Chemosphere, Vol. 38, No. 4, pp. 741-749, 1999

PII: S0045-6535(98)00219-7

LIGHT INDUCED TRANSFORMATION OF TRIBENURON-METHYL

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(Received in Germany 7 May 1998; accepted 9 June 1998)

ABSTRACT: To study the photostability of sulfonylurea herbicide tribenuron-methyl (methyl 2-[[[[N-(4-methoxy-6-methyl-1,3,5-triazin-2-yl) methylamino] carbonyl]amino]sulfonyl] benzoate), in the field, model experiments with organic solvents were performed. Irradiation of tribenuron-methyl in methanol, isopropanol and cyclohexane yielded 4-methoxy-6-methyl-2-aminomethyl-1,3,5-triazine; methyl-2-(aminosulfonyl) benzoate; N-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-N-methyl urea; N-(2-carbomethoxy phenyl)-N-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-N'-methyl urea; 2-(aminosulfonyl) benzoic acid, N-methyl saccharin and saccharin in considerable amounts. The rate of degradation in different solvents followed first-order kinetics with a statistically significant correlation coefficient. ©1998 Elsevier Science Ltd. All rights reserved

KEY WORDS : Tribenuron-methyl, photolysis, photoproducts, solvents, rate kinetics

INTRODUCTION

Tribenuron-methyl (methyl 2-[[[[N-(4-methoxy-6-methyl-1,3,5-triazin-2-yl) methyl amino]carbonyl]amino]sulfonyl] benzoate) a sulfonylurea herbicide has a wide spectrum of activity against many broad-leaved weeds in cereals like wheat, barley and oat (Ferguson *et al.*, 1985). Its exceptionally low rate of application (10 - 20 g a.i. ha^{-1}) at early post-emergence stage, selectivity to most cereal crops and low mammalian toxicity make it environment friendly. The mode of action of tribenuron-methyl is similar to that of other sulfonylurea herbicides, i.e., blocking the production of the essential branched-chain amino acids valine, leucine and isoleucine (Ray, 1985; Brown, 1990). In Scandinavia trials over four years have shown that it can also be used in cereals undersown with red clover and lucerne (Fahlgren, 1993). Absorption, translocation and foliar activity of clopyralid and tribenuron in perennial sowthistle (*Sonchus arvensis)* has been studied by Zollinger *et al.* (1992). York *et al.* (1994) observed that thifensulfuron plus tribenuron, commonly applied to wheat, could be applied post-emergent to triticale (*Triticosecale Wittmack*) during the tillering stage without adversely affecting the productivity of the crop.

The most common model for the plant surface is given by simulating the functional groups of the cuticle components (long chain alcohols, saturated unsaturated and hydroxylated fatty acids, triterpenes and sterols) with organic solvents like isopropanol, cyclohexane and cyclohexene. Hartmann and Schwack (1994) used organic solvents with selected functionalities as substitutes for components of plant waxes for photodegradation of triadimefon, a triazole fungicide. Therefore, this paper deals with the results of photochemical transformations of tribenuron-methyl in the presence of methanol, isopropanol and cyclohexane as representative model substances for the plant cuticle constituents.

MATERIALS AND METHODS

Chemicals : A technical sample of tribenuron-methyl (95% purity) was supplied by DuPont Far East Inc., New Delhi, India, and was purified further by repeated crystallisation from methanol until a constant m.p. of 141°C was achieved. Laboratory grade solvents and reagents were procured locally. All the solvents were dried and distilled before use.

Chromatrography and spectroscopy : Tribenuron-methyl and its degradates in the rate kinetics studies were analysed by HPLC (Thermo Separation Product model Spectra System P2000), equipped with a variable wavelength UV-150 UV-VIS detector and a Rheodyne injector (20 μL loop) and connected to a Datajet reporting integrator, the stationary phase consisted of a Lichrosorb C-18 column (250 mm x 4.6 mm i.d.) and the mobile phase was methanol:water (70:30, v/v) maintained at a flow rate of 0.8 mL min^{-1} with detector wavelength set at 230 nm. The photoproducts were separated by column chromatography using a glass column (45 cm x 2 cm i.d.) containing 250 g of 60-100 mesh preactivated silica gel at 120°C *n*-hexane and eluting the column with hexane and acetone in different ratios. Thin layer chromatography (TLC) was performed on 5 cm x 20 cm glass plates coated with silica gel G (0.5 mm) and iodine was used as visualizing agent. For the preparative TLC, 20 cm x 20 cm glass plates were used.

The ultraviolate-visible spectrum of tribenuron-methyl was recorded on a Hitachi Model U-2000 double beam UV-VIS spectrometer in methanol and water using a quartz cuvette (1 cm path length). The infra-red spectra of the photoproducts were recorded on a Nicolet Impact 700 FT-IR spectrophotometer using KBr disc and a nujol mull. ^{1}H-NMR spectra were recorded on a Varion EM 360L (60MHz) instrument. Deuterochloroform ($CDCl_3$) was used as solvent and tetramethylsilane (TMS) as the internal standard. Gas chromatography-mass spectroscopy (GC-MS) was performed on a HRGC-MEGA 2 series gas chromatograph coupled to a FISONS-TRIO 1000 ion trap mass spectrometer and connected to a Panasonic KX P1150 multimode printer. The ionization potential was 70 ev. The GC was equipped with a SE-54 capillary column (15 m x 0.25 mm i.d., film thickness 0.1-0.15 m). The column oven temperature was programmed to increase from 70 to 250°C at a rate of 10°C min^{-1}. Helium was used as carrier gas with a flow rate of 2 mL min^{-1}.

Irradiation and photoproducts: To produce enough of photoproducts for structural analysis, a solution of tribenuron-methyl (4000 ppm) in methanol, isopropanol and cyclohexane, respectively, was irradiated in a water-cooled quartz flask with UV-light from a medium pressure Hg vapour lamp (125 W, Philips) for 20, 18 and 26 h, respectively. After irradiation, the solvent was distilled off under reduced pressure and the residue so obtained was subjected to column chromatography on silica gel.

Synthesis of comparison compounds: *o*-Benzoic sulfimide or saccharin was synthesized according to the procedure described by Vogel (1989).

Methyl 2-(aminosulfonyl) benzoate: In a round bottomed flask (250 mL capacity) o-benzoic sulfimide (1.5 g), concentrated hydrochloric acid (8 mL) and methanol (150 mL) were taken and refluxed for 8 h on a water bath (Shkulev *et al.*, 1979). Methanol was distilled off by passing nitrogen gas and the remaining liquid was extacted with methylene chloride and dried over anhydrous sodium sulfate. Organic phase was then completely evaporated off. Solid product thus obtained was recrystallised from benzene ; m.p.115-116°C. The IR spectrum of the product showed the presence of C=O at 1710 cm^{-1} and O=S=O at 1341 cm^{-1} (asym.) and 1166 cm^{-1} (sym.). ^{1}H-NMR ($CDCl_3$) : δ 7.6-8.3 (m, 4H, aromatic), 5.8 (s, 2H, NH_2), 3.9 (s, 3H, OCH_3). GC-MS: m/z 215 (M^+), 199 (M^+-16), 184 (M^+-31), 120 (M^+-95), 105 (M^+-110).

4-Methoxy-6-methyl-2-aminomethyl-1,3,5-triazine: Tribenuron-methyl (500 mg) was stirred with aqueous hydrochloric acid (pH 3.0) at 40°C for 48 h. The reaction product was extracted with chloroform. Chloroform layer was separated , dried over anhydrous sodium sulfate and distilled off. A solid thus obtained was recrystallised from methanol; m.p.155°C. The IR spectrum showed the presence of N-H at 3256 cm-1 and C=N at 1558 cm-1. ^{1}H-NMR ($CDCl_3$) : δ 6.0 (bs, 1H, NH), 3.9 (s, 3H, OCH_3), 3.1 (d, 3H, NCH_3), 2.45 (s, 3H, CH_3). GC-MS : m/z 154 (M^+), 139 (M^+-15), 124 (M^+-30), 110 (M^+-44).

Photolysis kinetics: A solution of tribenuron-methyl (100 mL, 50 ppm) in methanol and isopropanol, respectively, was irradiated in quartz tubes under ultraviolet light from a medium pressure Hg vapour lamp. Samples (2 mL) in triplicate were removed at time intervals of 0, 15, 30, 45, 60, 90, 120, 150, 180, 210 and 240 min from both the solvents and analysed by HPLC.

RESULTS AND DISCUSSION

Isolation and identification of photoproducts:

Photolysis in methanol: A methanolic solution of tribenuron-methyl (I, 4000 ppm) on irradiation for 20 h, gave a mixture of a number of photoproducts (TLC). After solvent removal by vacuum evaporator, the residue was subjected to column chromatography. The separated products were further purified either by crystallisation from appropriate solvent or by preparative TLC. The following photoproducts were identified by IR, ^{1}H-NMR, GC-MS and comparison with authentic standards (Figure 1).

4-methoxy-6-methyl-2-aminomethyl-1,3,5-triazine (II): A colourless solid, recrystallised from methanol (m.p. 155°C). The infra-red spectrum of the product showed N-H stretching at 3256 cm-1 and C=N stretching at 1558 cm^{-1}. The ^{1}H-NMR spectrum exhibited a one proton broad singlet at δ 6.0 for NH, a three proton doublet at δ 3.1 for NCH_3 and two three proton singlets at δ 3.9 and 2.45 for OCH_3 and CH_3, respectively. The mass spectrum showed a molecular ion peak at m/z 154 (M^+) (fragments recorded in Table 1).

Methyl 2-(aminosulfonyl) benzoate (III): Recrystallised from ethanol (m.p. 115-116°C) , The infra-red spectrum showed two weak bands at 3383 and 3263 cm^{-1} for NH_2 group, a band at 1710 cm^{-1} corresponding to C=O group and two strong bands at 1341 cm^{-1} (asymmetric) and 1166 cm^{-1} (symmetric) for O=S=O group. ^{1}H-NMR spectrum showed the presence of four aromatic protons as multiplet at δ 8.3-7.6, two NH_2 protons at δ 5.8 and three OCH_3 protons at δ 3.95 and the mass spectrum showed a molecular ion peak at m/z 215 (M^+) with fragment ion peaks at m/z 199, 184, 135 and 104 (Table 1) .

Table 1: Mass Spectral Data of Photodegradation Products of Tribenuron -methyl in Organic Solvents.

Product	Mass Found (m/z)	Abundance (%)	Structure	Concentration (%)
II	154	100	M^+	
	139	5	$M^+ - CH_3$	
	124	70	CH_3NH/OCH_3	4
III	215	5	M^+	
	199	100	$M^+ - NH_2$	
IV	140	6	M^+	25
	125	6	$M^+ - CH_3$	
V	197	10	M^+	12
	181	100	$M^+ - NH_2$	
	153	35	$M^+ - (OCH_3 {}^+ CH_3)$	3
VI	211	100	M^+	
	196	17	$M^+ - CH_3$	2
VII	183	6	M^+	2
	169	3	$M^+ - CH_3$	
VIII	331	28	M^+	4
	300	45	$M^+ - OCH_3$	
	272	4	$M^+ - CONHCH_3$	
IX	317	15	M^+	2
	302	5	M^+ - CH3	
	274	5	M^+ - CONHCH3	
X	194	84	M^+	2.5
	179	51	$M^+ - CH_3$	
XI	271	11	M^+	1
	240	12	$M^+ - OCH_3$	
	207	100	$M^+ - SO_2$	
XII	286	100	M^+	1.5
	257	20	$M^+ - (CH_3)_2$	
	228	20	$M^+ - COOCH_3$	
XIII	258	2	M^+	2.2
	227	2	$M^+ - OCH_3$	
	213	12	$M^+ - CONH_2$	
XIV	201	8	M^+	6.5
	200	14	$M^+ - H$	
	184	62	$M^+ - OH$	
	120	100	$M^+ - SO_2NH$	
XV	183	62	M^+	10
	169	3	$M^+ - NH$	
XVI	197	20	M^+	1.5
	169	6	$M^+ - NCH_3$	
XVII	136	6	M^+	0.80
	105	15	C_6H_5CO	
XVIII	169	2	M^+	1.2
	140	4	$M^+ - NCH_3$	
XIX	257	2	M^+	1.5
	227	4	$M^+ - (CH_3)_2$	
	213	12	$M^+ - CH(CH_3)_2$	
XX	97	18	M^+	3
	81	100	$M^+ - NH_2$	

4-methoxy-6-methyl-2-amino-1,3,5-triazine (IV): The ^{1}H-NMR spectrum showed the presence of OCH_3 and CH_3 groups at δ 4.8 and 2.3, respectively. Its mass spectrum showed a molecular ion peak at m/z 140 (M^+) (Table 1).

N-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-N-methyl urea (V): A colourless solid purified by recrystallisation from methanol. ^{1}H-NMR spectrum showed the presence of NH_2, OCH_3 and CH_3 groups at δ 5.8, 4.1 and 2.5, respectively. The mass spectrum showed a molecular ion peak at m/z 197 (M^+) with fragment ion peaks at m/z 181, 153 and 126 (Table 1).

N-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-N,N'-dimethylurea (VI): The ^{1}H-NMR spectrum showed the presence of OCH_3, NCH_3, $NHCH_3$ and CH_3 groups at δ 4.1, 3.6, 3.2 and 2.6, respectively. Its mass spectrum showed a molecular ion peak at m/z 211 (M^+) (Figure 1).

N-(4-methoxy-6-methyl-1,3,5-triazin-2-yl) urea (VII): Purified by preparative TLC. The mass spectrum of this product showed a molecular ion peak at m/z 183 (M^+) with fragment ion peaks at m/z 155, 139 and 126 (Table 1).

N-(2-carbomethoxyphenyl)-N-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)-N'-methyl urea (VIII): The ^{1}H-NMR spectrum showed the presence of four aromatic protons at δ 8.4-7.5, six protons corresponding to two OCH_3 groups at δ 4.1, three protons for $NHCH_3$ group at δ 3.1 and three protons for CH_3 group at δ 2.6. Its mass spectrum showed a molecular ion peak at m/z 331 (M^+) (Figure 1).

N-(2-carbomethoxy phenyl)-N-(4-methoxy-6-methyl-1,3,5-triazin-2-yl) urea (IX): A brown solid which was purified by recrystallisation from benzene. It was tentatively identified by its mass spectrum which showed a molecular ion peak at m/z 317 (M^+) with fragment ion peaks at m/z 302, 274, 194, 126 and 108 (Table 1).

N-(2-carbomethoxyphenyl) urea (X): Identified tentatively by the mass spectrum which showed a molecular ion peak at m/z 194 (M^+) (Figure 1). The mass spectrum of X showed the typical fragment pattern of the substituted ureas as shown by Baldwin *et al.* (1968).

N-(2-carbomethoxyphenylsulfonyl)-N'-methylurea (XI), N-(2-carbomethoxy phenyl sulfonyl) - N',N'-dimethyl urea (XII) and N-(2-carbomethoxyphenylsulfonyl) urea (XIII) (Figure 1): A mixture of three photoproducts obtained were separated by preparative TLC and tentatively identified by GC-MS. The mass spectrum of these three photoproducts showed the molecular ion peaks at m/z 271 (M^+), 286 (M^+) and 258 (M^+) respectively (Table1).

2-(aminosulfonyl) benzoic acid (XIV): A colourless amphorphus solid purified by recrystallisation from benzene. The IR spectrum indicated the presence of NH_2 group as two weak absorption bands at 3361 and 3256 cm^{-1}, C=O group at 1721 cm^{-1} and O=S=O group by two strong bands at 1337 cm^{-1} (asymmetric) and 1179 cm^{-1} (symmetric). Its mass spectrum showed a molecular ion peak at m/z 201 (M^+) with fragment ion peaks at m/z 184, 121 and 77 (Table 1).

***o*-benzoic sulfimide or saccharin (XV):** A colourless solid purified by recrystallisation from hot water (m.p. 228°C). IR spectrum showed the presence of N-H, C=O and O=S=O stertching at 3322, 1648, 1341 and

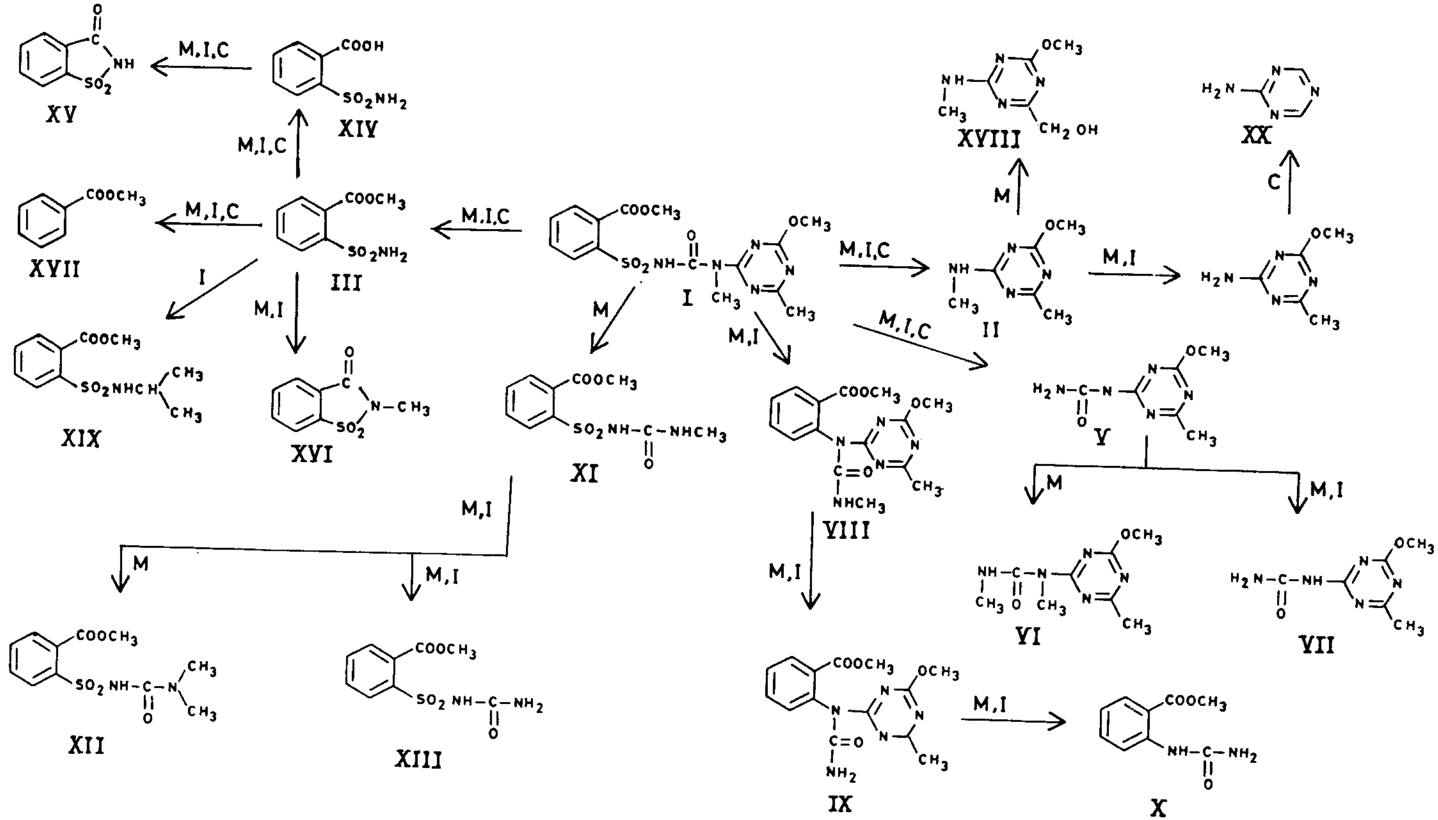

Figure 1. Photodegradation products of tribenuron - methyl (I) in methanol (M), isopropanol (I) and cyclohexane (C) under UV light.

1148 cm^{-1}, respectively. The mass spectrum showed a molecular ion peak at m/z 183 (M^{+}), (Figure 1). The structure of XV was further confirmed by comparing mass spectrum with authentic sample.

o-benzoic sulf-N-methylimide (XVI): The infra-red spectrum showed the presence of Ar-H stretching, C=O group and C-N stretching absorption bands at 3013, 1723 and 1216 cm^{-1}, respectively. Tentatively identified by mass spectrum which showed a molecular ion peak at m/z 197 (M^{+}) (Table 1).

Two minor photoproducts were tentatively identified by their mass spectra, which showed molecular ion peaks at m/z 136 (M^{+}) and 169 (M^{+}), as methyl benzoate (XVII) and 4-methoxy-6-hydroxy) cm^{-1}methyl-2-aminomethyl-1,3,5-triazine (XVIII), respectively (Figure 1).

Photolysis in isopropanol: Tribenuron-methyl (I) on irradiation in isopropanol in quartz tubes for 18 h yielded a number of photoproducts. Which were identified as II, III, IV, V, VII, VIII, IX, X, XIII, XIV, XV, XVI and XVII (Figure 1) by comparison of their IR, ^{1}H-NMR and mass spectra with those obtained earlier in methanol. Besides these, another photoproduct was identified by its mass spectrum which showed a molecular ion peak at m/z 257 (M^{+}) (Table 1). On the basis mass fragmentation pattern, it was tentatively identified as methyl 2-(isopropyl aminosulfonyl) benzoate (XIX, Figure 1).

Photolysis in cyclohexane: A solution of tribenuron-methyl (I) in cyclohexane on irradiation for 26 h. showed the formation of a number of photoproducts on TLC. IR, ^{1}H-NMR and mass spectra of isolated photoproducts were in good agreement with photoproducts II, III, V, XIV, XV and XVII identified earlier. Besides these photoproducts presence of another product was identified by GC-MS. It was tentatively identified as 2-amino-1,3,5-triazine (XX, Figure 1) by the mass spectrum which showed a molecular ion peak at m/z 97 (M^{+}) with a base peak at m/z 81 (Table 1).

Discussion: The UV spectrum of tribenuron-methyl (I) in water and methanol exhibited a band at 213.5 nm for allowed $\pi-\pi^*$ transition of the phenyl ring and a band at 258 nm which is essentially $n-\pi^*$ in character, resulting from the combined transition of the carbonyl group and lower energy band of the aromatic ring. These $\pi-\pi^*$ and $n-\pi^*$ transitions can lead to the production of either singlet or triplet excited states. Thus, no unique excited state can be invoked to explain the variety of photochemical reactions undergone by the various functional groups of tribenuron-methyl.

The identification of photoproduct II and III suggests that photoreaction of tribenuron-methyl in aqueous solution includes cleavage of sulfonylurea bridge, which is the most susceptible region for photolytic reaction of most of the sulfonylurea herbicides (Schneiders *et al.*, 1993). The photoproduct X may be obtained by de-esterification of photoproducts III, whereas photoproducts XI and XII may be formed from intermediates like 2-(aminosulfonyl) benzoic acid and 2-(N-methylaminosulfonyl) benzoic acid, respectively. Scission of SO$_2$NH bond of tribenuron-methyl may give photoproducts V, which further undergoes methylation (in methanol) and demethylation to yield photoproducts VI and VII, respectively. Cleavage of triazinyl amide linkage yields a major photoproducts N-(2-carbomethoxy phenylsulfonyl)-N'-methyl urea (XI) which also undergoes methylation (in methanol) and demethylation to give photoproducts XII and XIII, respectively. The minor photoproducts are formed from major photoproducts through various reactions like elimination of sulfonamide group (XVII), elimination of OCH_3 and CH_3 groups from photoproducts IV (XX), addition of isopropyl moiety in photoproducts III (XIX), hydroxylation of CH_3 group in triazine moiety (XVIII) etc. Contraction of sulfonylurea bridge to yield the photoproducts VIII. This process involves concerted elimination of SO_2 with the formation of methyl benzoate radical and 4-methoxy-6-methyl 1,3,5-triazin-2-yl urea radical. The later one undergoes intramolecular proton abstraction to form an intermediate which combines with methyl benzoate radical to yield photoproducts VIII. Photoproducts IX and X may be formed by demethylation and elimination of triazinyl moiety from photoproducts VIII, respectively.

Photolysis kinetics : The rate of Photodegradation of tribenuron-methyl was studied in methanol and isopropanol under UV-light. No degradation occurred in the dark, since 95% of tribenuron-methyl remained unchanged after 4 h. The rate of degradation of tribenuron-methyl was somewhat faster in isopropanol than in methanol. The statistically calculated half-live values for tribenuron-methyl in methanol and isopropanol were 2.41 h and 1.72 h, respectively (Table 2). The rate of Photolysis followed first-order kinetics with a significant correlation coefficient (r = 0.98) indicating the linear correlation between the time of irradiation and the concentration of tribenuron-methyl at different time intervals. The UV spectrum of tribenuron-methyl showed absorption maxima at 213.5 nm, that meant it absorbed maximum light at lower wavelength and thus underwent degradation.

Table 2: Rate constant (K), half-life ($t_{1/2}$) and correlation co-efficient (r) values for tribenuron-methyl in different solvent under UV-light

Solvents	Rate constant (K) (h^{-1})	Half-life (t1/2) (h)	No. of Replicates	Correlation coefficient (r)
Methanol	0.2874	2.41	3	-0.96
Isopropanol	0.4014	1.72	3	-0.99

CONCLUSION

Irradiation of tribenuron-methyl in different solvents under UV-light has given basic information about photoreactivity, photoproducts and possible photochemical pathways in the environment. These studies indicate that under the influence of light tribenuron-methyl undergoes cleavage of sulfonylurea bridge, scission of sulfonamide bond, cleavage of triazinyl amide linkage and contraction of sulfonylurea bridge. Thus, the formation of different products as a result of irradiation in different solvents simulating environmental conditions shows the possibility of detoxification of tribenuron-methyl in the field as a result of Photolysis. We can conclude that there will be a rapid breakdown of tribenuron-methyl on the leaf surface to non-toxic compounds.

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