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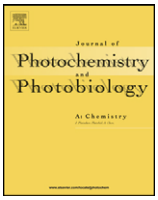

Photophysical and photochemical studies of thifensulfuron-methyl herbicide in aqueous solution

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ABSTRACT

The photophysical and photochemical studies of a sulfonylurea herbicide, thifensulfuron-methyl (THM), have been investigated in a buffered aqueous solution. In the first part, the influence of pH on the spectroscopic properties was studied. This allowed the determination of the ground and excited state acidity constants, $pK_a = 4$ and 4.4, respectively, thus exhibiting the potential existence of a photoinduced protonation in the singlet state. In the second part, the photolysis kinetics was studied at different pH and varying oxygen concentrations, using an HPK 125 W lamp and followed up by the identification of photoproducts formed under continuous photo-irradiation. The kinetics results suggest that the photolysis process is faster in acidic ($k = 3 \times 10^{-4}\ s^{-1}$) than in basic medium ($k = 9.8 \times 10^{-5}\ s^{-1}$). The photolysis products were identified by high performance liquid chromatography HPLC-DAD, HPLC–MS and HPLC–MS–MS. In order to obtain a better understanding of the photodegradation mechanism, a laser flash photolysis study was performed. By comparing the quenching rate constant ($k_q = 9.64 \times 10^8\ mol^{-1}\ l\ s^{-1}$) obtained from triplet state quenching by molecular oxygen and from the Stern–Volmer relation ($k_q = 0.41 \times 10^8\ mol^{-1}\ l\ s^{-1}$), the role of the singlet state in the photodegradation process was demonstrated. The photoproducts originating from both singlet and triplet excited states have been identified and hypothetical photodegradation pathways of the thifensulfuron-methyl in aqueous solution are proposed.

1. Introduction

A new class of agrochemical herbicides named sulfonylurea has been developed since the middle of the seventies [1]. The sulfonylurea herbicide structure consists of two chromophore groups connected by a sulfonylurea bridge. One group (R1) is constituted by an aliphatic, aromatic, or heterocyclic molecule while the other (R2) is principally a triazine, pyrimidine, or triazole [2,3]. Sulfonylureas are efficient at low doses (10–15 g ha^{-1}) [4] and the mode of action of these herbicides consists of inhibiting acetolactate synthase (ALS) which is a key enzyme in the biosynthesis of branched amino-acids (valine, leucine, and isoleucine) [5]. Because of their effectiveness, sulfonylureas have been widely used in agriculture but their fate in soil and water remain a major problem. Indeed three processes can occur concurrently in water or soil: chemical hydrolysis, microbial and photolysis degradation [6]. For example Cambon and Bastide [7] studied the hydrolysis kinetics of thifensulfuron-methyl in aqueous solutions buffered at different pH values (pH = 4, 5, 9, and 10), showing that the hydrolysis rate is pH dependent and follows a pseudo first-order kinetics. At high and low pH values the hydrolysis is faster with half-lives of 28.8 and 6.0 h at pH 4 and 10, respectively [7]. Concerning the degradation mechanism, in acidic solutions, two parallel reactions occurred, cleavage of the sulfonylurea bridge and opening of the triazine ring, whereas at alkaline pH, thifensulfuron-methyl hydrolyzed to thifensulfuron, which was then slowly transformed by cleavage of the sulfonylurea bridge and O-demethylation [7,8].

Although it is claimed that chemical hydrolysis and microbial degradation represent the main degradation pathways of sulfonylureas, several papers indicate that at neutral pH, photolysis could be an alternative pathway for the photodegradation of thifensulfuron-methyl [9–11]. This is the reason we have focused our attention on the photodegradation of sulfonylurea.

Whereas the photodegradation of sulfonylurea herbicides has been studied in the last decade [9–12] mainly from an analytical point of view, few studies refer to their photophysical and photochemical properties in solutions. This paper reports on the latter aspects, with reference to thifensulfuron-methyl herbicide in aqueous solution. A laser flash photolysis approach has been employed so as to better understand the role played by the excited (singlet or triplet) states. Following degradation, the photoproducts were

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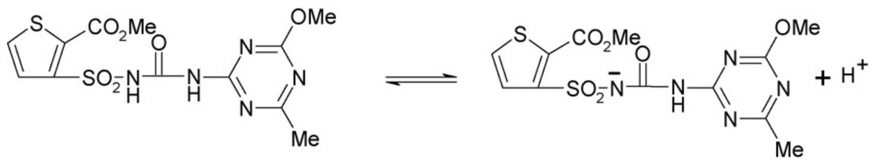


Scheme 1. Chemical structure of thifensulfuron-methyl as a weak acid, and its conjugate base.

analysed using LC/DAD (liquid chromatography diode array detector) and LC/MS (liquid chromatography, mass spectrometry).

2. Materials and methods

2.1. Reactants

[Thifensulfuron-methyl,3-[[[(4-methoxy-6-methyl-1,3,5-triazine-2-yl)amino]carbonyl]amino]sulfonyl]-2-thiophenecarboxylate (Scheme 1) (98% purity) acquired from Riedel-de Haen was used without further purification. This sulfonylurea is characterized by a high solubility in water which is 2400 mg l^{-1} at 25 °C at pH 6 [10]. 2-Amino-4-methoxy-6-methyl-1,3,5-triazine was purchased from Sigma–Aldrich (purity > 97%). It was used without further purification.

For photodegradation experiments, thifensulfuron-methyl (THM) was solubilized in phosphate buffers (H_3PO_4, KH_2PO_4, and K_2HPO_4). The water used for buffer preparation was purified with a Millipore Waters Milli-Q water system (MilliQ-50 18 MΩ). As the herbicide was not easy to be dissolved in acidic medium, a small quantity of ethanol 5% was added and this for all pH.

2.2. UV absorption, fluorescence emission and time resolved transient spectra

The UV absorption spectra were recorded with a double beam UVIKON 930 spectrophotometer (KONTRON INSTRUMENT), while fluorescence spectra were measured with a FP-6500 spectrofluorometer (JASCO).

Transient absorption experiments in the 20 ns–400 μs time scale were carried out on a nanosecond laser flash photolysis spectrometer from Applied Photophysics (LKS.60). Excitation (λ = 266 nm) was from the fourth harmonic of a Quanta Ray GCR 130-01 Nd:YAG laser (pulse width ≈ 9 ns), and was used in a right-angle geometry with respect to the monitoring light beam. The transient absorbance at preselected wavelength was monitored by a detection system consisting of a pulsed xenon lamp (150 W), monochromator, and a 1P28 photomultiplier. The signal from the photomultiplier was digitized by a programmable digital oscilloscope (HP54522A). A 32 bit RISC-processor kinetic spectrometer workstation was used to analyse the digitized signal. A 3 cm^3 volume of solution was used in a quartz vessel, and was stirred after each flash irradiation. Deoxygenation of the solutions was accomplished by nitrogen bubbling. The sample temperature was 297 K.

2.3. Irradiation experiments

The irradiation experiments were carried out in an open borosilicate (Pyrex) glass cell (cut-off at 295 nm, 50 ml volume), open to air with an optical window of 11 cm^2 area, equipped with a magnetic stirring bar and water circulating jacket. The light source was a HPK 125 W Philips mercury lamp with main emission wavelength at 365 nm, cooled with a water circulation maintained at 20 °C. Volumes of 25 ml of the aqueous solution of thifensulfuron-methyl (2.5×10^{-5} M) were irradiated. The radiant flux entering the irradiation system was measured using Uranyle oxalate from Fluka as actinometer [13] and a value of 1.63×10^{16} photon $cm^{-2}\,s^{-1}$ was found.

2.4. HPLC analysis

2.4.1. HPLC/DAD analysis

The concentration profile of THM during irradiation and the formation of intermediates were performed using a Shimadzu VP series high-pressure liquid chromatography (HPLC) system equipped with a photodiode array detector (HPLC-DAD). Analytical separation was performed using a column Hypersil BDS C18 (4 μm, 125 mm × 4 mm i.d.), flow rate of 1 ml min^{-1}, injection volume of 20 μl, and mobile phase 55:45 (v/v) methanol/water (pH set to 2.6 using formic acid). The detection wavelength was 245 nm. For photoproducts formation, the following gradient was used: 10% (methanol) at t = 0 min during 13 min, then increase to 60% for 20 min then 100% during 10 min.

2.4.2. LC/MS and LC/MS/MS analysis

The LC–MS and LC–MS–MS identification of photoproducts of the aerated solution was carried out with a Waters (Alliance 2695) HPLC system coupled to a Quattro LC triple quadrupole mass spectrometer (Micromass, Manchester, UK) equipped with a pneumatically assisted electrospray ionization source (ESI). Data acquisition and processing were performed by MassLynx NT 3.5 system. The system is also coupled with a UV–vis spectrophotometer. Analytical separation was performed: using a Nucleodur column C18 (5 μm, 250 mm × 4.6 mm i.d.), flow rate of 1 ml min^{-1}, wavelength for detection of 254 nm, mobile phase (buffered at pH 3 with sodium phosphate buffer) with the following gradient methanol/water: 40% (methanol) at t = 0 min, then increase to 70% for 3 min then decrease to 40% until 12 min.

The LC/MS identification of photoproducts of the deaerated solution was performed on a HP 1100 LC system (Hewlett-Packard GmbH) consisting of quaternary pump, degasser, autosampler, column oven, and DAD UV detector, interfaced with a HP 1100 MSD quadrupole mass spectrometer equipped with an electrospray ionization source. The chromatographic conditions were similar to those used previously for monitoring the evolution of intermediates by HPLC/DAD. The injection volume was 20 μl. The optimized electrospray parameters were: spray voltage, 4 kV; cone voltage, 80 V; drying gas (nitrogen), 12 l min^{-1}; nebulizer pressure, 55 psig; source temperature, 350 °C. Mass spectra were acquired in both positive and negative ion modes in a mass range of m/z 80–1000. The photoproducts were identified by mass spectroscopy.

2.5. Calculation of the quantum efficiencies

The quantum efficiencies were calculated using custom application software “photon” [11], and their value have been defined using the equation:

$$\phi = \frac{dn/dt}{\sum_{\lambda_1}^{\lambda_2} I_{abs}(\lambda)\,\Delta\lambda}$$

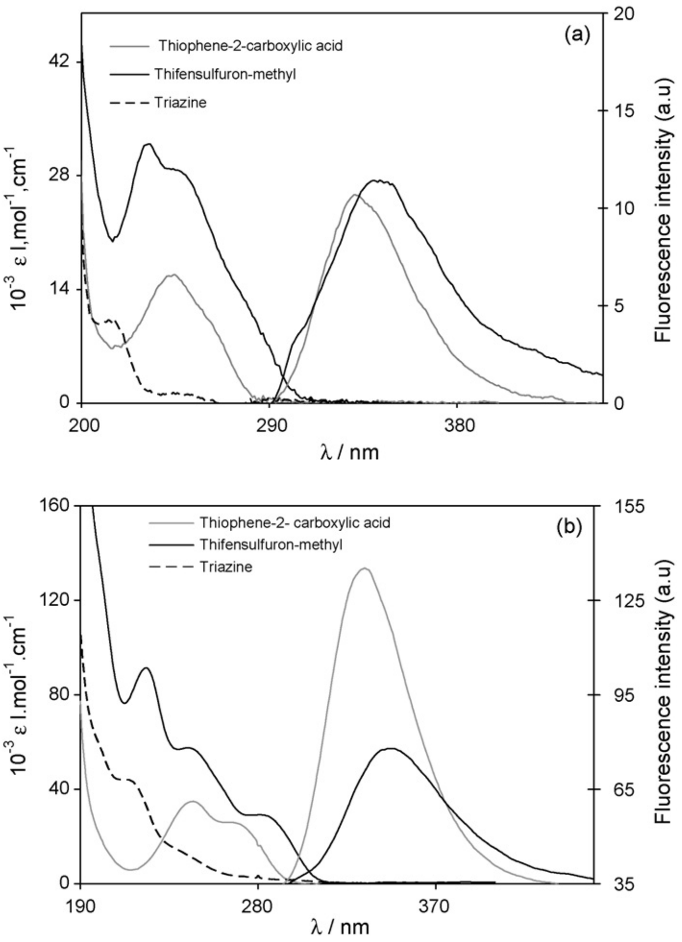


Fig. 1. Absorption and emission spectra (a) in aqueous solution in neutral medium and (b) in acid aqueous medium.

where dn/dt denotes the variation of the concentration of the substance for time t and I_{abs} is the absorbed light for the same time in the wavelength range studied.

2.6. Sample preparation and pre-concentration

During the irradiation, solution of thifensulfuron-methyl was collected at 3 and 7 h. As photoproducts were obtained at very low concentration, a pre-concentration step was dispensable to perform HPLC/MS analysis. Each sample was extracted on a solid phase extraction (SPE) cartridge isolute ENV$^+$ (50 mg, 6 ml). The solid phase was first conditioned with 3 ml of methanol and then 6 ml of deionised water. The solvent for elution is methanol.

3. Results and discussions

3.1. Photophysical properties of thifensulfuron-methyl (THM) in water

Fig. 1a presents the UV–vis absorption and fluorescence emission spectra of THM, thiophene and triazine in water at neutral pH. The UV–vis THM absorption spectrum shows several characteristic bands:

- *An intense band centred on 232 nm*. The very high molar extinction coefficient $\varepsilon_1 = 29\,600\,\mathrm{l\,mol^{-1}\,cm^{-1}}$ indicates that this band is mainly a π–π* transition. The literature [14] shows that for other sulfonylureas containing a triazinic chromophore, a characteristic intense band close to 232 nm is observed.
- *An intense band centred on 246 nm*. Comparison of the UV spectra of the pesticide in water with that of thiophene or triazine shows that this band is characteristic of the thiophene part of the herbicide. Considering its high molar extinction coefficient $\varepsilon_2 = 27\,300\,\mathrm{l\,mol^{-1}\,cm^{-1}}$, it can again be ascribed to a π–π* transition while the relatively weak shoulder centred on 280 nm is characteristic of the n–π* transition implying the non-binding electrons from the sulfur atom.

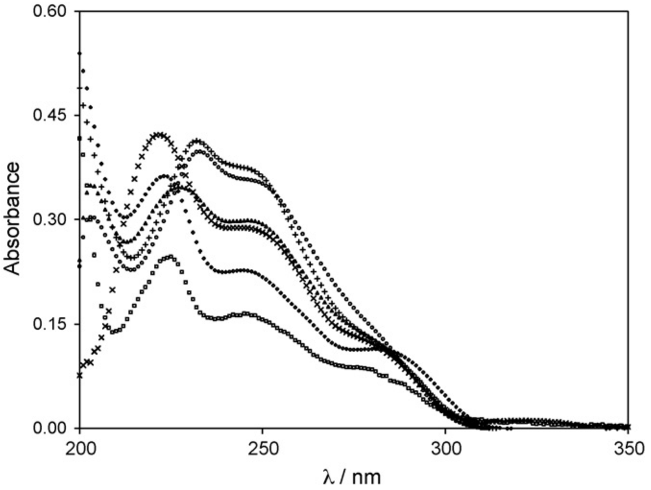


Fig. 2. Absorption spectra of thifensulfuron-methyl in different solvents: water (+), ethanol (○), methanol (△), acetonitrile (×), acid aqueous medium (◊), and hexane (□).

The fluorescence spectrum of THM in water Fig. 1a is characterized by the main band centred on 343 nm ($\lambda_{exc} = 279$ nm). Calculating the quantum efficiencies of fluorescence of thifensulfuron-methyl (given using naphthalene as reference [15]) yields a value of $0.0019 \pm 2 \times 10^{-4}$. For the fluorescence emission spectrum of thiophene, one band centred on 330 nm with a quantum efficiency of fluorescence $\varphi_F = 0.0021 \pm 2 \times 10^{-4}$ was found, which is very similar to the result obtained with THM. Since no fluorescence for triazine is observed, the result shows that the fluorescence of the THM is probably due to the thiophene part of the molecule. The deactivation of the excited singlet state by radiative way of THM as thiophene remains very low.

From Fig. 1a we can conclude that the absorption spectrum of THM represents the sum of the absorption spectra of thiophene derivatives and of the triazinic group while the emission spectrum of thiophene is not modified by the presence of the triazinic group. The absence of new specific bands and the small spectral shifts observed allow us to suppose that only weak interactions take place between the two chromophores and the sulfonylurea connecting bridge.

3.2. Photophysical properties of thifensulfuron-methyl in different media

The absorption spectra of thifensulfuron-methyl in different solvents were compared (Fig. 2) to obtain more information on the type of transition. The influence of solvent on the spectroscopic and photophysics properties of THM was interpreted using the solvatochromic Taft parameters [16]. The analysis is based on 3 parameters (see Table 1):

Table 1
Solvatochromic parameters.

Solvents	π^*	α	β
Ethanol	0.54	0.83	0.77
Methanol	0.60	0.93	0.62
Water	1.09	1.17	–
Acetonitrile	0.75	0.19	0.31
Hexane/heptane	−0.08	0.00	0.00

(1) The π^* parameter is an index of solvent polarity and polarizability.
(2) The α parameter describes the aptitude of solvent to donate a proton.
(3) The β parameter represents the acceptor character of solvent proton.

No correlation between the maximum absorption wavelength of THM and α and π^* parameters was noticed. On the other hand a correlation between the β parameter and the maximum absorption wavelength is observed and indeed a blue shift is observed when the β parameter decreases. These results can be explained by the existence of the pesticide in two forms, viz.

- *A molecular form*: this form is present in solvents with weak proton acceptor character (low β parameter). This is confirmed by the similarity of the absorption spectrum in acidified water.
- *An anionic form*: this form is present in solvents with a high proton acceptor character (high β parameter), i.e. solvents which can remove a proton from the molecule thus stabilizing it in the anionic form. The absorption spectrum in this case is identical to that obtained in aqueous medium for which the anionic form is predominant.

3.3. *Effect of pH on the thifensulfuron-methyl spectroscopic properties*

Taking into account the results concerning the solvent effect on the photophysics properties and the presence of a labile proton in the molecule, a pH effect on the spectroscopic properties was investigated.

Fig. 1b presents the UV–vis absorption and fluorescence emission spectra of THM, thiophene and triazine in acid aqueous solution. In the absorption spectrum of THM, the band centred on 280 nm is better defined in acidic than in neutral medium (Fig. 1a) and a hypsochromic shift of the band centred on 222 nm is observed when the pH decreases.

For the fluorescence spectra, a shift toward higher wavelengths (bathochromic shift) of 4 nm for thiophene, and 10 nm for thifensulfuron-methyl was observed in acidic when compared to neutral medium. Moreover, the quantum efficiency of thifensulfuron-methyl fluorescence is higher in acid ($\varphi_F = 0.011$) than in neutral medium ($\varphi_F = 0.0021$) and this is also the case for thiophene-2-carboxylic acid.

The absorption spectrum of THM as a function of pH is shown in Fig. 3a. Due to the presence of two isosbestic points (225 and 279 nm), it is possible to follow the evolution of THM absorbance as a function of pH at wavelength of 230 nm.

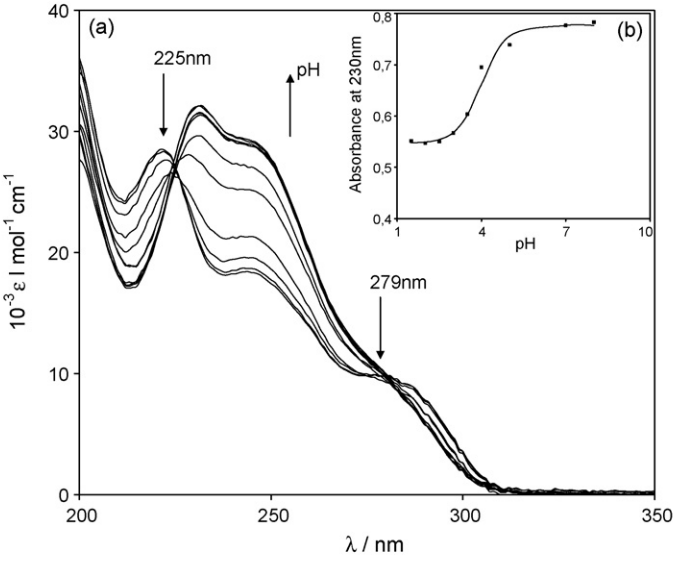


Fig. 3. (a) Absorption spectra of thifensulfuron-methyl *vs* wavelength: effect of pH. Insert: (b) variation of absorbance as a function of pH (λ = 230 nm).

The variation of the absorbance spectra as a function of pH (λ = 230 nm) makes it possible to determine the value of the apparent acid–base equilibrium constant in the ground state Fig. 3b. Adjustment of the curve by the following equation gives the pK_a value [17]:

$$\mathrm{ABS} = \frac{(\varepsilon_{\mathrm{SH}} - \varepsilon_{\mathrm{S^-}})C_0 \times 10^{-\mathrm{p}K_a}}{10^{-\mathrm{p}K_a} + 10^{-\mathrm{pH}}} + \varepsilon_{\mathrm{SH}}C_0$$

where C_0 is the initial concentration of thifensulfuron-methyl, $\varepsilon_{\mathrm{SH}}$ (21 900 l mol^{-1} cm^{-1}) and $\varepsilon_{\mathrm{S^-}}$ (31 300 l mol^{-1} cm^{-1}) are the molar extinction coefficients of the molecular and anionic forms respectively at 230 nm and ABS represents the absorbance at λ = 230 nm of a solution of thifensulfuron-methyl for each pH. The pK_a value of acid–base equilibrium (Scheme 1) determined in this condition is 4.0. Similar values were obtained for other sulfonylureas [5].

Although the curves exhibit two isosbestic points, only one pK_a value has been determined meaning that the deprotonation of the second proton does not occur within the pH range studied (pH 2–10).

The variation of the fluorescence signal as a function of pH was also studied. From Fig. 4a, it is shown that the emission intensity decreases when the pH increases. The evolution of the emission intensity as a function of pH allows us to determine the value of the acid–base equilibrium constant (cf. Fig. 4b). From this figure we can see that a similar value is obtained compared to the first method which leads us to suppose that the deactivation of the singlet state (k_d) occurs faster than the deprotonation (k'_1) (see Scheme 2).

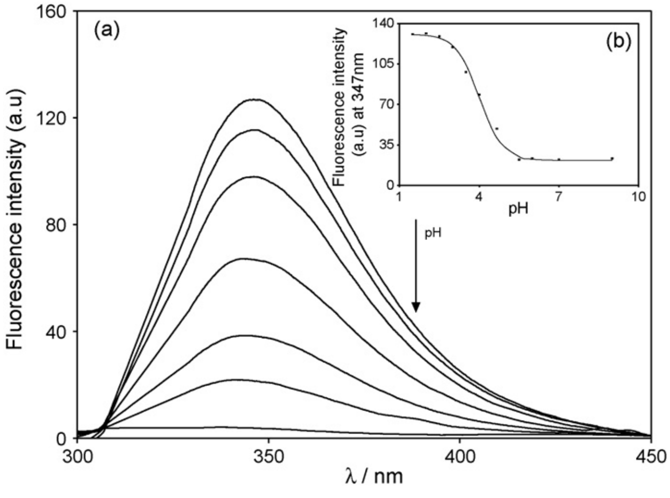
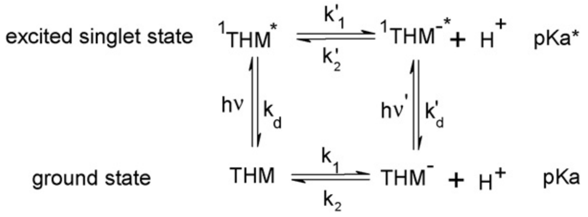


Fig. 4. (a) Emission spectra of thifensulfuron-methyl *vs* wavelength: effect of pH. Insert: (b) variation of fluorescence intensity as a function of pH (λ_{exc} = 279 nm; λ_{em} = 347 nm).



Scheme 2. Schematic representation of proton transfer for both the electronic ground and excited (S1) states in aqueous solution.

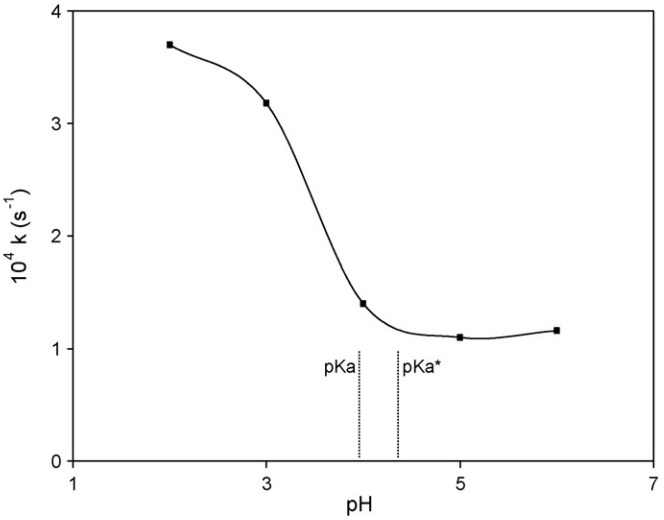


Fig. 5. Variation of photolysis rate constant k (s^{-1}) of thifensulfuron-methyl *vs* pH.

In this case the acid–base equilibrium constant of the excited singlet state was calculated using the Forster cycle [18]:

$$\mathrm{p}K_a^* = \mathrm{p}K_a + \frac{N_A hc}{2.303RT}(\bar{\nu}_{S^-} - \bar{\nu}_{SH})$$

where T is the absolute temperature, h is Planck's constant, N_A is Avogadro's number, c is the light speed, and $\bar{\nu}_{SH}$ and $\bar{\nu}_{S^-}$ are the frequency of neutral and anionic species respectively (cm^{-1}) ($\bar{\nu}_{SH} = 31\,645,56\,cm^{-1}$ and $\bar{\nu}_{S^-} = 31\,948,88\,cm^{-1}$).

Because of the absence of mirror-image symmetry between the absorption and emission spectra, the energy of the excited singlet state was given by the intersection between the emission and standardized absorption spectra ($E_{SH} = 382.8\,kJ\,mol^{-1}$ and $E_{S^-} = 388.4\,kJ\,mol^{-1}$ respectively for molecular and anionic form). In this condition a pK_a^* value of 4.4 was calculated meaning that thifensulfuron-methyl becomes less acid in the excited singlet state.

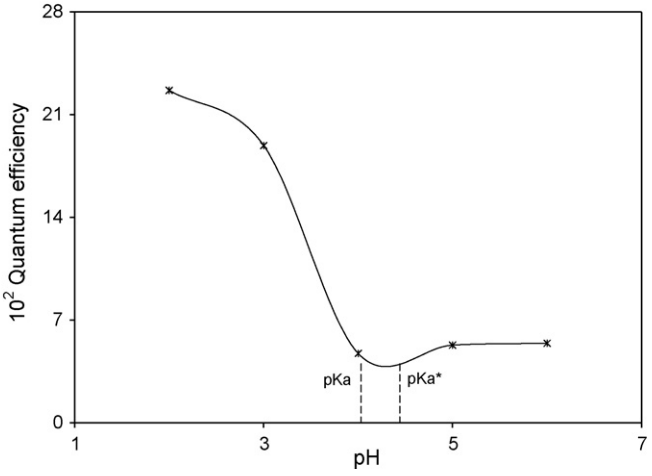


Fig. 6. Variation of quantum efficiency of thifensulfuron-methyl *vs* pH.

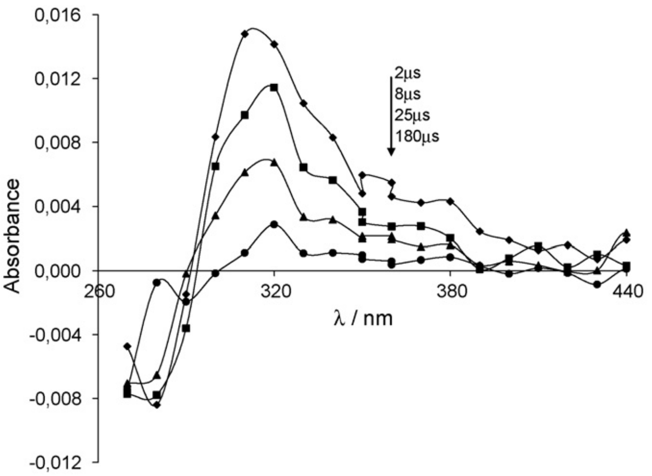


Fig. 7. Transient absorption spectra obtained by laser flash photolysis of thifensulfuron-methyl at pH 7 in deaerated solution.

3.4. Kinetic studies of the photodegradation

3.4.1. Influence of pH

The disappearance of THM obeys an apparent first-order kinetics. Fig. 5 shows the variation of the rate constant k of thifensulfuron-methyl as a function of pH. From this figure it appears that the photolysis rate constant is faster for the lowest pH when THM is in its neutral form. This result might be explained by a better wavelength match between the absorption and lamp emission spectra for the molecular form than for the anionic form.

The quantum efficiencies of photodegradation according to the pH were also plotted. Here too (Fig. 6), the results clearly show a better efficiency of the degradation at acidic pH since the quantum efficiency of the molecular form is at least three times higher than

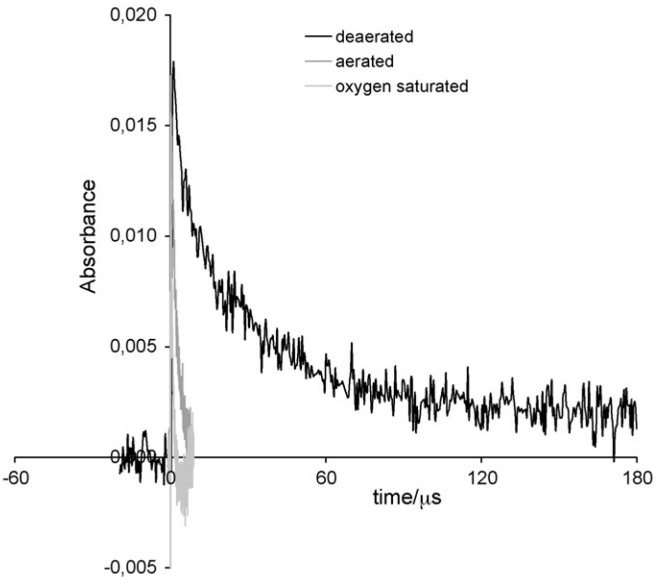


Fig. 8. Decay of transient absorption monitored at 320 nm of thifensulfuron-methyl at pH 7 as a function of oxygen concentration.

Table 2
Photodegradation kinetic parameters: rate constant k (s^{-1}), half-life $t_{1/2}$ (h^{-1}), observed rate constant k_{obs} (μs^{-1}) and lifetimes of triplet state τ (μs) of thifensulfuron-methyl under different oxygen concentration.

Medium	k (s^{-1})	$t_{1/2}$ (h)	R^2	ϕ	k_{obs} (μs^{-1})	$\tau = 1/k_{obs}$ (μs)
Deaerated	1.48×10^{-4}	1.3	0.9788	1.06×10^{-3}	0.0413	24.2
Aerated	1.13×10^{-4}	1.7	0.9734	6.24×10^{-4}	0.469	2.13
Oxygen saturated	0.60×10^{-4}	3.2	0.9407	4.56×10^{-4}	1.43	0.69

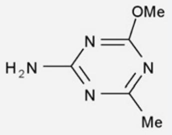
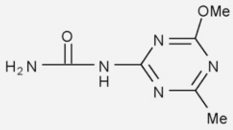
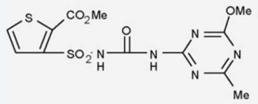
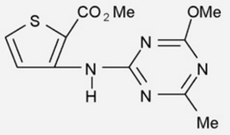
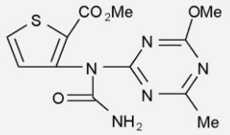
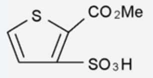
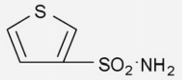
for the anionic form. These results show also that the photodegradation of the molecular form is pH dependent unlike in the case of the ionic form.

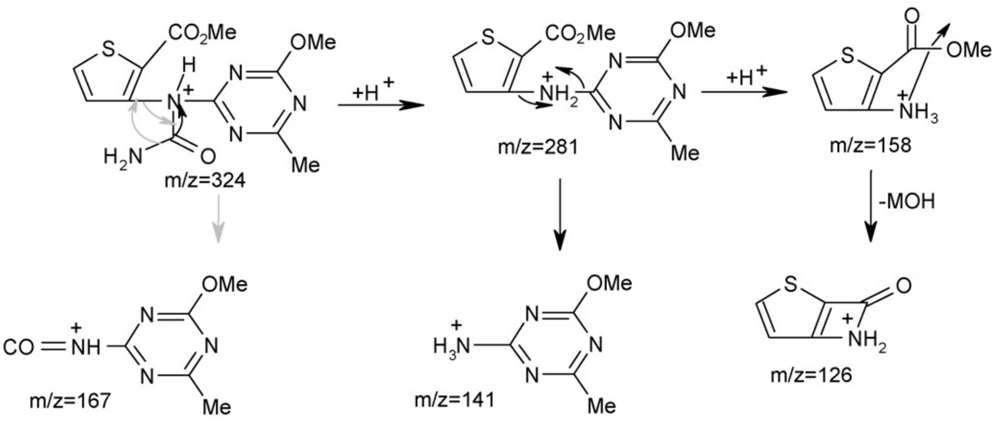
3.4.2. Laser flash photolysis studies

To establish the mechanism and kinetic details of THM degradation, a nanosecond laser flash photolysis technique was employed.

As shown in Fig. 7, the transient absorption spectrum obtained in deaerated aqueous solution presents a large band with a maximum at 320 nm and a shoulder at 370 nm. The intensity of this band decreases uniformly with time without formation of any significant band. Thus the transient absorption spectrum can be attributed to the T–T absorption without any transient species.

Table 3
HPLC retention times (Rt), m/z values from mass spectrometry, and UV data of thifensulfuron-methyl photoproducts.

Compound	Rt (min)	Mass (m/z) E_{S^-}	UV data, λ_{max} (nm)	Medium
 **T_1=AMMT**	3.8	139 (M−H), 141 (M+H)	195 nm219 nm245 nm (shoulder)	Deaerated/aerated
 **T_2**	7.5	184 (M+H), 167 and 141	195 nm223 nm245 nm (shoulder)	Deaerated/aerated
No identified **T_3**	10.2			Deaerated
 **T_4=TFSM**	18.3	410 (M+Na), 388 (M+H), 205, 184, 167 and 141	220 nm 232 nm 245 nm 280 nm	Deaerated/aerated
 **T_5/T_7**	21.8/23.2	281 (M+H), 249, 141	315 nm	Deaerated
 **T_6**	22.4	346 (M+Na), 324 (M+H), 292 (M–OMe)	300 nm	Deaerated
 **T_8**	1.7	221 (M−H), 163 (M–CO_2Me), 141 (M–SO_3H)	230 nm 260 nm	Aerated
 **T_9**	9.0	162 (M−H)	230 nm 270 nm	Aerated

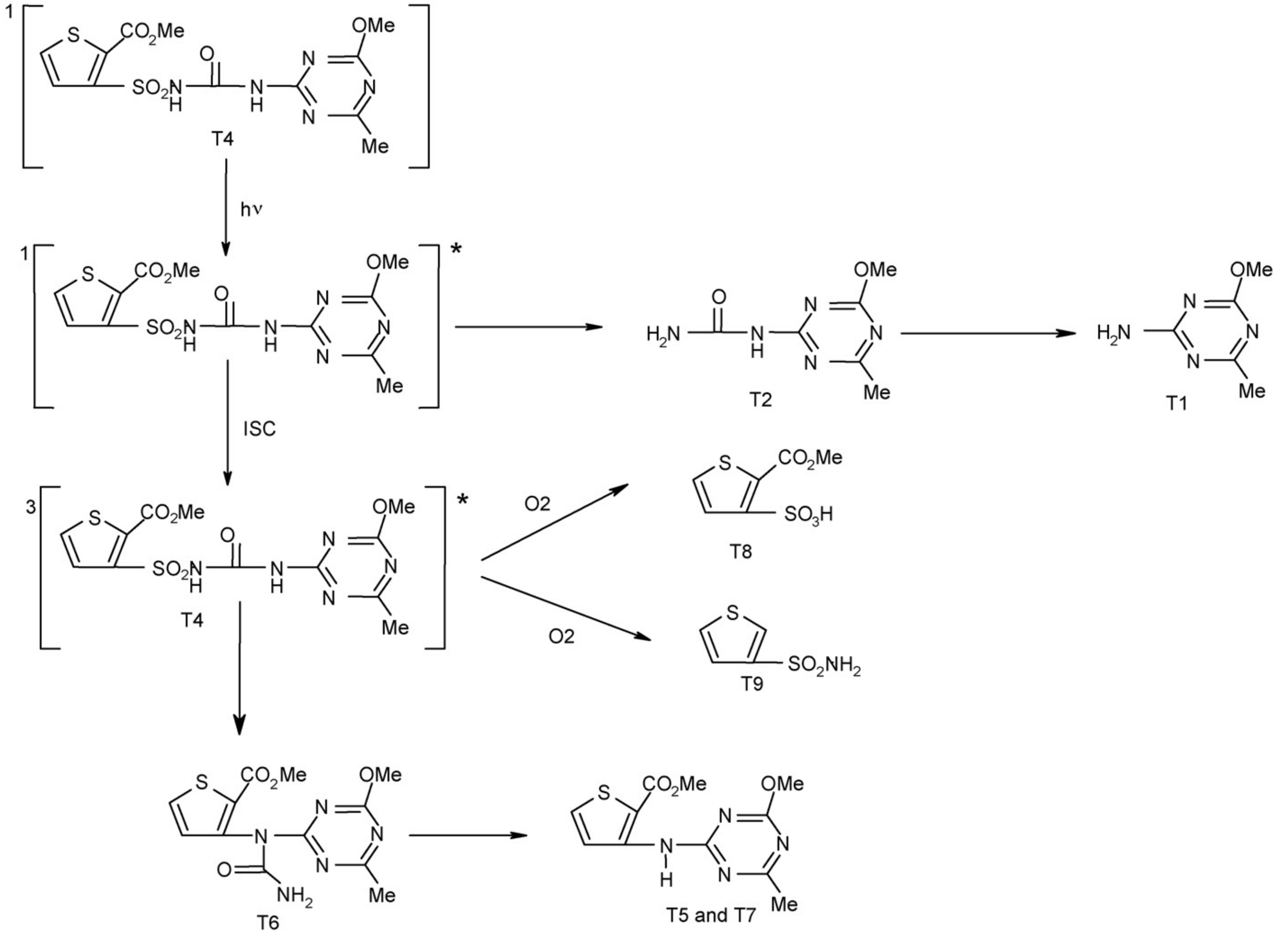


Scheme 3. Main likely mass fragmentations of both photoproducts T_5 and T_6.

Laser flash photolysis experiments were carried out in deoxygenated, aerated and oxygen saturated conditions (see Fig. 8). The oxygen quenching rate constant kinetic of triplet state was determined with the Stern–Volmer equation [19].

$$-\frac{d[T]}{dt} = (k_1 + k_2[O_2])[T] = k_{obs}[T]$$

where k_1 and k_2 represent respectively the rate constant for the triplet decay in the absence of oxygen and the second order rate constant for the quenching process. By plotting the triplet rate constant observed k_{obs} (Table 2) as a function of oxygen concentration, the quenching rate constant k_2 is deduced from the slope of the curve. A quenching process by molecular oxygen was observed as shown by the value of the rate constant $k_2 = 9.64 \times 10^8\ mol^{-1}\,l\,s^{-1}$, indicating that the quenching rate is diffusion-controlled. The effect of oxygen on the kinetic disappearance of the transient confirms the formation of a triplet state. The deactivation curve of the triplet state fitted well with exponential kinetics with a lifetime of 0.69 μs



Scheme 4. Hypothetical photodegradation pathway of thifensulfuron-methyl in aqueous solution (ISC: InterSystem Crossing).

in oxygen saturated conditions and 2.13 μs in aerated solution but no other transient species were detected in these experimental conditions. This result leads us to assume that the energy transfer between the triplet excited state of thifensulfuron-methyl and molecular oxygen is highly efficient. This energy transfer could generate reactive species such as singlet oxygen and superoxide anions which could be involved in the photodegradation processes.

Consequently, the photoproducts quantitatively formed in deaerated medium could be produced from the triplet excited state.

3.5. *Effect of oxygen concentration*

The kinetic rate constant was studied as a function of oxygen concentration in aqueous solution in order to obtain a better understanding of the thifensulfuron-methyl photodegradation mechanism.

The observed rate constants and half-lives, calculated by ln 2/k, in aqueous solution, are given in Table 2.

The study of the effect of oxygen concentration showed that the initial rate of thifensulfuron-methyl disappearance decreased with increasing oxygen concentration thus showing that the photodegradation of thifensulfuron-methyl is inhibited by oxygen.

As a result, the triplet state plays the main role in the photodegradation of thifensulfuron-methyl.

In order to determine whether the triplet state plays an important role in the photodegradation, the Stern–Volmer equation [19] was employed:

$$\frac{\phi_0}{\phi} = k_2\tau_0[\mathrm{O}_2] + 1$$

where ϕ_0 and ϕ represent, respectively, the quantum yield in the absence and in the presence of oxygen, and τ_0 is the lifetime of the triplet state in the absence of oxygen. By plotting the ϕ_0/ϕ *vs* oxygen concentration, we obtain a straight line, the value of $k_2\tau_0 = 1011.1\,\mathrm{mol}^{-1}\,\mathrm{l}$ is deduced from the slope of the curve. τ_0 has been determined by laser flash photolysis ($\tau_0 = 24.2\,\mu\mathrm{s}$). Under these conditions we determined that the quenching rate constant k_2 is equal to $0.41 \times 10^8\,\mathrm{mol}^{-1}\,\mathrm{l}\,\mathrm{s}^{-1}$. Since this value is lower than the calculated one ($k_2 = 9.64 \times 10^8\,\mathrm{mol}^{-1}\,\mathrm{l}\,\mathrm{s}^{-1}$), we can conclude that in addition to the triplet state, the singlet excited state also plays a role in the photodegradation mechanism of the pesticide.

3.6. *Identification of the photoproducts*

In order to avoid hydrolysis, degradation of THM and identification of photoproducts were carried out at pH 7. Using LC/DAD, two kinds of photoproducts were detected, viz. those containing the triazinic group for which the maximum of absorbance have wavelengths lower than 250 nm and those containing the thiophene group which absorb at wavelengths higher than 250 nm. The formation of these photoproducts can be explained as a result of the cleavage within the sulfonylurea bridge.

The use of LC/DAD and LC/MS, as well as LC/MS/MS in negative and positive ions allowed us to suggest different photoproducts (Table 3).

3.6.1. *Deaerated medium*

Photoproduct T_1: This product quickly eluted shows a UV spectrum typical of a triazine derivative. Mass spectroscopy revealed quasi-molecular ions at $m/z = 140.9$ (M+H)$^+$. The product was identified by direct comparison of its UV, MS and chromatographic data with those of standard product 2-amino-4-methoxy-6-methyl-1,3,5-triazine (AMMT).

Photoproduct T_2: The UV spectrum shows that this product also contains a triazine derivative and this conclusion was corroborated by the mass spectrometric data which revealed characteristic fragments of the triazine derivative at $m/z = 167$ and 140.9 as reported [9,11,20]. Moreover, quasi-molecular ions in positive mode at $m/z = 184$ (M+H)$^+$ as well as the literature data allowed us to propose a structure for T2 (cf. Table 3).

It has been found that T_1 and T_2 are stable with regard to oxygen concentration and it is likely that the mechanism involves the first excited singlet state.

Product T_4: T_4 was identified as being THM using the molecule as standard. The LC–MS/MS main data in positive mode of THM are $m/z = 410$, 388, 205, 167, 141 corresponding to (M+Na), (M+H), thiophene and triazine derivatives respectively.

Photoproduct T_5: The mass spectrum in positive mode of this product presents three characteristics peaks, the first is the quasi-molecular ion peak at $m/z = 281$ (M+H), the second is a fragment ion peak at $m/z = 249$ corresponding to (M–OMe) while the third one, is a fragment ion peak at $m/z = 141$ corresponding to triazine derivative.

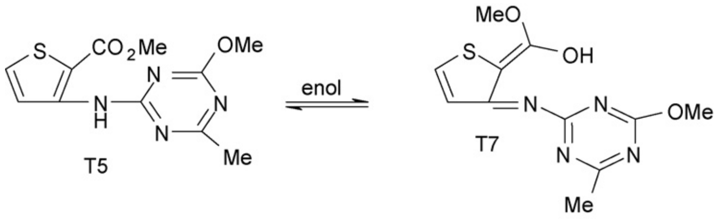
The main fragment ions of this photoproduct is shown in Scheme 3.

A similar compound was also found by Schneiders et al. [21,22]. It is the major hydrolysis product of rimsulfuron at pH 7 and at pH 9.

Photoproduct T_6: The mass spectrum of APCI in positive mode of T_6 showed an abundant peak at $m/z = 346$ (M+Na), a quasi-molecular ion peak at $m/z = 324$ (M+H), and a fragment ion peak at $m/z = 292$ corresponding to (M–OMe). The absorption UV spectrum of this product presents a large band at 300 nm due to an extended conjugated system and a greater dipole moment between the triazine and thiophene parts, that could explain the high absorption observed at 300 nm. We have also observed other fragment ion peaks with mass–mass spectrometric in positive mode at $m/z = 281$, 167, 158, 141 and 126. The main fragmentation of T_6 is shown in Scheme 3. This process involves concerted elimination of SO_2 through contraction of sulfonylurea bridge to generate T_6.

A similar product was identified as primary hydrolysis product of rimsulfuron at pH 5 by Schneiders et al. [21,22]. Elimination of SO_2 was also observed as photoproduct of the tribenuron-methyl by Bhattacharjee and Dureja [23] and as photolysis product of the triflusulfuron-methyl by Chafik [24].

Photoproduct T_7: The mass spectrum of APCI in positive mode of this product, was similar to that of T_5: an abundant peak at $m/z = 281$ (M+H) and a fragment ion peak at $m/z = 249$ corresponding to (M–OMe). The absorption UV spectrum of this product presents a high absorption at about 315 nm. As a conclusion, T_7 and T_5 could be isomeric enol.



Since photoproducts T_5, T_6 and T_7 were quantitatively generated in deaerated medium we can conclude that they are produced from triplet excited state.

3.6.2. *Aerated medium*

Other photoproducts in aerated medium were identified with mass–mass spectrometry in negative mode.

Photoproduct T_8: The mass–mass spectrum of T_8 presents a quasi-molecular ion peak at $m/z = 221$ (M−H), and a fragment ion peaks at $m/z = 163$ and 141 corresponding to (M–CO_2Me) and (M–SO_3H) respectively. It was tentatively identified as being $C_6H_6S_2O_5$.

Photoproduct T_9: The mass–mass spectrum of T_9 presents a quasi-molecular ion peak at $m/z = 162$ (M−H) which was tentatively identified as being sulfonamid thiophene.

Scheme 4 represents photoproducts obtained from the singlet and triplet excited states and summarizes the hypothetical photodegradation pathways of THF in aqueous solution.

Since photoproducts T_8 and T_9 were quantitatively generated in aerated medium, we can suppose that the mechanism required simultaneously both triplet excited state and oxygen molecules.

4. Conclusion

In this work the photophysical properties and photodegradation of thifensulfuron-methyl were investigated in different media. The results clearly show that the photodegradation process is more efficient at $pH < pK_a(S_0)$ and that the protonated form is more easily photodegraded than the ionic form. The photolysis mechanism involves both first excited singlet and first triplet states but the latter appears to be more widely implicated in the photodegradation mechanism. The main photoproducts obtained derive from the elimination of SO_2 and the contraction of the sulfonylurea bridge.

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