Photolysis and hydrolysis of rimsulfuron

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Abstract: The degradation in the liquid phase of rimsulfuron and its commercial 250 g kg^{-1} WG formulation (Titus®) was investigated. Photolysis reactions were carried out at 25 °C by a high-pressure mercury arc (Hg-UV) and a solar simulator (Suntest), while the hydrolysis rate was determined by keeping aqueous buffered samples in the dark. The effects of solvent and water pH on reaction kinetics were studied, and the results compared to literature data. Photoreactions of the commercial product in organic solvents were faster than pure rimsulfuron. Under simulated sunlight in water, the half-life for the photolysis reaction ranged from one to nine days at pH 5 and 9, respectively. The hydrolysis rate was as high as the photolysis rate, but decreased on increasing water pH. The main metabolite identified in neutral and alkaline conditions as well as in acetonitrile was *N*-[(3-ethylsulfonyl)-2-pyridinyl]-4,6-dimethoxy-2-pyridinamine, while *N*-(4,6-dimethoxy-2-pyrimidinyl)-*N*-[(3-(ethylsulfonyl)-2-pyridinyl)]urea and minor metabolites prevailed in acidic conditions.

Keywords: rimsulfuron; Titus®; photolysis; hydrolysis; suntest; Hg-UV-arc

1 INTRODUCTION

In the last decade, a new class of agrochemicals named sulfonylureas has been developed and offered on the market. Some of the reasons for the rapid and good acceptance of sulfonylureas include their low application rates and favourable environmental and toxicological properties.[1] The mode of action of these herbicides is related to inhibition of acetolactate synthase, an enzyme involved in the branched-chain amino acid biosynthesis in plants.[2,3] Rimsulfuron, 1-(4,6-dimethoxypyrimidin-2-yl)-3-(3-ethylsulfonyl-2-pyridylsulfonyl)urea, is a selective sulfonylurea herbicide (Figure 1; **1**) for the post-emergence control of weeds in many crops. It was distributed in Europe in 1992 by Du Pont.

Although several articles have appeared during the last few years about the effectiveness of this herbicide on crops and its hydrolytic behaviour, its transformation under light irradiation has received little attention. Schneiders *et al*,[4] using ^{14}C-labelled rimsulfuron, showed that degradation in aqueous solutions and the soil environment does not depend on irradiation under natural sunlight, though the compound undergoes hydrolysis reactions. However, the same authors observed some effects of natural light at pH 5.

It has been also suggested that photochemical investigation may contribute toward a better understanding of pesticide behaviour in the environment.[5,6] More information on the degradation time of active ingredients, and consequently, on their activity and environmental fate, can be obtained by studying jointly the kinetics of both photolysis and hydrolysis reactions.[7,8]

Since 1981, the European Chemical Industry Ecology and Toxicology Centre (ECETOC) has discussed experimental methods for assessing the photodegradation of chemicals in the environment and set out the criteria which such methods should meet in order to be both scientifically adequate and environmentally relevant.[9,10]

This paper deals with the application of our laboratory method (derived from ECETOC directions) for assessing the abiotic degradation of rimsulfuron in aqueous solutions. Moreover, owing to the post-emergence use of this herbicide, a large amount of the technical product remains on the exposed site of leaves[11] and may interact with the waxy and fatty substances which cover the surface of the latter.[12,13] For this reason photodegradation in organic solvents of the pure standard active ingredient and its technical

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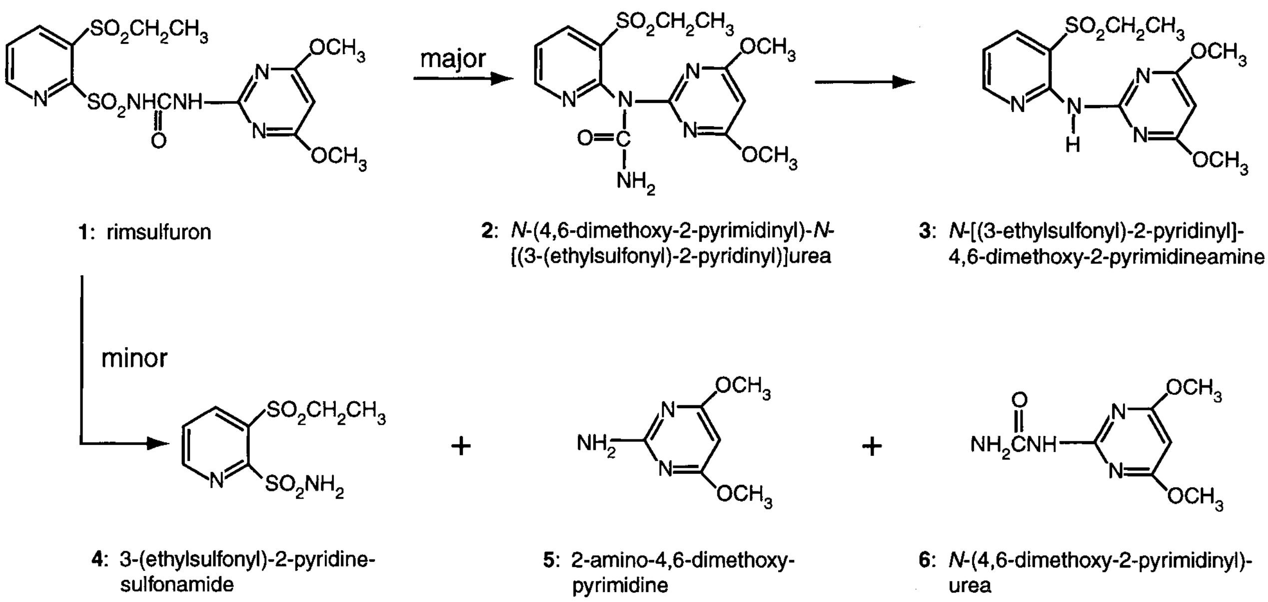

Figure 1. Chemical structure and degradation pathways of rimsulfuron.[4]

product (Titus®) were also studied. The comparative behaviour of the herbicide in organic and aqueous solutions is reported.

2 EXPERIMENTAL METHODS

2.1 Literature data

Rimsulfuron is a white odourless solid, solubility <10 mg litre^{-1} in distilled water and 7,300 mg litre^{-1} in buffer solution at pH 7; pKa = 4.1; $K_{ow} = 0.034$ at pH 7; vapour pressure = 1.1×10^{-4} Torr at 25 °C. It has little or no toxicological effects on mammals with oral LD_{50} >5000 mg kg^{-1} in rats and with dermal LD_{50} >2000 mg kg^{-1} in rabbits.[1,4,14]

2.2 Materials

All solvents (pesticide grade), reagents (analytical grade) and filters (disposable sterilised packet) were purchased from Fluka and Sigma-Aldrich (Milan, Italy). Ultrapure water was obtained with a Milli-Q system (Millipore). Rimsulfuron 250 g kg^{-1} WG (Titus®) was purchased from an agrochemical store in Italy. A stock solution of pure standard AI (98%; Dr Ehrenstorfen, Germany) in acetonitrile (1000 mg litre^{-1}) was prepared. This solution was maintained in the dark at +4 °C and used to prepare both aqueous and organic working solutions (10 mg litre^{-1}).

A stock solution containing 100 mg AI litre^{-1} was also prepared from the commercial formulation under the same conditions. This solution was pre-filtered over a membrane (0.8 µm) before preparing final solutions (10 mg AI litre^{-1}). Actual concentrations were determined using the analytical procedure described below. All working solutions were divided into two parts. One of these portions was used for the irradiation experiment, the other as control, keeping it in the dark. Aqueous solutions were prepared using phosphate buffers at pH 5, 7, and 9, at ionic strength 0.05 M.

All glass apparatus was heat-sterilised by autoclaving for 60 min at 121 °C before use, and buffer solutions were filtered using sterilised ultra-filters (0.2 µm). Aseptic handling materials and laboratory facilities were used throughout the study to maintain sterility.

2.3 Procedures

Photochemical reactions were performed by a solar simulator (Suntest CPS+, Heraeus) equipped with a Xenon lamp (1.1 kW), protected with a quartz plate (total passing wavelength: $300\,nm < \lambda < 800\,nm$). The irradiation chamber was maintained at 25 °C both through circulating water from a thermostatic bath and a conditioned airflow.

The photodegradation of samples was also carried out in a Pyrex reactor (250 ml) at 25 °C using a high-pressure mercury arc (Hg-UV, Philips HPK 125 W) covered with a borosilicate protecton (total passing wavelength: $310\,nm < \lambda < 580\,nm$), and the same concentration as in the Suntest experiments.

Before beginning the experimental work, the light emission effectiveness of both the irradiation systems was tested by using the uranyl oxalate method.[15,16] The disappearance of rimsulfuron at various illumination times was determined by liquid chromatography after 0.2-µm membrane filtration.

Control samples, having the same initial concentration as irradiated samples, were kept in the dark at the same temperature. The amount of herbicide was determined at the same times as the irradiated samples to measure hydrolytic disappearance or to confirm that the degradation process would only be the result of photochemical reactions.

Metabolites of pure rimsulfuron were only quantified in aqueous and acetonitrile solutions kept in the dark and under Suntest irradiation.

2.4 Analytical standards for rimsulfuron metabolites

Compounds **2** and **3** (Figure 1) were prepared according to literature methods.[17] Owing to the impossibility of achieving or preparing all substances, minor metabolites were quantified as pyrimidine amine (2-amino-4,6-dimethoxypyrimidine; **5**, Figure 1), purchased as pure standard (98%) by Aldrich (Milan, Italy). However, all chemical structures were confirmed by [^{1}H]NMR (Varian 300 MHz), mass spectrometry (HP 5971), and FTIR (Perkin Elmer 1710), which gave spectra comparable to literature findings.[17–19]

2.5 HPLC Analysis

Analyses were performed on a HP 1090 (Hewlett Packard) liquid chromatograph equipped with a diode array detector (fixed at 230 nm), and a Dionex Omnipac PCX-500 5-μm packed column (18 cm long, 3.2 mm ID.) plus guard column. The mobile phase used for all experiments was acetonitrile + water (1 + 1 by volume) adjusted to pH3 with phosphoric acid, flow rate 1 ml min^{-1}.

Retention times (minutes) for each substance in Fig 1 were: 8.4 (**1**), 6.5 (**3**), 4.5 (**2**), 3.6 (**6**), 2.8 (**5**), 2.4 (**4**). The detection limit of the analytical method for the determination of rimsulfuron was 0.01 mg litre^{-1}. Metabolites were also determined and confirmed by an ion spray LC/MS/MS technique on a Perkin Elmer API 300 coupled with a Waters 600 pump.[20]

2.6 Calculations

Knowledge of the reaction order is essential for finding the correct integrated rate equation. Kinetic parameters were calculated using the zero-, first- and second- (Langmuir–Hinshelwood) order equations.[21] The determination coefficient (r^2) was used to check the best fit.

Owing to the coexistence of hydrolysis and photolysis reactions in aqueous solutions during the irradiation experiments, the herbicide photolysis contribution was obtained adding the quantity $(C_0–C_t)_{dark}$, which disappeared in time *t* in the solution kept in darkness, to the remaining $(C_t)_{light}$ concentration detected in the irradiated solution at the same time. C_0 is the initial concentration of the herbicide; C_t is the concentration at time *t*. The procedure used is not fully rigorous because the synergistic effect between photolysis and hydrolysis is not taken into account (eg concentration depletion during the whole degradation reaction). However, both reactions are first-order (see below) and the calculations are theoretically a good approximation.

3 RESULTS AND DISCUSSION

The experimental set-up is summarised in Table 1. Three replicates were carried out for each experiment. The kinetic parameters were calculated considering all replicates for each experiment. The Hg-UV irradiation system (Pyrex reactor) was found to be more effective (28.7%) than the Xenon-Suntest system as the disappearance of oxalate was 9.4×10^{-4} and 6.7×10^{-4} mol s^{-1}, respectively.

Table 1. Experimental set-up

Environment:	Acetonitrile	Methanol	Water
Light source:	Darkness	Darkness	Darkness
	Suntest	–	Suntest
	Hg-UV arc	Hg-UV arc	Hg-UV arc
pH:	–	–	5
	–	–	7
	–	–	9

Table 2 summarises the kinetic parameters of rimsulfuron degradation under Suntest and Hg-UV arc irradiation. The values of determination coefficients (r^2) indicated that in each solution the degradation process occured following first-order kinetics. Figure 2 and Table 3 show the fraction $[1-(C_0–C_t)/C_0]$ of both pure rimsulfuron and that from the commercial formulation remaining in the acetonitrile solution during either Suntest or Hg-UV arc irradiation. $(C_0–C_t)/C_0$ is the fraction disappeared at time *t*.

The reaction rate of the formulated product in acetonitrile was always greater than that of the pure compound. This result may be due to the presence of co-formulates which can sensitise the photolysis reaction.[12] Obviously, the reaction was always faster under the Hg-UV arc than Suntest irradiation because of the lower energy of the latter energy source. While the pure standard solution used as control in the dark did not show any significant degradation during the experimental time (i e 60 h), approximately 5% of the technical product was degraded from 50 h onwards. However, we suggest that in both cases the disappearance of rimsulfuron in acetonitrile could depend only on the photochemical reaction.

Figure 3 shows the degradation of rimsulfuron in methanol. A fast degradation was observed having a half-life of 97.5 h at 25 °C in the dark (Table 2). From the calculated degradation under Hg-UV arc irradiation it is possible to realise how much the contribution of light could be in the transformation process of this herbicide. Indeed, Table 2 shows a photolysis half-life of 19.8 h, a value close to the half-life of the whole process in methanol, which is 12.3 h. The degradation rate of the formulated product in methanol, either in the dark or under Hg-UV arc irradiation, was only slightly faster than that of the pure standard (Figure 4, Table 2).

Half-lives of photolysis reactions in the organic solvents used here are comparable to those of hydrolysis in an aqueous environment (see below). This probably means that the photolysis of rimsulfuron is a very important process in organic environments and

Table 2. Kinetic parameters of rimsulfuron degradation under Suntest or Hg-UV arc irradiation: reaction order (*n*), determination coefficient (r^2), half-life ($t_{0.5}$), kinetic constant (*k*). Values obtained on the basis of three replicate experiments

Reaction[a]	*Environment*	*Light source*	*n*	r^2	$t_{0.5}$ (*h*)	*k* (h^{-1})
Photolysis of P S	Acetonitrile[b]	Suntest	1	0.967	79.5	0.00871
Photolysis of F P		Suntest	1	0.993	42.3	0.01640
Photolysis of P S		Hg-UV arc	1	0.974	29.7	0.02332
Photolysis of F P		Hg-UV arc	1	0.998	20.2	0.03435
Degradation of P S	Methanol	darkness	1	0.984	97.5	0.00711
Photolysis of P S		Hg-UV arc	1	0.970	19.8	0.03508
Total reaction of P S		Hg-UV arc	1	0.998	12.3	0.05653
Degradation of F P		darkness	1	0.999	81.7	0.00848
Photolysis of F P		Hg-UV arc	1	0.998	19.5	0.03562
Total reaction of F P		Hg-UV arc	1	0.993	9.6	0.07211
Hydrolysis of P S	Water, pH 5	darkness	1	0.993	243.9	0.00284
Photolysis of P S		Suntest	1	0.986	29.7	0.02333
Total reaction of P S		Suntest	1	0.998	20.2	0.03426
Photolysis of P S		Hg-UV arc	1	0.981	25.7	0.02692
Total reaction of P S		Hg-UV arc	1	0.991	16.2	0.04267
Hydrolysis of P S	Water, pH 7	darkness	1	0.955	196.8	0.00352
Photolysis of P S		Suntest	1	0.974	117.0	0.00592
Total reaction of P S		Suntest	1	0.988	65.4	0.01059
Photolysis of P S		Hg-UV arc	1	0.995	19.0	0.03653
Total reaction of P S		Hg-UV arc	1	0.998	15.0	0.04621
Hydrolysis of P S	Water, pH 9	darkness	1	0.994	24.1	0.02873
Photolysis of P S		Suntest	1	0.993	222.0	0.00312
Total reaction of P S		Suntest	1	0.996	18.8	0.03690
Photolysis of P S		Hg-UV arc	1	0.996	7.2	0.09628
Total reaction of P S		Hg-UV arc	1	0.997	5.0	0.13950

[a] PS = pure standard; FP = formulated product.

[b] No degradation was observed in the darkness for rimsulfuron P.S. and only 5% of AI was degraded at the end of experiment for rimsulfuron F.P.

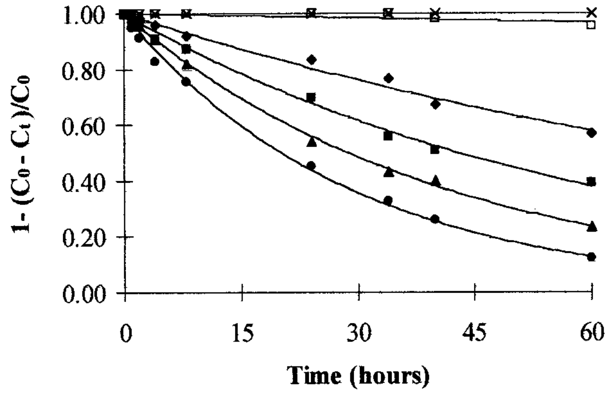

Figure 2. Fraction of rimsulfuron remaining in acetonitrile: (×) PS and (□) FP in the dark; (◆) PS and (■) FP during Suntest irradiation; (▲) PS and (●) FP during Hg-UV arc irradiation.

degradation on the leaf surface is also possible, particularly in sunny areas and seasons.

In Figs 5–7 are plotted the remaining fractions of rimsulfuron in buffered aqueous solutions as a function of time. The corresponding kinetic data are listed in Table 2. As described by Schneiders *et al*[4] the hydrolysis rate of rimsulfuron in the dark depends on pH, and the reactions always follow first-order kinetics. Thus, the hydrolytic reaction rate without irradiation is reported as being higher in acidic (pH 5: $t_{0.5} = 112.8\,h$) and alkaline (pH 9: $t_{0.5} = 9.6\,h$) environments than in neutral conditions (pH 7: $t_{0.5} = 172.8\,h$). The same authors observed a slight shift of pH from 7.0 to 7.6 in the dark, whereas the pH value remained constant during irradiation under natural sunlight. Moreover, exposure to light does not affect the degradation reaction rate and reaction products under either neutral or alkaline conditions. However, they mentioned accelerated degradation in acidic solutions and the appearance of minor polar by-products. We never observed an increase in pH under any experimental conditions. Notably, the hydrolysis reaction rate in the dark increased on increasing the pH, whereas the calculated rate of photolysis under simulated sunlight decreased, with a slope closer to the hydrolysis curve, but having an opposite sign (Fig. 8). The crossing-point indicates that at pH 7.3 (a diffuse pH value both in biotic and abiotic environments) the two reactions occur at the same rate. Therefore, the sunlight effect at pH 9 ($t_{0.5\text{photo}} = 222.0\,h$) is not completely negligible with respect to the hydrolysis reaction ($t_{0.5\text{hydro}} = 24.1\,h$), while the photolysis contributions at pH 7 ($t_{0.5\text{photo}} = 117.0\,h$) and pH 5 ($t_{0.5\text{photo}} = 29.7\,h$) were higher than the hydrolysis contributions at the same pH values ($t_{0.5\text{hydro}} = 196.8\,h$ and 243.9 h, respectively). Our results are in good agreement with previous data[4] as the whole reaction (photolysis +

Table 3. Rimsulfuron remaining in acetonitrile during irradiation and in the darkness

	Rimsulfuron (mg litre^{-1}) (±SD)					
	Darkness		*Suntest*		*Hg-UV arc*	
Hours	*PS*	*FP*	*PS*	*FP*	*PS*	*FP*
0	10.02 (±0.01)	10.12 (±0.01)	10.02 (±0.01)	10.12 (±0.01)	10.02 (±0.01)	10.12 (±0.01)
1	10.02 (±0.01)	10.12 (±0.01)	9.72 (±0.02)	10.00 (±0.02)	9.70 (±0.02)	9.46 (±0.02)
2	10.02 (±0.01)	10.12 (±0.03)	9.73 (±0.03)	9.63 (±0.05)	9.55 (±0.03)	9.13 (±0.06)
4	10.02 (±0.01)	10.12 (±0.05)	9.61 (±0.03)	9.09 (±0.05)	9.07 (±0.03)	8.27 (±0.06)
8	10.02 (±0.02)	10.11 (±0.05)	9.19 (±0.03)	8.71 (±0.06)	8.19 (±0.04)	7.55 (±0.06)
24	10.01 (±0.02)	10.00 (±0.05)	8.33 (±0.03)	6.97 (±0.06)	5.41 (±0.04)	4.50 (±0.06)
34	10.01 (±0.02)	9.99 (±0.05)	7.67 (±0.03)	5.57 (±0.06)	4.30 (±0.04)	3.28 (±0.06)
40	10.00 (±0.02)	9.89 (±0.05)	6.74 (±0.03)	5.09 (±0.06)	3.98 (±0.04)	2.59 (±0.06)
60	10.00 (±0.02)	9.58 (±0.05)	5.69 (±0.03)	3.92 (±0.06)	2.36 (±0.04)	1.21 (±0.06)

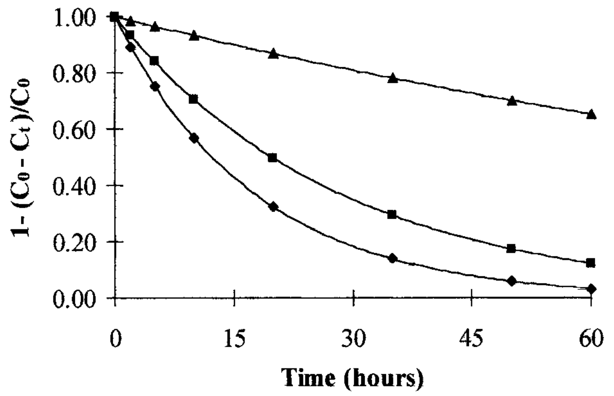

Figure 3. Fraction of pure rimsulfuron remaining in methanol: (◆) total reaction during Hg-UV arc irradiation; (■) calculated photolysis (Hg-UV arc); (▲) degradation in the dark.

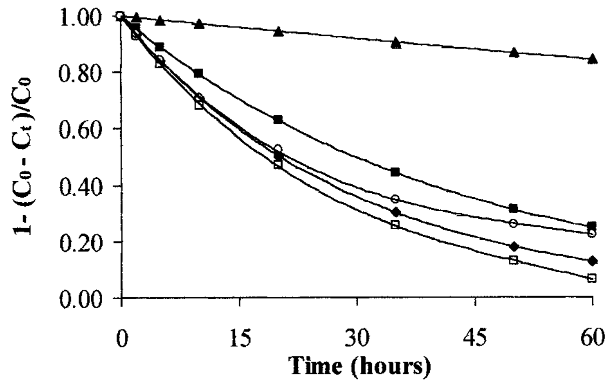

Figure 5. Fraction of rimsulfuron remaining in water (pH 5): (◆) total reaction (Suntest); (■) calculated photolysis (Suntest); (□) total reaction (Hg-UV arc); (○) calculated photolysis (Hg-UV arc); (▲) hydrolysis.

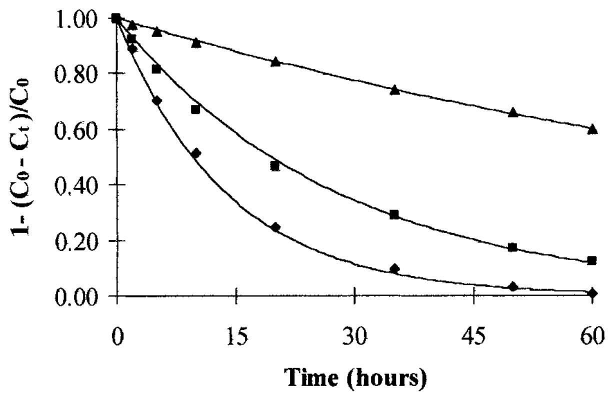

Figure 4. Fraction of rimsulfuron formulated product remaining in methanol: (◆) total reaction during Hg-UV arc irradiation; (■) calculated photolysis (Hg-UV arc); (▲) degradation in the dark.

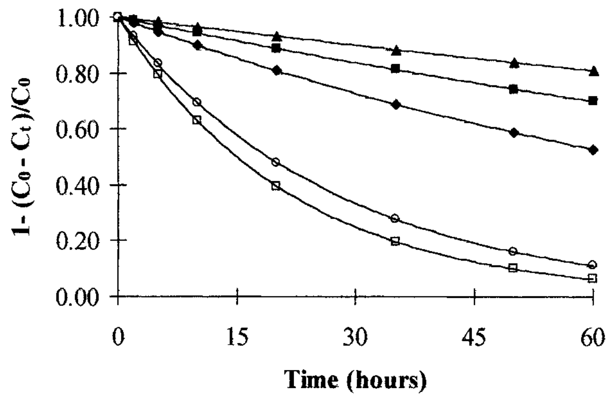

Figure 6. Fraction of rimsulfuron remaining in water (pH 7): (◆) total reaction (Suntest); (■) calculated photolysis (Suntest); (□) total reaction (Hg-UV arc); (○) calculated photolysis (Hg-UV arc); (▲) hydrolysis.

hydrolysis) under sunlight is faster in acidic (pH 5: $t_{0.5}=20.2\,h$) and alkaline (pH 9: $t_{0.5}=18.8\,h$) conditions than in neutral solutions (pH 7: $t_{0.5}=65.4\,h$).

Data obtained under Hg-UV arc irradiation confirm the above findings, as the calculated half-lives of photo-reactions are always lower than the measured half-lives of hydrolysis. Hg-UV results are very reproducible, and for such a reason it was not possible to distinguish different behaviour among the solvents. The quantities of each metabolite determined at the half-life time of pure rimsulfuron in acetonitrile and aqueous solutions kept in the dark or irradiated under the Suntest are reported in Table 4. Data are expressed as a percentage of the initial herbicide concentration.

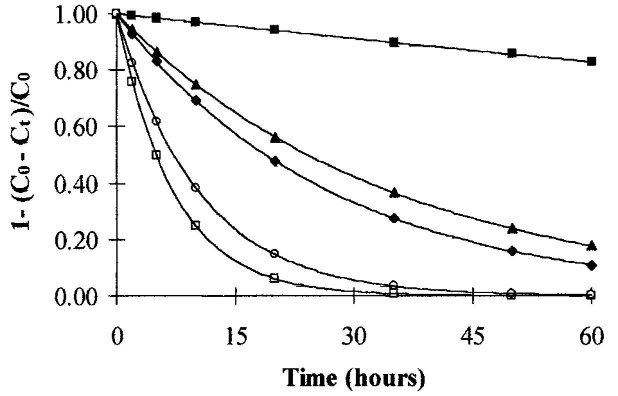

Figure 7. Fraction of rimsulfuron remaining in water (pH 9): (◆) total reaction (Suntest); (■) calculated photolysis (Suntest); (□) total reaction (Hg-UV arc); (○) calculated photolysis (Hg-UV arc); (▲) hydrolysis.

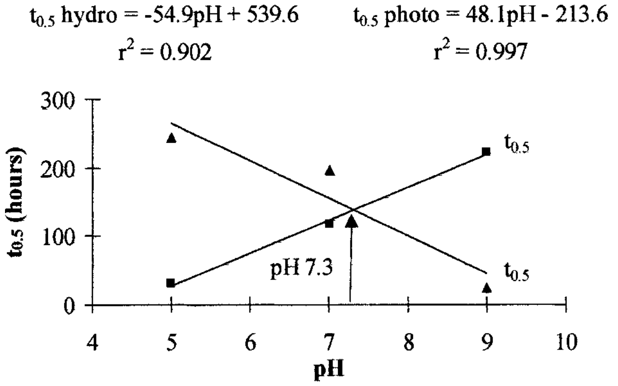

Figure 8. pH dependence of degradation half-life of pure rimsulfuron: (■) calculated photolysis in water (Suntest); (▲) hydrolysis (in the dark).

The main metabolite was always compound **3**, with the exception of hydrolysis in acidic water, where compound **2** prevailed, and the irradiated sample in the same environment, where minor metabolites (**4**, **5**, **6**) were prevalent. Metabolite **2** was also high in the alkaline hydrolytic process.

Rimsulfuron easily undergoes intramolecular nucleophilic substitution, which transforms it into compound **2** either *via* the hydrolysis or photolysis reaction (Fig 1). Such a product is only a transient degradation product[17] both in acetonitrile and neutral and alkaline aqueous solutions. The transformation of rimsulfuron and compound **2** in acidic conditions into the metabolite **3** is most likely very low because protonation of electron-donor groups occurs.[18]

At pH 5 the hydrolysis reaction rate is slow ($t_{0.5}$ = 243.9 h) and the irradiated energy in the Suntest can directly transform rimsulfuron and compound **2** into metabolites **4**, **5** and **6** (Fig 1). In this case a small amount of 2-pyridinesulfonamide-3-sulfonic acid and 2-hydroxypyridine-3-sulfonic acid was also found in the reaction mixture.

4 CONCLUSION

Our experiments confirm that rimsulfuron degradation depends on both pH and light. The photolytic process under simulated sunlight was as important as the hydrolytic effect. The half-life in the darkness was *c* 1 day in acidic and alkaline pH, and increased up to eight days in neutral medium. Noticeable differences in the metabolite composition were found when the reaction environment was changed. The main metabolite was compound **3** in neutral and alkaline conditions as well as in acetonitrile, whereas **2** and minor metabolites prevailed in acidic solutions.

The photolysis process in organic solvents also occurred with a first-order kinetic reaction and was as fast as the analogous reaction in neutral and alkaline aqueous conditions. This implies that degradation on the leaf surface is also possible. Having in mind that rimsulfuron is used on post-emergence treatments, in which it can be distributed both on the soil surface and plant leaves, and degradation of the formulated product occurs faster than of the pure standard for field purposes it may be necessary to recommend rates higher than those indicated in the laboratory or glasshouse to take into account the field fate of the herbicide.

Table 4. Metabolites of pure rimsulfuron determined at half-life time under Suntest irradiation and in the darkness

			Compound (%)[a]		
Reaction	*Environment*	*Light source*	**2**[b]	**3**[b]	**4**+**5**+**6**[b]
Degradation	Acetonitrile	Darkness	–[c]	–[c]	–[c]
Photolysis	Acetonitrile	Suntest	9.8	33.8	6.4
Hydrolysis	Water, pH 5	Darkness	35.5	9.7	4.8
Total reaction[d]	Water, pH 5	Suntest	14.5	0	35.5
Hydrolysis	Water, pH 7	Darkness	5.2	31.2	13.6
Total reaction[d]	Water, pH 7	Suntest	6.1	30.6	13.3
Hydrolysis	Water, pH 9	Darkness	13.7	28.4	7.9
Total reaction[d]	Water, pH 9	Suntest	3.1	33.2	13.7

[a] Based on initial rimsulfuron content.

[b] See fig 1.

[c] No degradation observed up to 60 h.

[d] Hydrolysis + photolysis.

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