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Degradation of Sulfosulfuron, a Sulfonylurea Herbicide, As Influenced by Abiotic Factors

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A laboratory experiment was conducted to study the stability of sulfosulfuron [1-(2-ethylsulfonylimidazo-[1,2-*a*]pyridin-3-ylsulfonyl)-3-(4,6-dimethoxypyrimidin-2yl) urea] in a controlled environment of pH, temperature, solvent, and surface. In another experiment the photostability of sulfosulfuron was studied after irradiation under sunlight. Under alkaline condition, it yielded 1-(2-ethylsulfonylimidazo[1,2-*a*]-pyridin-3-yl-3-(4,6-dimethoxypyrimidin-2-yl) amine, and under acidic condition it degraded to 1-(2-ethylsulfonylimidazo[1,2-*a*] pyridin)-3-sulfonamide and 4,6-dimethoxy-2-aminopyrimidine. Photodegradation included breaking of a sulfonylurea bridge, as in the case of acidic hydrolysis and contraction of the sulfonylurea bridge was the major pathway of alkaline hydrolysis.

KEYWORDS: Sulfosulfuron; stability; pH; temperature; photolysis

INTRODUCTION

Sulfosulfuron [1-(2-ethylsulfonylimidazo[1,2-*a*]pyridin-3-yl-sulfonyl)-3-(4,6-dimethoxypyrimidin-2-yl)urea] has been recently introduced by Monsanto, under the trade name Leader. The herbicide is recommended for use in cereals against a broad range of weeds (*1*).

Dermiyati and Yamamoto (*2*) reported that decreasing the temperature from 30 to 4 °C reduced the degradation rate of halosulfuron-methyl in two different soils at 50% water-holding capacity; average half-lives at the two temperatures were 13 and 98 days, respectively, in both of the soils.

Sulfonylurea herbicides were hydrolyzed more quickly in acidic than in alkaline conditions (*3*, *4*). The primary hydrolytic mechanism is acidic cleavage of the sulfonylurea linkage. The sulfonylurea linkage is susceptible to attack by water on the carbonyl carbon, producing CO_2 and the corresponding aryl sulfonamide and amino heterocyclic portions of the molecule. In addition to acidic hydrolysis, some sulfonylurea herbicides are also subject to hydrolytic degradation under alkaline conditions. Pyridine-2-sulfonylureas, including flazasulfuron, rimsulfuron, flupyrsulfuron-methyl, and trifluromethylpyridine (SL-160), are subject to a novel degradation mechanism that occurs much more rapidly than acidic cleavage (*5*). Another herbicide, halosulfuron-methyl, also degraded through bridge contraction and rearrangement (*6*). These herbicides underwent an interesting contraction and rearrangement of the sulfonylurea linkage (*7*). The mechanism is an intramolecular nucleophilic addition and elimination reaction (*5*, *8*).

Tribenuron-methyl was rapidly photodecomposed in sunlight; the half-lives were ∼2 h in organic solvents and ∼7 days in water (*9*). Unlike other sulfonylureas, extensive direct photodegradation of sulfosulfuron was observed when it was exposed to simulated sunlight (*10*). There are several reports of degradation of this class of herbicide under the influence of temperature (*2*), pH (*11*, *12*), and light (*13*, *14*).

Being nonvolatile and thermally unstable, sulfosulfuron could not be analyzed by gas chromatography. A high-performance liquid chromatographic (HPLC) method for qualitative and quantitative determination of sulfosulfuron in soil and plant samples was developed in our laboratory.

The extraction of the herbicide from various matrices using organic solvents and subsequent cleanup to remove interferences pose problems for quantitative recovery of pesticides, especially in the case of sulfonylurea herbicides. During analysis it was observed that standard solutions of sulfosulfuron even when stored in a refrigerator did not produce reproducible results after a month when injected on HPLC.

This paper presents the degradation of sulfosulfuron as influenced by various abiotic factors such as temperature, pH, light, solvent, and type of surface.

MATERIALS AND METHODS

Chemicals. Analytical grade sulfosulfuron (98.85% purity) was supplied by Monsanto India Ltd., New Delhi, India. Solvents were distilled prior to use. All chemicals and reagents were of analytical grade. HPLC grade solvents were used for HPLC analysis.

Alkaline Hydrolysis. Sulfosulfuron (500 mg) was dissolved in methanol (10 mL) and stirred with 1% methanolic KOH (15 mL, pH ≅10) at 40 °C for an hour. The reaction product was neutralized with 0.1 M hydrochloric acid and extracted with ethyl acetate (3 × 25 mL). The organic phase was passed through anhydrous sodium sulfate and evaporated to dryness. The solid mass was crystallized in ethanol when a brown crystalline product (compound **I**, **Figure 1**) was obtained, mp 152−154 °C. Its IR and ^{1}H NMR identified the product.

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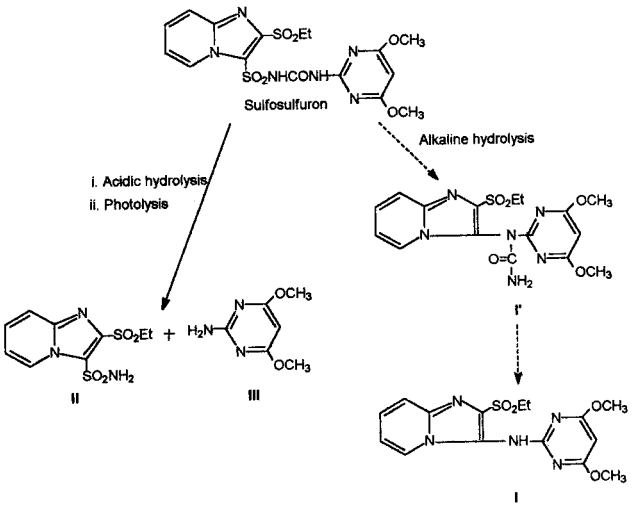

Figure 1. Hydrolytic and photodegradation products of sulfosulfuron formed during the study.

Acid Hydrolysis. Sulfosulfuron (500 mg) was dissolved in methanol (20 mL) and stirred with 2.5 mL of concentrated hydrochloric acid (pH 2.5) at 35 °C for 10 h. The reaction was stopped; the contents were neutralized with sodium bicarbonate solution (25% aqueous) and partitioned with ethyl acetate (3 × 25 mL). The ethyl acetate layer was separated, dried over anhydrous sodium sulfate, and distilled off to dryness. The crude product was chromatographed over silica gel using a glass column (30 cm × 2 cm i.d.), eluted with hexane and hexane/benzene (9:1 v/v). Compound **II** was separated as a yellowish solid (mp 193 °C), and compound **III** was separated by preparative thin-layer chromatography (TLC) as a white solid (mp 94−96 °C).

Rate of Hydrolysis. Buffer solutions of pH 4.0, 7.0, and 9.2 were prepared by dissolving one phosphate buffer tablet of corresponding pH in 100 mL of deionized water, and the pH of each solution was confirmed by pH meter.

One milliliter (100 μg) of stock solution of sulfosulfuron in HPLC grade acetonitrile was transferred into each glass-stoppered test tube containing 19 mL of buffer solutions of pH 4.0, 7.0, and 9.2 and distilled water (pH 6.8). Contents were mixed and incubated at 28 ± 1 °C for 10 days in triplicate. The controls were also maintained in triplicate simultaneously. Samples (5 mL) were drawn every alternate day and extracted with dichloromethane (3 × 10 mL). The extracts were combined and passed through anhydrous sodium sulfate. Solvent was evaporated on a rotary evaporator under vacuum to dryness, and residues were dissolved in acetonitrile prior to injection in the HPLC. The degradation products formed in different pH solutions were identified by comparison with the authentic products prepared, as described earlier.

Effect of Temperature. Standard solutions of sulfosulfuron (0.5 and 1.0 μg mL^{-1} in acetonitrile) in glass-stoppered test tubes were incubated at 10, 25, 40, 50, and 75 °C for 6 h. After every hour, solutions in duplicate were injected in the HPLC and analyzed.

Effect of Light. Acetonitrile solution of sulfosulfuron (1.0 μg mL^{-1}) in 10 mL glass-stoppered test tubes was irradiated under sunlight for 11 days at temperature of 30 ± 1 °C in triplicate. Samples were injected in the HPLC at 0, 3, 5, 7, 9, and 11 day intervals. Dark controls at room temperature (30 ± 1°C) and refrigerator temperature (10 ± 1 °C) were maintained and analyzed under similar conditions.

Effect of Surface Type and Area. One milliliter of standard solution of sulfosulfuron in acetonitrile (1.0 mg mL^{-1}) was transferred to glass volumetric flasks of different capacities, namely, 1, 2, 5, 10, and 25 mL. The contents were swirled several times to provide maximum contact with the glass surface. Each capacity volumetric flask in triplicate was maintained at 10 ± 1 °C. In another set of experiments acetonitrile solution was transferred in triplicate to volumetric flasks (5 and 10 mL capacities) made of polypropylene and maintained at 10 ± 1 °C. The samples were analyzed by HPLC after an hour of contact with two surfaces.

Effects of Solvents. One milliliter of sulfosulfuron (100 mg) stock solution in acetonitrile and acetone was transferred into two separate glass-stoppered test tubes containing 19 mL of either acetonitrile or acetone, respectively, and the contents were mixed thoroughly. The solutions in triplicate were maintained at 10 ± 1 °C for 15 days. The acetone solution samples were drawn at intervals, the solvent was evaporated, and the residues were dissolved in acetonitrile prior to injection in the HPLC. Acetonitrile solutions were injected directly. The fresh standard solution (5 μg mL^{-1}) of sulfosulfuron in acetonotrile was used as the standard to evaluate the stability of sulfosulfuron in the two solvents.

In another set of experiments triplicate solutions of sulfosulfuron in acetonitrile were incubated at 10 ± 1° C for 160 days and analyzed at specific intervals.

High-Performance Liquid Chromatography. Sulfosulfuron and its predicted degradation products were analyzed by an HPLC technique. The method employed a Hewlett-Packard HPLC (series 1100), equipped with a degasser, a quaternary pump, a photodiode array detector connected with a Rheodyne injection system (20 μL loop), and a computer (model Vectra) for carrying out the analysis. The stationary phase consisted of a Lichrospher C-8 column (250 mm × 4 mm i.d.), and the mobile phase consisted of acetonitrile/water/orthophosphoric acid (80:20:0.1 v/v/v) with a flow rate of 1 mL min^{-1}. The detector wavelength was adjusted at 212 nm according to the UV spectra of the compound. At λ_{max} 212 nm compounds sulfosulfuron, **I**, **II**, and **III** eluted at retention times (t_R) of 2.423, 2.372, 2.242, and 2.104 min, respectively.

Fourier Transform Infrared Spectroscopy (FT-IR). The infrared spectra of the compounds were recorded on a Nicolet Impact 700 FT-IR spectrophotometer (model Impact 400) using $CHCl_3$ and a KBr disk.

Nuclear Magnetic Resonance (NMR). ^{1}H NMR spectra were recorded on a Varian EM 360 L (60 MHz) instrument. Deuteriochloroform was used as the solvent and tetramethylsilane (TMS) as the internal standard.

Degradation Data Analysis. The degradation data were analyzed statistically, and a degradation curve was obtained using the linear regression equation. The dependent variable was sulfosulfuron concentration and the independent variable, time (days after treatment). The half-life ($t_{1/2}$) was calculated from the curve for first-order rate kinetics.

RESULTS AND DISCUSSION

Effect of Surface Type and Area. The experiment with glass and polypropylene volumetric flasks showed that the stability of sulfosulfuron was not affected by the surfaces. The glass surface did not adsorb sulfosulfuron in 3 days at 10 ± 1 °C. However, Princes and Guinivan (*15*) reported adsorption of chlorimuron-ethyl on a glass surface. There was no loss of herbicide when the area of glass surface was increased.

Effect of Organic Solvents. The stability of sulfosulfuron was studied in acetone and acetonitrile. These are two solvents in which standard solutions were prepared and stored for experimental and HPLC analysis. There was a gradual decline in the recovery of sulfosulfuron in both solvents, which was not significant up to 3 days, but thereafter degradation was slightly faster in acetone than in acetonitrile. The degradation in standard solution is of prime importance as it is common practice to store standard solutions for further investigations including chromatographic analysis. For use as standard solutions, acetonitrile was a better solvent than acetone. Sulfosulfuron degraded at almost similar rates in both of the solvents. Continuous degradation of sulfosulfuron in both acetone and acetonitrile at 10 ± 1° C was observed (**Table 1**), so much so that only 20−25% was recovered in 4 months; it was completely degraded in 160 days. The fresh solution of sulfosulfuron in acetonitrile was, therefore, used in all future investigations.

Thermal Degradation of Sulfosulfuron. The stability of sulfosulfuron in acetonitrile was examined at different temper-

Table 1. Recovery of Sulfosulfuron from Standard Solution (20 μg mL^{-1}) Prepared in Two Different Solvents at 10 ± 1 °C

	amount recovered[a] (μg mL^{-1})	
time (days)	acetonitrile	acetone
0	20.0	20.0
3	19.7	19.4
5	19.4	18.8
7	19.2	18.6
9	18.9	18.4
11	18.7	17.8
80	10.8	9.3
120	4.9	3.6
160	BDL[b]	BDL

[a] Average of three replicates. [b] Below detection limit.

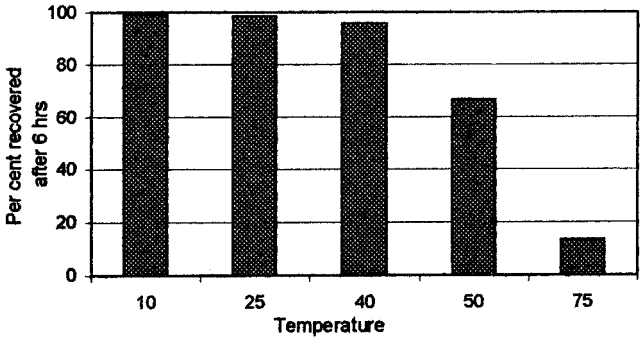

Figure 2. Degradation of sulfosulfuron in acetonitrile at different temperatures.

atures ranging from 10 to 75 °C. The quantitative recoveries were observed up to 40 °C. The average recoveries declined to 65.8 and 13.5% at 50 and 75 °C in 6 h, respectively (**Figure 2**). Singles et al. (*7*) reported that the rate of thermal degradation of flupyrsulfuron-methyl in soil at 10 °C was half that at 20 °C. The degradation of sulfonylurea herbicides is mainly dependent on pH and temperature (*11*, *14*). It was concluded that the experimental working temperature for sulfosulfuron must be maintained below 40 °C. Any experiment conducted at higher temperature than this, such as in the summer season, or any operation such as rotary evaporation conducted at a temperature above 40 °C would thermally degrade the compound, and hence there is need to be cautious in this regard. Temperature during rotary evaporation should not exceed 40 °C.

Alkaline Hydrolysis. The product formed in alkaline hydrolysis was identified by its IR and ^{1}H NMR as 1-(2-ethylsulfonylimidazo[1,2-*a*]pyridin-3-yl-3-(4,6-dimethoxypyrimidine-2-yl) amine (**I**, **Figure 1**). The IR spectrum showed the presence of an −NH group, and O═S═O absorbance was seen at 3394, 1565, 1380, and 1137 cm^{-1}. ^{1}H NMR spectra further confirmed the structure by showing a broad singlet of the −NH proton at δ 2.1, a triplet at δ 1.3 due to $-CH_3$, a quartet at δ 3.10−3.39 due to $-CH_2$, singlets at δ 3.70 and 5.60 due to OCH_3 and a proton of the pyrimidine ring, and a multiplet at δ 7.02−8.02 due to aromatic protons. The hydrolyzed product eluted differently from the original compound on HPLC.

Acid Hydrolysis. Compound **II** was identified as 1-(2-ethylsulfonylimidazo[1,2-*a*]pyridin)-3-sulfonamide after IR and ^{1}H NMR study (**Figure 1**). The IR spectrum showed the presence of −NH as stretching and bending absorbance at 3361 and 1551 cm^{-1}, besides its O═S═O stretching at 1363, 1313, 1151, and 1137 cm^{-1}. In the ^{1}H NMR spectrum, the presence of an ethyl group was confirmed as it showed a triplet and a quartet (J = 7 Hz) at δ 3.21 and 3.63, respectively. Four aromatic protons resonated at δ 7.06−7.83 as a multiplet.

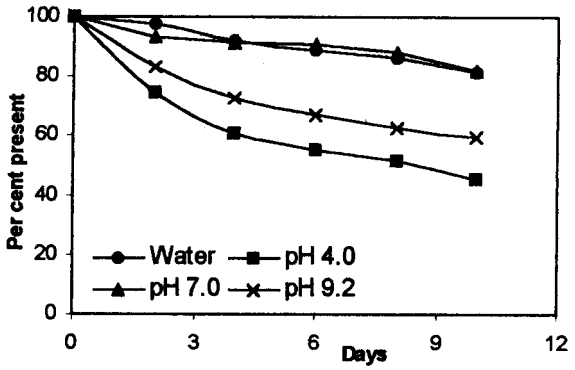

Figure 3. Degradation pattern of sulfosulfuron at 28 °C at different pH values and in distilled water.

Table 2. Regression Equations, Correlation Coefficients (r), and Half-Lives ($t_{1/2}$) of Sulfosulfuron at Four Different pH Values (28 °C)

pH	regression equation	r	$t_{1/2}$ (days)
4.0	$Y = 1.956 - 0.0321x$	−0.967	9.3
7.0	$Y = 1.995 - 0.074x$	−0.959	40.6
9.2	$Y = 1.972 - 0.0216x$	−0.969	13.9
6.8 (distilled water)	$Y = 2.006 - 0.0086x$	−0.990	35.0

The IR spectrum of compound **III** showed absorbance at 3414.3 and 1585 cm^{-1} for an −NH group, and C−N stretching was also observed at 1374 cm^{-1} (**Figure 1**). The ^{1}H NMR spectrum confirmed the presence of methoxy groups and a proton of pyrimidine ring as it showed singlets at δ 3.95 and 5.48, respectively. On the basis of the above spectral analysis compound **III** was assigned the structure of 4,6-dimethoxy-2-aminopyrimidine.

Kinetics of Sulfosulfuron Hydrolysis. To study the effect of pH on the rate of sulfosulfuron hydrolysis, aqueous solutions of different pH values, namely, 4.0, 6.8, 7.0, and 9.2, were used. The rate of degradation at 28 °C followed first-order kinetics with significant rate constant and r values (**Table 2**). Degradation was lowest under neutral conditions (distilled water and pH 7.0) and occurred both in acidic and in alkaline conditions (**Figure 3**). Hydrolysis was more rapid in acidic condition, pH 4.0 ($t_{1/2}$ = 9.3 days), than alkaline condition, pH 9.2 ($t_{1/2}$ = 13.9 days). The half-lives were 35.0 and 40.6 days in distilled water and at pH 7.0, respectively. Results indicated that sulfosulfuron is more stable under neutral condition and that the degradation rate is high in acidic condition.

The hydrolysis product under alkaline condition showed that there was rearrangement due to the presence of a base. Sulfonyl bridge contraction and rearrangement may be the major mode of degradation of sulfosulfuron under alkaline condition. Breaking of a urea bridge was the path of degradation under acidic condition (**Figure 1**).

The degradation of sulfosulfuron in soil and, in turn, its persistence in soil will be influenced by soil pH.

Photodegradation of Sulfosulfuron. After irradiation of 11 days, sulfosulfuron decomposed with first-order rate kinetics. To correct for temperature effects, dark controls were kept at room temperature, and they showed very slow degradation as compared to the irradiated sample. The half-life was observed to be 9.1 days under sunlight. The result (**Figure 4**) showed that there was no significant difference in degradation, maintained at room temperature and in the dark. However, dissipation in these controls was much higher than in the solution incubated

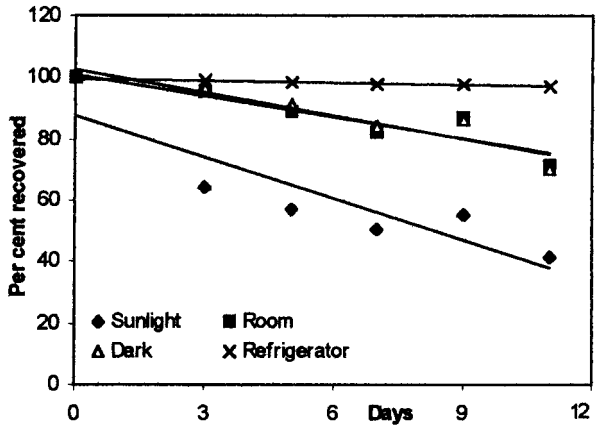

Figure 4. Comparative degradation pattern of sulfosulfuron under sunlight with respect to room, dark, and refrigerator conditions.

at 10 ± 1 °C. This could be due to thermal degradation (temperature = 46 °C), which accounted for ~30% loss in photodegradation. The rate of degradation of sulfosulfuron in different types of controls and in sunlight followed the order sunlight > room temperature ≅ dark > refrigerator.

The photodegradation products were analyzed by HPLC and compared with the authentic degradation products prepared in our laboratory. Compounds were identified as 1-(2-ethylsulfonylimidazo[1,2-*a*]pyridin)-3-sulfonamide (**II**) and 4,6-dimethoxy-2-aminopyrimidine (**III**) (**Figure 1**). The t_R values of photodegraded products were the same as for authentic products prepared in the laboratory. The mechanism of phototransformation is the hydrolysis of the sulfonylurea bridge.

Conclusion. Hydrolysis of sulfosulfuron under different pH conditions has provided the basic information about the stability of the compound in various conditions. Sulfosulfuron degraded at a faster rate in acidic (pH 4.0) than in alkaline condition (pH 9.2) and least in neutral pH. Temperature plays a role in environmental degradation during the early hours of application of the sulfonylurea compound under field condition. Irradiation has conveyed the possible degradation pattern of the compound under field conditions. By combining all of the physicochemical effects, that is, pH, sunlight, temperature etc., the total effect can be drawn from rate kinetics study in soil.

Sulfosulfuron herbicide is affected by various abiotic factors. It is unstable in organic solvents such as acetonitrile even at 10 ± 1 °C (refrigerator) beyond 10 days and degraded completely in 5 months. It is also influenced by temperature above 40 °C. Summer season (temperature > 40 °C) and laboratory operations at temperatures >40 °C would degrade sulfosulfuron. Herbicide was susceptible to acid and alkaline hydrolysis ($t_{1/2}$ = 9.3 and 13.9 days, respectively). 1-(2-Ethylsulfonylimidazo[1,2-*a*]pyridin-3-yl-3-(4,6-dimethoxypyrimidine-2-yl) amine was identified as the major product of alkaline hydrolysis, whereas 1-(2-ethylsulfonylimidazo[1,2-*a*]pyridin)-3-sulfonamide and 4,6-dimethoxy-2-aminopyrimidine were identified as acidic hydrolytic degradation products. Thus, contraction and rearrangement were the mode of degradation under alkaline conditions, and breaking of the urea bridge was the path of degradation under acidic condition. Sulfosulfuron underwent photodegradation ($t_{1/2}$ = 9.1 days) and formed 1-(2-ethylsulfonylimidazo[1,2-*a*]pyridin)-3-sulfonamide and 4,6-dimethoxy-2-aminopyrimidine.

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LITERATURE CITED

(1) Hageman, N. R.; Blank, S. E.; Cramer, G. L.; Isakson, P. J.; Ryerson, D.K.; Parrish, S. K. MON 37500: a new selective herbicide to control annual and perennial weeds in wheat. *Proc. West. Soc. Soil* **1996**, *49*, 78−82.

(2) Dermiyati, S. K.; Yamamoto, I. Degradation of the herbicide halosulfuron-methyl in two soils under different environmental conditions. *J. Pestic. Sci.* **1997**, *22*, 282−287.

(3) Hemmamda, S.; Calmon, M.; Calmon, J. P. Kinetics and hydrolysis mechanism of chlorsulfuron and metsulfuron-methyl. *Pestic. Sci*. **1994**, *40*, 71−76.

(4) Singh, S. B.; Kulshrestha, G. Effect of pH on hydrolysis of chlorimuron-ethyl, a sulfonylurea herbicide. *Pestic. Res. J.* **2000**, *12*, 235−238.

(5) Haga, T.; Tsujii, Y.; Kimura, F.; Sakashita, N.; Fujikawa, K. In *Synthesis and Chemistry of Agrochemicals II*; ACS Symposium Series 443; Baker, D. R., Feynes, J. G., Moberg, W. K., Eds.; American Chemical Society: Washington, DC, 1991; pp 107−121.

(6) Mehrsheikh, A. Halosulfuron methyl. In *Metabolic Pathways of Agrochemicals*; Roberts, T. R., Ed.; The Royal Society of Chemistry Information Services: Cambridge, U.K., 1998; Part 1, pp 516−520.

(7) Singles, S. K.; Dean, G. M.; Kirkpatrick, D. M.; Mayo, B. C.; Langford-pollard, A. D.; Barefoot, A. C.; Bramble, F. Q., Jr. Fate and behaviour of flupyrsulfuron-methyl in soil and aquatic systems. *Pestic. Sci.* **1999**, *55*, 288−300.

(8) Moran, S. J.; Kurtzweil, M. L. Sufosulfuron. In *Metabolic Pathways of Agrochemicals*; Roberts, T. R., Ed.; The Royal Society of Chemistry Information Services: Cambridge, U.K., 1998; Part 1, pp 555−560.

(9) Bhattacharjee, A. K.; Dureja, P. Light induced transformation of tribenuron-methyl in aqueous solution. *Pestic. Sci*. **1999**, *55*, 183−188.

(10) Brown, H. M.; Gaddamidi, V.; Lee, P. W. Sulfonylureas. In *Metabolic Pathways of Agrochemicals*; Roberts, T. R., Ed.; The Royal Society of Chemistry Information Services: Cambridge, U.K., 1998; Part 1, pp 451−473.

(11) Beyer, E. M., Jr.; Duffy, M. J.; Hay, J. V.; Schluter, D. D. Sulfonylureas. In *Herbicides*: *Chemistry*, *Degradation and Mode of Action*; Kearney, P. C., Kaufman, D. D., Eds.; Dekker: New York, 1988; Vol. 3, pp 117−189.

(12) Brown, H. M. Mode of action, crop selectivity and soil relations of the sulfonylurea herbicides. *Pestic. Sci.* **1990**, *29*, 263−281.

(13) Choudhury, P. P.; Dureja. P. Phototransformation of chlorimuron-ethyl in aqueous solution. *J. Agric. Food Chem.* **1996**, *44*, 3379−3382.

(14) Pusino, A.; Braschi, I.; Petretto, S.; Gessa, C. Photodegradation of herbicide triasulfuron. *Pestic. Sci.* **1999**, *55*, 479−481.

(15) Princes, J. L.; Guinivan, R. A. Analysis of chlorimuron-ethyl in crops by high-performance liquid chromatography. *J. Agric. Food Chem.* **1988**, *36*, 63−69.

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