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Photochemical behaviour of oxyfluorfen: a diphenyl-ether herbicide

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Abstract

The photochemical behaviour in different solvents of the herbicide oxyfluorfen [2-chloro-1-(3-ethoxy-4-nitrophenoxy)-4-(trifluoromethyl) benzene (CAS RN 42874–03–3)] was studied. Photochemical reactions were carried out by using a high pressure mercury arc and a solar simulator. Kinetic parameters and quantum yields were determined. Identification of the photoproducts was performed by GC-MS and the main compounds were confirmed by [^{1}H] NMR. The photochemical reactions were also carried out in the presence of either a singlet or a triplet quencher, and in the presence of either a radical initiator or a radical inhibitor. Results indicate that the first excited singlet state can undergo both homolytic and heterolytic cleavage of the ethyl-oxygen bond in the side chain of oxyfluorfen. Moreover, the presence of reduction products in the reaction mixture is supposed to occur via a monoelectron transfer process with the formation of a transient exciplex during the reaction. ©1999 Published by Elsevier Science S.A. All rights reserved.

Keywords: Photophysical properties; Photodegradation; Kinetic parameters; Herbicides; Oxyfluorfen; Liquid phase

1. Introduction

Oxyfluorfen is a diphenyl ether herbicide (**1**, Scheme 1), acting as a protoporphyrinogen oxidase inhibitor and used for pre- or post-emergence to control monocotyledonous and broad-leaved weeds at rate in the range 0.25–2.0 kg of active ingredient (a.i.) per hectare. The herbicide is degraded at temperature >50°C [1]. As oxyfluorfen is not metabolised in plants and is subjected to very little translocation, phototransformation is suggested as a possible abiotic degradation process. Solubility in water is 0.1 mg l^{-1}, and although photodecomposition in water is rapid, the process is comparably slower on soil. Microbial degradation is not a major factor. Half-life in soil approximately ranges 30–56 days [2]. The organic matter content of soil seems to influence oxyfluorfen persistence and activity [3–6].

Diphenyl ether herbicides require light to exhibit phytotoxic activity [7–9]. However, the nature of the light activated mechanism is still unknown. The photochemical reactions of substituted diphenyl ethers in liquid phases have been described by Nakagawa and Crosby [10] and Ruzo et al. [11], but no information is available on the photochemical behaviour of oxyfluorfen.

It is worth referring to contributions that have appeared in the past. Hageman [12] reported work on diphenyl ether, 1,4-diphenoxybenzene, and some substituted diaryl ethers (methyl- and/or methoxy-derivative) irradiated by the unfiltered UV light of a high pressure mercury lamp at 25°C. The reactions observed were: cleavage of the ether bond(s) followed by H-abstraction from the solvent yielding phenols and benzene derivatives, and a photo-Claisen type rearrangement yielding 2- and/or 4-hydroxybiphenyl derivative. Another experiment showed that diphenyl ether was converted to *o*-phenyl phenol, *p*-phenyl phenol, and a small amount of phenol, by UV light in several solvents. *p*,*p*′-Ditolyl ether was similarly converted to 2-(*p*-tolyl)-4-methylphenol and *p*-cresol, indicating that the photochemical rearrangement proceeds via C–O bond cleavage and recombination of the radical (quinoid) fragments. These reactions were reported as intra molecular and occurring via an excited singlet state or via a short-lived triplet [13].

The sunlight photolysis of the herbicide nitrofen (2,4-dichloro-phenyl *p*-nitrophenyl ether) in aqueous methanol solution was described as a photonucleophilic displacement of nitrophenate by the hydroxide ion of

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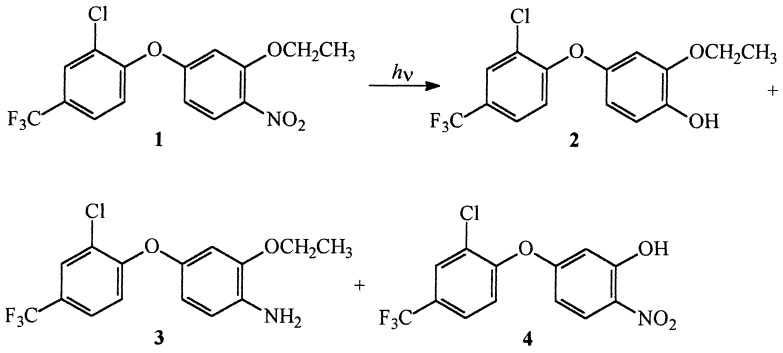


Scheme 1.

water giving rise to 2,4-dichlorophenol and *p*-nitrophenol. Apparently, oxygen does not influence the formation of photoproducts [10].

Other substituted diphenyl ethers were studied under 300 nm irradiation in water, cyclohexane and methanol solutions. The major reaction pathways observed involve reductive dehalogenation, decarboxymethylation, reduction of nitro substituents, and cleavage of the ether linkage to yield phenols. Nucleophilic substitution by the solvent was also observed [11].

Having in mind that the photochemical study of diphenyl ethers may be informative on the dependence of their herbicidal activity on light absorption, two main objective were targeted. These deal with the photochemical behaviour of oxyfluorfen in various solvents and the decomposition products arising under light irradiation in acetonitrile solution, respectively. Data obtained in this study could be very useful in understanding the environmental behaviour of oxyfluorfen.

2. Materials and methods

All the solvents (pesticide grade), reagents (analytical grade) and filters (disposable sterilised packet) were purchased from Fluka and Sigma-Aldrich (Milan, Italy). Ultrapure water was obtained with a Milli-Q system (Millipore). Oxyfluorfen pure standard (98%; M.W. 361.7) was purchased from Dr. Ehrenstorfen (Germany). All the solvents and solutions were filtered using sterilised ultra-filters (0.2 μm). Aseptic handling materials and laboratory facilities were used throughout the study to maintain sterility.

UV spectra were recorded by using a Uvikon 930 spectrophotometer. Fluorescence and phosphorescence spectra were obtained with a Jobin Yvon 3D spectrofluorimeter. The fluorescence spectrum was recorded in acetonitrile using diphenylanthracene (DPA) as actinometer. The phosphorescence spectrum was recorded, under liquid nitrogen, in the ethylether/2-methylbutane/ethanol (5 : 5 : 2) mixture (EPA), using acetophenone as actinometer.

The intersystem crossing quantum yield [14] was determined by using the sensitised isomerization of α-methylstilbene. 10 ml of oxyfluorfen solution in benzene (8.1×10^{-2} M) was irradiated at 360 nm in the presence of α-methylstilbene (20 mg) with a high pressure mercury arc (Helios-Italquarz, 125 W) surrounded by a Pyrex water jacket. The lamp was immersed in 2 M KNO_3 solution in order to cut-off all the emission below 330 nm. The cis-trans isomerization was determined via GLC. Benzophenone was used as actinometer.

The degradation of oxyfluorfen was carried out in an immersion apparatus equipped with a high-pressure mercury arc (125 W) surrounded by a Pyrex water jacket and in a solar simulator (Suntest CPS+, Heraeus) furnished with a 1.1 KW xenon lamp, at 21°C. All the experiments were carried out in the atmospheric environment. Oxyfluorfen at the concentration of 0.1 mM in acetonitrile, methanol, and *n*-hexane was used in the degradation tests. The solutions were analysed via HPLC with a HP 1090 instrument equipped with a diode array detector. C18 (5 μm) Perkin Elmer HS-5HCODS column was used at 0.6 ml min^{-1} flow rate. 7 : 3 acetonitrile–water mixture was adopted as mobile phase. The oxyfluorfen retention time was 6.34 min.

The photodegradation quantum yields were determined using uranyl oxalate as actinometer. The identification of photoproducts was performed on the reaction mixture obtained in acetonitrile under irradiation with the mercury arc. To avoid the formation of a multitude of little by-products, which could be an hindrance for the understanding the degradation pathway, the reaction was stopped after 1 h of irradiation, when 20% of starting compound was converted. A Hewlett-Packard 5971 mass selective detector on a Hewlett-Packard 5890 gas chromatograph was used [OV-1 capillary column between 70–250°C (12°C/min)]. Further analyses were achieved on a Finnigan SSQ 7000 mass spectrometer.

The products thus obtained were: 2-chloro-1-(3-ethoxy-4-hydroxyphenoxy)-4-(trifluoromethyl)benzene **2** [MS, *m/z* (relative abundance): 334 (21%), 332 (64), 313 (11), 304 (38), 303 (25), 251 (100), 223 (22), 179 (7), 125 (11)]; 2-chloro-1-(3-ethoxy-4-aminophenoxy)-4-(trifluoromethyl) benzene **3** [MS, *m/z* (relative abundance): 333 (30%), 331 (89), 304 (33), 303 (45), 302 (80), 276 (31), 274 (100), 238 (13), 211 (15), 179 (7), 124 (36)];

2-chloro-1-(3-hydroxy-4-nitrophenoxy)-4-(trifluoromethyl) benzene **4** [MS, *m/z* (relative abundance): 335 (18), 333 (52), 280 (17), 252 (100), 223 (11), 179 (8), 132 (8), 69 (16), 63 (19)].

The reaction mixture was then concentrated under a mild vacuum in a rotating evaporator, nitrogen fluxed, and separation of metabolites was achieved by thin layer chromatography (TLC) on $60F_{254}$ plates (E. Merck) using as solvent system a mixture of acetonitrile / chloroform / methanol (30: 5 : 65). On recovered products [^{1}H] NMR spectra were recorded. Brucker 300 AM instrument was used and the acquisitions were performed in $CDCl_3$: compound **2** (chemical shifts are reported in δ): 7.72 (s, 1 H), 7.25 (s, 1 H), 7.5–6.7 (m, 4 H), 3.92 (q, 2 H, $J = 7$ Hz), 3.2 (bs, 1 H), and 1.34 ppm (t, 3 H, $J = 7$ Hz); compound **3**: 7.73 (s, 1 H), 7.5–7.0 (m, 4 H), 7.24 (s, 1 H), 3.92 (q, 2 H, $J = 7$ Hz), 3.5 (bs, 2 H), and 1.33 ppm (t, 3 H, J = 7 Hz); compound **4**: 7.72 (s, 1 H), 7.5–7.2 (m, 4 H), 7.15 (s, 1 H), and 3.1 ppm (bs, 1H).

Afterwards, to have information on photoproducts yielding under a longer irradiation time, the reaction was extended and GCMS analysis was repeated at 24 h irradiation.

Main metabolites were: 2-chloro-1-(3-ethoxy-4-hydroxyphenoxy)-4-(trifluoromethyl) benzene **2**; 2-chloro-1-(3-hydroxy-4-nitrophenoxy)-4-(trifluoromethyl) benzene **4**; 1-(3-ethoxy-4-nitrophenoxy)-4-(trifluoromethyl) benzene **5** [MS, *m/z* (relative abundance): 327 (69), 251 (100), 223 (25), 163 (8), 91 (8), 63 (9)]; and 2-chloro-1-(2-hydroxy-4-ethoxy-3-nitrophenoxy)-4-(triflurometyl) benzene **6** [MS, *m/z*: 377 (100), 358 (10), 301 (18), 267 (16), 251 (18), 239 (12), 95 (8), 69 (16)].

Unfortunately the concentrations of compounds **5** and **6** were too low to obtain their effective separation by TLC and registration of clear NMR signals.

3. Results and discussion

3.1. Photophysical properties of oxyfluorfen

The UV spectra of oxyfluorfen in methanol, acetonitrile, and *n*-hexane are illustrated in Fig. 1. Each spectrum exhibits an absorption at 267–276 nm, which could be assigned to a $\pi \rightarrow \pi^*$ transition and an absorption at 310–325 nm, probably due to a $n \rightarrow \pi^*$ transition. In Table 1 are summarised

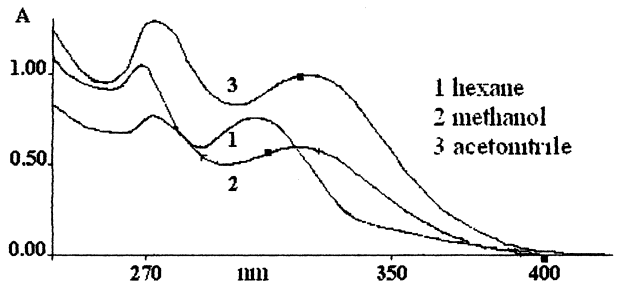


Fig. 1. UV spectra of oxyfluorfen (0.1 mM) in different solvents.

Table 1
UV absorption maxima and extinction coefficients of oxyfluorfen in different solvents

Solvent	λ_1 (nm)	ϵ (M^{-1} cm^{-1})	λ_2 (nm)	ϵ (M^{-1} cm^{-1})
n-hexane	267	8213	310	5390
Methanol	270.5	6432	325	5351
Acetonitrile	275.5	7566	323	5700

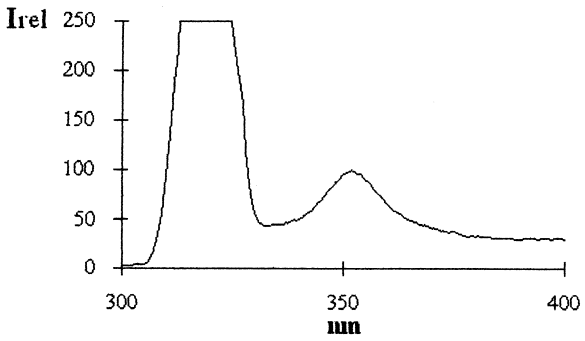


Fig. 2. Fluorescence spectrum of oxyfluorfen (0.1 mM in acetonitrile versus DPA as actinometer); $\lambda_{exc} = 323$ nm; $\lambda_{em} = 350$ nm.

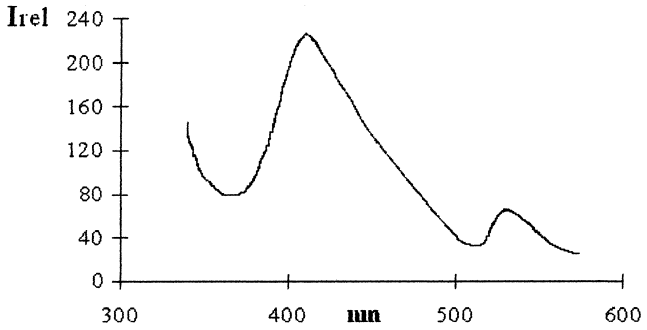


Fig. 3. Phosphorescence emission of oxyfluorfen (0.1 mM in EPA versus acetophenone as actinometer); $\lambda_{exc} = 330$ nm; $\lambda_{em} = 411$ nm.

the absorption maxima and the corresponding extinction coefficients evaluated by the Lambert–Beer law. Moreover, oxyfluorfen shows a low emission band at 350 nm ($\lambda_{exc} = 323$ nm) in the fluorescence spectrum (Fig. 2), and an emission band at 411 nm ($\lambda_{exc} = 330$ nm) in the phosphorescence spectrum with $\Phi_{ph} = 4.0 \times 10^{-3}$ (Fig. 3). These data allow the calculation the energy of the first excited singlet state and that of the lowest excited triplet state at 346 kJ mol^{-1} ($\tau = 1.77 \times 10^{-8}$ s) and 291.1 kJ mol^{-1}, respectively. The intersystem crossing quantum yield was $\Phi_{isc} = 2.9 \times 10^{-2}$.

3.2. Photodegradation of oxyfluorfen

Figs. 4 and 5 show the degradation curves of **1** in different solvents (methanol, acetonitrile and *n*-hexane), obtained under Suntest and UV mercury arc irradiation, respectively. The quantum yields were 0.473, 0.554, and 0.959

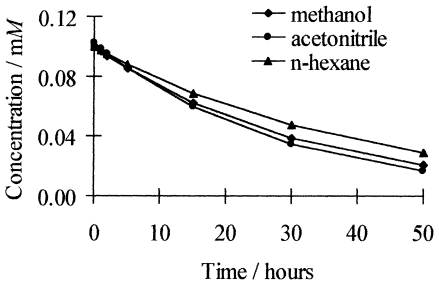


Fig. 4. Degradation curves of oxyfluorfen (0.1 mM) in different solvents (Suntest).

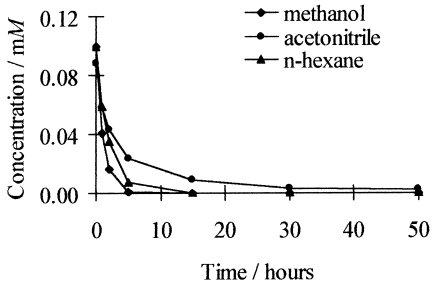


Fig. 5. Degradation curves of oxyfluorfen (0.1 mM) in different solvents (UV mercury arc).

in acetonitrile, methanol, and *n*-hexane, respectively. The kinetic parameters of the degradation reactions are listed in Table 2. All the reactions fit a first kinetic order. No significant reaction was observed in the dark.

The products obtained after light irradiation lasting of one-hour are depicted in Scheme 1. Afterwards the reaction was stopped. Three main products were observed: **2**, **3**, and **4**. Product **2** exhibits a nitro group substituted by a hydroxy group. There is also a reduction product (**3**), where the nitro

Table 2
Kinetic parameters of oxyfluorfen degradation and quantum yields

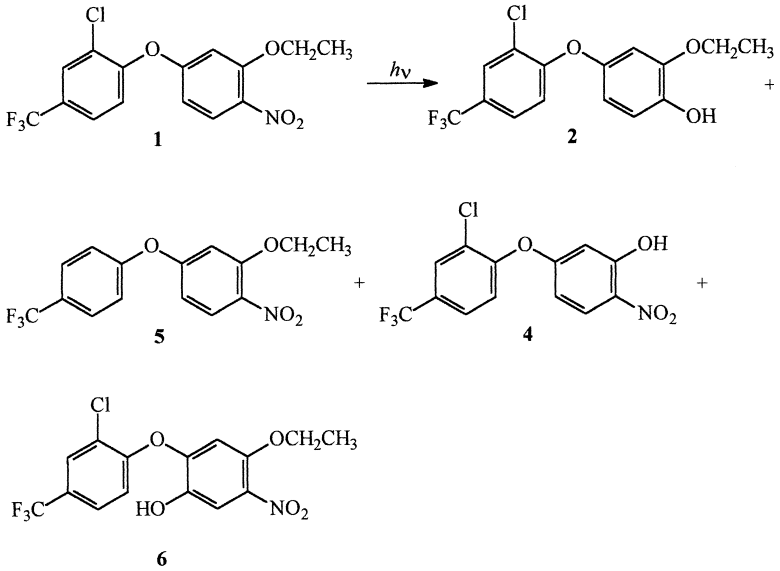
Solvent	Irradiation source	τ ($s \times 10^{-3}$)	k ($s^{-1} \times 10^{5}$)	Φ
Acetonitrile	Suntest	84.2	0.822	0.473
Acetonitrile	UV	7.1	9.83	
Methanol	Suntest	86.4	0.803	0.554
Methanol	UV	4.5	15.40	
n-hexane	Suntest	100.4	0.692	0.959
n-hexane	UV	4.8	14.59	

group is transformed in an amino group, and a product (**4**), where the ethoxy group became a hydroxy group. The reduction of the nitro to amino group was also reported by Ruzo et al. [11].

Interestingly, when the photochemical reaction was allowed to occur for 24 h, a different reaction mixture was observed and a host of minor compounds appeared. As described for clearness in Scheme 2, two additional degradation products (**5**) and (**6**) were found to be of some chromatographic relevance, whereas compound **3** was not more detectable. Note that product **5**, which is probably obtained from the homolytic cleavage of the carbon-chlorine bond, was observed at trace level. Owing to their low concentration we only can hypothesise on structures of compounds **5** and **6** on the basis of GCMS spectra.

Fig. 6 clearly shows the depletion of compound **3** after 5 h of irradiation and its definitive disappearance at 15 h meanwhile compounds **5** and **6** appeared after 15 h and 8 h of irradiation, respectively. Noteworthy is that the yield of formation of metabolite **2** shows a valley at 5 h corresponding with the maximum yield of **3.** Yielding of metabolite **4** is steady rising along the entire irradiation time.

For a better understanding of the oxyfluorfen photochemical degradation mechanism some experiments were also



Scheme 2.

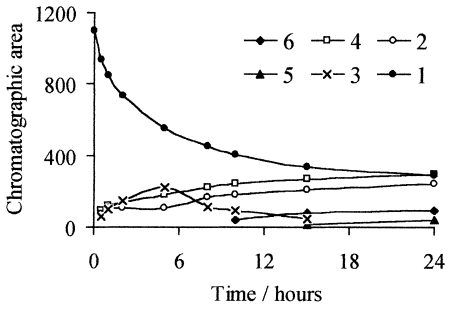


Fig. 6. Yield of formation with irradiation time for main metabolites of oxyfluorfen in acetonitrile.

Table 3
Kinetic data on oxyfluorfen (0.1 mM in acetonitrile) degradation in the presence of: triplet quencher (biphenyl at different molar ratios); singlet quencher (pyridazine); radical initiator (AIBN); radical inhibitor (benzoquinone)

Added substance	Molar ratio	τ ($s \times 10^{-3}$)	k ($s^{-1} \times 10^{5}$)
–	1:0	84.2	0.82
Biphenyl	1:2.5	15.5	4.44
Biphenyl	1:5	19.2	3.61
Biphenyl	1:10	17.9	3.86
Pyridazine	1:10	724.6	0.096
AIBN	1:10	82.3	0.84
Benzoquinone	1:10	49.5	1.40

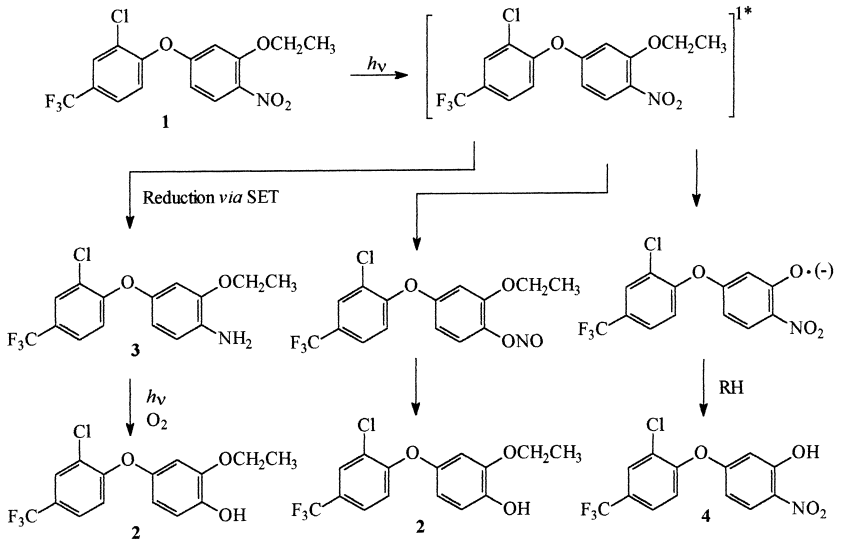
carried out under the Suntest irradiation system. The reaction was performed in the presence of either a singlet [pyridazine ($E_S = 318\,kJ\,mol^{-1}$)] or a triplet quencher [biphenyl ($E_T = 274\,kJ\,mol^{-1}$, $E_S = 391\,kJ\,mol^{-1}$)]. We wished to clarify whether the photochemical reaction occurred through the first excited singlet state or through the first excited triplet state.

The presence of a singlet quencher considerably inhibits the reaction as evidenced from kinetic data reported in Table 3. Meanwhile, the presence of a triplet quencher does not inhibit the reaction, but the degradation rate seems to increase with the rising of the molar ratio biphenyl/oxyfluorfen (Table 3). All these data are in agreement with a mechanism involving the first excited singlet state.

Furthermore, we have performed the degradation of **1** (0.1 mM in acetonitrile) in the presence of a radical initiator (2,2'-azobisisobutyro-nitrile, AIBN, 1 mM). As we did not observe any change in the reactivity of the substrate (Table 3), the reaction was carried in the presence of a radical inhibitor. Benzoquinone was selected because its UV spectrum does not overlap with the absorption maximum of oxyfluorfen [15]. Moreover, in this case we did not obtain significant data to support a radical mechanism for the photolysis of oxyfluorfen, because the rate constant (k) slightly increased from $0.82 \times 10^{-5}\,s^{-1}$ to $1.40 \times 10^{-5}\,s^{-1}$ with the presence of the radical inhibitor.

Finally, we tested the photochemical degradation of oxyfluorfen in acetonitrile without the presence of air because of the relatively high solubility of O_2 in acetonitrile [16]. Argon was used to saturate the solution, but no significant changes in the degradation rate was observed.

All these data fit the following hypothesis on the degradation mechanism of **1** (Scheme 3). The first excited singlet state may undergo either an homolytic or heterolytic photolysis of the alkyl-oxygen bond in the side chain to give compound **4**, after abstraction of a hydrogen atom or of a proton from the solvent. On the other hand a reduction reaction can give compound **3** which is then converted into compound **2** via a photonucleophilic substitution [10,11]. Otherwise, the compound **2** can be obtained directly from the nitro substituted compound **1** via a transposition reaction of the nitro group to nitrite and the subsequent formation of the radical [17]. It is noteworthy that, while the transposition of the nitro group is described to occur in the triplet state, our results



Scheme 3.

could represent the first example of this reaction through the first excited singlet state. Despite these facts, it is difficult to explain the formation of the reduction product **3**. It is known that nitroarenes can be reduced to amino derivatives via an electron transfer process with the formation of radical anion of the nitroarene derivative followed by hydrogen abstraction [18]. Although this type of mechanism is probably involved in the observed degradation of **1**, a compound acting as donor in the reaction process was not identified. Furthermore, the reduction of nitroarenes is usually obtained in acidic medium, while this condition is not present in the degradation protocol used in this work. At the same time, it is not easy to explain the formation of compounds **5** and **6** in Scheme 2 when the degradation is performed for a prolonged time (i.e. 24 h). We speculate that on increasing the concentration of by-products (see Scheme 3) the occurrence of additional reaction pathways take over and not easily predictable compounds are formed.

Therefore, and as evidenced by several authors, the increase of herbicidal activity with the light exposure of oxyfluorfen could be due to the formation of more polar (and hydrophilic) compounds designed as **2**, **3**, **4**, and **6**.

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