Hydrolysis kinetics of the sulfonylurea herbicide Sulfosulfuron

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The kinetics of hydrolytic degradation of Sulfosulfuron was investigated to predict the fate of the herbicide in an aqueous environment. The study revealed that the hydrolytic degradation of Sulfosulfuron followed first-order kinetics. The degradation of the herbicide was dependent on pH and temperature. Hydrolysis rate was faster in acidic condition ($t_{1/2} = 9.24$ d at pH 4.0) than alkaline environment ($t_{1/2} = 14.14$ d at pH 9.2). Several fold increase in the degradation rate was found when temperature was increased from $10 \pm 1°C$ ($t_{1/2} = 518$ h) to $50 \pm 1°C$ ($t_{1/2} = 10$ h). Activation energy (E_a) was also calculated as $63.87 \, KJ \, mol^{-1}$, which is required for the hydrolytic degradation of the molecule. Both media pH and temperature effects were coupled together and derived a complex equation to estimate the overall effect of these two abiotic factors. The major degradation mechanism of the compound was the breaking of the sulfonylurea bridge yielding corresponding sulfonamide and aminopyrimidine. The possible significance of the results to persistence of the herbicide in the field condition is discussed.

Keywords: kinetics; pH; temperature; Sulfosulfuron; Arrhenius equation

1. Introduction

Studies related to the fate of pesticides in the environment are required for predicting the potentiality of groundwater contamination and behaviour in the aquatic environment. Hydrolytic degradation and its kinetics in the normal pH and temperature range are of utmost importance to predict the persistence of a particular pesticide in the ecosystem.

The processes responsible for the dissipation of sulfonylurea herbicides are chemical hydrolysis, microbial degradation and photodegradation [1,2]. Temperature and pH are the two main abiotic factors, which are responsible for hydrolysis of the sulfonylurea bridge [1]. The hydrolytic pathway of sulfonylurea herbicides is well understood [3–9]. The primary hydrolytic mechanism is acidic cleavage of the sulfonylurea linkage [10–12]. Another mechanism of hydrolysis is bridge contraction and rearrangement of the sulfonylurea bridge. This is mainly in the case of pyridine-2-sulfonylureas [9,13–15].

Besides the fate of sulfonylurea herbicides in the environment, there are problems of degradation during sample handling [9,16]. During extraction and clean up of these compounds from different matrices by organic solvents, hydrolysis creates interferences

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for qualitative recovery of pesticides. Therefore, the knowledge of the stability of these compounds in different solvents is necessary to monitor the recovery results.

Sulfosulfuron {1-(2-ethylsulfonylimidazo [1, 2-a] pyridin-3-ylsulfonyl)-3-(4, 6-dimethoxy pyrimidin-2yl)} (Figure 1) is a sulfonylurea herbicide introduced for selective weed control in winter wheat. The herbicide is applied at a dose of 25 g a.i. ha^{-1} at post emergence to control various grassy and dicot weeds [17]. This herbicide differs from other sulfonulurea herbicides in terms of efficacy as it is able to control grass weeds also, which may be due to the imidazo-pyridine group in its structure [17].

The objectives of this study were to evaluate the hydrolysis kinetics of Sulfosulfuron as a function of temperature and pH and the prediction of its fate in different aqueous environments.

2. Experimental

2.1 *Chemicals*

Analytical grade Sulfosulfuron (98.8%) was supplied by Monsanto India Ltd. (New Delhi, India). Acetonitrile (Merck®, India) was HPLC grade and water was double distilled and filtered through Milli Q apparatus before use as mobile phase. All chemicals and reagents used were of analytical grade.

2.2 *LC apparatus*

The reverse phase LC system (Hewlett Packard, series 1100) consisted of a quaternary pump with a manual injector (20 µl fixed loop) and a photodiode array detector. A computer using the 'ChemStation' software program integrated peak areas automatically.

Sulfosulfuron

Molecular weight: 470.5   Vapour pressure: 3.1×10^{-8} Pa (20°C)

Water solubility : 18 mg L^{-1} (pH 5.0) K_{oc} : 5–89

            1.63 mg L^{-1} (pH 7.0)

            482 mg L^{-1} (pH 9.0)

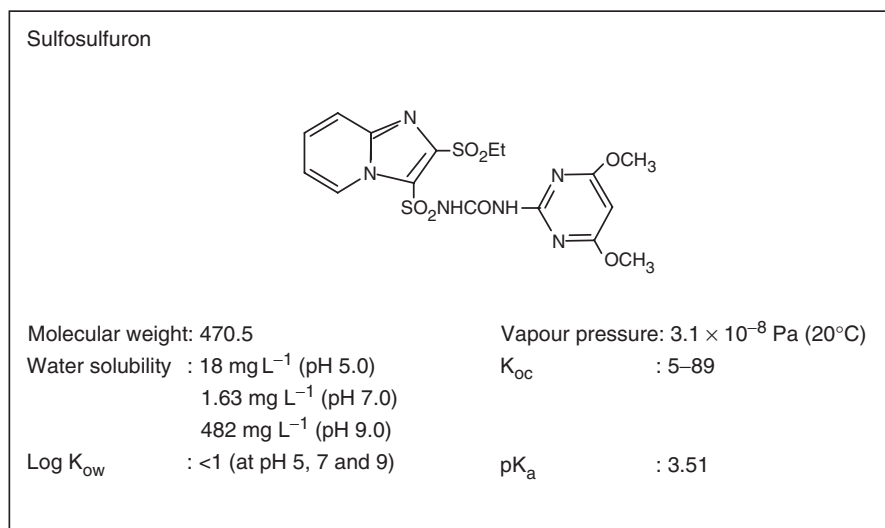Log K_{ow} : <1 (at pH 5, 7 and 9) pK_a : 3.51

Figure 1. Chemical structure and physico-chemical properties of Sulfosulfuron.

2.3 *Chromatographic conditions*

Chromatographic conditions for the analysis of Sulfosulfuron were developed earlier in our laboratory and the same was used for this investigation [18]. The chromatographic analysis was performed at ambient temperature (25–30°C) on a LiChrospher C-8 column (250 mm × 4 mm i.d., Merck, Dermstadt, Germany). The mobile phase comprised of an isocratic mixture of acetonitrile/water/orthophosphoric acid (80 : 20 : 0.1; v/v/v) at a flow rate of 1 mL min^{-1} for quantification. The photodiode array was set at 212 nm. A 20 μL portion of sample was injected each time. The approximate retention time for Sulfosulfuron was 2.42 min. The limit of determination of Sulfosulfuron was 0.25 μg g^{-1}.

2.4 *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 deionised water and the pH of each solution was confirmed by pH metre. Five mL (100 μg mL^{-1}) of stock solution of Sulfosulfuron in HPLC grade acetonitrile was transferred into each glass stoppered test tube and diluted to 100 mL with buffer solutions of pH 4.0, 7.0, 9.2 and distilled water (pH 6.8). Contents along with control were mixed and incubated at 28 ± 1°C for 10 days in a B.O.D. incubator at 70% R.H. (Macro Scientific works, New Delhi, India). The samples were maintained in triplicate. Samples (5 mL) were drawn every alternate day and extracted with dichloromethane (3 × 10 mL). The extracts were combined and passed through anhydrous sodium sulphate. Solvent was evaporated on rotary evaporator (Heidolph, Dermstadt, Germany) under vacuum to dryness and residues dissolved in acetonitrile prior to analysis by HPLC. The formation of degradation products in different pH solutions was confirmed by comparison with the authentic products prepared earlier, as reported in the literature [18].

2.5 *Rate of thermal degradation*

A standard stock solution of Sulfosulfuron was prepared after dissolving 10 mg of the compound in 100 mL acetonitrile in a volumetric flask. The stock solution was diluted 100 times to get 1 μg mL^{-1} concentration. Sulfosulfuron solutions (0.5 and 1.0 μg mL^{-1}) in glass-stoppered test tubes were incubated at 10, 25, 35, 50 and 75°C for six hours. After every hour, solutions in duplicate were analysed by HPLC. At 75°C treatment, the analysis was done after concentrating the solution, as the concentration of Sulfosulfuron was below the detectable limit. The temperature dependence of reaction rate was best explained by the Arrhenius equation:

$$\ln k = \ln A - E_a/RT \qquad (1)$$

Graphical representation of this equation can be obtained when $\ln k$ (degradation constant) was plotted against $1/T$. Where the parameter A, which is given by the intercept of the line at $1/T = 0$, is called the preexponential or frequency factor, E_a is activation energy (J mol^{-1}), obtained from the slope of the line ($-E_a/RT$), R is universal gas constant and T is absolute temperature (K).

2.6 *Data analysis*

Hydrolysis data were analysed and the degradation curve obtained using a simple linear regression equation. The dependent variable was Sulfosulfuron concentration and independent variable was time (days/hour after treatment). The $t_{1/2}$ value (half life) was calculated from the degradation constant (first order rate kinetics) $t_{1/2} = -0.693/k$.

3. Results and discussion

The degradation pattern of Sulfosulfuron under different temperatures and pH followed first order rate kinetics as we found from the regression equation and high correlation coefficient (Figure 2). Our earlier report on the degradation pattern of Sulfosulfuron showed that the dissipation of the herbicide was independent of time [9]. Sarmah and Sabadie [11] also found similar results for other sulfonylurea herbicides.

The study showed that temperature and pH had a distinct role on the degradation of Sulfosulfuron (Table 1). With the increase of temperature from $25 \pm 1°C$ to $50 \pm 1°C$ there was a 20-fold increase in degradation rate ($t_{1/2}$ were 21.66 and 0.52 days, respectively). There was a significant increase (8-fold) in degradation of Sulfosulfuron, when the solution temperature increased from $15°C$ to $35°C$ (Table 2). Morrica *et al.*, [7] reported that the change in temperature from 15 to $25°C$ in acidic conditions (pH 3.6) decreased the half-life of Imazosulfuron by a factor of ~ 4.0 and 3–5-fold increase in the rate of hydrolysis was found for each $10°C$ increase in temperature. Thermal degradation of sulfonylurea herbicides depends on the individual structural configuration, as different half-lives were reported for different sulfonylureas [5,6,8,19]. Thermal degradation of Sulfosulfuron was comparable with Imazosulfuron, as both are imidazo-pyridine sulfonylurea herbicides [7]. The study revealed that the temperature-dependent degradation reaction of Sulfosulfuron followed the Arrhenius equation, as the plot of $\ln k$ against $1/T$ produced a straight line (Figure 2). A linear regression line, $\ln k = -7.69\,(1/T) + 13.87$ fitted the experimental points in the equation for Sulfosulfuron within the temperature range of 10 to $75°C$. The activation energy (E_a) was calculated as $63.87\,KJ\,mol^{-1}$, by multiplying the slope by the universal gas constant. So, this much energy is required to
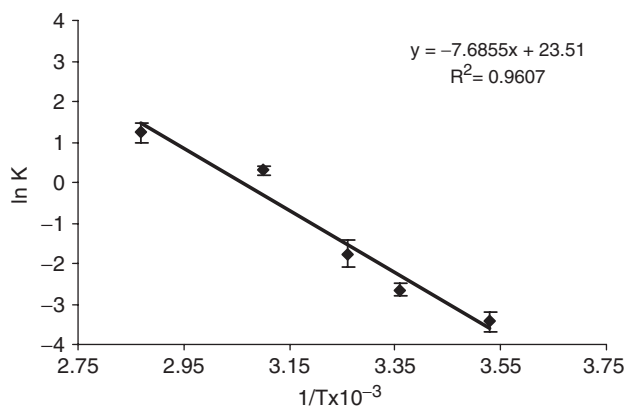

Figure 2. Graphical representation of Arrhenius equation by plotting $\ln k$ *vs.* $1/T \times 10^{-3}$.
Notes: Error bars showing standard deviation of means.

activate Sulfosulfuron hydrolysis. The activation energy of other members of sulfonylurea herbicides has also been reported in a similar range [6,7,19].

Media pH has a definite role in the hydrolysis of the sulfonylurea bridge of Sulfosulfuron. With the increase of [H$^+$], there was a marked difference in the hydrolytic degradation of the herbicide. The results of Sulfosulfuron degradation under the influence of pH are presented in Table 3. The recoveries of Sulfosulfuron were 81.3, 45.2, 81.7 and 59.8% in distilled water (pH 6.8), and at pH 4.0, 7.0 and 9.2 after 10 days of incubation. With the increase of pH from 4.0 to 7.0 there was 4.4-fold increase in the half-life (Table 3). On the other hand, there was an increase in the degradation rate by 2.8 fold as

Table 1. Recoveries of Sulfosulfuron at different temperatures after six hours of incubation.

Temperature (°C)	Amount added (µg mL^{-1})	Amount found (µg mL^{-1})	Recovery (%)
10	0.5	0.496 ± 0.003	99.2
	1.0	0.992 ± 0.007	99.2
25	0.5	0.492 ± 0.011	98.4
	1.0	0.979 ± 0.009	97.9
35	0.5	0.479 ± 0.012	95.9
	1.0	0.973 ± 0.008	97.3
50	0.5	0.333 ± 0.009	66.6
	1.0	0.649 ± 0.017	64.9
70	0.5	0.068 ± 0.004	13.5
	1.0	0.125 ± 0.013	12.5

Table 2. Degradation constants (k) and half-lives ($t_{1/2}$) of Sulfosulfuron at different temperatures.

Temperature (°C)	k^t (h^{-1})	$t_{1/2}$ (h)
10 ± 1	0.0013	517.78
25 ± 1	0.0027	257.85
35 ± 1	0.0071	96.93
50 ± 1	0.0677	10.23
75 ± 1	0.3332	2.08

Notes: Conc. $0.5 \, \text{mg} \, \text{L}^{-1}$, r^2 of all values >0.986.

Table 3. Variation of rate constant (k^h) and half-life ($t_{1/2}$) as influenced by pH at 28 ± 1°C.

pH	Percent degradation of Sulfosulfuron days					k^h (day^{-1})	$t^{1/2}$ (days)
	2	4	6	8	10		
4.0 ± 0.1	25.3	38.9	44.5	48.5	54.8	0.075	9.24
6.8 ± 0.1	2.4	8.1	11.1	13.9	18.7	0.020	34.65
7.0 ± 0.1	6.8	8.5	9.5	12.1	18.3	0.017	40.74
9.2 ± 0.1	17.0	27.2	32.6	37.3	40.3	0.049	14.14

pH increased from 7.0 to 9.2. Typical trend of sulfonylurea compound hydrolysis observed was that degradation was faster in acidic condition than alkaline pH [9,20,21].

To predict the fate of Sulfosulfuron in aqueous medium, we combined the two distinct parameters responsible for hydrolysis. The Arrhenius equation was combined with the regression equation of pH-acquired hydrolysis, as previously reported by Dinelli *et al.* [6]. By combining the two equations, the Arrhenius equation can be written as:

$$\ln k_2 = \left(\frac{-E_a}{R}\right)\left(\frac{1}{T_2} - \frac{1}{T_1}\right) + \ln k_2 \tag{2}$$

where, k_1 and k_2 were degradation constants at T_1 and T_2.

Substituting the $\ln k_1$ by the pH dependent regression equation, taking the temperature of hydrolysis at 28°C, T_1, as $(273 + 28) = 301$, and expressing E_a in $J\,mol^{-1}$, we obtain the combined equations:

$$\ln k = \left(\frac{63870}{R}\right)\left(\frac{1}{T} - \frac{1}{301}\right) + (-0.49\text{pH} - 0.65) \tag{3}$$

and:

$$\ln k = \left(\frac{63870}{R}\right)\left(\frac{1}{T} - \frac{1}{301}\right) + (0.48\text{pH} - 7.44) \tag{4}$$

for the pH range of 4.0 to 7.0 and 7.0 to 9.2, respectively.

On a typical aquatic environment of pH range between 6.5 and 7.5 and temperatures in the range of 10 to 15°C, the half-life of Sulfosulfuron varied and will be in the range of 40 ± 2 days.
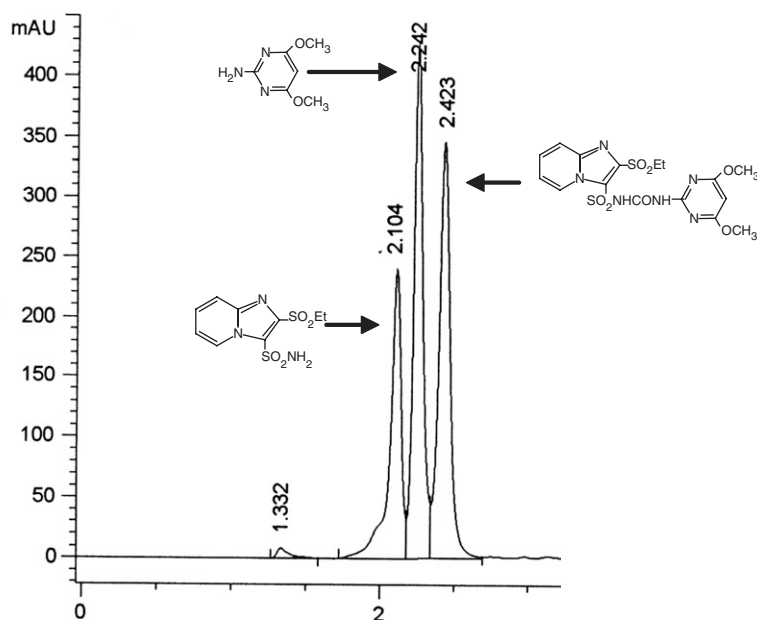

Figure 3. Chromatogram of Sulfosulfuron and its hydrolysis products along with their respective structure.

On the basis of this study, it was concluded that hydrolytic degradation of Sulfosulfuron was dependent both on pH and temperature. The major mechanism of the hydrolytic degradation was the breaking of sulfonylurea bridge. The linkage is susceptible to attack by water on the carbonyl carbon, producing CO_2 and the corresponding sulphonamide and amino heterocyclic portion of the molecule (Figure 3). Sarmah *et al*. [12] reported that the hydrolysis involving attack by neutral water was at least 100-fold faster when the sulfonylurea herbicides were undissociated (acidic conditions) than when they were present as the anion at near neutral pH. The major degradative pathways at pH > 7 were contraction of the sulfonylurea bridge followed by intramolecular rearrangement [9]. The mechanism was an intramolecular nucleophilic addition and elimination reaction [13]. In agreement with the literature report, Sulfosulfuron degraded faster in acidic pH than alkaline condition. But the difference in their pattern is not so distinguishable as reported for other sulfonylurea herbicides [20].

4. Conclusion

Herbicide contamination of soil and groundwater is a common problem in the environment. In this study, we have examined the hydrolytic behaviour of Sulfosulfuron in aqueous media. The results show that the hydrolysis of Sulfosulfuron is highly dependent of both the pH of water and temperature. Under acidic media, the sulfonylurea herbicide degrades faster than under alkaline and neutral conditions. Unlike other groups of herbicides, Sulfosulfuron degrades at a faster rate with increasing temperature. The major hydrolytic degradation mechanism of the compound was the breaking of the sulfonylurea bridge yielding the corresponding sulfonamide and aminopyrimidine. Thus, it may be concluded that degradation of Sulfosulfuron in aqueous medium can be predicted under different environmental conditions and the persistence problem is not alarming.

References

[1] E.M. Beyer Jr, M.J. Duffy, J.V. Hay, and D.D. Schluter, in *Herbicides: Chemistry, Degradation and Mode of Action*, edited by P.C. Kearney and D.D. Kaufman (Marcel Dekker, Inc, New York, 1988), Vol. 3, pp. 117–189.
[2] S.T. Maheswari and A. Ramesh, Environ. Monit. Assess. **127**, 97 (2007).
[3] B.M. Berger and N.L. Wolfe, Environ. Toxicol. Chem. **15**, 1500 (1996).
[4] J.P. Cambon and J. Bastide, J. Agric. Food Chem. **44**, 333 (1996).
[5] G. Dinelli, A. Bonetti, P. Catizone, and G.C. Galletti, J. Chromatogr. **656**, 275 (1994).
[6] G. Dinelli, A. Vicari, A. Bonetti, and P. Catizone, J. Agric. Food Chem. **45**, 1940 (1997).
[7] P. Morrica, F. Barbato, R.D. Iacavo, S. Seccia, and F. Ungaro, J. Agric. Food Chem. **49**, 3816 (2001).
[8] G.E. Schneiders, M.K. Koeppe, M.V. Naidu, P. Horne, A.M. Brown, and C.F. Mucha, J. Agric. Food Chem. **41**, 2404 (1993).
[9] S. Saha and G. Kulshrestha, J. Agric. Food Chem. **50**, 4572 (2002).
[10] C. Bertrand, A. Witczak-Legrand, J. Sabadie, and J. Cooper, J. Agric. Food Chem. **51**, 7717 (2003).
[11] A.K. Sarmah and J. Sabadie, J. Agric. Food Chem. **50**, 6253 (2002).
[12] A.K. Sarmah, R.S. Kookana, M.J. Duffy, A.M. Alston, and B.D. Harch, J. Agric. Food Chem. **56**, 463 (2000).

[13] T. Haga, Y. Tsujii, F. Kimura, N. Sakashita, and K. Fujikawa, in *Synthesis and Chemistry of Agrochemicals II*, edited by D.R. Baker, J.G. Feynes, and W.K. Moberg (American Chemical Society Symposium Series 443, Washington, DC, 1991), pp. 107–121.

[14] A. Mehrsheikh, in *Metabolic Pathways of Agrochemicals*, edited by T.R. Roberts (The Royal Society of Chemistry Information Services, Cambridge, UK, 1998), pp. 516–520.

[15] S.K. Singles, G.M. Dean, D.M. Kirkpatrick, B.C. Mayo, A.D. Langford-Pollard, A.C. Barefoot, and F.Q. Bramble Jr, Pestic. Sci. **55**, 288 (1999).

[16] L. Benke, L. Bura, and E. Majzik, Presented at the 10th IUPAC International Congress on the Chemistry of Crop Protection Basel **2**, 242 (2002).

[17] N.R. Hageman, S.E. Blank, G.L. Cramer, P.J. Isakson, D.K. Ryerson, and S.K. Parrish, Proc. West Soc. Soil **49**, 78 (1996).

[18] S. Saha, S.B. Singh, and G. Kulshrestha, J. Environ. Sci. Health Part B **38**, 337 (2003).

[19] A. Vicari, R.L. Zimdahl, B.K. Cranmer, and G. Dinelli, Weed Sci. **44**, 672 (1996).

[20] S. Hemmamda, M. Calmon, and J.P. Calmon, Pestic. Sci. **40**, 71 (1994).

[21] S.B. Singh and G. Kulshrestha, Pestic. Res. J. **12**, 235 (2000).