

Photochemical Degradation of Acifluorfen in Aqueous Solution

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To elucidate the photochemical behavior of diphenyl ether herbicides in superficial waters, the photodegradation of acifluorfen, 5-[2-chloro-4-(trifluoromethyl)phenoxy]-2-nitrobenzoic acid (CAS Registry No. 50594-66-6), was studied in water and acetonitrile. All experiments were carried out under laboratory conditions using a solar simulator (xenon arc) or jacket Pyrex reaction cell equipped with a 125 W high-pressure mercury lamp. The calculated polychromatic quantum efficiencies (Φ_{solvent}) of acifluorfen in different solvents are as follows (units are degraded molecules photon⁻¹): $\Phi_{\text{water}} = 10^{-4}$, $\Phi_{\text{acetonitrile}} = 10^{-4}$, $\Phi_{\text{methanol}} = 10^{-4}$, and $\Phi_{\text{hexane}} = 10^{-2}$. The results obtained in this work are in good agreement with the literature value of monochromatic quantum yield. HPLC-MS analysis (APCI and ESI in positive and negative modes) was used to identify acifluorfen photoproducts. These results suggest that the photodegradation of acifluorfen proceeds via a number of reaction pathways: (1) decarboxylation, (2) dehalogenation, (3) substitution of chlorine group by hydroxyl or hydrogen groups, and (4) cleavage of ether linkage, giving phenols. Photorearrangement products were studied by other investigators. No such products were observed. In addition, it was found that the trifluoro functional group on acifluorfen was not affected by any transformation, and no products of a nitro group reduction were found.

Keywords: *Herbicides; diphenyl ether; acifluorfen; photodegradation; HPLC-MS analysis*

INTRODUCTION

Acifluorfen is a diphenyl ether herbicide used in postemergence for the selective control of most broadleaf weeds in soybeans and rice (1, 2). Its phytotoxic activity is observed upon sunlight irradiation (3, 4).

The lifetime of pesticides is mostly governed by biotic degradation and soil adsorption (5). Soil adsorption is strongly dependent on its physicochemical properties such as (1) pH, (2) clay mineral content, (3) soil carbon content and nature, and (4) quality of humic substances (6–8). The half-life of acifluorfen in different soils can range from 23 days to >112 days (8). As a result, the half-life of acifluorfen is sufficiently long that it may be washed away toward surface waters (rivers and lakes). Therefore, hydrolysis and photolysis are potentially important processes responsible for the destruction of the herbicide (9, 10). As a result, the study of the photochemical degradation of acifluorfen is warranted.

In aqueous solution, the rate of the direct photodegradation of acifluorfen follows a first-order kinetics reaction, and up to now, the only identified photoproduct has been 2-chloro-1-(4-nitrophenoxy)-4-(trifluoromethyl)benzene arising from the decarboxylation of acifluorfen (11). However, studies of photolysis of phenyl ethers, diphenyl ethers, and similar molecules (12–15) have shown that other numerous reactions can be

expected, such as dehalogenation, reduction of the nitro group, cleavage of the ether linkage, giving phenols, substitution by solvent, and photo-Claisen-type rearrangement, yielding biphenyl compounds.

To identify the largest number of photoproducts and to elucidate the complete pathway for acifluorfen photodecomposition, all experiments were carried out under laboratory conditions using a solar simulator and an immersion apparatus equipped with a high-pressure mercury arc lamp surrounded by a Pyrex jacket.

The limit of pesticide concentration in drinking water is fixed by European Union directives at 0.1 $\mu\text{g L}^{-1}$ for all active matter. As a result, analytical methods used to identify the photoproducts must reach a limit of detection of $\sim 0.02 \mu\text{g L}^{-1}$. Recent progress in direct coupling of liquid chromatography–mass spectrometry (HPLC-MS) (16, 17) allowed good sensitivity and identification of a large number of photoproducts.

MATERIALS AND METHODS

Herbicide. Acifluorfen, 5-[2-chloro-4-(trifluoromethyl)phenoxy]-2-nitrobenzoic acid, CAS Registry No. 50594-66-6, IUPAC name 5-(2-chloro- α,α,α -trifluoro-*p*-tolylloxy)-2-nitrobenzoic acid, C₁₄H₇ClF₃NO₅, was used: molecular weight, 361.7 g mol⁻¹; vapor pressure, 0.01 mPa (20 °C); solubility in water, 120 mg L⁻¹ (23–25 °C); stability, thermal decomposition at 235 °C, stable in aqueous solution between pH 3 and 9, UV decomposition (1).

The acifluorfen used for the photodegradation experiments was obtained from Fluka–Riedel de Haën (Sigma-Aldrich Chimie). A standard from Cil cluzeau info labo (Paris La defense, France) was used as analytical reference.

Quantum Efficiencies. The determination of polychromatic quantum efficiencies (Φ) was carried out using a solar

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light simulator (Suntest CPS+, Heraeus), equipped with a 1.1 kW xenon arc lamp. The concentrations used ranged from 5×10^{-5} to 1.2×10^{-4} mol L⁻¹. Incident photonic flux was measured by chemical actinometry using uranyl oxalate from Fluka–Riedel de Haën (Sigma-Aldrich Chimie). The quantum efficiencies were calculated using custom application software, "photon" (18, 19). This software calculated the number of absorbed photons from the pesticides' absorption spectrum, the emission spectrum of the source, and the actinometric results. Kinetic studies of photodegradation (<10% of degradation) gave the number of photodegraded molecules during the same time.

Photophysical Properties. UV–visible absorption spectra were recorded with a Uvikon 930 spectrophotometer (Kontron Instruments). Fluorescence and phosphorescence spectra were obtained with an SFM 25 spectrofluorometer (Kontron Instruments). The phosphorescence spectrum was recorded, in liquid nitrogen temperature, in ethyl ether/2-methylbutane/ethanol (EPA), respectively 5:5:2 in volume.

Photochemical Procedures. For kinetics studies and photoproduct identification, the experiments were carried out under laboratory conditions with a solar light simulator (Suntest CPS+, Heraeus) equipped with a 1.1 kW xenon arc lamp. The concentration of irradiated solutions was $\sim 10^{-4}$ mol L⁻¹ in pure water (MilliQ-50 18 M Ω). Most experiments were carried out under atmospheric conditions at 20 °C. The role of oxygen has been studied in acetonitrile with a jacketed Pyrex immersion apparatus equipped with a high-pressure mercury arc lamp (125 W).

Photoproduct Identification. Six samples of 15 mL were irradiated in the Suntest. At regular intervals a sample was collected, stocked, and then gathered with the others in one solution to observe the highest variety of photoproducts in the same HPLC-MS analysis. The obtained sample was pre-concentrated by three successive liquid–liquid extractions with ethyl acetate (1:1, v/v). The organic phase was evaporated under vacuum at 30 °C, and the dry residue was then dissolved in 1 mL of methanol.

Kinetics Experiments. Aqueous solutions (225 mL) of acifluorfen were irradiated in the Suntest. Products were irradiated for 140 h, and every 10 h samples were collected and analyzed directly (without preconcentration).

¹H NMR Analysis. Acifluorfen, from Riedel de Haën and from Cluzeau, was dissolved in a mixture of CDCl₃ and DMSO (80:20) and analyzed using a Bruker Avance 200 spectrometer.

HPLC Conditions. For the kinetic studies a Hypersil BDS C₁₈ column (5 μ m, 125 \times 4 mm) was used. An isocratic elution (66:34, % v/v) was carried out using a mobile phase of acetonitrile/water (with H₃PO₄ buffer to reach pH 3). The flow rate was 1 mL min⁻¹, injection volume 10 μ L, and wavelength of detection 254 nm.

Photoproduct Identification. An HPLC-MS apparatus [Hewlett-Packard (HP) 1100 series lc-msd] equipped with a precolumn and a Hypersil HP Elite column (5 μ m, 150 \times 3 mm) was used (column was thermostated at 40 °C). The injection volume was 2 μ L. An elution gradient was carried out with methanol/water (+10⁻⁴ M ammonium formate) from 100 to 0% water in 50 min. The flow rate was set at 0.4 mL min⁻¹. The MS detection was performed using two related techniques: electrospray ionization (ESI), in positive and negative modes, and atmospheric pressure chemical ionization (APCI), using nitrogen as atomizing gas. Ionization conditions of ESI analysis were as follows: capillary potential, 300 V; N₂ flow, 13 L min⁻¹; pressure, 55 psig. Ionization conditions of APCI were as follows: capillary potential, 1750 V; N₂ flow, 6 L min⁻¹; vaporization temperature, 185 °C.

RESULTS AND DISCUSSION

Photophysical Properties of Acifluorfen. Acifluorfen in aqueous solution shows two maxima in the UV–visible absorption spectrum (Figure 1), the first one at $\lambda = 296$ nm ($\epsilon_{296} = 8000$ L mol⁻¹ cm⁻¹) and the second one at $\lambda = 197$ nm ($\epsilon_{197} = 32400$ L mol⁻¹ cm⁻¹). The

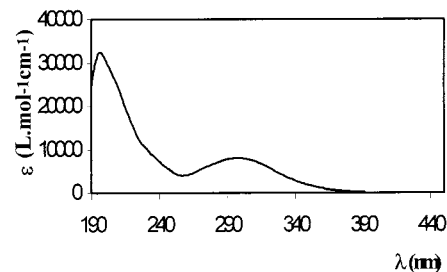


Figure 1. Absorption spectrum of acifluorfen in aqueous solution.

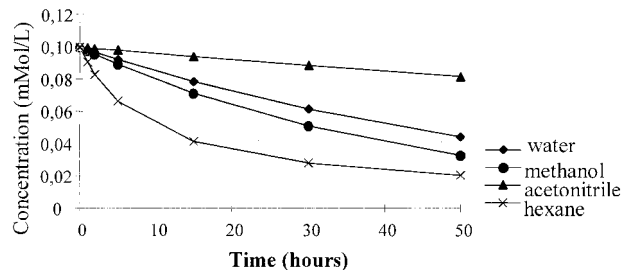


Figure 2. Photodegradation of acifluorfen in different solvents (Suntest).

Table 1. Quantum Efficiency (Φ) of Acifluorfen in Different Solvents

solvent	Φ (molecules/photon)
hexane	$\approx 10^{-2}$
methanol	3.6×10^{-4}
water	1.8×10^{-4}
acetonitrile	1.2×10^{-4}

solar light spectrum slightly overlaps the first absorption band, meaning that a direct photodegradation is possible in natural conditions. To estimate the photochemical stability of molecules, the quantum yield (for monochromatic light) or the quantum efficiency (for polychromatic light) is a useful parameter. The quantum efficiencies of acifluorfen in water, acetonitrile, and methanol (Table 1) using the "photon" software have been found to be close to 10^{-4} degraded molecules per absorbed photon. The results obtained in this study are in good agreement with those obtained by other investigators (20) using monochromatic radiation. The quantum efficiency obtained in hexane ($\Phi \approx 10^{-2}$ degraded molecules per absorbed photon) was higher. The photodegradation is faster in hexane (Figure 2) despite a hypsochromic shift of the first absorption band (in hexane $\lambda_{\max} = 274$ nm with $\epsilon_{274} = 4990$ L mol⁻¹ cm⁻¹). A free radical mechanism is often suspected when the photodegradation is favored in nonpolar solvents. So, for a better understanding of the acifluorfen photochemical degradation mechanism, some experiments were carried out in the Suntest ($C_{\text{acifluorfen}} = 10^{-4}$ mol L⁻¹ in acetonitrile) with a radical initiator, 2,2'-azobis(2-methylpropionitrile) (AIBN) ($C_{\text{AIBN}} = 10^{-3}$ mol L⁻¹). Table 2 shows that the half-life of irradiated acifluorfen was reduced in the presence of AIBN. On the other hand, the introduction of a well-known inhibitor of radicals, 1,4-benzoquinone ($C_{\text{benzoquinone}} = 10^{-3}$ mol L⁻¹), increased the half-life from 107.3 to 1861.5 h. Of course, this reduction of the photodegradation rate may be a result of other phenomena such as a screen effect or a triplet quencher activity. This is consistent with recently published results (22) that put in evidence the triplet state involvement in the acifluorfen photodegradation. To investigate if 1,4-benzoquinone can act as a triplet

Table 2. Suntest Kinetic Data of Acifluorfen Photodegradation ($C_{\text{acifluorfen}} = 10^{-4} \text{ mol L}^{-1}$ in Acetonitrile) in the Presence of Radical Initiator (AIBN) and Radical Inhibitor (Benzoquinone) ($C = 10^{-3} \text{ mol L}^{-1}$)

added substance	molar ratio (pesticide/added substance)	$t_{0.5}$ (h)	k (h^{-1})
AIBN	1:0	107.3	0.0065
	1:10	32.9	0.0210
benzoquinone	1:10	1861.5	0.00037

Table 3. Energy of the First Excited Singlet (S_1) and Triplet States (T_1) of Acifluorfen in Acetonitrile

	S_1	T_1
λ_{max} (nm)	297	402.9
ΔE (kJ mol^{-1})	410	291.8

quencher, the energies of the first excited singlet and triplet states were determined from the absorption, fluorescence (in acetonitrile), and phosphorescence spectra (in EPA). Results are summarized in Table 3. The energy levels determined for acifluorfen ($E_{S_1} = 410 \text{ kJ mol}^{-1}$, $E_{T_1} = 291 \text{ kJ mol}^{-1}$) show that 1,4-benzoquinone cannot act as a triplet quencher ($E_{T_1, \text{benzoquinone}} = 287 \text{ kJ mol}^{-1}$) because its triplet state energy is not low enough. Effectively, to have an efficient triplet-triplet transfer, the difference between the two levels must be at least 15 kJ mol^{-1} (22). On the other hand, the light screen effect cannot be neglected because 1,4-benzoquinone absorbs wavelengths $>280 \text{ nm}$ (23) ($\epsilon_{\text{max, benzoquinone}} = 1047$ at 290 nm) and the ratio of pesticide to 1,4-benzoquinone is in favor of 1,4-benzoquinone. The results using AIBN are in favor of a free radical mechanism, but recent work (20) has shown that the photodegradation kinetics were pH-dependent. This result is consistent with a heterolytic mechanism. These results are not incompatible. Like Vialaton and colleagues (20), we think that the first excited triplet state may undergo either a homolytic or a heterolytic photolysis, giving competitive nucleophilic substitution and homolytic decarboxylation or substitution.

Analysis of the Initial Compound. HPLC analysis of the standard from Cluzeau (Figure 3) showed one well-defined peak, whereas the chromatogram of the acifluorfen (Riedel de Haën) used for the photodegradation experiments pointed out the presence of a secondary product (from chromatographic area $\sim 15\%$). Additional ^1H NMR and HPLC-MS analyses (Table 4) have suggested a positional acifluorfen isomer, which could be 5-[2-chloro-5-(trifluoromethyl)phenoxy]-2-nitrobenzoic acid obtained as a byproduct during acifluorfen synthesis (2). The samples used for the photodegradation experiments contained $\sim 15\%$ of 5-[2-chloro-5-(trifluoromethyl)phenoxy]-2-nitrobenzoic acid, which can be photodegraded during the herbicide irradiation. This presence could not be neglected, and consequences on the previous pathways can be expected.

Identification of the Photoproducts. An aqueous solution of acifluorfen is stable in the dark but gives a lot of photoproducts under irradiation. After irradiation with a solar simulator, Suntest ($\lambda \geq 290 \text{ nm}$), the preconcentrated solutions were analyzed using HPLC-MS (ESI analysis, in positive and negative modes). All results are summarized in Table 5. Figure 4 shows a characteristic chromatogram of acifluorfen solution gathering several samples collected at different times of irradiation. The APCI results are consistent with the ESI results.

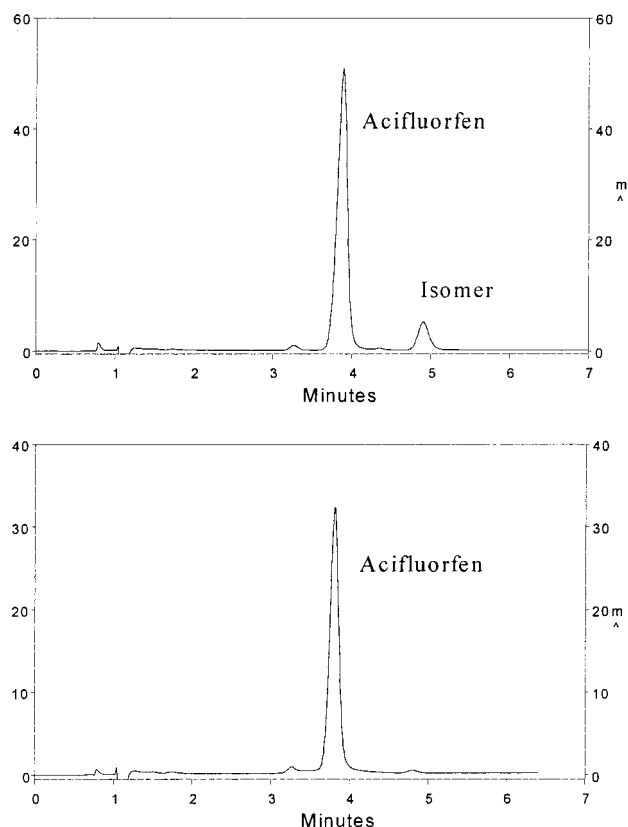


Figure 3. HPLC-UV chromatograms of acifluorfen (a) from Riedel de Haën and (b) from Cluzeau in aqueous solution (detection $\lambda = 254 \text{ nm}$).

Table 4. HPLC-MS Analysis of Acifluorfen (from Riedel de Haën): Retention Times (t_R), Molecular Peaks ($M - H$) $^{\pm}$, and Fragments Detected with Electrospray Ionization (Negative Mode)

compd	t_R (min)	($M - H$) $^{\pm}$ (amu)	fragments (amu)
acifluorfen	35.1	360	316; 195
isomer	37.2	360	316; 249; 195

On the basis of the molecular peaks and fragments detected, we can suggest different structures for the photoproducts detected by HPLC-MS. The single structure confirmed, at the moment, is the 1,4-nitrophenol (product E). Product E and the 1,4-nitrophenol from Acros gave the same result with HPLC and HPLC-MS. The structure proposed for product C is in agreement with previously reported results using GC-MS analysis (23, 24). The cleavage of the ether linkage of the herbicide molecule gives products A and B (13, 14). The complementary fragments of these molecules [2-chloro-4-(trifluoromethyl)phenol and 3-(trifluoromethyl)chlorobenzene], which should have been detected at 196 and 180 amu, respectively, were not observed. There are three possible explanations: (1) analytical, these parts of the molecule are too polar and they are eluted in the HPLC dead volume or they are not detected by MS ionization; (2) sample preparation, their solubility in ethyl acetate is not sufficient to be extracted during the preconcentration; (3) photochemical, they are quickly photodegraded.

In the negative detection mode (Table 5) two different peaks ($t_R = 28.1$ and 30.3 min) were observed with the same m/z ratio (376 amu). These two products with the same mass and almost the same retention times have been found to be two isomers of position (G_1 and G_2) coming from the presence of 5-[2-chloro-5-(trifluoro-

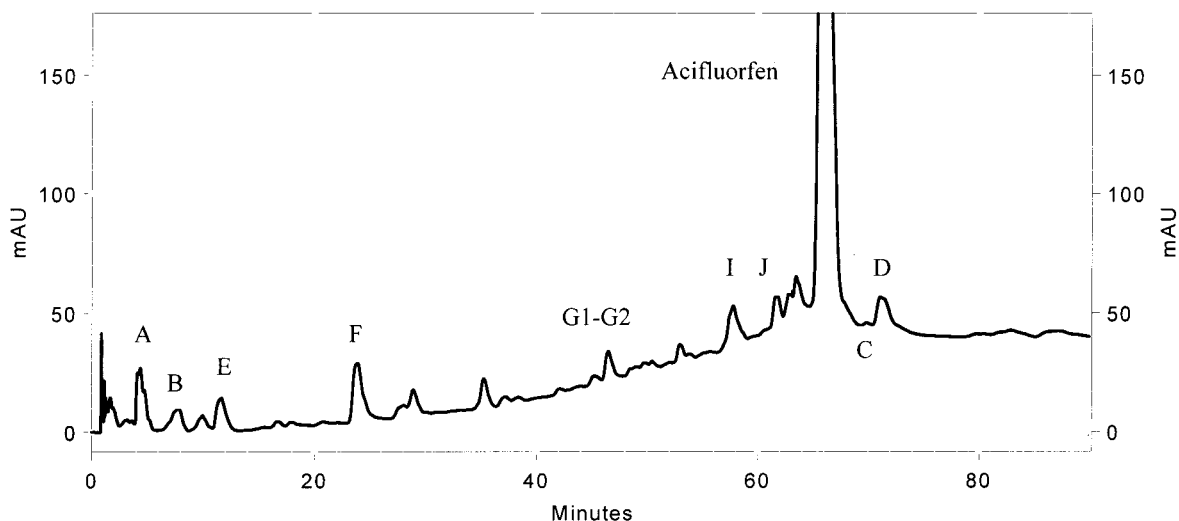
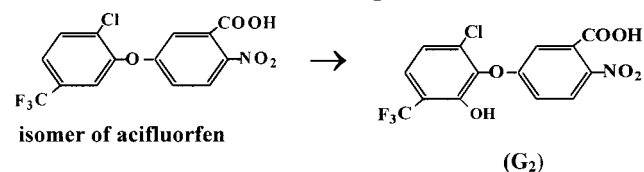


Figure 4. HPLC-UV chromatogram of aqueous irradiated solution of acifluorfen (detection $\lambda = 254$ nm).

Table 5. Retention Times (t_R), Molecular Peaks ($M + H$)⁺, and Fragments Detected with Electrospray Ionization (Positive and Negative Modes)

compd	t_R (min)	positive mode		negative mode	
		($M + H$) ⁺ (amu)	fragments (amu)	($M - H$) ⁻ (amu)	fragments (amu)
acifluorfen	35.1	362	384 ($M + Na$) ⁺	360	316; 195
isomer	37.2	360	316; 249; 195		
A	3.9	184			not detected
B	8.7	201			
C	42.7	334		332	
D	43.8	318	340 ($M + Na$) ⁺ ; 300		not detected
E	19.1	140	162 ($M + Na$) ⁺	138	
F	20.6			342	307; 249; 227; 195
G ₁	28.1	not detected		376	332; 285; 231; 193
G ₂	30.3			376	332; 313; 255
I	39			348	332; 249
J	40			298	249; 113

Scheme 1. Formation of Photoproduct G₂



methyl)phenoxy]-2-nitrobenzoic acid in acifluorfen (Scheme 1).

Kinetic Studies. After 140 h under simulated light (Suntest), 75% of acifluorfen was converted, whereas 99.6–100% was recovered after the same period in darkness. The evolution of some characteristic photoproducts (A, D, E, G₁, and I) was analyzed using HPLC. Figures 5–7 show chromatographic areas versus irradiation time. In water the major photoproduct comes from the decarboxylation (D) of the acifluorfen. The maximum concentrations are obtained after 30 h of

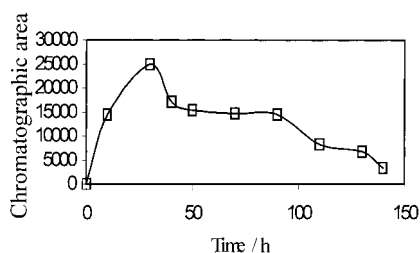


Figure 5. Evolution of photoproduct D from the decarboxylation of acifluorfen.

irradiation and have been evaluated at $1.1 \cdot 10^{-5}$ mol L⁻¹ (taking ϵ close to the acifluorfen one). After this delay, the quantity of product D decreased, a result that is consistent with its photodegradation. Products A and E appear after product D; their concentrations increase to reach a maximum after 100 h of irradiation (Figure

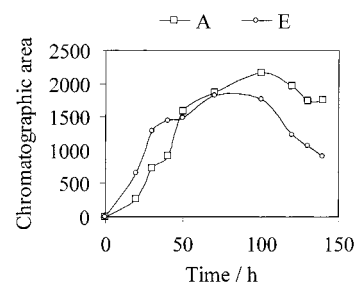


Figure 6. Evolution of photoproduct A and 1,4-nitrophenol (E) during Suntest irradiation.

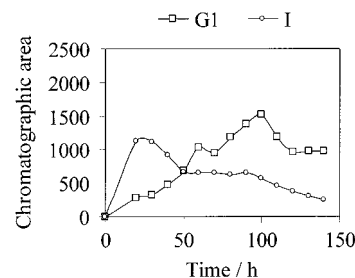
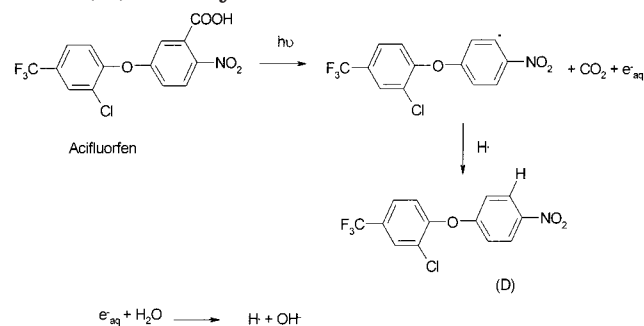


Figure 7. Evolution of photoproducts G₁ and I during Suntest irradiation.

Table 6. Kinetic Parameters of Acifluorfen UV Photodegradation with or without Oxygen (*k* Is the Pseudo-Rate Constant Calculated for First-Order Kinetics)

atmosphere	$t_{1/2}$ (h)	k (h^{-1})
air	6.6	0.1044
argon	21.4	0.0323

Scheme 2. Photodegradation Pathway of Acifluorfen Decarboxylation (Product D) Proposed by Pusino and Gessa (11): Homolytic Mechanism



4). There is no delay between the appearance of products E (1,4-nitrophenol) and A (4-hydroxy-2-nitrobenzoic acid), suggesting that the formation of product E is not only due to the photodegradation of product A but comes also from the photolysis of the ether function of product D. The decrease of product E, observed after 100 h, shows that 1,4-nitrophenol is not a final residue and that other reactions occur, such as a hydroxylation or an opening of the aromatic ring. However, even after 150 h of irradiation and beyond, the quantity of these third-generation photoproducts is under the threshold of HPLC-MS detection, and no product have been identified.

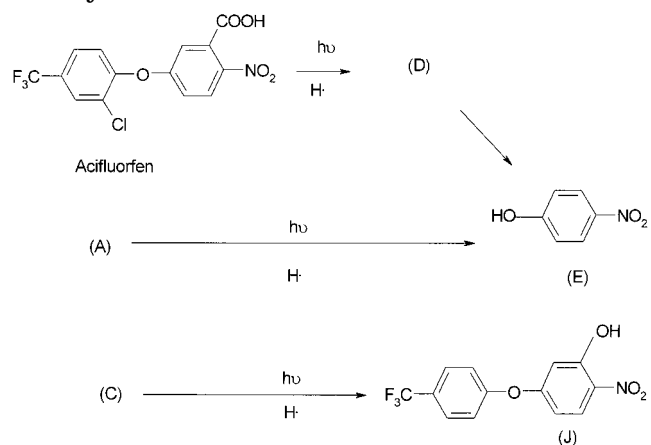
Compound (G_1), from the hydroxylation of acifluorfen, appeared at the beginning of the irradiation. It was detected at the end of the 20th hour (Figure 7), and its quantity increased regularly during the following 120 h and then decreased. Concerning product I, maximal concentration is reached during the first 20 h and then gradually decreases, which can be explained by a competition of several pathways. Products from the photolysis of product I ether function have not been detected.

Role of Oxygen. The role of oxygen was tested in acetonitrile using a jacketed Pyrex immersion apparatus equipped with a high-pressure mercury arc lamp. Argon was used to saturate the solution. Under inert atmosphere the kinetic rate of photolysis clearly decreased from 0.1044 h^{-1} , in air conditions, to 0.0323 h^{-1} (Table 6). These results are in opposition with other published results. For Pusino and Gessa (11), in distilled water the half-time of photolysis decreased under inert conditions, and for Vialaton et al. (20) no oxygen influence was observed. As a result, to date, the role of oxygen in acifluorfen photodegradation is unclear, particularly with respect to a solvent or wavelength dependence of the photodegradation of acifluorfen.

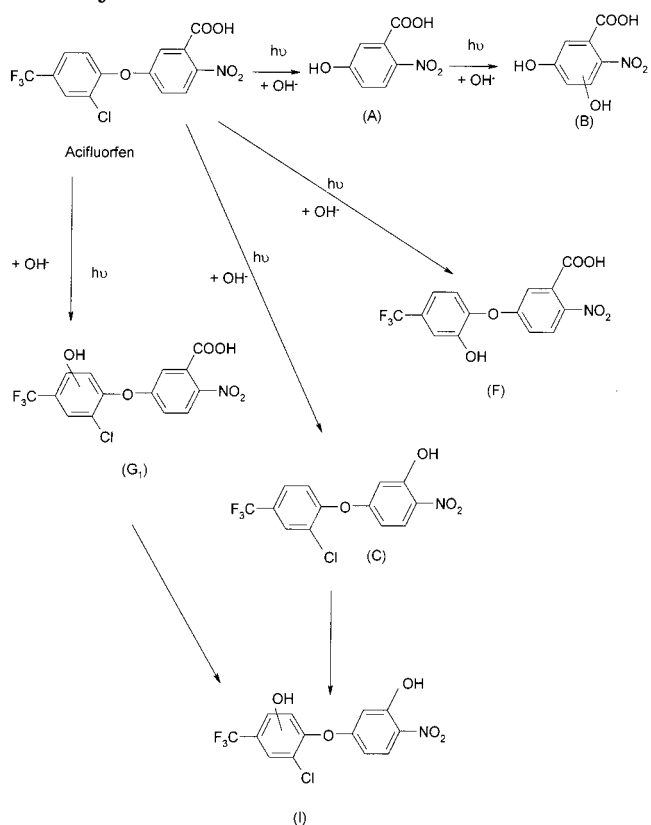
Photodegradation Pathway. The irradiation of acifluorfen gives numerous photoproducts. Our results suggest several competitive pathways.

Photodecarboxylation. The principal photoproduct obtained was decarboxylated product D. Pusino and Gessa (11) suggested that the mechanism for this reaction involved the formation of a phenyl radical by loss of a hydrated electron and carbon dioxide (Scheme

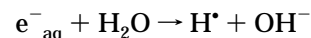
Scheme 3. Photodegradation Pathway of Acifluorfen: Homolytic Substitutions



Scheme 4. Photodegradation Pathway of Acifluorfen: Heterolytic Substitutions



2). Afterward, the phenyl radical can couple with the hydrogen atom formed by the reaction of the hydrated electron with water.



This reaction gives two other possibilities of reaction: **H[•] Abstraction.** The formation of free radical $\text{H} \cdot$ can explain the appearance of products E, 1,4-nitrophenol, and J (Scheme 3).

Nucleophilic Substitution by OH^- . The presence of hydroxyl groups (Scheme 4) can explain the hydrolysis of different molecules (acifluorfen giving products G_1 , F, and C or hydroxylation of product A giving product B). Moreover, the results of Vialaton et al. (20) have put in evidence an increase of the scission of the ether linkage with the hydroxyl ion concentration. Therefore,

cleavage of the aromatic ether linkage is probably a photonucleophilic displacement, as was suggested in nitrofen photodegradation (25), as well as in the photostitution of Cl by a hydroxyl group.

Conclusion. Acifluorfen in aqueous solution absorbs light around 300 nm. Therefore, when it is exposed to sunlight, it can be photodegraded. We have identified 11 photoproducts. The identification of numerous photoproducts indicates that acifluorfen in aqueous medium can undergo many photochemical reactions. As Vialaton et al. (20) have suggested, the photodegradation of acifluorfen is the result of competitions between nucleophilic substitutions by OH⁻ and a radical mechanism (photodecarboxylation and H abstraction).

The photoproducts formed, in their turn, can be phototransformed. As the photodegradation goes on, the increasing concentration of byproducts gives other competitive absorption and reactions, so the prediction of the involved mechanism is not easy.

Photorearrangement products observed by other investigators were not identified due to a less energetic irradiation ($\lambda > 290$ nm). In addition, it was found that the trifluoro functional group on acifluorfen was not affected by any transformation. On the other hand, the chloro functional group on the aromatic ring undergoes photodehalogenation. No product of nitro group reduction were found, in agreement with the literature (12).

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