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Kinetic and mechanistic aspects of the direct photodegradation of atrazine, atraton, ametryn and 2-hydroxyatrazine by 254 nm light in aqueous solution

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ABSTRACT: Atrazine (**1**), Atraton (**2**) and Ametryn (**3**) are photodegraded upon 254 nm irradiation, yielding 2-OH-atrazine (**4**) as a photoproduct. Dealkylation products are also generated, and 4-ethylamino-6-isopropylamino-(1,3,5)-triazine was also found as a photoproduct of **3**. The main photoreaction is proposed to be an addition–elimination, yielding **4**, which subsequently photodegrades. The ease of photodegradation depends on the electron availability at position C-2, the observed order of photoreactivity being **1** > **3** > **4** > **2**. Copyright © 2003 John Wiley & Sons, Ltd.

KEYWORDS: dealkylation; herbicides; photodegradation; photolysis; photohydrolysis; addition–elimination; reaction mechanism; triazines

INTRODUCTION

There is serious environmental concern about the levels of *s*-triazine herbicides in groundwater and drinking water supplies. Of particular importance in this respect are chlorotriazine derivatives, such as atrazine, which have been amongst the most widely used herbicides in Europe and the United States.[1,2] These may have a variety of toxic effects,[3] and although legislation restricts their use, their persistence in the environment requires the development of cheap and reliable methods for their destruction.

Various techniques have been suggested for the elimination of atrazine and related compounds from drinkable water, including biological degradation,[4] adsorption,[4] oxidation by ozone,[5,6] or the Fenton reaction,[7–9] direct and catalysed photolysis,[10–14] sonolysis[12] and radiolytic decomposition.[15] Amongst the photocatalysts tested, titanium dioxide,[10,11] polyoxometalates,[12] riboflavin[13] and porphyrin and phthalocyanine derivatives[14] have been shown to be particularly efficient.

However, the rational design of new treatment methodologies requires a mechanistic understanding of the reaction pathways involved in the degradation process.[16] The direct photolysis of atrazine in water has been studied[10,17–19] and suggested to produce 2-OH-atrazine as the major product.[10] However, little information is available on the subsequent fate of this compound, and mechanistic details concerning the way in which 2-OH-atrazine is generated remain obscure. In this paper we will focus on some of these aspects, reporting a study of the direct photolysis of atrazine (**1**) and related compounds, atraton (**2**), ametryn (**3**) and 2-hydroxyatrazine (**4**), in aqueous solutions using 254 nm light (Scheme 1).

EXPERIMENTAL

Compounds **1**–**4** were Pestanal certified standards from Riedel de Häen. Their purity was checked by gas chromatography, and they were used without further purification. Organic matter-free freshly doubly distilled water was used to make up all solutions. In all cases the solutions were allowed to equilibrate with air at atmospheric room temperature and pressure.

The pH values of the different solutions were not far from those typical of riverine water (ca 6), due to their typical macroscopic pK_1 value, ca 5.[20–22] pH measurements were carried out at 298.0 K using a combined glass

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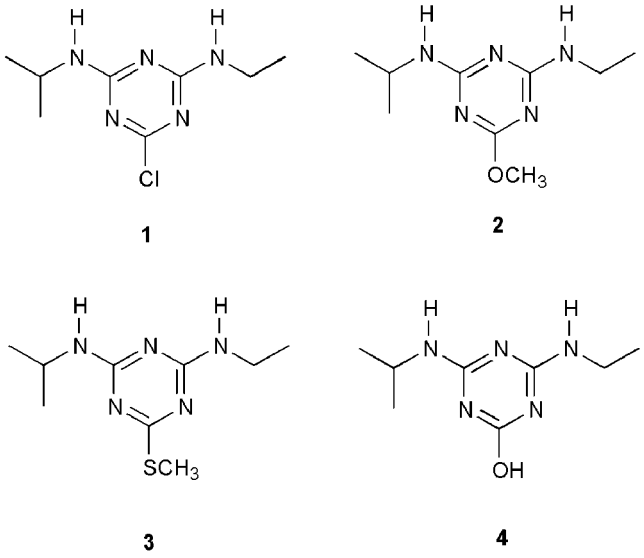


Scheme 1. Compounds used in this study

electrode, previously calibrated with commercial buffers of pH 7.02 ± 0.01 and 4.00 ± 0.01. The accuracy achieved in the measurement of pH was within ± 0.02 units.

Spectrophotometric measurements using a continuous flow of solution were made using a Milton Roy Spectronic 3000 double-beam array spectrophotometer. A 10 mm pathlength and 1.0 mL capacity quartz cells was used. All other spectrophotometric measurements in which solution flow was not needed were taken on a double-beam Kontron Uvikon 941 Plus spectrophotometer, using standard quartz cells with 10 mm pathlength and 3.5 mL capacity. Both systems were thermostated to within ± 0.1 K by water flow.

A Merck-Schuhardt TNN 15/32 irradiation system was used for irradiation, supplying essentially monochromatic light at 254 nm. In order to carry out continuous spectrophotometric monitoring of the photodegradation, inlet and outlet valves were coupled to one of the quartz cells, and a peristaltic pump, allowing a flow-rate between 1 and 1000 ml h^{-1}, was used to obtain a smooth, non-turbulent flow inside the cell (ca 12 mL min^{-1}). The lamp was jacketed with a glass container and thermostated to within ± 0.1 K by water flow.

All relevant data were converted into ASCII code and analysed using *ad hoc* software packages. Reported rate constants are average values obtained from replicated experiments, whose reproducibility was within 5%.

Samples used for product analysis were directly extracted from the reaction mixture at different irradiation times, and stored frozen at ca 253 K prior to analysis. The samples were used directly, without any further work-up procedure.

Product analysis were carried out by high-performance liquid chromatography (HPLC) and gas chromatography–mass spectrometry (GC–MS). Changes in the Cl^- content of the photosylate were recorded for **1** using a properly calibrated Cl^- selective electrode. In the case of **3** the photosylate was analysed for the presence of methanethiol by derivatization with monobromobimane[23] and subsequent measurement of the fluorescence emission in a single-beam, 1 cm pathlength Aminco Bowman Series 2 luminescence spectrometer.

HPLC analyses were performed with a Waters system equipped with a flow unit, automatic injection, column oven with temperature control and a photodiode-array UV–visible detector, using a detection wavelength of 220 nm. The flow-rate was 1.2 mL min^{-1} and 100 mL of the sample were injected in all cases. The linearity of response of the detector to all analysed products was tested. A reversed-phase 250 mm × 4.6 mm i.d. column, packed with C-18 Intertsil (5 μm), was used. The mobile phases consisted of acetonitrile and 5 mM acetic acid (pH ≈ 4.5), using the solvent gradient 0:100 (0 min), 75:25 (15 min), 100:0 (20 min), 0:100 (25 min).

GC–MS analyses were carried out using a DB-XLB (60 m × 0.25 mm i.d., 0.25 μm film thickness) capillary column, with splitless injection and a Thermo Finnigan Trace GC 2000 apparatus, equiped with a CTC Analitics GCPAL injector. Mass spectrometric detection was carried out using a Thermo Finnigan PolarisQ apparatus equiped with an ion trap in the full-scan mode and by selecting the different molecular ions characteristic of the compounds under study.

The main photoproducts observed are listed in Table 1.

To complement and reinforce the experimental studies, electronic structure calculations were carried out with the Gaussian 98 suite of programs.[24] The theoretical model, denoted B3LYP, is based on density functional theory,[25,26] and the 6–31G(d,p) basis set was used. Full geometry optimization was carried out in the gas phase, a frequency calculation on each optimal geometry resulting in no imaginary frequencies.

Table 1. Main photoproducts observed upon 254 nm steady-state irradiation

	Detection method		
Compound	GC–MS	Fluorescence	HPLC
1	—	—	2-Hydroxyatrazine
2	Desisopropylatraton	—	2-Hydroxyatrazine
3	4-ethylamine-6-isopropylamine-1,3,5-triazine	MeSH	2-Hydroxyatrazine

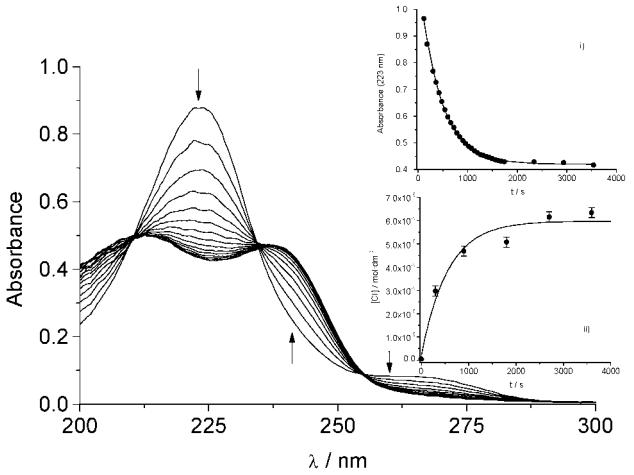


Figure 1. Spectral changes observed at various times from 5 min to 1 h following 254 nm irradiation of 51 μM atrazine (pH ≈ 6.0, 5% MeOH, T = 298.0 K, 1 h of irradiation). Insets: (i) change in absorbance observed at 223 nm and (ii) change in [Cl^-] observed upon irradiation as a function of irradiation time

RESULTS

The UV absorption spectrum of **1** in aqueous solution (pH ≈ 6, 5% MeOH) shows absorptions at 263 and 223 nm, with molar absorption coefficients 3500 and 34 400 l mol^{-1} cm^{-1}, in good agreement with previous reports on this and the related compound terbuthylazine.[10,19] The 223 nm band has previously been assigned to a π to π^* transition.[27] The nature of the longer wavelength transition is, as yet, unclear. However, Mason has assigned the band observed at 260 nm in *sym*-triazine in water to the n to π^* transition.[28] Upon irradiation with 254 nm light, these bands were seen to decrease in intensity and new absorptions grew in at 238 and *ca* 205 nm. In the initial stages of the reaction, good isosbestic points were observed (Fig. 1), indicating clean interconversion to the primary products. Upon prolonged photolysis (up to 8 h) the absorbance at 238 nm was seen to decrease and a less well defined spectrum was observed.

The kinetics of the initial process were followed by studying the decrease in the absorption of **1** at 223 nm and the build-up of the new absorption at 238 nm. In both cases, the kinetics fitted good first-order behaviour, with rate constants $(2.30 \pm 0.03) \times 10^{-3}$ s^{-1} (223 nm, Fig. 1, inset i) and $(2.5 \pm 0.2) \times 10^{-3}$ s^{-1} (238 nm), which are identical within experimental error. The values are also close to those previously reported for the direct photolysis of aqueous solutions of **1**.[10] The irradiation was also found to lead to a release of Cl^-, which was monitored as indicated previously (Fig. 1, inset ii), showing a slightly lower rate constant, although within the same order of magnitude [$(1.8 \pm 0.3) \times 10^{-3}$ s^{-1}]. This difference may be associated with photolysis leading to other reactions competing with photosubstitution of Cl^-. Furthermore, irradiation was seen to lead to a decrease in the pH of the solution that was not compensated by the buffering effect of **1** or its photoproducts.

The products of the initial stages of photolysis were studied by HPLC. Upon 60 min of irradiation with 254 nm light of a 51 μM solution of **1** in 5% MeOH–H_2O, loss of **1** (retention time t_R = 16.3 min) was found to be accompanied by the simultaneous quantitative recovery of a product (99%, t_R = 12.7 min), that was identified as **4** by comparison with an authentic sample, in agreement with previous reports.[10,29] Kinetic analysis of these results was complicated by consecutive photodegradation of this photoproduct. However, the rate constant for formation of **4** as measured by HPLC appears to be markedly lower than the rates of photodegradation obtained from the UV spectral changes, suggesting parallel routes for atrazine photodegradation. In support of this, some HPLC peaks due to minor components were also observed. These have not yet been identified, although the GC–MS results show no signs of dealkylated products.

At longer times, degradation of the major primary photoproduct, **4**, was observed by both UV–visible spectrophotometry and HPLC. The photodegradation of **4** was also studied in separate experiments. Its absorption spectrum, highly dependent on the acidity of the medium (Fig. 2), showed absorption maxima at 215 nm in basic medium (pH ≈ 12.2, $\epsilon \approx 45\,800$ l mol^{-1} cm^{-1}), and at λ <200 nm and also 240 nm in acidic medium (pH ≈ 2.3, ϵ(238 nm) ≈ 15 200 l mol^{-1} cm^{-1}). On this basis, the two macroscopic pK_a values observable for **4** under common acidity conditions were obtained from the change in absorbance at both 215 and 240 nm (Fig. 2, inset), exhibiting values pK_1 = 5.2 ± 0.1 and pK_2 = 10.8 ± 0.4,

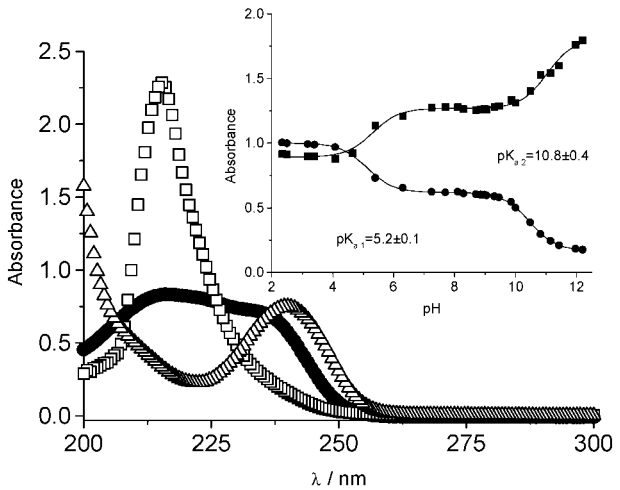


Figure 2. Spectra of **4** under different conditions of acidity. (□) Basic medium; (△) acidic medium; (●) pH ≈ 6. Inset: determination of the two macroscopic pK_a values; (■) 215 nm; (●) 240 nm

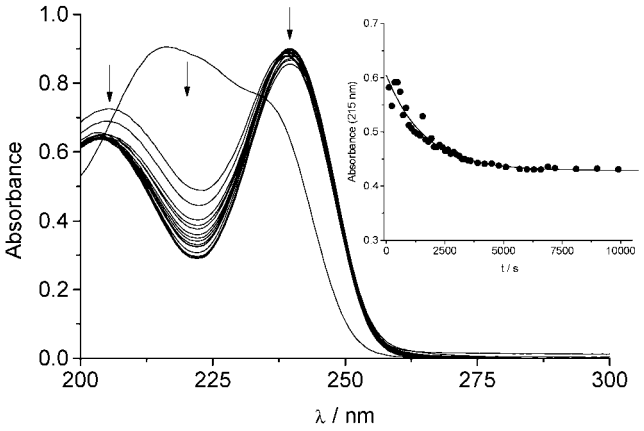


Figure 3. Spectral changes observed at various times from 5 min to 4 h following 254 nm irradiation of 50 μM 2-OH-atrazine (pH ≈ 6.0, 5% MeOH, T = 298.0 K, 3 h of irradiation). Inset: change in absorbance observed at 215 nm as a function of irradiation time

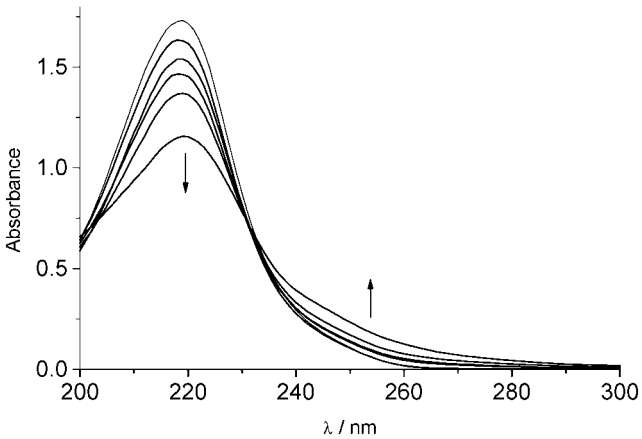


Figure 4. Spectral changes observed at various times from 3 min to 4 h following 254 nm irradiation of 51 μM atraton (pH ≈ 6.0, 5% MeOH, T = 298.0 K, 4 h of irradiation)

in good agreement with those previously obtained using capillary zone electrophoresis and capillary isoelectric focusing methods.[22]

Upon steady-state irradiation at 254 nm of a 50 μM solution of **4** (pH ≈ 6, 5% MeOH–H_2O), spectral changes were observed (Fig. 3), with the formation of new bands at ca 204 and 238 nm. The initial spectrum at pH ≈ 6 (Fig. 3) results clearly from combination of the absorption bands mentioned earlier (Fig. 2). As for **1**, irradiation led to a decrease in the pH of the solution that was not compensated by the buffering effect of **4** or its photoproducts, consequently affecting the shape of the observed spectra (Fig. 3). This notwithstanding, a photodegradation rate of $(6.2 \pm 0.6) \times 10^{-4}$ s^{-1} was estimated from the observed absorbance changes.

To help understand the mechanism of photodegradation of these compounds, the photodegradation of aqueous solutions of two other (1,3,5)-*s*-triazine derivatives, **2** and **3**, was also studied. Solutions of 51 μM of **2** in 5% MeOH–H_2O, pH ≈ 6.0, show an absorption spectrum with maximum at 220 nm ($\epsilon \approx 33075$ l mol^{-1} cm^{-1}), and a weak shoulder at 250 nm ($\epsilon \approx 2115$ l mol^{-1} cm^{-1}). Upon irradiation, a decrease in the absorbance at 220 nm was observed, with corresponding increases in absorbances at ca 250 nm and <200 nm (Fig. 4). From the decrease in absorbance at 220 nm, a rate constant of $(2.57 \pm 0.04) \times 10^{-5}$ s^{-1} was determined. HPLC studies showed that the 2-hydroxy derivative was one of the photoproducts, in agreement with the literature.[29] In addition, GC–MS experiments on the photolysate showed that desisopropylatraton was formed by dealkylation.

Solutions of 51 μM of **3** in 5% MeOH–H_2O, pH ≈ 6.1, show an absorption maximum at 222 nm ($\epsilon \approx 36575$ l mol^{-1} cm^{-1}) and a weaker band at 270 nm ($\epsilon \approx 3918$ l mol^{-1} cm^{-1}). Upon irradiation a decrease in absorbance at 222 nm was observed to be accompanied by the formation of a new absorption at shorter wavelengths (Fig. 5). The photodegradation followed first-order kinetics (Fig. 5, inset i), with a rate constant of $(2.2 \pm 0.5) \times 10^{-3}$ s^{-1}. HPLC studies showed that **4** was the main photoproduct, in agreement with the literature.[29] GC–MS studies on the photolysate evidenced the formation of 4-ethylamino-6-isopropylamino-1,3,5-triazine. Fluorimetric measurements upon derivatization of the photolysate with monobromobimane showed an increase in the intensity of fluorescence during the first 30 min, followed by a slight and slower decrease (Fig. 5, inset ii).

Table 2 summarizes the different rate constants obtained for the 254 nm-initiated photodegradation of triazines **1**–**4**. No obvious linear free energy relationship

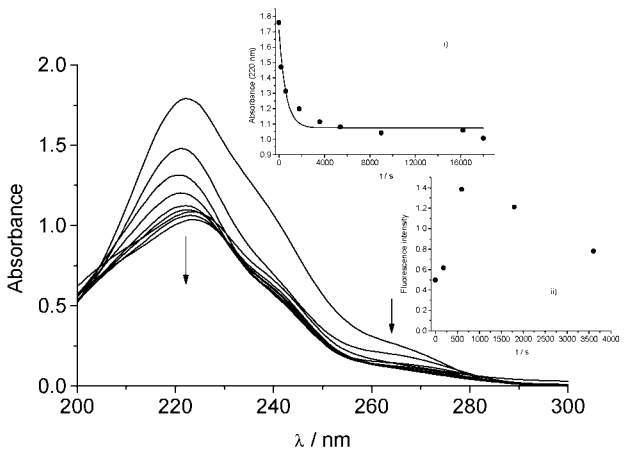
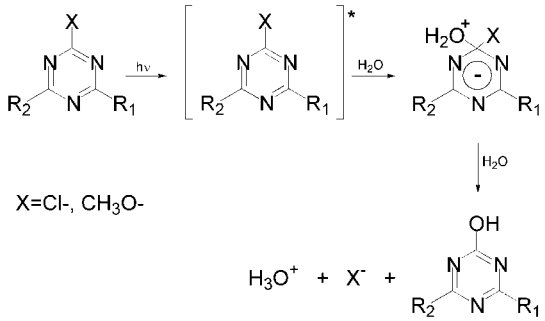


Figure 5. Spectral changes observed at various times from 5 min to 5 h following 254 nm irradiation of 51 μM **3** (pH ≈ 6.10, 5% MeOH, T = 298.0 K, 5 h of irradiation). Insets: (i) change in absorbance observed at 220 nm and (ii) change in the intensity of fluorescence emission at 480 nm upon derivatization of the photolysate with monobromobimane (λ_{exc} = 394 nm) as a function of irradiation time

Table 2. Rate constants obtained spectrophotometrically for the photodegradation of triazines **1–4**

Compound	k (s^{-1})
1	$(2.3 \pm 0.03) \times 10^{-3}$ [a]
	$(2.5 \pm 0.2) \times 10^{-3}$ [b]
2	$(2.57 \pm 0.04) \times 10^{-5}$
3	$(2.2 \pm 0.5) \times 10^{-3}$
4	$(6.2 \pm 0.6) \times 10^{-4}$

[a] Detection at $\lambda = 223$ nm.
[b] Detection at $\lambda = 238$ nm.



Scheme 2. Mechanism of photodegradation proposed for compounds **1** and **2**

was found between these rate constants and the substituent inductive or steric effects. A study of the photodegradation with a wider range of 1,3,5-triazine herbicides is planned in which both kinetic and quantum yield data will be measured to check on the existence of any useful structure-reactivity correlations.

Theoretical calculations carried out at the B3LYP/6–31G(d,p) level allowed us to analyse the Mulliken charges at position 2 of the different triazines, evidencing in all cases an electronic deficiency in this position (Table 3).

DISCUSSION

The photodegradation of four related 1,3,5-triazines was studied in aqueous solutions using 254 nm light. Two main degradation pathways are observed, photosubstitution at the 2-position, leading generally to the 2-hydroxy derivative, and dealkylation on the amine side-chains. Photohydroxylation at the 2-position has also been observed with various other 1,3,5-triazines,[30] and seems to be a common reaction for this class of compounds. Three mechanisms can in principle be considered for this: (i) homolytic dissociation of the carbon–substituent bond at the 2-position, followed by reaction of the triazinium/triazinyl radical with water or HO^-, (ii) addition of water/HO^- followed by elimination of the other substituent or (iii) a charge-transfer process involving the formation of the triazinium radical cation, followed by nucleophilic attack of water/HO^-. Intermediacy of charge-transfer species has been suggested in the photosubstitution of 1-nitronaphthalene by hydroxide ion.[31] However, the mechanism is unlikely in this case since triazines are known to have very high oxidation potentials.[32] Furthermore, homolytic dissociation is unlikely to be an important mechanism in the case of triazines, since 2-hydroxy products are observed on photolysis of a wide variety of 1,3,5-triazines having very different dissociation energies for the 2-substituent bonds.[21,33] We therefore believe that the main mechanism involves addition–elimination. Support for this comes from charge calculations. Table 3 shows that all **1–4** are electronically defficient at C-2 which is in agreement with the addition of water/HO^- at such a position. Moreover, the electron deficiency is less important for **2** and **4**, in line with the fact that the photodegration is slower for these derivatives, as evidenced by the observed rate constants (Table 2).

Table 3. Calculated Mulliken charges at position 2 [B3LYP/6–31G(d,p)]

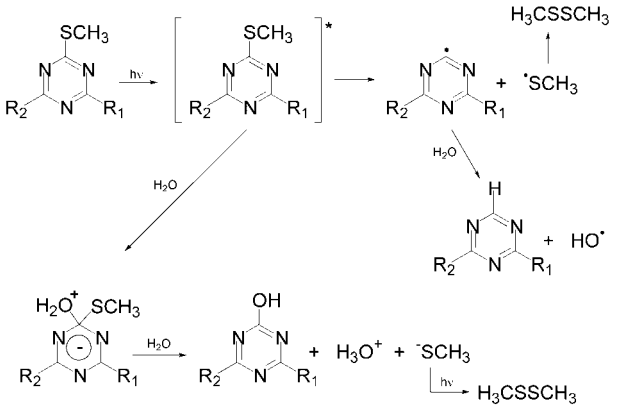
Compound	Charge at position 2
1	0.266696
2	0.685101
3	0.272177
4	0.656304

Therefore, the behaviour observed for **1** and **2** can be rationalized in terms of the mechanism shown in Scheme 2, which would explain the increase in [Cl^-] for **1**, and also as the decrease in the pH of the medium observed for all **1–4**.

In the case of **3**, an initial increase in the concentration of thiol (MeSH) was observed, followed by a loss of MeSH. This could be due to the photolysis of MeSH to yield $MeS^{\bullet}$, with subsequent reduction of the thiol concentration. Furthermore, the detection of 4-ethylamino-6-isopropylamino-(1,3,5)-triazine indicates homolysis of the C—S bond followed by H abstraction by the resulting triazinyl radical. This observation is in agreement with previous findings for 2-methylthio-(1,3,5)-triazines.[27,34] All the observations for **3** can be rationalized in terms of the mechanism shown in Scheme 3.

Despite the fact that **4** is the one of the main photoproducts of photodegradation of **1–3**, the same being valid for analogous (1,3,5)-triazine herbicides with different substituents,[16] no detailed product analyses are available for its photodegradation. From the observations for **1–3**, dealkylation in the lateral chain could be expected.

For this mechanistic route, dealkylation of the amino groups, the mechanism is less clear. Theoretical calculations show that the lone electron pairs on the side-chain nitrogen atoms are included in the electron delocalization



Scheme 3. Mechanism of photodegradation proposed for compound **3**

of the heterocyclic ring, thus facilitating a potential dealkylation of the alkyl side-chains. Therefore, it is possible that dealkylation is a relatively minor route with this excitation source (254 nm), resulting from some dissociative pathway ocurring at higher excitation energies. Joint experimental and theoretical studies are in progress in order to compare the effects of different excitation wavelengths to test this and to analyse in detail the reaction mechanism.

CONCLUSION

Compounds **1**–**3** undergo 254 nm-initiated photodegradation, leading to **4** as one of the main photoproducts, as shown by HPLC. Dealkylation products were also observed by GC–MS in the case of **2**, and 4-ethylamino-6-isopropylamino-(1,3,5)-triazine in the case of **3**. An addition–elimination mechanism is proposed for **1**–**3**, leading to **4**, which would subsequently undergo photodegradation. The observed order of reactivity upon irradiation is **1** > **3** > **4** > **2**, in accordance with the electron availability at position C-2. No linear free energy relationship was found between the observed rate constants and substituents inductive or steric effect.

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