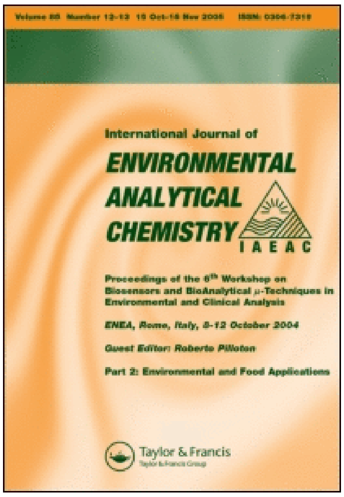


International Journal of Environmental Analytical Chemistry
Publication details, including instructions for authors and subscription information:
http://www.informaworld.com/smpp/title~content=t713640455

Asulam in Aqueous Solutions: Fate and Removal Under Solar Irradiation

Carole Catastini[a]; Mohamed Sarakha[a]; Gilles Mailhot[a]
[a] Laboratoire de Photochimie Moléculaire et Macromoléculaire, CNRS, Université Blaise Pascal, Aubière Cedex, France

To cite this Article Catastini, Carole , Sarakha, Mohamed and Mailhot, Gilles(2002) 'Asulam in Aqueous Solutions: Fate and Removal Under Solar Irradiation', International Journal of Environmental Analytical Chemistry, 82: 8, 591 — 600
To link to this Article: DOI: 10.1080/03067310290009479
URL: http://dx.doi.org/10.1080/03067310290009479

Intern. J. Environ. Anal. Chem., Vol. 82, No. 8–9, pp. 591–600

ASULAM IN AQUEOUS SOLUTIONS: FATE AND REMOVAL UNDER SOLAR IRRADIATION

CAROLE CATASTINI, MOHAMED SARAKHA and GILLES MAILHOT*

Laboratoire de Photochimie Moléculaire et Macromoléculaire, CNRS Université Blaise Pascal, UMR 6505, 24 Avenue les Landais, F-63177 Aubière Cedex, France

(Received 24 August 2001; In final form 10 January 2002)

The photodegradation of the pesticide asulam (methyl[(4-aminophenyl)sulfonyl]carbamate) in aqueous solutions ($1.0 \times 10^{-4}\,\mathrm{mol\,L^{-1}} = 23\,\mathrm{mg\,L^{-1}}$) has been investigated with and without Fe(III). The asulam disappearance were measured by direct photolysis at 254 nm as a function of pH and oxygen concentration. Different photoproducts have been identified, among them a blue condensation product which was only observed upon selective direct excitation of asulam. In the presence of Fe(III) and by excitation at 365 nm, we obtained the complete mineralisation of asulam, while no complete transformation of organic carbons into CO_2 was observed by direct photolysis. The continuous formation of $^{\bullet}OH$ radicals generated from the excitation of Fe(III) species allowed the total mineralisation of asulam. Information is also given about the fate of asulam in aqueous solutions under solar irradiation.

Keywords: Asulam; Water; Solar irradiation; Photodegradation; Fe(III)

INTRODUCTION

The contamination of aquatic bodies by synthetic chemicals is one of the great environmental problems. Among the synthetic chemicals, pesticides have been widely developed in the last 50 years. More than 120 formulations are used in French agriculture. Due to the intensive use of pesticides each year they can be found in surface waters. Despite the generally low concentration ($< \mu\mathrm{g\,L^{-1}}$) in the river, it is of great interest from an environmental point of view to know the persistence of the parent compound and also the nature of the photogenerated products in water.

When the pesticides does not absorb solar light, its transformation can be photoinduced by different absorbing species, present or added in the aquatic medium (Nitrate [1], Humic substances [2], Fe(III) aquacomplexes [3], ...). In our laboratory, we have previously investigated the degradation of various pollutants photoinduced by Fe(III) [4]. Fe(III) aquacomplexes are known to undergo photolysis upon irradiation with wavelengths $\lambda > 300$ nm, yielding to Fe(II) and hydroxyl radicals ($^{\bullet}OH$) [5,6]. Hydroxl radicals, which are known to be strong oxidant agents, react efficiently but not selectively with most organic substrates with rate constants that are limited

---

*Corresponding author. Fax: +33 4 73 40 77 00. E-mail: gilles.mailhot@univ-bpclermont.fr

ISSN 0306-7319 print: ISSN 1029-0397 online
DOI: 10.1080/03067310290009479

by diffusion. In all cases, we concluded that the degradation photoinduced by Fe(III) was an interesting process for the elimination of pollutants in aqueous solution.

In this work, we investigated the direct photolysis and the photoinduced degradation by Fe(III) of asulam in aqueous solutions. The pesticide asulam is a translocation herbicide, which is absorbed by leaves and roots causing slow chlorosis in susceptible plants. It interferes with cell division and expansion and is used to control the growth of grass [7].

EXPERIMENTAL SECTION

Reagents and Solutions

$Fe(ClO_4)_3$, $9H_2O$ (97%) was purchased from Fluka and used without further purification. Asulam (methyl[(4-aminophenyl)sulfonyl]carbamate) was a Dr. Ehrenstroler-Schäfers product ($>$ 96%). Tetrabutylammonium hydrogen sulfate (TBA) used in water for the HPLC eluent was a Fluka product (purum, $>$ 97%). Methanol was from Carlo Erba (HPLC grade). All solutions were prepared with deionized ultrapure water ($\rho = 18.2\,M\Omega\,cm$). pH measurements were carried out with an Orion pH meter to 0.01 unit. The ionic strength was not controlled.

In order to study the influence of oxygen on asulam disappearance, the solutions were deoxygenated by bubbling argon for 30–40 min at 22°C. For prolonged, irradiation time and kinetic measurements, nitrogen bubbling was maintained during the irradiation.

Apparatus

UV–visible spectra were recorded on a Cary 3 double beam spectrophotometer.

HPLC experiments were carried out using a Hewlett-Packard 1050 chromatograph equipped with a monochromatic UV–visible detector and a fluorescent detector. The flow rate was $1\,mL\,min^{-1}$. The eluent was a mixture of an aqueous solution of TBA (10 mM) and methanol, respectively 70/30 v/v. The column was Waters spherisorb ODS2 C_{18} (250 mm long $\times$ 4.6 mm i.d., 5 µm p.d.).

Several devices were used for the irradiations. To determined the photodegradation at 254 nm a low pressure mercury lamp (PHILIPS TUV 6 W) was used. The beam was parallel, and the reactor was a quartz cell of 1 cm path length. Kinetic experiments were carried out in: (i) a cylindrical stainless steel chamber with three high pressure mercury lamps (Philips HPW type 125 W), the emission of which at 365 nm was selected by an inner filter and in the middle a reactor a water-jacketed Pyrex tube (diameter = 2.8 cm); (ii) a six fluorescent lamps reactor (Duke GL 20 W) was used for irradiations at 310 nm. The quartz reactor was placed along the symmetry axis.

The quantum yield defined as the ratio of the number of transformed molecules and the number of absorbed photons during the same irradiation time. This reflects the efficiency of the photochemical reaction. The chemical actinometry, which permits the determination of incident light intensity, was obtained by using ferrioxalate [8] ($I_{o\,254\,nm} = 2.03 \times 10^{14}$ photons $cm^{-2}\,s^{-1}$).

Solutions were also exposed to natural sunlight in a Pyrex vessel. Experiments were carried out in Clermont-Ferrand (latitude 46° N, altitude 420 m) in June.

Analysis

The Fe(II) concentration was determined by complexometry with *o*-phenanthroline, using $\varepsilon_{510} = 1.118 \times 10^4\,\mathrm{L\,mol^{-1}\,cm^{-1}}$ for the Fe(II)-phenanthroline complex [8].

The method to measure the monomeric concentration of Fe(III) (with HQSA, 8-hydroxyquinoline-5-sulfonic acid) was modified from Kuenzi's procedure [9] and described elsewhere [4]. Under our experimental conditions (concentration $= 3.0 \times 10^4\,\mathrm{mol\,L^{-1}}$ and $\mathrm{pH} = 3.50$), $Fe(OH)^{2+}$ [$Fe(OH)^{2+}$ refers to $Fe((H_2O)_5OH)^{2+}$] is the predominant monomeric Fe(III) hydroxy complex [5]. However, the concentration of monomeric species rapidly decreased after the dissolution of ferric perchlorate in water. The disappearance was attributed to the formation of soluble aggregates, the first step toward the formation of soluble polymeric species and the precipitation of amorphous $Fe(OH_3)$ [10]. It appeared that the percentage of $Fe(OH)^{2+}$ strongly depended on the age of the ferric solution, on the starting concentration [5] and on the temperature. By the HQSA method we were able to determine the percentage of $Fe(OH)^{2+}$ in solution:

$$\%Fe(OH)^{2+} = \frac{[Fe(OH)^{2+}]}{[Fe(III)]_{tot}} \times 100$$

$[Fe(III)]_{tot}$ is the concentration of total dissolved Fe(III). The $\sim 100\%$ of $Fe(OH)^{2+}$ was obtained by weighting the desired amount of $Fe(ClO_4)_3$ and by using the resulting solution immediately after dissolution.

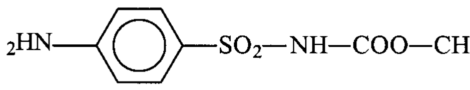
Total Organic Carbon was analysed in a TOC analyser Shimadzu Model TOC-5050A which is based on the combustion infrared gas analysis method. The calibration curve within the range 1–15 $\mathrm{mg\,L^{-1}}$ was obtained by using potassium hydrogen phthalate and sodium hydrogen carbonate for organic and inorganic carbon, respectively.

Laser Flash Photolysis

Transient absorption experiments in the 20 ns to 400 μs time scale were carried out on a nanosecond laser flash photolysis spectrometer from Applied Photophysics (LKS.60). Excitations at 266 nm was from the fourth harmonic of a Quanta Ray GCR 130-01 Nd:YAG laser respectively. The laser pulse with a width of 5 ns was used in a right-angle geometry with respect to the monitoring light beam. A 3 $\mathrm{cm^3}$ volume of solution was used in a quartz cuvette and was stirred after each flash irradiation. Individual cuvette samples were used for a maximum of three consecutive experiments. In order to carry out irradiation with the same percentage of $Fe(OH)^{2+}$, the solutions were prepared for each set of experiments. The transient absorbances at preselected wavelength were monitored by a detection system consisting of a pulsed xenon lamp (150 W), monochromator, and a 1P28 photomultiplier. A spectrometer control unit was used for synchronizing the pulsed light source and shutters with the laser output. The signal from the photomultiplier was digitized by a programmable digital oscilloscope (HP54522A). A 32 bit RISC-processor kinetic spectrometer workstation was used for analysis.

RESULTS

Characterisation of Asulam in Aqueous Solutions

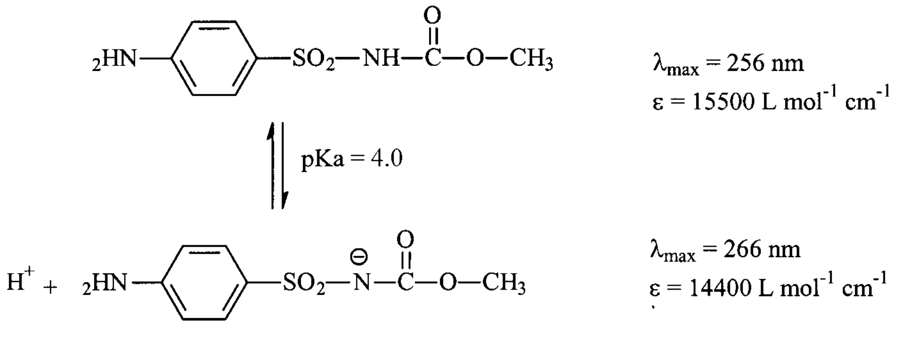


Asulam

SCHEME 1

Asulam (methyl[(4-aminophenyl)sulfonyl]carbamate) is soluble in water with a reported maximum solubility of $5\,g\,L^{-1}$ ($2.17 \times 10^{-2}\,mol\,L^{-1}$) [11]. The concentration of asulam used throughout this work was $1.0 \times 10^{-4} mol\,L^{-1}$ ($23\,mg\,L^{-1}$). Such high concentration with respect to the environmental, conditions was used to perform precise analytical measurements, e.g., detection and identification of photogenerated products. No degradation of asulam was observed in the dark at room temperature after several days.

The acid-base equilibrium of asulam, $pK_a = 4.0$ at 22°C was determined from the evolution of the spectrum as a function of pH. This pK_a is attributed to the protonation of the nitrogen adjacent to the sulfonyl group as reported for sulfacetamide [12]. The UV–visible spectrum (Fig. 1) of both forms present an intense band centred at about 260 nm.



SCHEME 2

The UV–visible spectrum of asulam in aqueous solutions and the solar emission show a small overlap.

Fe(III) and Asulam in Aqueous Solutions

The solution of asulam and Fe(III) was stable in the dark at room temperature for several hours in terms of asulam concentration. No complexation was detected between asulam and Fe(III). The UV–visible spectrum of asulam and Fe(III) mixture was a sum of the individual spectra of asulam and Fe(III). Moreover, the kinetics of $Fe(OH)^{2+}$ disappearance in the dark (followed by complexometry with HQSA, see experimental part) was not affected by the presence of asulam. This again confirms

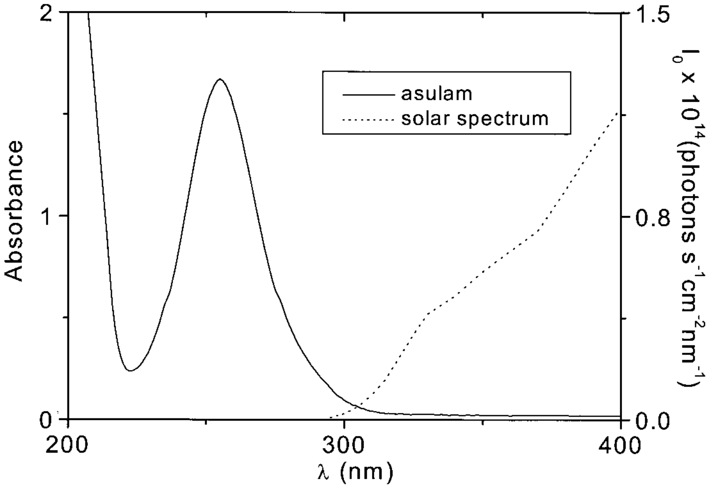


FIGURE 1 UV–visible spectrum of asulam (—) and solar emission in June (- - -).

TABLE I Quantum yields of asulam disappearance as a function of pH and oxygen concentration. [asulam] = 1.0×10^{-4} mol L^{-1} and $\lambda_{irr} = 254$ nm

[*Oxygen*] (mol L^{-1}) [13]	*pH* = 2.0	*pH* = 6.0	*pH* = 11.8
1.39×10^{-3}	0.055	0.10	0.08
0.29×10^{-3}	0.053	0.24	0.19
$< 10^{-5}$	0.07	0.87	0.52

that no interaction between asulam and Fe(III) is observed in aqueous solutions and in the dark.

Photodegradation of Asulam in Aqueous Solutions

The asulam disappearance by direct photolysis was calculated as a function of pH and oxygen concentration (Table I). Such disappearance was expressed by the photochemical quantum yield (see Experimental Section). The irradiations were performed at 254 nm.

The degradation of asulam by direct photolysis is not negligible, and the results show an increase of the degradation when the concentration of oxygen decreases.

Aerated aqueous solutions of asulum (1.0×10^{-4} mol L^{-1} = 23 mg L^{-1}) at pH = 6.0 under UV irradiation (λ = 254 nm) rapidly turned blue with an increase of the colour with the irradiation time. A broad band appeared in the 500–650 nm region with an absorption maximum at 560 nm. These characteristics are similar to those reported earlier [14] for the photooxidation of sulfanilamide. The kinetic of the blue photoproduct formation under irradiation and its UV–visible spectrum are represented in Fig. 2. In addition to the blue product, only observed in the presence of oxygen, we demonstrated the formation of *para*-sulfanilic acid as a major product. Its presence was observed upon irradiation of asulam in the presence and in the absence of oxygen. In the aerated solution, hydroquinone and benzoquinone were also formed as minor photoproducts.

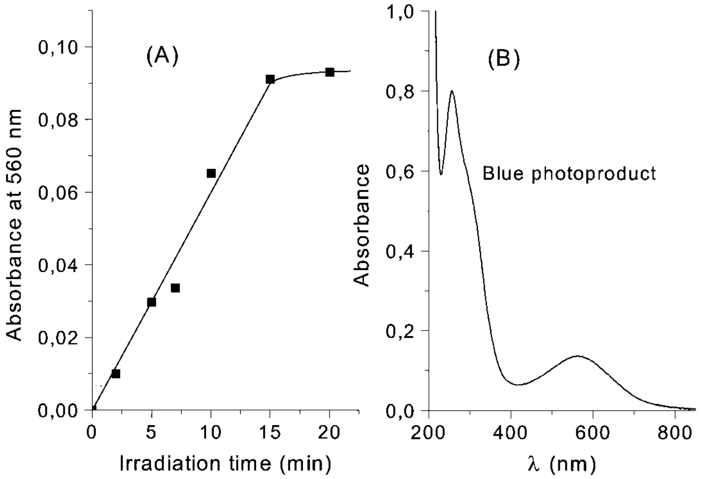


FIGURE 2 (A) Kinetics of the blue photoproduct formation as a function of irradiation ($\lambda = 254$ nm) time. (B) UV–visible spectrum of the blue photoproduct.

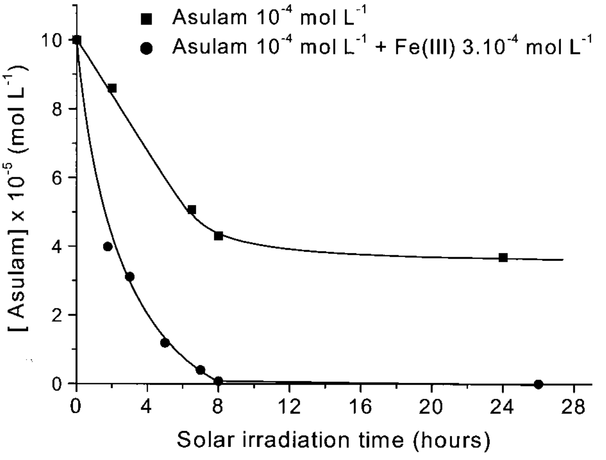


FIGURE 3 Kinetics of asulam disappearance upon solar irradiation with (●) and without (■) Fe(III). [asulam] = 1.0×10^{-4} mol L^{-1}.

A non-negligible degradation of asulam under solar irradiation (Fig. 3) was observed. However, the disappearance of asulam levelled off when about 60% conversion was achieved. This is most likely due to the formation of the blue product which prevent further excitation of asulam.

Laser Flash Photolysis

Nanosecond laser photolysis at 266 nm of asulam in oxygen-free solutions (0.05 mM) revealed immediately after the pulse the formation of a short lived transient. Its absorption spectrum showed two adsorption bands at 320 and 440 nm (Fig. 4). By monitoring the absorbance at 440 nm as a function of time, a first order decay with a rate of

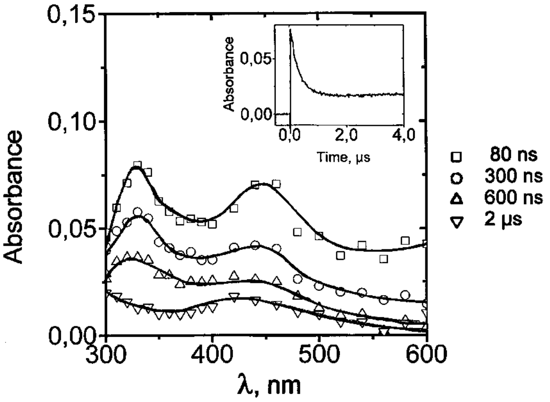


FIGURE 4 UV–visible spectra of the transients produced during the irradiation at 254 nm of a solution of asulam (5.0×10^{-5} mol L^{-1}). The insert shows the signal obtained at 440 nm.

$2.0 \times 10^6\,s^{-1}$ was obtained. This leads to a lifetime in deoxygenated solution of $\tau_o = 470$ ns. Experiments undertaken with various concentrations of oxygen showed an efficient quenching of the observed transient. This led us to the conclusion that the transient can probably be assigned to the triplet state. In an oxygenated solution ($[O_2] = 1.4 \times 10^{-3}$ M), the decay was complete within 200 ns and it followed a pseudo-first order kinetics with a rate constant of k_{obs}. The quenching rate constant, k_q, was obtained by monitoring the triplet–triplet (T–T) absorption decays at fixed wavelengths for various oxygen concentrations by employing the Stern–Volmer relation $k_{obs} = \tau_o + k_q\,[O_2]$. k_q was found to be 1.5×10^{10} mol^{-1} L s^{-1} showing that the quenching process is a diffusion-controlled process.

Photodegradation of Asulam in the Presence of Fe(III)

It has been well established that, upon irradiation, Fe(III) aquacomplexes undergo a photochemical process giving rise to hydroxyl radical and Fe(II) through an internal electron transfer [5,6].

$$Fe^{3+} + H_2O \xrightarrow{h\nu} Fe^{2+} + {}^{\bullet}OH + H^+$$

The degradation of asulam photoinduced by Fe(III) upon solar irradiation appears from Fig. 4. The concentration of asulam continuously decreased, and the total conversion was achieved after 8 h of irradiation.

It is worth noting that in the presence of Fe(III), we do not observe the formation of the blue photoproduct. The presence of hydroquinone and benzoquinone were demonstrated by HPLC coinjection. The latter represents the major photoproduct since it accounts for 35% of asulam conversion. We also detected the presence of *para*-sulfanilic acid and sulfanilamide as minor photoproducts.

Mineralisation

Moreover, in the presence of Fe(III), we observed the complete disappearance of the organic carbon from the solution for longer irradiation time. This disappearance is

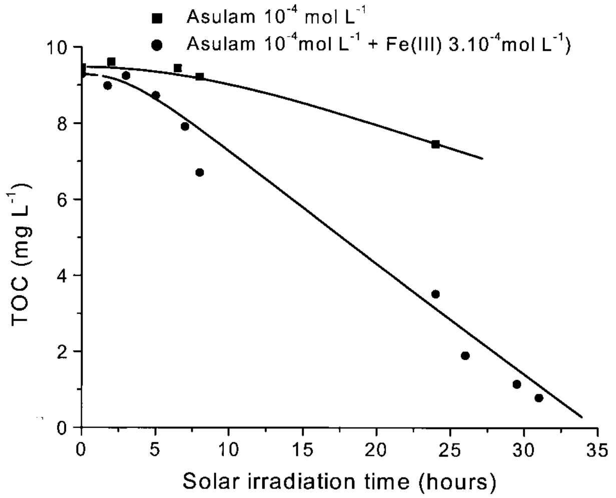
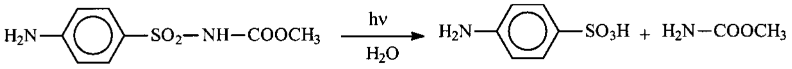


FIGURE 5 Disapperance of the total organic carbon from the aqueous solutions upon solar irradiation. (■) asulam ($1.0 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$) and (●) asulam ($1.0 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$) + Fe(III) ($3 \times 10^{-4}\,\mathrm{mol\,L^{-1}}$).

probably due to the transformation of the organic into CO_2. This was confirmed by the total organic carbon (TOC) analysis. The degradation of the total organic carbon as a function of solar irradiation time is shown in Fig. 5. A parallel experiments was performed without Fe(III) for a long period of irradiation and we never obtained the complete mineralisation of asulam.

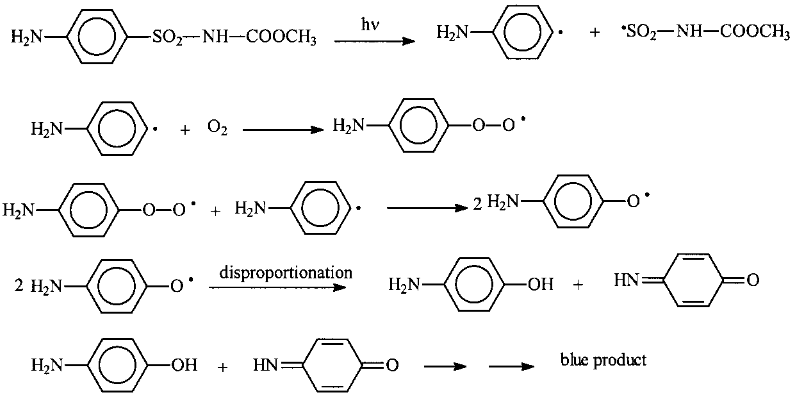
DISCUSSION

Upon direct excitation of asulam in aqueous solutions within the S_1 band, i.e., 254 nm, a variety of photoproducts have been found. Among them hydroquinone, *para*-sulfanilic acid, benzoquinone and a blue product represent the major ones. The disappearance of asulam as well as the formation of the photoproducts were shown to depend on oxygen concentration: the asulam disappearance decreased when the concentration of oxygen increased. Laser flash experiments clearly showed the involvement of the triplet state of asulam. The quenching process was found to be a diffusion controlled process ($k = 1.5 \times 10^{10}\,\mathrm{mol^{-1}\,L\,s^{-1}}$). The asulam disappearance was also shown to be pH dependent. This is most likely due to the presence of the neural form of asulam which is predominant at pH < 4.0. The formation of *para*-sulfanilic acid can be explained by the hydrolysis of asulam in its triplet state by the cleavage of the S–N bond:



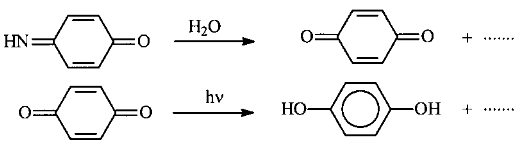
SCHEME 3

The formation of hydroquinone, benzoquinone and the blue product was only observed in aerated solution. The mechanism involve the homolytic scission of the C–S bond. In the presence of oxygen, the formation of the 4-aminophenoxyl radical may be proposed. Such a species leads by disproportionation to aminophenol and benzoquinone monoimine. These two photoproducts have been reported to give rise to dye substances (blue product) [15].



SCHEME 4

The presence of hydroquinone and benzoquinone in trace concentration may be due to the hydrolysis of benzoquinone monimine [16].



SCHEME 5

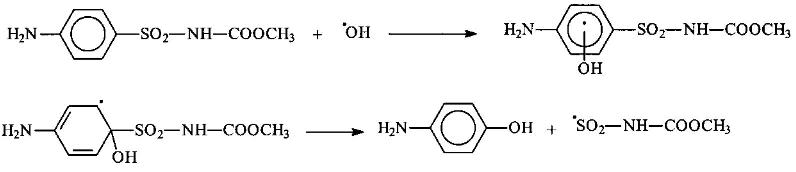
The induced degradation of asulam by excitation of Fe(III) aquacomplexes is due to the continuous formation of hydroxyl radicals from the predominant hydroxy Fe(III) species, namely $Fe(OH)^{2+}$, via the following electron transfer process:

$$Fe(OH)^{2+} \xrightarrow{h\nu} Fe^{2+} + {}^{\bullet}OH$$

where $Fe(OH)^{2+}$ refers to $[Fe(H_2O)_5(OH)]^{2+}$.

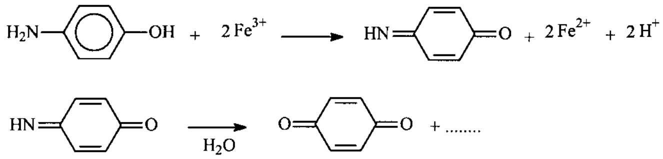
This photoredox process is of great interest for two reasons: (i) the process can be induced by excitation with solar light ($\lambda > 300\,nm$) [5] and (ii) the generated hydroxyl radicals react efficiently with most organic compounds [17].

The addition of $^{\bullet}OH$ radicals to the aromatic ring has been widely reported for various substrates [18]. In the case of asulam, the reaction leads to the formation of the adduct $^{\bullet}OH$–asulam, which is the main precursor of the formation of the products. The presence of benzoquinone (the major photoproduct) and hydroquinone may be explained via the formation of 4-aminophenol.



SCHEME 6

In the presence of Fe(III), 4-aminophenol can be oxidised according to the reported reactions [15] leading to the formation of benzoquinone monoimine which is hydrolised into benzoquinone.



SCHEME 7

Sulfanilic acid, present in trace concentration, may be formed by addition of hydroxyl radical to the SO_2 group followed by the cleavage of the S–N bond.

The continuous formation of hydroxyl radicals by excitation of iron aquacomplexes leads to the complete degradation of the starting compound as well as the generated photoproducts up to the complete mineralisation of the solution. This was also achieved by exposition to solar light. On the contrary, by direct photolysis of asulam, we have never reached the complete mineralisation.

References

[1] L. Meunier and P. Boule, *Pest. Manag. Sci.*, **56**, 1077–1085 (2000).
[2] D. Vialaton, C. Richard, D. Baglio and A.-B. Paya-Perez, *J. Photochem. Photobiol.*, **119**, 39–45 (1998).
[3] P. Mazellier, J. Jirkovsky and M. Bolte, *Pestic. Sci.*, **49**, 259–267 (1997).
[4] N. Brand, G. Mailhot and M. Bolte, *Environ. Sci. Technol.*, **32**, 2715–2720 (1998).
[5] B.C. Faust and J. Hoigné, *J. Atmos. Environ.*, **24A**, 79–89 (1990).
[6] H.J. Belkemberg and P. Warneck, *J. Phys. Chem.*, **99**, 5214–5221 (1995).
[7] C. Tomlin, The Pesticide Manual, 12th edn. British Crop Protection Council, Surrey, UK, pp. 40–41 (2000).
[8] J.G. Calvert and J.G. Pitts, *Photochemistry*. Wiley, New York, pp. 783–786 (1966).
[9] W.H. Kuenzi, *Die Hydrolyse von Eisen* (*III*). PhD dissertation ETH No. 7016. Zurich, Switzerland (1982).
[10] C.M. Flynn, *Chem. Rev.*, **84**, 31–41 (1984).
[11] C. Tomlin, *The Pesticide Manual*, 10th edn., p. 49. Crop Protection Publication, Bath (1994).
[12] S. Sabharwal, K. Kishore and P.N. Moorthy, *Radiat. Phys. Chem.*, **44**(5), 499–506 (1994).
[13] S.L. Murov, I. Carmichael and G.L. Hug, *Handbook of Photochemistry*, 2nd edn., p. 293. Marcel Dekker Inc., New York (1993).
[14] T. Ahmad and I. Ahmad, *Pakistan J. Pharm. Sci.*, **2**, 13–17 (1989).
[15] C.B. Brown and J.F. Corbett, *J. Soc. Cosmet. Chem.*, **34**, 191–211 (1979).
[16] J.F. Corbett, *J. Chem. Soc.* (*B*), 213–215 (1969).
[17] G.V. Buxton, C.L. Greenstock, W.P. Helman and A.P. Ross, *J. Phys. Chem. Ref. Data*, **17**, 513–886 (1988).
[18] U. Stafford, K.A. Gray and P.V. Kamat, *J. Phys. Chem.*, **98**, 6343–6350 (1994).