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ORIGINAL PAPER

# Photodegradation of atrazine and ametryn with visible light using water soluble porphyrins as sensitizers

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**Abstract** The photodegradation of the herbicides atrazine and ametryn with visible light in aerated neutral aqueous solutions and 5, 10, 15, 20-tetrakis (2,6-dichloro-3-sulfophenyl) porphyrin or 5, 10, 15, 20-tetrakis (4-sulfophenyl) porphyrin as sensitizers are reported for the first time. Our findings show that the degradation percentage reached 30% for atrazine and 63% for ametryn. The final photoproducts were characterized as dealkylated *s*-triazines. Photolysis of the pesticides in the presence of a singlet oxygen quencher showed only a minor contribution of this type of mechanism, while a bimolecular quenching reaction between the triplet state of the sensitizer and the pesticides is excluded by flash photolysis studies. It is proposed that the mechanism may involve the formation of a superoxide radical anion from the triplet state of the sensitizer and molecular oxygen, followed by a radical decomposition pathway.

**Keywords** Porphyrins · Atrazine · Ametryn · Photodegradation · Visible light · Oxygen

## Introduction

The quantity of pesticides and their metabolites present in surface and underground waters have been increased dramatically in the last decades. The inherent negative consequences for ecosystems and human health are pressing the efforts for the development of new technologies for water treatment, which are more efficient and environmentally clean. Photooxidation processes have major potential in this area (Legrini et al. 1993; Burrows et al. 2002; Oller et al. 2005; Lichtfouse et al. 2005). In particular, the photo-assisted degradation of organic pollutants in water in the presence of solar light, oxygen and a sensitizer is considered to be a very promising and low-cost methodology (Gryglik et al. 2004; Xiong et al. 2005).

Porphyrins and phthalocyanines have relatively high molar absorption coefficients in the visible region and high quantum yields for the formation of the corresponding photoexcited triplet states. This, together with their long-lived triplet state, makes them very strong potential candidates for efficient harvesting of sunlight for use as good sensitizers (Tai et al. 2005). The excited triplet state of the sensitizers can promote the activation of the pollutant molecule by electron or atom transfer (type I mechanism), by energy transfer to molecular oxygen, forming the highly reactive singlet oxygen species ($^1O_2$), which can then promote the oxidation of pollutants (type II mechanism) or by superoxide radical (Foote 1991; De Rosa et al. 2002; Burrows et al. 2002).

Atrazine (**1**) and ametryn (**2**) (Fig. 1) are extensively used herbicides, with high persistence in the environment. Atrazine is still one of the most widely used pesticides worldwide. It degrades slowly in waters, with negligible breakdown in neutral or slightly alkaline waters ($t^{1/2} \geq 2$ years). At pH 5 and temperature 20 °C, the half-life is about 12

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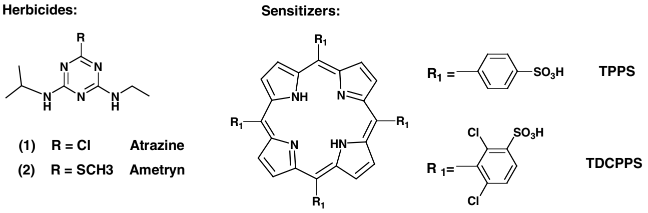

**Fig. 1** Herbicides and porphyrins used in photodegradation studies

weeks. This herbicide has relatively low adsorption in soil and easily migrates, leaching to water.

Photodegradation of atrazine or ametryn by $O_2$ in the presence of sunlight or simulated sunlight has been reported using different sensitizers, such as methylene blue, rose bengal, flavin nucleotide, phthalocyanines and a naturally occurring hemin (Rejto et al. 1983; Héquet et al. 2000). However, as far as we know, porphyrins have not been applied as sensitizers with these compounds. For practical purposes, there is an urgent need for more efficient sensitizers, in addition to more mechanistic information (Azenha et al. 2003).

Recently, we have shown that 5, 10, 15, 20-tetrakis (2,6-dichloro-3-sulfophenyl) porphyrin (TDCPPS) and some of its metal complexes are efficient sensitizers for the degradation of phenols and chlorophenols in water (Monteiro et al. 2005; Silva et al. 2004). In the present work, we extend these studies to the photodegradation of atrazine and ametryn using the water soluble porphyrins TPPS and TDCPPS (Fig. 1) as sensitizers. To obtain mechanistic information, photodegradation has also been performed in the presence of a singlet oxygen quencher, as well as flash photolysis studies with different concentrations of pesticides.

For practical applications, the recovery of the sensitizer is important, and with the systems studied this can be achieved by filtration over clays or other species.

## Experimental

Atrazine (**1**), desethylatrazine (DEA), deisopropylatrazine (DIA), desethyldeisopropylatrazine (DEIA), 2-hydroxyatrazine (HA), desethyl-2-hydroxyatrazine (DEHA) and ametryn (**2**) were purchased from Riedel-de Häen, sodium azide ($NaN_3$) was purchased from Aldrich, methanol and acetonitrile for HPLC analysis, were purchased from Merck. All other chemicals and solvents were obtained from commercial sources and used as received or distilled and dried by standard procedures. In photolysis reactions, distilled water (pH $\approx$ 6.5) was used. Millipore (Milli-Q academic system) water was used in HPLC analysis.

The synthesis and characterisation of 5, 10, 15, 20-tetrakis (phenyl) porphyrin and 5, 10, 15, 20-tetrakis (2,6-dichlorophenyl) porphyrin and its sulfophenyl derivatives TPPS and TDCPPS (Fig. 1) have been described elsewhere (Gonsalves et al. 1996).

Standard solutions (10 $\mu$M) of pesticides, sensitizers and possible degradation products were prepared by dissolving the required amount of solid in distilled water. For atrazine and ametryn, several days equilibration was necessary to obtain homogenous solutions.

UV/visible absorption spectra were recorded in quartz cells on a Shimadzu 2100 spectrometer. The pH control was made using a Crison micro-pH 2000 apparatus. HPLC/UV analysis was performed with an Agilent 1100 series system equipped with a reverse phase C18, Zorbax ODS column (220 mm $\times$ 4.5 mm i.d., 5 $\mu$m) and a UV-visible detector set at 222 nm. Analysis was carried out with 0.15% ammonium acetate in water:acetonitrile (50:50 v/v) as an eluent, using a flow rate of 1.4 mL/min and an injection volume of 20 $\mu$L.

Experiments with GC-FID were performed with an Agilent 6890 GC system and hydrogen as a carrier gas (55 cm/s), using an HP-5 capillary column (30 m $\times$ 0.32 mm i.d., 0.25 $\mu$m film thickness). The oven temperature program was as follows: 55 °C (1 min); 35 °C/min; 250 °C (5 min); injector temperature was 250 °C, and detector temperature was 260 °C. The samples were prepared by the extraction of the reaction mixtures with dichloromethane and concentration of the extracts under reduced pressure.

For photolysis experiments, an Applied Photophysics LKS 60 micro reactor was used, with monochromatic wavelength set at ca. 350 nm from a low pressure mercury lamp.

Transient absorption decays were measured with an Applied Photophysics LKS 60 ns laser flash photolysis kinetic spectrometer, using the third harmonic (355 nm) of a Spectra-Physics Quanta Ray GCR 130-01 Nd:YAG laser for excitation, a Hamamatsu 1P28 photomultiplier for detection and a Hewlett-Packard Infinium oscilloscope (1 GS $s^{-1}$). Triplet flash photolysis lifetime measurements were made on aerated and argon saturated solutions of sensitizer ($\sim 2 \times 10^{-5}$ M) in 50:50 acetonitrile:water, with different concentration of pesticides in the range $1 \times 10^{-3}$–$2 \times 10^{-5}$ M.

### Pesticide photodegradation

Aqueous samples containing the pesticide ($4.3 \times 10^{-6}$ M) and sensitizer ($4.3 \times 10^{-6}$ M) were prepared. The pH was controlled and adjusted if necessary with sodium hydroxide or hydrochloric acid, 0.1 M solutions.

Continuous irradiation of the aerated solutions was carried out for 24 and 120 h. The reaction was monitored by both HPLC and UV/visible spectroscopy, to allow the evaluation of the extent of degradation of pesticide and sensitizer, respectively. Degradation products were identified by HPLC-UV by co-injection of available standards. The reaction products were also identified by GC-FID analysis

**Table 1** Photosensitized degradation of atrazine after 24 h at different pH values irradiated at 350 nm[a]

| Entry | pH | Sensitizer | Degradation (%) |
|---|---|---|---|
| 1 | 2.1 | – | 63 |
| 2 | 7.2 | – | 0 |
| 3 | 12.0 | – | 17 |
| 4 | 2.1 | TPPS | 59 |
| 5 | 5.8 | TPPS | 0 |
| 6 | 12.0 | TPPS | 28 |
| 7 | 2.1 | TDCPPS | 64 |
| 8 | 7.2 | TDCPPS | 5 |
| 9 | 12.0 | TDCPPS | 31 |

[a] Water solutions of pesticide ($4.3 \times 10^{-6}$ M) and (if present) the sensitizer ($4.3 \times 10^{-6}$ M).

following the extraction of the reaction mixtures with dichloromethane and concentration on a rotary evaporator.

Photolysis was performed of aqueous solutions of TPPS or TDCPPS, in the above concentrations, in the presence of the singlet oxygen quencher ($NaN_3$, $4.3 \times 10^{-4}$) to obtain mechanistic insights.

## Results and discussion

Because of the known tendency of charged porphyrins to form aggregates in solution and the consequent influence of this on the photophysical properties, it has previously been shown (Monteiro et al. 2005) that at the concentrations and pH used for this study, aggregates of TPPS and TDCPPS were not formed.

A series of reactions were performed at different pH values, both in the absence and presence of TPPS or TDCPPS, to evaluate the pH effect on atrazine photodegradation. The results were obtained after 24 h irradiation and are summarized in Table 1.

Atrazine rapidly degrades in the presence of strong acids (pH 2, entries 1, 4 and 7). Under these conditions, atrazine degradation appeared only to depend on pH, and not to be affected by the use and type of sensitizer. A more moderate degradation is observed in the presence of strong bases, (pH 12, entries 3, 6 and 9). The only reaction product observed by HPLC was 2-hydroxyatrazine (HA), indicating the occurrence of hydrolysis at these extreme pH values. At near pH 7 (entries 2, 5 and 8) no degradation of atrazine was observed. These results led us to test longer irradiation times for effective photoreactions at this pH near 7, where there was no hydrolysis of atrazine.

To study the effect of sensitizers TPPS and TDCPPS on the degradation of the pesticide, the reactions were performed in the pH interval 6–7, during 120 h of irradiation. Results are collated in Table 2.

Under these conditions, reaction in the presence of TPPS and TDCPPS led to 30 and 21% atrazine degradation, respectively. TPPS is completely degraded at the end of the reaction, while only 56% of TDCPPS degradation was observed, after this irradiation time (Table 2, entries 1 and 2). The different degrees of degradation of TDCPPS under atmospheric pressure or oxygen bubbling (entries 2 and 5) can be related to the extent of the reaction. As indicated in the literature, porphyrins can be photooxidized in the presence of visible light and oxygen to bilinone derivatives (Cavaleiro et al. 1990).

To test for possible participation of singlet oxygen in the photodegradation of atrazine, photolysis was also performed in the presence of $NaN_3$ (entries 3 and 4). This singlet oxygen quencher did not produce any significant effect on atrazine degradation, strongly suggesting that the atrazine degradation mechanism with both sensitizers does not proceed by the type II mechanism involving singlet oxygen.

However, the presence of oxygen seems to be important, as an increase in the degradation was observed when the reaction mixture was bubbled with $O_2$ for 30 min before photolysis (Table 2, entry 5).

To obtain more information about the possible occurrence of a type I mechanism, quenching of the triplet state of sensitizer by the pesticide was studied. Flash photolysis experiments were carried out on deaerated solutions of TDCPPS with 355 nm excitation, and the decay of the transient absorptions studied at 460 nm, (the T-T absorption maximum of the sensitizer triplet state), in the presence of different concentrations of pesticide.

As low solubility makes it difficult to obtain concentrations of atrazine in pure water above $1 \times 10^{-5}$ M, this study

**Table 2** Photosensitized degradation of atrazine in neutral water solution, following 120 h of irradiation at 350 nm[a]

| Entry | Sensitizer | | pH | Atrazine degradation (%) | Identified photoproducts | Porphyrin degradation (%) |
|---|---|---|---|---|---|---|
| 1 | TPPS | – | 7.4 | 30 | DEA, DIA | 100 |
| 2 | TDCPPS | – | 6.5 | 21 | DEA, DIA | 56 |
| 3 | TPPS | $NaN_3$ | 7.5 | 32 | DEA, DIA | 100 |
| 4 | TDCPPS | $NaN_3$ | 6.7 | 19 | DEA | 85 |
| 5 | TDCPPS | $O_2$ | 6.5 | 34 | DEA, DIA | 42 |
| 6 | – | – | 7.2 | 11 | – | – |
| 7 | – | $NaN_3$ | 6.0 | 9 | – | – |

[a] Pesticide solutions ($4.3 \times 10^{-6}$ M), sensitizer ($4.3 \times 10^{-6}$ M) and (if present) $NaN_3$ ($4.3 \times 10^{-4}$ M).

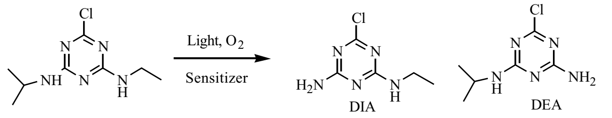

**Fig. 2** Photoproducts of atrazine identified by HPLC/UV and GC/FID

was performed in acetronitrile: water (50:50%) mixtures as solvent, following a control test that photolysis in this solvent led to the same degradation products of atrazine as in pure water.

The decay time of the triplet state in dearated solution is $\approx 250\ \mu s$ both alone and with atrazine $\approx 1 \times 10^{-3}$ M pesticide. This leads to an upper limit for the reaction between sensitizer triplet and atrazine $k_q \leq 4\ M^{-1}\ s^{-1}$. In contrast, the triplet states of the sensitizers are efficiently quenched by oxygen. However, as will be described in a future publication, triplet decay may produce a long-lived intermediate.

From these results, the involvement of singlet oxygen and direct reaction between sensitizer triplet and pesticides seems unlikely. The fact that photodegradation depends on the presence of oxygen suggests that the mechanism may involve formation of superoxide radical anion from reaction between triplet sensitizer and molecular oxygen. However, the concentration of this species should be low as these sensitizers have high quantum yields for singlet oxygen formation (Monteiro et al. 2005) and the reaction via superoxide formation should be a minor pathway, in agreement with the low atrazine degradation. The superoxide radical anion may also lead to hydroxyl radical formation, which can be one of the active species in the photodegradation of atrazine. However, in these reaction conditions (pH, λ), the generation of radical $HO^{\bullet}$ must occur only in trace amounts, which is confirmed by the absence of hydroxylated products.

$$^{3}S^{*} + O_2 \longrightarrow {}^{1}O_2 + S$$

$$^{3}S^{*} + O_2 \longrightarrow S^{\bullet +} + O_2^{\bullet -}$$

$$O_2^{\bullet -} + H^{+} \rightleftharpoons HO_2^{\bullet}$$

$$2\ HO_2^{\bullet} \longrightarrow H_2O_2 + O_2$$

$$H_2O_2 \xrightarrow{h\nu} 2\ HO^{\bullet}$$

The dealkylated products, DEA and DIA (Fig. 2) were obtained and characterized by HPLC-UV and GC-FID independent of the sensitizer and reaction conditions used. These were identified by comparing their chromatographic behaviour with that of authentic samples.

With the dealkylated compounds, it has recently been shown in studies with bacterial assemblages in natural water, to determine cytotoxicity of atrazine photodegradation products, that DEA and DIA do not have any significant toxic effect on bacterial heterotrophic activity. Instead these photoproducts may be growth substrates for bacterial assemblages in natural water (Zeng et al. 2004).

**Table 3** Photosensitized degradation of ametryn in neutral water solution, during 120 h of irradiation at 350 nm[a]

| Entry | Sensitizer | | pH | Ametryn degradation (%) | Porphyrin degradation (%) |
|---|---|---|---|---|---|
| 1 | TPPS | – | 7.4 | 63 | 100 |
| 2 | TDCPPS | – | 6.5 | 40 | 42 |
| 3 | TPPS | $NaN_3$ | 5.8 | 77 | 100 |
| 4 | TDCPPS | $NaN_3$ | 6.7 | 32 | 64 |
| 5 | – | – | 6.5 | 4 | – |
| 6 | – | $NaN_3$ | 7.0 | 17 | – |

[a] Pesticide solutions ($4.3 \times 10^{-6}$ M), sensitizer ($4.3 \times 10^{-6}$ M) and (if present) $NaN_3$ ($4.3 \times 10^{-4}$ M).

The photodegradation of ametryn with TPPS and TDCPPS was carried out under similar irradiation conditions used for atrazine and the results are presented in Table 3. Although suggestions have been given of the importance of C-S homolysis in degradation of this herbicide, our experiments with porphyrin photosensitizer do not allow us to detect this.

The use of TPPS as sensitizer led to more photodegradation than TDCPPS (63% degradation of ametryn with the first sensitizer compared with 40% with the second one (entries 1 and 2)).

The degradation of the pesticide in the presence of TPPS and $NaN_3$ appears to lead to a higher conversion than with the sensitizer alone (entry 3). However, this result can be explained, as it was also observed that $NaN_3$ alone leads to 17% ametryn degradation (entry 5). We can thus conclude that singlet oxygen is not important in the photodegradation mechanisms of these two herbicides with TPPS.

However, the reaction of TDCPPS in the presence of this singlet oxygen scavenger may have led to a slight decrease in the percentage of degradation, indicating some possible contribution from a type II mechanism, involving singlet oxygen. As with atrazine, flash photolysis studies show that the decay of the triplet state of the sensitizer is not affected by the presence of ametryn. Again, the photosensitized degradation mechanism most probably involves superoxide radical anion.

## Conclusion

The herbicide atrazine shows 30% photodegradation with visible light in the presence of the water soluble porphyrins TPPS or TDCPPS as sensitizers, following 120 h irradiation, while ametryn shows 63% breakdown. The reaction products are dealkylated derivatives, which in the case of atrazine are suggested to be of low toxicity. Although more detailed mechanistic studies are needed, this study suggests that the mechanism involved in the photodegradation of atrazine using TPPS or TDCPPS probably proceeds via $O_2^{-\bullet}$ and $HO^{\bullet}$

radicals. With ametryn, using TDCPPS there may be some contribution of singlet oxygen.

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