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Abiotic Degradation of Iodosulfuron-methyl-ester in Aqueous Solution

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The abiotic degradation of iodosulfuron-methyl-ester was investigated under both alkaline and acidic pH conditions in the dark, and results showed it to be a rather stable molecule in neutral or slightly alkaline environments. Photochemical reactions were studied using a high-pressure mercury arc lamp, and results showed that direct phototransformation is possible under normal environmental conditions ($\lambda > 290$ nm). High-performance liquid chromatography (HPLC-UV and HPLC-MS) analyses were used to identify the degradates and to study the kinetics of photodecomposition and hydrolysis. Five main products of iodosulfuron-methyl-ester degradation were tentatively identified, and one of them (4-methoxy-6-methyl-1,3,5-triazin-2-amine) was confirmed using an authentic standard. Among the phototransformation mechanisms, photosubstitution of the iodide atom by a hydroxyl group, photodissociation of the N–S bond, and photoassisted hydrolysis were observed. The quantum efficiencies (multiwavelength quantum yield) of the photodegradation under different conditions were determined, and values of 0.054 ± 0.02 (pH 9.6), 0.08 ± 0.02 (pH 7), and 0.044 ± 0.008 (pH 5.3) were obtained.

INTRODUCTION

Sulfonylurea herbicides are now being widely used in agriculture because of their low application rates (2–75 g/ha), good crop selectivity, and very low animal toxicity (*1*). While numerous papers have dealt with the chemical hydrolysis of sulfonylureas because it is claimed to represent the main abiotic degradation pathway (*2–4*), some recent papers indicate that photodegradation is an alternative means to chemical hydrolysis (*5–7*). Indeed, the chemical degradation rates of sulfonylureas are pH-dependent, and generally, these compounds are more susceptible to chemical hydrolysis at acidic rather than at neutral or weakly basic pH values (*8*). We can therefore envision photodegradation becoming an important pathway at neutral pH.

Sulfonylureas can be considered as bichromophoric molecules with the general formula $X-SO_2-NH_2-CO-NH-Y$ where X is an aromatic or a heterocyclic ring (benzene, pyridine, thiphene) connected by a sulfonylurea bridge to Y, which is an N-heterocycle (triazine or pyrimidine). The mechanism of photodegradation involves three principal competitive pathways viz. (i) photoassisted hydrolysis of the sulfonylurea bridge, (ii) photodissociation of the C–S bond, and (iii) photodissociation of the N–S bond. Photodissociation of either N–S or C–S bonds appears to depend mainly on the substitutent borne by the aromatic ring but can also depend on the wavelength or solvent used during photodegradation (*9*). Chovelon et al. studied the photodegradation of cinosulfuron and triasulfuron in aqueous buffered solutions at wavelengths >290 nm and observed the formation of the sulfonyl derivative $HO_3S-NH-CO-NH-$triazine (C–S cleavage), the urea $NH_2-CO-NH-$triazine (N–S cleavage), and the amine NH_2-triazine (photo-assisted hydrolysis) and showed that $HO_3S-NH-CO-NH-$triazine is the main photoproduct, which was attributed to the oxygen group attached to the benzene ring weakening the C–S bond (*5, 10*). On the other hand, Chovelon et al. only observed this for an N–S cleavage for triasulfuron in acetonitrile solution (*9*). In a recent work on the photodegradation of chlorsulfuron, Yang et al. mainly observed an N–S cleavage of the sulfonyl-urea bridge (*11*), which was interpreted by the presence of the

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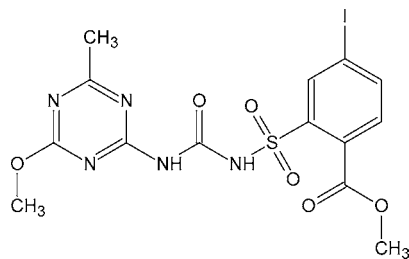|| SCA Service Central D'analyse.

Figure 1. Iodosulfuron-methyl-ester chemical structure.

ortho chloro group attached to the benzene ring reinforcing the photochemical stability of the C−S bond. The same conclusion was drawn by Morrica et al. (*12*) concerning the photodegradation of imazosulfuron.

Iodosulfuron-methyl-ester (referred to from here as iodosulfuron) is a triazinyl sulfonylurea herbicide (**Figure 1**) bearing both an ester and an iodide group on the benzene ring. It is commercially available as Husar, Chekker, Sekator, Hoestar Super, and Tribute for early postemergence control of annual grass and broadleaved weeds in cereal and applied at 5−35 g active ingredient per hectare (*13*). Like other sulfonylureas, iodosulfuron is an inhibitor of acetolactate synthase.

Similar to other sulfonylureas, the physical and chemical behaviors of iodosulfuron are pH-dependent. However, no study concerning its abiotic degradation has been published.

These studies had two main objectives viz. (i) to describe the photochemical and chemical behaviors of iodosulfuron at a range of aqueous pH levels and (ii) to identify the main decomposition products from photodecomposition or hydrolysis in the dark.

MATERIALS AND METHODS

Chemicals. The iodosulfuron-methyl-ester (methyl 4-iodo-2-[({[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl}amino)sulfonyl]-benzoate] was a gift from Bayer Crop Science. Methanol used for high-performance liquid chromatography (HPLC) analysis (HPLC grade) was purchased from Merck. The water used for the liquid chromatography mobile phase and buffer preparation was purified with a Millipore water system (Milli Q 50 system). 4-Methoxy-6-methyl-1,3,5-triazin-2-amine was purchased from Sigma Aldrich.

The solubility of iodosulfuron in water is 20 mg L^{-1} at pH 4, 25 g L^{-1} at pH 7, and 65 g L^{-1} at pH 9. At pH 7, the chemical degradation of iodosulfuron is slow (half-life $t_{1/2} > 365$ days) (*14*).

Spectrometer Apparatus. The UV−visible absorption and fluorescence spectra were recorded using a double-beam Uvikon 930 Spectrophotometer (Kontron Instruments), and an SFM 25 Spectrofluorometer (Kontron Instruments), respectively.

Photodegradation Equipment. Two photochemical reactors with HPK 125 W arc lamps were used, viz. a cylindrical vessel made of Pyrex for $\lambda \geq 290$ nm and another with a quartz window for more energetic wavelengths from $\lambda \geq 230$ nm. Experiments were carried out at 19 °C.

Kinetic Experiments. Twenty-five milliliters of phosphate buffer solutions of iodosulfuron (C = 4.9×10^{-5} mol L^{-1}) adjusted to different pH values using NaOH or H_3PO_4 were irradiated in the reactors. At selected time intervals, samples were collected and analyzed directly using HPLC. The same procedure was used for hydrolysis experiments, but samples were kept in the dark.

Determination of the Kinetic Partial Order with Respect to Protons. The hydrolysis degradation rate of iodosulfuron with respect to protons can be evaluated by the following expression where r is the hydrolysis degradation rate of iodosulfuron

$$r = k \text{ [iodosulfuron]}$$

with $k = k_A \text{ } [H^+]^a + k_B \text{ } [OH^-]^b + k_N'$ where k_A, k_B, and k_N' represent the rate constants for acid, basic, and neutral forms, respectively, and
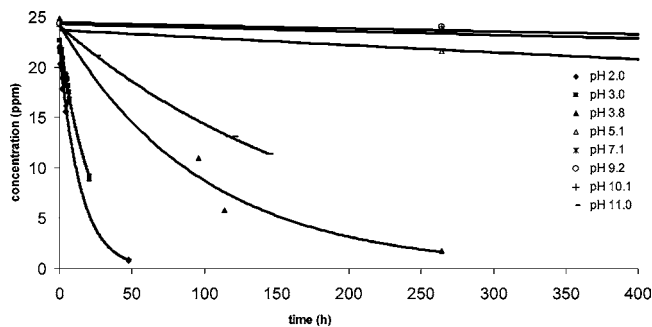

Figure 2. Kinetics of disappearance of iodosulfuron-methyl-ester in aqueous solutions at different pH values.

a and *b* represent the kinetic partial orders with respect to proton and hydroxide ions. Considering only acid pH (pH < 7), k_B and k_N' can be neglected. Consequently, k can be rewritten

$$k = k_A \text{ } [H^+]^a$$

and

$$\log k = \log k_A + a \log [H^+]$$

hence

$$\log k = \log k_A - a \text{ pH}$$

From this equation, the kinetic partial order with respect to protons, a, can be determined from the slope of log k as a function of pH.

Quantum Efficiencies. The polychromatic quantum efficiency values (Φ) were calculated using a custom application software, "photon" (Kontron instrument). Photonic incident flux was measured by chemical actinometry using uranyl oxalate from Fluka.

Two values were established, viz. quartz quantum efficiency [Φ_{quartz}] and Pyrex quantum efficiency [Φ_{Pyrex}], to predict the influence of wavelength on the iodosulfuron photodegradation.

HPLC-UV Analysis. HPLC analyses were conducted using a Varian 9010 instrument equipped with a UV−visible detector. The column used was a Hypersil BDS C_{18} column (5 μm, 125 mm × 4 mm) eluted with a gradient of methanol (A) and water (B) (pH was set up at 2.70 with phosphoric acid). The gradient used was 95% (B) at t = 0, to 45% (B) at t = 30 min, and 45% (B) during 7 min. The flow rate was set up at 1 mL min^{-1}, and the injection volume was 20 μL.

Photoproduct Identification. As photoproducts were obtained at very low concentrations, a preconcentration step was required to perform HPLC-MS analysis. In this context, 6 mL of each sample was extracted on a solid phase extraction cartridge Isolute ENV$^+$ (International Sorbent Technology) packed with 25 mg of styrene−divinylbenzene copolymer. The solid phase was first conditioned with 4 mL of methanol and then 6 mL of deionized water. The solution was then eluted with 500 μL of methanol and analyzed by HPLC-MS.

HPLC-MS Analysis. The identification of photoproducts was performed using HPLC-MS apparatus (Hewlett-Packard hp 1100 series LC-MSD) equipped with the same column used for kinetic studies (thermostated at 40 °C) and under the same operating conditions. The injection volume was 20 μL. MS detection was performed using an electrospray ionization (ESI) in the positive mode. Ionization conditions of ESI analysis were as follows: capillary potential, 300 V; N_2 flow, 13 L min^{-1}; and pressure, 55 psig.

RESULTS AND DISCUSSION

Kinetic Study of the Hydrolysis of Iodosulfuron. Figure 2 shows the variation of iodosulfuron concentrations at different pH values as a function of time. At all pH values, iodosulfuron degradation follows apparent first-order kinetics since the curves $\ln(C/C_0)$ vs time give a straight line. The rate constants (k) were calculated from the slopes of the curves, and **Figure 3** presents

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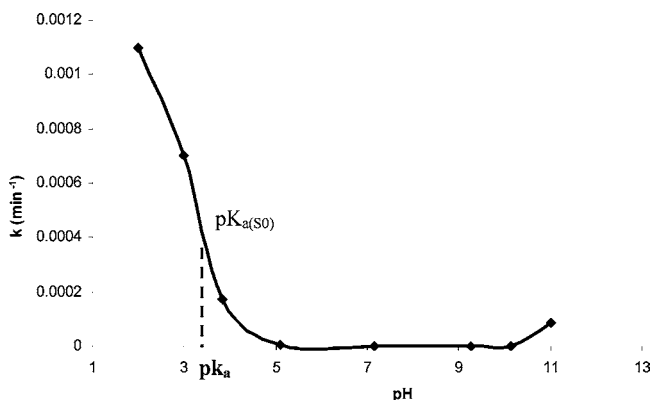
Figure 3. Evolution of the constant rate (k) of iodosulfuron-methyl-ester degradation vs pH values (kinetic order = 1).
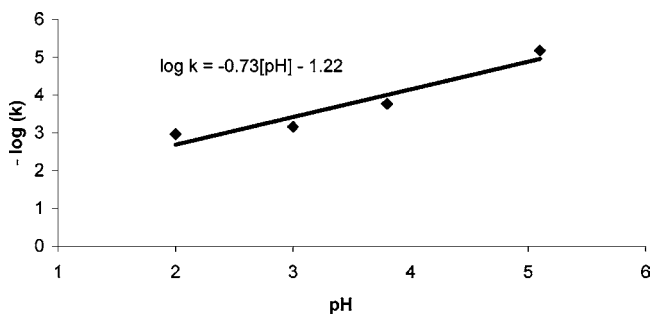
Figure 4. Evoluation of the logarithm of the constant rate (k) of iodosulfuron-methyl-ester degradation vs pH values.

the evolution of the rate constant (k) of hydrolysis vs pH. Just as in the case of other sulfonylureas, the influence of pH is particularly significant in acidic and alkaline media (*8*).

The determination of the kinetic partial order with respect to protons determined according to the procedure described in the Materials and Methods gives a value of 0.7 (**Figure 4**), which implies that the kinetic partial order for the hydrolysis reaction is close to one with respect to proton ions. Because at acidic pH and to a lesser extent at basic pH the hydrolysis degradation rates become large, the photodegradation studies will be performed at neutral pH.

Identification of the Degradation Product. The extracted solutions were analyzed by HPLC-MS, and **Table 1** (products **a**–**d**) gives their masses, relative fragmentations, retention times, and proposed molecular structures. In a recent study (*15*), it has been reported that in acid solutions the main reaction that occurs, corresponding to a breakdown of the sulfonylurea bridge, gives sulfonamide and *s*-triazine derivatives as byproducts. In basic medium, the mechanism differs as nucleophilic substitution of the methoxy group of the *s*-triazine derivatives by a hydroxyl group occurs. In our case and in acidic solution, we did obtain as the main product of degradation an s-triazine derivative (4-methoxy-6-methyl-1,3,5-triazin-2-amine) (product **a** confirmed by an authentic standard), but it was impossible to see the sulfonamide derivative. Products **c** and **d** were also obtained at low pH. Product **d** comes from a hydrolysis of the ester group to a carboxylic acid group while product **c** was obtained according to a procedure proposed by Sabadie et al. (*16*) for chlorsulfuron, another herbicide of the sulfonylurea family. Product **c** results from an acid-catalyzed hydrolytic breakdown of the triazine ring.

Photophysical Properties of Iodosulfuron-methyl-ester. **Figure 5** shows the absorption spectra of iodosulfuron in aqueous medium at different pH values (from 2.1 to 8.2). Iodosulfuron UV–vis spectra at pH 7 show three maxima, the

first one close to 198 nm with ϵ = 33313 L mol^{-1} cm^{-1}, the second close to 234 nm with ϵ = 31669 L mol^{-1} cm^{-1}, and the last at λ = 288 nm with ϵ = 1595 L mol^{-1} cm^{-1}.

The pH curves display a measurable absorption tail up to 320 nm. According to an EC (94/37/CE) directive, photodegradation must be taken into account if the molar extinction coefficient is ≥ 10 L mol^{-1} cm^{-1} for $\lambda \geq 290$ nm, and this is pertinent in our case with ϵ = 1416 L mol^{-1} cm^{-1} at λ = 290 nm (pH 7).

The inset of **Figure 5** also shows the variation of the molar extinction coefficient (ϵ_λ) of iodosulfuron as a function of pH of the medium at λ = 250 nm. An increase in ϵ_{250nm} for pH ranging from 2 to 5 is observed while at higher pH the curve levels off. On the other hand, the absorption bands at λ = 205 nm do not change significantly with pH. In addition, the UV spectra clearly present at least one isobestic point at λ = 226 nm within the pH region studied, reflecting the presence of one acid–base equilibrium.

To precisely determine the ground state pK_a value, different methods were used. First, the absorbance as a function of pH was plotted and a pK_a value of approximately 3 was found. A second method was to calculate the pK_a value according to the following standard formula (eq 1)

$$pK_a(S_0) = pH - \log \frac{Abs_{AH} - Abs}{Abs - Abs_{A^-}} \tag{1}$$

in which Abs represents the absorbance of a solution, Abs$_{AH}$ represents the absorbance of the molecular form, and Abs$_A$ represents the absorbance of the anionic form. According to this formula, a value of pK_a = 3.3 was obtained. In this context, it is reasonable to consider 3.3 as a value for the p$K_{a(S_0)}$; it is interesting to note that such a value corresponds to the inflection point of **Figure 3**. For a pH higher than 3.3, iodosulfuron is in its ionic form while at lower pH, iodosulfuron is in its molecular form.

The absorption and fluorescence (λ_{exc} = 277 nm) spectra of iodosulfuron in water buffered at pH 7 are presented in **Figure 6** after normalization to 100, so as to calculate the energy of singlet excited states. The fluorescence spectrum shows a band with a maximum at λ = 303 nm. In these conditions, the intersection of the absorption and fluorescence spectra (at λ = 289 nm) gives a wavelength whose corresponding energy is that of the first excited state, S$_1$ (*17*). Under these conditions, the energy of the first excited singlet state is calculated to be 414 kJ mol^{-1} at pH 7. As the acid–base behavior of most organic molecules can be affected by electronic excitation, the p$K_{a(S_1)}$ value for the first singlet excited state can be estimated using the following relation derived from the Förster formula

$$pK_A(S_1) = pK_a(S_0) + \frac{0.625}{T}\Delta\bar{v} \tag{2}$$

where T is the absolute temperature and $\Delta\bar{v}$ is the difference (cm^{-1}) between the frequencies of maximum emission in anionic and molecular forms. To determine the p$K_{a(S_1)}$ of iodosulfuron, the fluorescence spectra were taken at both low and high pH (pH 2 and 9, respectively) so as to be certain that both molecular and anionic forms were present. From these data, the p$K_{a(S_1)}$ value obtained from eq 2 is 5.3, indicating that iodosulfuron becomes less acidic upon excitation and that the most reactive form of sulfonylurea (neutral form) will be present under a wider range of pH.

Study of the Photodegradation of Iodosulfuron. To estimate the photochemical stability of iodosulfuron in aqueous
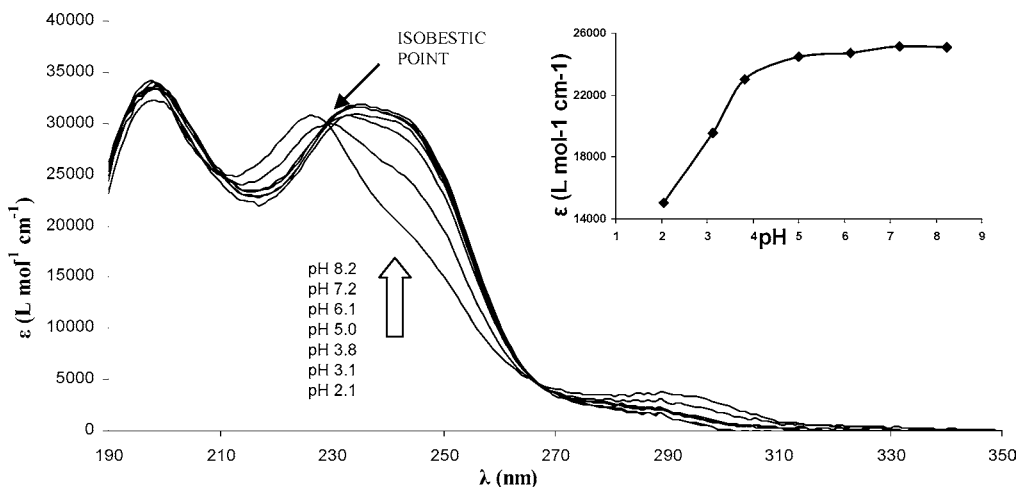
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Figure 5. Absorption spectra of iodosulfuron-methyl-ester in phosphate buffer at different pH values. Inset: Variation of λ_{250nm} vs pH.

Table 1. Degradates of Photodegradation and Hydrolysis of Iodosulfuron Detected and Tentatively Detected by HPLC-MS

IUPAC name	Compound	R_t (min)	Mass (m/z) ES$^+$
IODOSULFURON methyl 4-iodo-2-[({[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl}amino)sulfonyl] benzoate		33.8	530 (M+Na)$^+$, 508 (M+H)$^+$
product **a** 4-methoxy-6-methyl-1,3,5-triazin-2-amine		3.3	141 (M+H)$^+$
product **b** N-(4-methoxy-6-methyl-1,3,5-triazin-2-yl)urea		10.6	184 (M+H)$^+$, 141 (-CONH$_2$)
product **c** methyl 2-[({[({[(acetylamino) carbonyl]amino}carbonyl)amino]carbonyl}amino)sulfonyl]-4-iodobenzoate		20.9	535 (M+Na)$^+$, 513 (M+H)$^+$
product **d** 4-iodo-2-[({[(4-methoxy-6-methyl-1,3,5-triazin-2-yl) amino]carbonyl}amino)sulfonyl]benzoic acid		23.9	494 (M+H)$^+$, 366 , 215 , 141 (-C$_8$H$_6$I N O$_5$ S)
product **e** methyl 4-hydroxy-2-[({[(4-methoxy-6-methyl-1,3,5-triazin-2-yl)amino]carbonyl}amino)sulfonyl]benzoate		28.3	398 (M+H)+, 366 , 215 , 141 (-C9 H8 I N O5 S)

solution the quantum efficiencies (with polychromatic light), [Φ_{quartz}] and [Φ_{Pyrex}] were evaluated using the "photon" software (*18*, *19*). To check whether photodegradation is pH-dependent, quartz quantum efficiencies were measured at different pH

values and values of 0.054 ± 0.02 (pH 9.6), 0.08 ± 0.02 (pH 7), and 0.044 ± 0.008 (pH 5.3) were obtained. From these results, it appears that the Φ_{quartz} of iodosulfuron is indeed pH-dependent, with a maximum value of 0.08 ± 0.02 at pH 7 and

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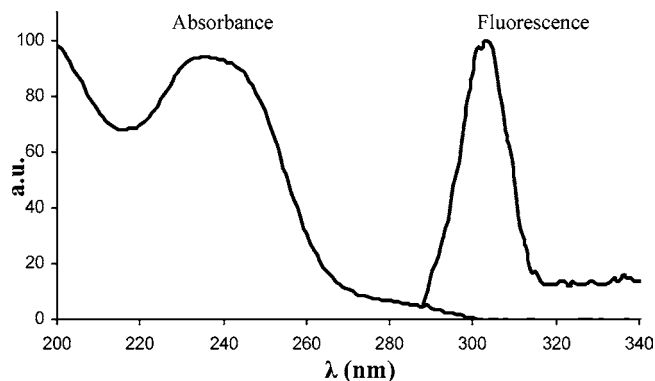
Figure 6. Absorption and fluorescence spectra of iodosulfuron-methyl-ester at pH 7.

Figure 7. Evolution of iodosulfuron and photoproduct **c** in a Pyrex reactor.

a minimum of 0.044 ± 0.008 at pH 5.3. To predict iodosulfuron persistence under sunlight irradiation, [Φ_{Pyrex}] was also evaluated. A value of $\Phi_{Pyrex} = 0.086$ was obtained in buffered water at pH 7. It can be observed that the results of the quantum efficiencies for both quartz and Pyrex reactors are similar, showing that the influence of wavelength is limited.

Three main photoproducts were identified by HPLC-MS (**Table 1**, photoproducts **a**, **b**, and **e**). Two of them were also observed in the hydrolysis experiment (products **a** and **b**).

It has previously been shown that product **a** resulted from hydrolysis (cf. **Table 1**); however, under the photochemical conditions employed (pH 7, $T = 19$ °C), such a reaction should not occur (cf. **Figure 3**). We can therefore assume that photoproduct **a** results from photoassisted hydrolysis of the sulfonylurea bridge. This reaction is a typical degradation pathway of sulfonylureas under irradiation (*5*, *9*), and such a reaction is faster under irradiation than in the dark. Indeed, during irradiation, the pK_a is shifted toward higher values [p$K_{a(S_0)}$ = 3.3 and p$K_{a(S_1)}$ = 5.3], and at pH 7, the fraction of the neutral form, which is the more reactive one, is higher than that obtained in the dark.

Photoproduct **b** results from photodissociation of the N−S bond, a classical homolytic reaction of amine photochemical deprotection. Recently, it has been reported that carbon−sulfur photodissociation occurred with some sulfonylureas (*5*, *9*, *10*), but here, this degradation represents only a minor pathway. It appears that the photodissociation of either N−S or C−S bonds depends on the substitutent borne by the benzenic derivative. It is interesting to note that **b** was also observed by direct hydrolysis at acidic pH values.

Photoproduct **e** results from a photosubstitution of iodide atoms by hydroxyl groups. To compare the formation of photoproduct **e** with the degradation of iodosulfuron, the evolution of the concentration (ppm) of both molecules during irradiation was reported (**Figure 7**). For this, we have considered that because these products have similar chemical structures, their absorption coefficients at $\lambda = 240$ nm should also be similar. As can be seen from this **Figure 7**, photoproduct **e** represents at $t = 50$ h, 20% of the initial concentration of iodosulfuron, indicating that this photoproduct is formed in great quantities.

In conclusion, our study showed that iodosulfuron is a rather stable molecule in the dark under neutral or slightly alkaline pH conditions. We have shown that the direct phototransformation of iodosulfuron-methyl-ester is possible under normal environmental conditions ($\lambda > 290$ nm) and represents a pathway for natural attenuation. The main photoproducts of iodosulfuron come from photosubstitution of the iodide atoms
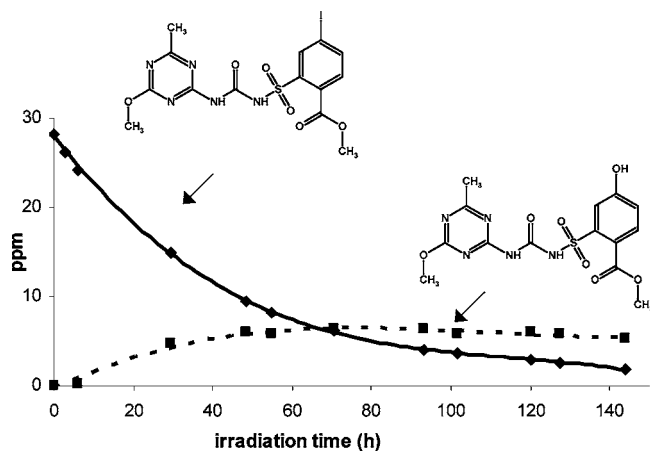
by hydroxyl groups, photohydrolysis of the urea bridge, and photodissociation of the N−S bonds present in the sulfonylurea bridge.

LITERATURE CITED

(1) Beyer, E. M.; Duffy, M. J.; Hay, J. V.; Schlueter, D. D. *Sulfonylureas in Herbicide: Chemistry, Degradation and Mode of Action*; Keaney, P. C., Kaufmann, D. D., Eds.; Dekker: New York, 1987; pp 117−189.

(2) Sarmah, A. K.; Kookana, R. S.; Duffy, M. J.; Alston, A. M.; Harch, B. D. Hydrolysis of triasulfuron, metsulfuron-methyl and chlorsulfuron in alkaline soil and aqueous solutions. *Pest Manage. Sci.* **2000**, *56*, 463−471.

(3) Cambon, J. P.; Bastide, J. B. Hydrolysis kinetics of thifensulfuron methyl in aqueous buffer solutions, *J. Agric. Food Chem.* **1996**, *44*, 333−337.

(4) Badon, R.; Bastide, J. B.; Sabadie, J. Rèactivitè de l'herbicide metsulfuron methyl, synthëse des produits de dègradation. *Chemosphere* **1990**, *21*, 289−293.

(5) Vulliet, E.; Emmelin, C.; Grenier-Loustallot, M. F.; Paisse, O.; Chovelon, J. M. Simulated sunlight-induced photodegradations of triasulfuron and cinosulfuron in aqueous solutions. *J. Agric. Food Chem.* **2002**, *50*, 1081−1088.

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

(7) Harvey, J., Jr.; Dulka, J. J.; Anderson, J. J. Properties of sulfometuron-methyl affecting its environmental fate: Aqueous hydrolysis and photolysis, mobility and adsorption on soils, and bioaccumulation potential. *J. Agric. Food Chem.* **1985**, *33*, 590−596.

(8) Sarmah, A. K.; Sabadie, J. Hydrolysis of sulfonylurea herbicides in soils and aqueous solution: A review. *J. Agric. Food Chem.* **2002**, *50*, 6253−6265.

(9) Vulliet, E.; Emmelin, C.; Chovelon, J. M. Influence of pH and irradiation wavelength on the photochemical degradation of sulfonylureas. *J. Photochem. Photobiol.*, A **2004**, *163*, 69−75.

(10) Courminbouef, C.; Carnal, F.; Weber, J.; Chovelon, J. M.; Chermette, H. Photodegradation of sulfonylurea molecules: Analytical and theoretical DFT studies. *J. Phys. Chem. A* **2003**, *107*, 10032−10038.

(11) Yang, X.; Wang, X.; Kong, L. Photolysis of chlorsulfuron and metsulfuron-methyl in methanol. *Pestic. Sci.* **1999**, *44*, 751−754.

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(12) Morrica, P.; Barbato, F.; Dello Iacovo, R.; Seccia, S.; Ungano, F. Kinetics and mechanism of imazosulfuron hydrolysis. *J. Agric. Food Chem* **2001**, *49*, 3816−3820.

(13) Hacker, E.; Bieringer, H.; Willms, L.; Ort, O.; Koecher, H.; Kehne, H. Iodosulfuron plus mefenpyr-diethyl- a new foliar applied herbicide for weed control in cereals. *Proc. Br. Crop Prot. Conf.-Weeds* **1999**, *1*, 15−22.

(14) www.apvma.gov.au/publications/prsiod.pdf.

(15) Braschi, I.; Calamai, L.; Cremonini, M.; Fusi, P.; Gessa, C.; Pantani, O. A.; Pusino, A. Kinetic and hydrolysis mechanism of triasulfuron. *J. Agric. Food Chem.* **1997**, *45*, 4495−4499.

(16) Sabadie, J.; Rèactivitè de l'herbicide chlorsulfuron; synthèse et structure de ses produits de dégradation. *Weed Res.* **1992**, *32*, 137−142.

(17) Braun, A. M.; Maurette, M. T.; Oliveros, E. Rappel des principes fondamentaux de la photochimie. *Technologie Photochimique*; Presses Polytechniques Romandes: Lausanne, Switzerland, 1986; pp 26−142.

(18) Guittonneau, S.; Konstantinou, I.; Emmelin, C.; Albanis, T.; Meallier, P. Determination of photochemical lifetime of pesticides in aqueous medium with solar light. *Fresenius Environ. Bull.* **2001**, *10* (4), 353−356.

(19) Guittonneau, S.; Maestracci, M.; Meallier, P.; Moutie, L. Logiciel de calcul de rendement quantique en lumiëre polychromatique. *Actes of XXVëme Congrës du Groupe Franáais des Pesticides*; Montpellier, France, 1995; 17−18 May.