as the two compounds which resulted from the simple breakdown of the sulfonylurea bridge (*68*).

Nicosulfuron, which belongs to the substitute pyridine-sulfonylurea herbicides, exhibits a pyridyl-sulfonylurea bridge in place of the usual phenyl-sulfonylurea group (**Figure 1c**). From a recent work on hydrolysis of nicosulfuron, it was concluded that the main degradation pathway for this compound was the hydrolysis of the sulfonylurea bridge (*69*), whereas the bridge contraction was more prevalent for other compounds within this category such as rimsulfuron (*37, 63−65*) and flupyrsulfuron-methyl (*67, 68*).

Degradation of Sulfonylurea Herbicides in the Presence of Minerals. Degradation of several sulfonylurea herbicides in the presence of minerals was investigated with a view to realize a simplified model of the soil, and obtained results were compared to the conclusions derived from hydrolysis studies (*31, 40, 42*). For instance, the observed degradation rates of 12 sulfonylureas in two water−sediment systems could be explained by both biotic and chemical process (*33*). In native sediments at neutral pH, microbial degradation was found to be prevalent, however at lower pH, chemical hydrolysis became more important. The results of Berger and Wolfe (*31*) allowed a direct comparison of the degradation rates of the herbicides in water and in sediments. Influence of clay mineral on the adsorption and degradation of sulfonylurea herbicides has been investigated by few researchers in the past. For example, Pantani et al. (*70*) reported a partial decomposition of cinosulfuron to several products after undergoing adsorption from the organic solvent on Al-montmorillonite. One of these was identified as the correspondent hydroxy-*s*-triazine (R_2−OH). Others have investigated the behavior of sulfonylurea deposition on various dry minerals such as kaolinite, silica gel, alumina, and bentonite, and suggested degradation pathways for bensulfuron methyl (*36*), chlorimuron ethyl (*71*), chlorsulfuron (*72*), or metsulfuron methyl (*73*). These pathways were found to be similar to those previously proposed for chemical hydrolysis.
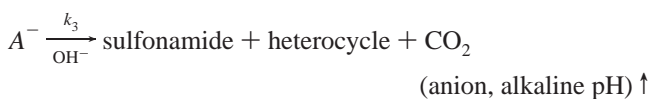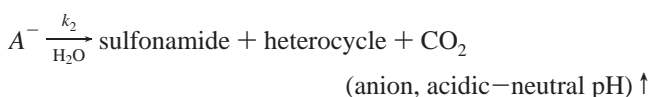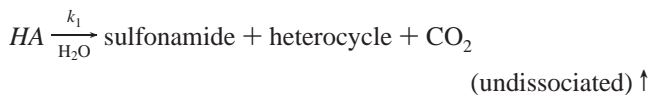
Degradation of rimsulfuron adsorbed on Al-hectorite was investigated by Pantani et al. (*74*) and they proposed a degradation mechanism that involved the similar bridge contraction products (**1**) and (**2**) as previously formed during hydrolysis (*37*). In contrast, Ukrainczyk and Rashid (*75*) described the rapid

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disappearance of nicosulfuron deposited on clay minerals, however, the identification of the degradation product was not reported. Elsewhere, degradation on solid humic acid was investigated for chlorsulfuron, metsulfuron methyl (*35*), bensulfuron-methyl, and chlorimuron ethyl (*36, 44*), and the observed pathways were similar to those described for hydrolysis studies for the same compounds.

Unlike most sulfonylurea herbicides that are weak acids and exhibit only a limited affinity for various minerals (*76, 77*), nicosulfuron (pK_a = 4.3) showed an unexpectedly strong interaction with clay minerals (*75*). However, in contrast to the findings of Ukrainczyk and Rashid (*75*), Sabadie (*69*) reported slower degradation of this compound at 30 °C after its deposition on various oven-dried minerals that included kaolinite, silica gel, H$^+$-bentonite, montmorillonite K10, and alumina. Although these minerals did not seem to provoke the expected rapid degradation, catalyzed by clay surface as reported earlier (*75*), the measured half-lives appeared to be in close approximation to those described for bensulfuron-methyl (*36*) and were higher than chlorimuron ethyl (*44*) under similar experimental conditions.

Model for pH vs Hydrolysis Rate. It has been well established that for weak acids, such as the sulfonylureas, there exists an equilibrium between the undissociated and the negatively charged dissociated molecules in aqueous solution (*1*). Hence, depending upon the pH of the system, the molecules of the herbicide can be present as anions or as the conjugate acid. On the basis of the ionization constants (pK_a) of these molecules, the anions can thus experience either slightly acidic to neutral or alkaline environments. The most important and the first step in the hydrolysis process involves the cleavage of the sulfonylurea linkage via attack by water, or at higher pH, by the hydroxyl ions. On the basis of this, Sarmah et al. (*34*) has developed a model to describe the pH-dependent hydrolysis rate (in aqueous buffer) for three sulfonylurea herbicides: chlorsulfuron, metsulfuron-methyl, and triasulfuron. The main assumptions of the model were that, over the pH range of 4−12, the observed rate of sulfonylurea hydrolysis is the sum of the following three simultaneous reactions: (a) hydrolysis of the undissociated sulfonylurea molecules; (b) hydrolysis of the anionic species of sulfonylurea molecules at near neutral pH; and (c) hydrolysis of the anionic species of sulfonylurea molecules by hydroxide ion.

The three reactions can be represented as follows:

$$HA \xrightarrow[H_2O]{k_1} \text{sulfonamide} + \text{heterocycle} + CO_2$$

$$(\text{undissociated}) \uparrow$$

$$A^- \xrightarrow[H_2O]{k_2} \text{sulfonamide} + \text{heterocycle} + CO_2$$

$$(\text{anion, acidic−neutral pH}) \uparrow$$

$$A^- \xrightarrow[OH^-]{k_3} \text{sulfonamide} + \text{heterocycle} + CO_2$$

$$(\text{anion, alkaline pH}) \uparrow$$

The equation is based on the concept of the Henderson−Hasselbach equation, which can be written as follows:

$$[SU] = [HA] + [A^-] \tag{1}$$

where [*SU*] is the concentration of sulfonylurea herbicides, HA is acid, and A$^-$ is the conjugate base. The above three processes
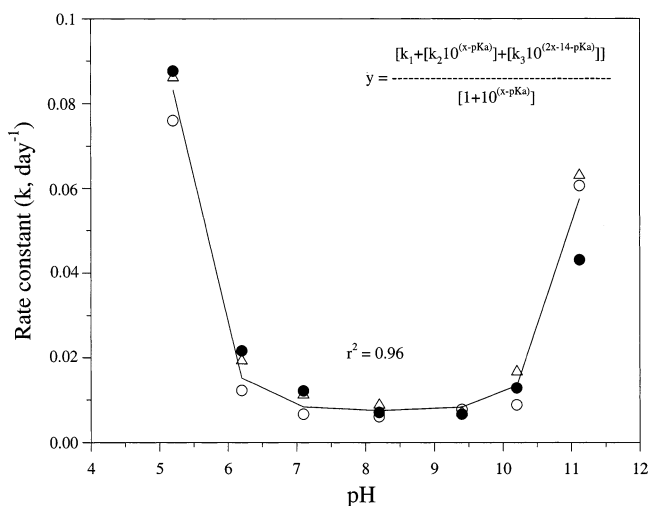
Figure 7. Hydrolysis rate constants (day^{-1}) of triasulfuron (●), metsulfuron-methyl (○), and chlorsulfuron (△) in aqueous buffer solution as a function of pH. Symbols represent measured data, whereas the solid lines represent the fit of eq 3.

can be thus represented as follows:

$$-\frac{d(\ln[SU])}{dt} = Y \tag{2}$$

where

$$Y = \frac{[k_1 + [k_2 10^{(X-pK_a)}] + [k_3 10^{(2X-14-pK_a)}]]}{[1 + 10^{(X-pK_a)}]} \tag{3}$$

In equation 3, k_1, k_2, and k_3 are the rate constants for each of the hydrolysis reactions, X is the pH of the buffer solutions, and pK_a is the dissociation constant of the sulfonylurea herbicide. Each of the individual rate constants exhibits a temperature dependence that conforms to the Arrhenius equation, and under constant temperature these rate constants will be constant. When the pH is held constant, then the right-hand side of the eq 3 is constant and the rate of loss of sulfonylurea herbicide follows the pseudo-first-order kinetics (*34*). **Figure 7** shows the functional relationship between the hydrolysis rate constants and pH for three sulfonylurea herbicides at a constant temperature of 25 °C. A nonlinear regression was used to estimate the values for the rate constants k_1, k_2, and k_3 for each of the three compounds, and the relative magnitude of the model-estimated rate constants was in the order $k_3 > k_1 \gg k_2$ for each compound investigated (**Table 2**). This study confirmed similar findings reported in the past (*1, 31*) that sulfonylurea hydrolysis occurs most readily via hydroxyl ion attack of the bridge carbonyl (alkaline conditions) and that hydrolysis involving attack by neutral water is at least 1000-times faster when the molecule is undissociated (acidic conditions) than when it is present as the anion at near neutral pH.

Transformation of Sulfonylurea Herbicides in Soil. Many persistence evaluation experiments of sulfonyurea herbicides in soil can be found in the literature (e.g., *1, 6, 25, 29, 58, 76−78*). Although these studies presented some results of undeniable agronomic interest, an extensive knowledge of sulfonylurea behavior in soil seemed to be lacking in regard to their implication in the environment: phytotoxicity of residues, remnants of degradation products, presence of "bound residues", and groundwater pollution.

Transformation of sulfonylurea herbicides in soil occurs twice through chemical degradation and microbial breakdown (*1*, *2*, *24*). To assess the relative importance of these two processes, degradation in sterilized (no microbial activity) and nonsterilized soil has been compared (*15*, *28*, *29*). Several studies were undertaken with one or a few sulfonylureas such as sulfometuron methyl (*45*), metsulfuron methyl (*79*), triasulfuron (*29*), thifensulfuron (*80*), and chlorsulfuron (*25*, *78*). A comparative study on microbial and chemical transformation of eleven sulfonylurea herbicides in soil was recently described by Berger et al. (*27*), where most of these herbicides were mainly transformed by microorganisms, although chemical hydrolysis played a significant role. For instance, tribenuron methyl seemed to degrade chemically, however, thifensulfuron methyl appeared to undergo transformation only through microbial action. This, perhaps, explains why it is difficult to isolate microorganisms able to degrade sulfonylureas in pure culture (*81*).

*Sulfonylurea Herbicides Without Pyridinic (R$_1$) and Triazinic Ring (R$_2$) (**Figure 1a**).* For sulfonylurea herbicides without pyridinic and a triazine ring, the breakdown normally occurs at the bridge linkage. Degradation of amidosulfuron followed first-order dissipation kinetics in soils and observed half-live varying from 14 to 231 days (*82*) and a good correlation was obtained among temperature, soil pH, organic matter content, and soil moisture (*7*, *83*). A laboratory degradation study on an acidic soil (pH 5.2), at 20 °C and 21% moisture content, showed that amidosulfuron degraded with first-order kinetics; however, the corresponding amino-pyrimidine (R$_2$−NH$_2$) did not appear to be a degradation product in this silt loam soil (*82*). However, it is noteworthy that the same authors confirmed the amino-pyrimidine as a major hydrolysis product of amidosulfuron in aqueous solution (*43*). The authors speculated that amino-pyrimidine could be formed transiently before being biologically transformed into demethylated hydroxypyrimidines. Recently, detection of an *O*-desmethyl metabolite of amindosulfuron also suggested occurrence of biotic degradation (*84*).

The low half-life observed for bensulfuron methyl (1−3 weeks), a herbicide commonly used in aquatic vegetation management, essentially resulted from abiotic degradation (*85*). Similar observations were also reported in flooded rice fields (*86*, *87*).

Degradation of chlorimuron ethyl in soil was reported to be pH dependent (*2*, *88*), and the identified degradation products (phenylsulfonamide, R$_1$−SO$_2$−NH$_2$; aminopyrimidine, R$_2$−NH$_2$; and saccharin) suggest that chemical hydrolysis of the sulfonylurea bridge is the primary mode of degradation in air-dry soil, whereas microbial degradation (*O*-desmethyl chlorimuron) and chemical hydrolysis both occur in moist soil (*27*, *89*, *51*, *52*). A complete degradation pathway of chlorimuron ethyl in soil was proposed by Fuesler and Hanafey (*90*).

The degradation rate for sulfonylurea herbicides is dependent on several factors such as temperature, pH, moisture content, and the biological activity of the soils (*1*, *6*, *24*). For example, measured degradation half-lives for primisulfuron methyl in microbially active soils were found to vary from 5 (*91*) to 30 days (*92*, *93*), but were 4-fold higher in sterile soil, confirming the decisive contribution of biological processes (*94*). Observed degradation products (phenylsulfonamide and saccharin) suggested that the initial hydrolyzation of the sulfonylurea bridge occurred both chemically and biologically.

In acidic soils, microorganisms did not seem to play a major role in the initial step of degradation of sulfometuron methyl (sulfonylurea bridge hydrolysis), and saccharin appeared as the principal degradation product (*45*, *95*). This herbicide was found

to undergo decomposition in alkaline soils as well; however, it was speculated that soil microbial action was the rate-limiting step because the compound was found to be relatively stable under neutral and alkaline conditions (*48*). The degradation rate for sulfometuron methyl was found to increase with increases in soil temperature and moisture content in soils from the midwestern United States, and the half-lives ranged from 2 to 5 weeks (*50*). A complete metabolic pathway of sulfometuron methyl in field soil was recently discussed by Trubey et al (*96*).

Both pyrazosulfuron ethyl and halosulfuron methyl (*7*) are distinguishable from other sulfonylureas by their R$_1$ moiety (pyrazole in place of the aromatic ring). Their rate of dissipation in soil seemed to follow first-order kinetics and increased with increasing temperature and lower soil pH (*97*). Another sulfonylurea with pyrimidine and triazine rings is the imazosulfuron, which has a complex imidazole ring as R$_1$ moiety. Mikata et al. (*98*) reported for this compound a significant difference in degradation rates between aerobic and anaerobic conditions (half-lives of approximately 60 and 3 days, respectively), with a proposed degradation pathway as the cleavage of sulfonylurea bond and monodemethylation.

*Sulfonylurea Herbicides with Triazinic Ring [R$_2$] (Without Pyridinic Ring [R$_1$]) (**Figure 1b**).* Good examples of this group of sulfonylureas are the chlorsulfuron, metsulfuron-methyl, and triasulfuron having a distinct aromatic ring (R$_1$), and perhaps these three are most widely researched compounds under laboratory and field conditions, involving aqueous hydrolysis, soil degradation, and mobility in the field and laboratory columns. By far, the behavior of chlorsulfuron in the soil and water environment, the first sulfonylurea to be discovered and commercialized, generated many studies as discussed recently by Strek (*25*, *78*).

Chlorsulfuron. Numerous studies were conducted in the past under laboratory and field conditions and under varied environmental conditions investigating the fate and behavior of these three compounds. The rate of degradation of most soil-applied herbicides increases with an increase in temperature (*99*) and a decrease of soil pH (*3*, *100*−*102*). Effects of other important factors such as soil moisture and organic matter content on the degradation rate for chlorsulfuron were well documented in the past (*103*, *104*). In most of these studies, a pseudo-first-order description was often observed (*105*, *106*) and measured half-lives in acidic or neutral soils varied according to experimental conditions: from 8 days at pH 5.2 (*107*), 20−30 days (*27*, *53*), 30−70 days (*60*, *104*, *108*, *109*), and up to 168 days at pH 7.5 (*110*). Observed half-lives in alkaline soils varied from 20 to 90 days (*15*, *23*, *111*, *112*). Good correlation of soil pH versus half-lives was also proposed (*3*, *76*).

It has been well documented that both microbial and aqueous hydrolysis degradation are responsible for chlorsulfuron dissipation in soil. Half-lives comparison between sterile and nonsterile soils was established (*25*, *27*, *113*, *114*) which confirmed the relative importance of each degradation path. Degradation rates were positively correlated with microbial biomass (*76*), which assumed a greater role, especially in alkaline soils (*28*).

Chlorosulfonamide (R$_1$−NH$_2$) was first identified as a degradation product of chlorsulfuron in soil (*101*, *110*), and this simple breakdown of the sulfonylurea bridge was earlier described as the prevalent degradation process for chlorsulfuron in soil (*1*, *115*). However, the discovery of a new significant degradation compound resulting from the *O*-demethylation of chlorsulfuron (*116*) suggested further studies, and comparable

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degradation pathways as described previously for aqueous hydrolysis were later identified in soil under laboratory conditions as shown in **Figure 5** (*25*). Similar results were also reported with the occurrence of an unexpected product identified as a ring-opened carbamoyl guanidine under field dissipation studies involving chlorsulfuron (*78*).

Metsulfuron-Methyl. The chemical structure of the herbicide metsulfuron-methyl appears to be comparable with that of chlorsulfuron, having a carboxymethyl substitute in place of Cl in R_1 moiety (*117*). Like chlorsulfuron, degradation rates of metsulfuron-methyl were also affected by soil temperature, moisture content, and soil pH. Measured half-lives in acidic or neutral soils varied from 5 to 190 days (*92, 111, 114*). The effect of soil organic matter content on metsulfuron-methyl degradation was studied in relation to soil depth in the UK (*76*) and in Swedish soils (*111*), and the results obtained were in good agreement with results obtained for chlorsulfuron in New Zealand soils (*118*).

It was demonstrated that chemical hydrolysis and microbial breakdown simultaneously play a role in soil degradation of metsulfuron methyl (*79*), and that microbial degradation was an important factor for field dissipation (*119*). However, chemical hydrolysis appeared to be a major factor at pH < 6, whereas at pH greater than 6, the herbicide was degraded by microbial activity (*27, 120*). From a laboratory incubation study, Pons and Barriuso (*121*) reported the metsulfuron methyl half-life to vary from as low as 5 days in an acidic soil (pH 5.2) to 69 days in an alkaline soil (pH 8.1). In the same study, under sterile conditions, the half-life increased to 139 days in alkaline soil, however, there was no change in an acidic soil. Although a simple breakdown of the sulfonylurea bridge was earlier postulated to be the prevalent degradation mechanism for metsulfuron methyl in soil (*1*), work by Pons and Barriuso (*121*) suggested that there were two main metabolic pathways of degradation of metsulfuron-methyl: hydrolysis of the sulfonylurea bridge and *O*-demethylation of the methoxy-triazine moiety, which supports the earlier findings (*35, 42, 46, 121, 122*). This was further evidenced in a recent work on the degradation of metsulfuron-methyl, where Li (*30*) demonstrated that the metabolic pathways of metsulfuron-methyl involved *O*-demethylation and sulfonylurea bridge cleavage, as well as a third mechanism, triazine ring opening. This ring opening after *O*-demthylation was also observed in alkaline hydrolysis conditions for metsulfuron-methyl (*34*) and under acidic conditions for prosulfuron in aqueous buffer solution at pH 5 (*57*).

Triasulfuron. Considerable variation in the results of degradation studies involving triasulfuron in soil can be found in the literature, which applies to acidic, neutral, or alkaline soils. Despite comparable temperature conditions (20 °C), measured half-lives seemed to vary significantly in a number of laboratory and field investigations. Therefore, no general conclusion can be easily made with regard to their degradation half-lives. For example, in two different soils at pH 5.8, half-lives were found to vary from from 33 days (*77*) to 198 days (*99*), whereas it was found to be 20 days (*27*) at pH 7.2, and 120 days (*77*) at pH 7.4. Effects of varied temperature and moisture contents on triasulfuron degradation were well documented in different soil types under varied laboratory conditions (*29, 15, 76, 104*), and the role of soil organic matter on the rate of degradation was specified (*107*). Estimated first-order half-lives of 44−46 days were reported in alkaline soils (pH 8.7−10.1) in the field depending on the experimental conditions (*23*).

Earlier work demonstrated the importance of microbial activities being primarily responsible for the disappearance of triasulfuron from soils, particularly at lower temperatures (*29, 123*). Measured half-lives in microbially active soils (pH 6.5 or 7.2) were found to be four times lower than those in sterile soils (*27, 93*). In contrast, however, the microbial breakdown process appeared to be much higher in alkaline soils, although it was speculated that the type of microorganisms present in the soil may have been the cause of rapid disappearance of triasulfuron in soils of southern Australia having extremely high pH values (*15*).

Other Sulfonylurea Herbicides of this Class (R_1: Aromatic Ring; R_2: Triazinic Ring). An example of this group of sulfonylureas having a distinct aromatic and a triazine ring is the tribenuron-methyl. The compound consists of *N*-methyl substituent on the sulfonylurea bridge that induces high hydrolysis rates (*2, 31*) and a very rapid degradation rate ($t_{1/2} \sim$ 8 days at 20 °C, pH 7.2) in agricultural soils (*2, 7, 24*). However, similar degradation kinetics in sterile and nonsterile soil also suggested a purely chemical transformation (*27*).

There is a dearth of information on the soil degradation studies involving cinosulfuron or prosulfuron whose microbial transformations have been described (*7*), and the newly identified metabolites will be useful for further soil degradation studies (*124*). Ethametsulfuron-methyl degrades in soil through pH-dependent chemical hydrolysis and microbial degradation (*7*). Observed degradation rates for ethatmetsulfuron-methyl were reported to be similar to those of chlorsulfuron, but chemical transformation appeared to be relatively greater (*27*). Low hydrolysis half-lives of triflusulfuron-methyl (3.7 and 32 days, at pH 5 and 7, respectively) contribute to the rapid degradation of this herbicide in soil (*7*).

Because of its R_1 thiofene moiety, thifensulfuron-methyl appears to be a compound of particular interest. Observed degradation rates for this herbicide in soils were nearly 20 to 50 times faster than that of chlorsulfuron (*24, 27*). Previous work has shown that the compound is degraded microbially (*58, 125*), and the initial degradation product in soil has been identified as herbicidally inactive thifensulfuron acid (*59, 80*). Steric and electronic features of thifensulfuron-methyl that may account for its rapid deesertification in soil and water have been described (*126*). Comparison of degradation curves in sterile and nonsterile soils (*27, 80*) suggested a first microbial deesertification step followed by chemical processes as described later in hydrolysis kinteics under aqueous buffer solutions (*32*).

*Sulfonylurea Herbicides With Pyridinic Ring (R_1) (**Figure 1c**).* An example of sulfonylureas having a pyridinic ring is the maize-selective sulfonylurea, rimsulfuron, which has been found to rapidly degrade in soil (*7, 63*). For example, in an alluvial soil suspension of pH 8.1, Martins and Mermoud (*63*) measured a half-life of 7.5 days, a value slightly lower than that (∼24 days at pH 6.5 and 25 °C) observed by Schneiders et al. (*37*). This difference in the observed half-lives can be attributed to the differences in the experimental conditions. Under field conditions rimsulfuron degraded rapidly with a half-life of 5.6 day and the major metabolite was formed by a contraction of the sulfonylurea bridge forming *N*-(3-ethylsulfonyl-2-pyridinyl)-4,6-dimethoxy-2-pyridineamine (*7*), which suggest that alkaline conditions favored hydrolysis (*60*). In contrast, similar degradation curves were observed for rimsulfuron in aerobic and anaerobic soils, while the same sulfonylurea bridge contraction, e.g., rimsulfuron → (**1**) → (**2**), described previously during hydrolysis appeared as the major degradation path of the herbicide in soil as shown below. The cleavage of the sulfonylurea bridge, however, was a minor degradation pathway (*37*).

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Rimsulfuron → (1) → (2) → (4)
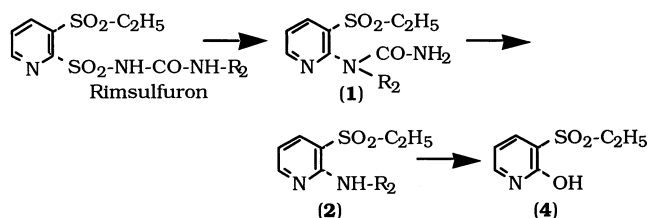
Marucchini and Luigetti (*60*) have developed an analytical procedure to detect the compound (**2**), however, this important degradation product did not accumulate in the soil. Its maximum concentration occurred after 20 days of incubation, thereafter it decreased, and, as shown above, the 2-hydroxypyridine (**4**) then became the major rimsulfuron soil degradation product (*127*).

Field soil half-lives of about 100 days were measured for flupyrsulfuron methyl (*67*). Therefore, lower values (from 9 to 25 days at 20 °C) were obtained under laboratory conditions in various nonsterile European soils, and both chemical and microbial breakdown seemed to be implicated (*66*). The aerobic soil studies showed the existence of three main degradative pathways depending on the soil pH (*68*) as depicted below.


R$_1$-SO$_2$-NH$_2$ Flupyrsulfuron methyl

(2′)

(3′)
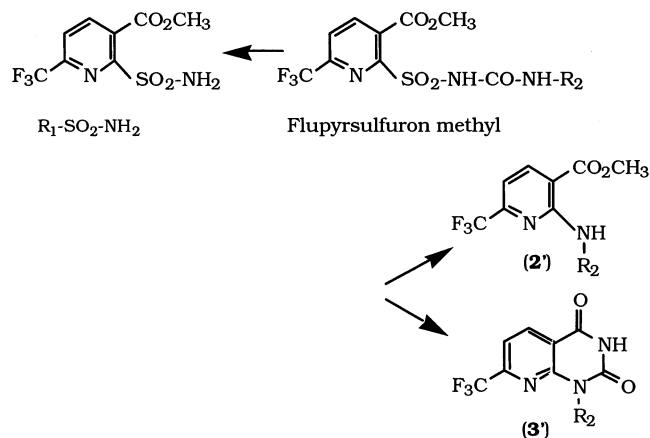
At pH > 6.6, contraction and ipso-rearrangement of the sulfonylurea bridge predominated, giving **3′** (which further underwent successive *O*-demethylation of two R$_2$ methoxy substitutes), and bridge contraction **2′**. In more acidic soils, formation of sulfonamide (R$_1$−SO$_2$−NH$_2$) also implicated sulfonylurea bridge breakdown.

Research on the transformation of other compounds in soil belonging to this substituted pyridinesulfonylurea group is lacking, though some useful information is available on the sorption and transport behavior of nicosulfuon under laboratory investigation (*75, 128, 129*) and flazasulfuron (*130*) in soil.

CONCLUSION

An overview of past and recent work on the hydrolysis of some sulfonylurea herbicides in aqueous buffer and soil is presented. It is clear from the discussion that the literature is replete with information on the behavior of these herbicides in aqueous and soil environments, and their persistence and disappearance in our environment is a function of a multitude of factors contributing to their actions in soil or water. Observed hydrolysis reaction rates are temperature-, and in particular, pH-dependent. All sulfonylurea herbicides hydrolyze more rapidly in water at acidic pH, but remained fairly stable in neutral solutions (**Figures 2** and **3**). Sulfonylurea bridge breakdown was earlier postulated as the predominant pathway of chemical

hydrolysis for this group of herbicides. In fact, some of these herbicides with molecular structure including an aromatic ring as [R$_1$] and pyrimidine ring as [R$_2$] are hydrolyzed according to the following equation:

$$R_1 - SO_2 - NH - CO - NH - R_2 + H_2O \rightarrow$$
$$R_1 - SO_2 - NH_2 + NH_2 - R_2 + CO_2$$
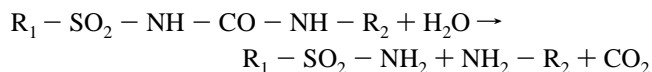
Often, degradation products may be further transformed, as in saccharin formation from chlorimuron ethyl (**Figure 5**). An unexpected concomitant degradation path was observed for hydrolysis of all sulfonylureas with R$_2$ as methoxytriazinic ring, *O*-demethylation of the methoxy substitute followed by hydrolytic cleavage of the triazine as presented in **Figure 6**. In the case of a few sulfonylureas with R$_1$ as pyridinic ring, breakdown of the sulfonylurea bridge appears as a minor degradation path, while sulfonylurea bridge contraction is preponderant. All these extensive studies about hydrolysis appeared particularly indispensable to establish and understand the pathways of degradation of sulfonylurea herbicides in soil, which occurs twice, i.e., first through chemical degradation (abiotic) that is pH dependent, and later through biotic processes involving microorganisms. Similar pathways have been generally recognized, however, biotic transformations may be specific to the compound itself, such as *O*-demethylation of chlorimuron ethyl, deesterification of thifensulfuron methyl, and formation of a ring-opened carbamoyl guanidine from chlorsulfuron.

ACKNOWLEDGMENT

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