JOURNAL OF PHYSICAL ORGANIC CHEMISTRY
J. Phys. Org. Chem. 2005; **18:** 148–155

Developments in the mechanism of photodegradation of triazine-based pesticides[†]

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Received 13 November 2003; revised 12 April 2004; accepted 28 April 2004

ABSTRACT: Developments in the mechanisms of the direct, photosensitized and photocatalyzed photodegradation and of photochemically generated hydroxyl radical-based degradation of triazine-based pesticides are reviewed. Recent results are accounted for: steady-state irradiation photoproducts suggest the participation of both singlet and triplet excited states in the direct photodegradation of triazines, their concurrency being confirmed by luminescence studies. Both low-lying excited states have been theoretically characterized. Laser flash photolysis and pulse radiolysis studies evidence the participation of short-lived radical cations and radical anions, in addition to $HO^{\bullet}$ adducts, in the mechanism of photodegradation. E° values were estimated for both the triazine (*ca.* ~ 1.1 V vs NHE) and triazinyl radical cation (2.3 ± 0.1 V vs NHE) and also the pK_a for the $HO^{\bullet}$ adduct of triazines (*ca.* ~ 11). Sub-diffusion control rate constants were measured for the one-electron oxidation of triazines by $SO_4^{\bullet -}$ and $(UO_2^{2+})^*$, one-electron reduction by e^{-}_{aq} and $HO^{\bullet}$ addition. Copyright © 2004 John Wiley & Sons, Ltd.

KEYWORDS: herbicides; pesticides; laser flash photolysis; photodegradation; pulse radiolysis; radical anions; radical cations; triazines

INTRODUCTION

Intensive agricultural methods have led to dramatic increases in the variety and quantities of agrochemicals with different degrees of resistance to degradation in natural waters. An efficient alternative to their natural degradation involves the use of UV–visible radiation, sometimes combined with $HO^{\bullet}$ precursors, photosensitizers or photocatalysts. As a consequence, a large variety of photochemical/photophysical processes may take place.

A huge research effort has been put into identifying photoproducts arising from the photodegradation of different pesticides. In contrast, as will become evident through this paper, there is a dramatic lack of detailed mechanistic studies of the corresponding photodegradation processes, most of those available being merely speculative. Few or no reaction rate, spectroscopic or thermodynamic data have been reported for excited states and short-lived and stable reaction intermediates. It turns out that it will be difficult to model the environmental fate of agrochemicals or predetermine it synthetically unless detailed mechanistic studies become available.[1]

We have recently succinctly reviewed the reaction pathways and mechanisms of the photodegradation of different types of pesticides, including triazines.[1] Here, we concentrate on the mechanistic developments in the field, with emphasis on studies incorporating mechanistic discussion. Most of such available discussions are either minimal or difficult to associate with experimental findings. For the sake of simplicity, the studies are chronologically classified into four broad categories: direct, photosensitized and photocatalyzed photodegradation and indirect degradation by reaction with photochemically produced $HO^{\bullet}$ radicals. Unavoidably, some studies show a certain extent of overlap between these categories. Unless otherwise stated, when discussing triazines we refer to 1,3,5-triazines. We shall use common names, much more convenient than the systematic ones. Table 1 compiles the different structures and common and systematic names for the different triazines reported (in order of appearance).

RESULTS AND DISCUSSION

Direct photodegradation of triazine pesticides

Atrazine, propazine and simazine, when irradiated in aliphatic alcohols at 254 nm, formed the corresponding

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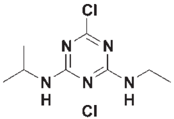
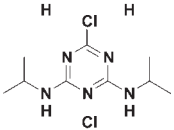
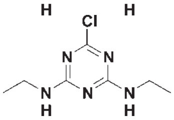
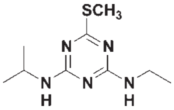
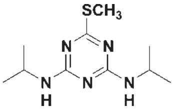
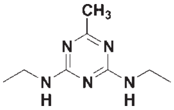
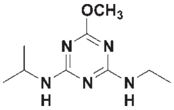
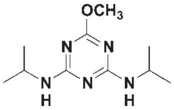
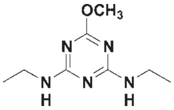
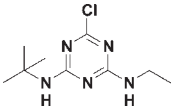
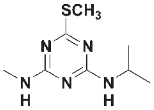
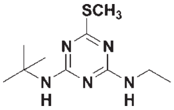
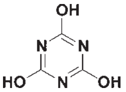
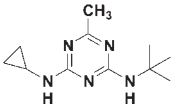
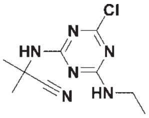
[†] Selected article presented at the Seventh Latin American Conference on Physical Organic Chemistry (CLAFQO-7), 21–26 September 2003, Florianópolis, Brazil.

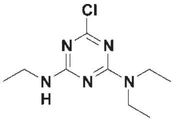
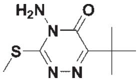
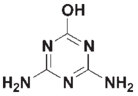
Contract/grant sponsor: Ministerio de Ciencia y Tecnología; *Contract/grant number:* PPQ2000-0449-C02-01.
Contract/grant sponsor: Xunta de Galicia; *Contract/grant number:* PGIDT01PX110306PN.

Table 1. Structures and common and systematic names of the different triazines reported (in order of appearance)

Structure	Names
	Atrazine 6-Chloro-*N*-ethyl-*N*′-isopropyl-1,3,5-triazine-2,4-diamine
	Propazine 6-Chloro-*N*,*N*′-diisopropyl-1,3,5-triazine-2,4-diamine
	Simazine 6-Chloro-*N*,*N*′-diethyl-1,3,5-triazine-2,4-diamine
	Ametryne *N*-Ethyl-*N*′-isopropyl-6-methylthio-1,3,5-triazine-2,4-diamine
	Prometryne *N*,*N*′-Diisopropyl-6-methylthio-1,3,5-triazine-2,4-diamine
	Simetryne *N*,*N*′-Diethyl-6-methylthio-1,3,5-triazine-2,4-diamine
	Atraton *N*-Ethyl-*N*′-isopropyl-6-methoxy-1,3,5-triazine-2,4-diamine
	Prometon *N*,*N*′-Diisopropyl-6-methoxy-1,3,5-triazine-2,4-diamine
	Simeton *N*,*N*′-Diethyl-6-methoxy-1,3,5-triazine-2,4-diamine
	Terbutylazine *N*-*tert*-Butyl-6-chloro-*N*′-ethyl-1,3,5-triazine-2,4-diamine
	Desmetryne *N*-Isopropyl-*N*′-methyl-6-methylsulfanyl-1,3,5-triazine-2,4-diamine
	Terbutryne *N*-*tert*-Butyl-*N*′-ethyl-6-methylsulfanyl-1,3,5-triazine-2,4-diamine
	Cyanuric acid 1,3,5-Triazine-2,4,6-triol
	Irgarol *N*-*tert*-Butyl-*N*′-cyclopropyl-6-methyl-1,3,5-triazine-2,4-diamine
	Cyanazine 2-(4-Chloro-6-ethylamino-1,3,5-triazin-2-ylamino)-2-methylpropionitrile

Continues

Table 1. Continued

Structure	Names
	Triethazine 6-Chloro-*N*,*N*,*N*′-triethyl-1,3,5-triazine-2,4-diamine
	Metribuzine 4-Amino-6-*tert*-butyl-3-methylsulfanyl-4*H*-1,2,4-triazin-5-one
	Ammeline 4,6-Diamino-5*H*-1,3,5-triazin-2-ol

2-alkoxy analogues. Irradiation of the same compounds in water led in high yields to their 2-hydroxy derivatives. Ametryne, prometryne and simetryne led, upon 254 nm irradiation, to their corresponding 2-*H* analogues. 2-Alkoxytriazines such as atraton, prometon and simeton and also as 2-hydroxytriazines did not undergo any photochemical process upon 254 nm irradiation in alcohols or water. The authors suggest, as a mere hypothesis, that the photodegradation of 2-Cl-triazines may take place via photosolvolysis, and suggest an intermediate C-2-centred carbocation, formed upon heterolytic cleavage of the C—Cl bond, as 'an attractive alternative'. They also hypothesize the formation of 2-*H* derivatives from 2-MeS-triazines, possibly via a concerted rearrangement involving an intramolecular hydrogen shift. The 260 nm absorbance of the triazines is suggested as responsible for the observed photoreactions.[2] These authors also studied the 300–360 nm irradiation of 2-Br, 2-F, 2-I and 2-azido analogues of atrazine, propazine and simazine in aliphatic alcohols, that yielded 2-alkoxy- and 2-hydroxytriazines. The authors suggest, based on product analysis, that the mechanism involves various competitive pathways: radical coupling, H-abstraction, hydrolysis and radical trapping. Irradiation of atrazine, propazine and simazine and their 2-F analogues in aliphatic alcohols at $\lambda > 290$ nm resulted in multiple photoproducts. *N*-Dealkylated photoproducts were identified, and the authors suggest the involvement of a Chugaev-type cyclic transition state in the dealkylation process.[3]

The decomposition rate of atrazine in aqueous solution upon 254 nm irradiation showed a half-life of $t_{1/2} = 2.5$ min, whereas with polychromatic light within the sunlight spectrum it was much larger. Such comparison is, clearly, rather casual, as the effects of monochromatic and polychromatic radiations should not be compared. It is not even clear from the data whether the observed effect means that different excited states are involved, which would undoubtedly have mechanistic relevance. A complex degradation mechanism was proposed based exclusively on the final and intermediate byproducts, including dealkylation, deamination, dehalogenation and amino-group ring insertion. On this basis, the authors claim a significant involvement of radicals in these processes.[4]

The photodegradation of propazine with a xenon lamp in distilled water took place slightly faster than in artificial seawater containing humic acids. 2-hydroxypropazine was found as the main metabolite in both cases. Deisopropylpropazine and 2-*H* analogues were also observed as photoproducts. No photosensitization effect was observed from the humic acids, indicating inefficient energy transfer from their excited states. On these grounds, the authors propose dealkylation, hydroxylation and dehalogenation as the main photodegradation pathways. However, no short- or long-lived intermediates or even precursor excited states were identified, and no kinetic elucidation was carried out.[5]

Irradiation of simazine at 254 nm followed first-order kinetics. A linear relationship was observed between the observed first-order rate constants and the UV intensity: 0.0864 min^{-1} (0.09 W), 0.161 min^{-1} (0.20 W) and 0.356 min^{-1} (0.38 W), leading, according to the authors, to an intriguing 'second-order rate constant' of 0.92 ± 0.06 W^{-1} min^{-1}, which may reflect the effect of the UV intensity (W) on the pseudo-first order rate constant. The observed linear dependence really reflects the fact that the process involved arises from a one-photon absorption, rather than a two- or multi-photon absorption. Based on the observed photoproducts, the authors propose simazine $\rightarrow$ 2-OH-simazine $\rightarrow$ 2-OH-4-ethylamino-6-aminotriazine, i.e. dechlorination followed by dealkylation. Such a mechanistic sequence must involve different short-lived intermediates, unidentified by the authors. A combination of UV irradiation with ozonation was effective in increasing the rate of simazine disappearance, but led also to dealkylation, deamination and dechlorination byproducts.[6]

The photodegradation of atrazine, propazine, simazine, terbutylazine, ametryne and atraton using a xenon lamp was studied in aqueous buffered solutions (pH 7–9) containing a small percentage of MeCN. Quantum yields for the different 2-Cl-triazines ($\Phi = 0.048$–0.062) and ametryne ($\Phi = 0.043$) were comparable, and in MeCN and hexane for terbutylazine were about half of their values in aqueous solution. An activation energy $E_a \approx 13\,\mathrm{kJ\,mol^{-1}}$ was estimated for the photodegradation of terbutylazine. Such E_a value, doubtless, involves several steps, not all of which need to be of photochemical origin. It is unclear to what extent E_a values corresponding to an overall photodegradation process and not to a single elementary step are useful at all. Atraton did not degrade under the experimental conditions, with $\Phi < 0.002$.[7]

Photodecomposition of 4-amino-1,2,4-triazin-3,5-diones and 4-amino-1,2,4-triazinethiones in O_2-containing aqueous solutions at different acidities leads to deamination, decarboxylation and dealkylation reactions, the last being slow and non-selective. The authors put forward and discuss mechanisms for such processes. Small differences in the substituents at the heterocyclic ring lead to large changes in the photodegradation rate and selectivity of deamination and decarboxylation, whereas dealkylation is slow and non-selective.[8]

Atrazine undergoes very efficient degradation on UV–visible irradiation using a medium-pressure mercury lamp. The degradation is more efficient at lower acidities, which might be a result of HO^- concentration, with k (pH 2) $= 0.26\,\mathrm{min^{-1}}$, k (pH 7) $= 0.30\,\mathrm{min^{-1}}$ and k (pH 12) $= 0.39\,\mathrm{min^{-1}}$. The main photodegradation pathway is dehalogenation to the 2-OH derivative, which ultimately leads to cyanuric acid. The authors suggest that the formation of the 2-OH derivative could result either from homolytic C—Cl cleavage, followed by e^- transfer from $C^{\bullet}$ to $Cl^{\bullet}$ and hydrolysis of the carbocation, or rather heterolytic C—Cl cleavage in the excited state of atrazine, which should be favoured by polar solvents such as water.[9]

The antifouling agent irgarol undergoes sunlight photodegradation in aqueous solution, leading to a product that is persistent in sunlight-exposed aqueous solution.[10] Previously, the same authors had found that whereas the photodegradation of irgarol is significantly accelerated in natural waters, this is not the case with its photodegradation products, which are not affected by natural photosensitizers.[11]

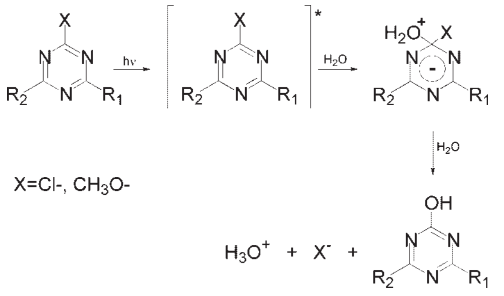
The rate of UV ($\lambda > 290\,\mathrm{nm}$) photodegradation of atrazine, simazine and prometryne in aqueous solutions and natural waters depends on the nature of the triazines and follows first-order kinetics. The number of photodegradation products detected, using flow injection–mass spectrometric and flow injection–tandem mass spectrometric techniques suggests, as evidenced in other papers cited above, various degradation routes resulting in complex and interconnected pathways.[12]

The kinetics of the photodegradation of atrazine and ametryne in fresh and coastal salt water from Barbados were measured under irradiation with simulated sunlight and 254 nm UV radiation. The observed first-order rate constants were higher for ametryne, with reduced rates in seawater and soil slurries relative to fresh water. Reaction rates increased in the presence of Fe^{3+} at pH 3, which the authors attribute to photo-Fenton type processes. Such rate enhancement was found lower at typical environmental pHs.[13]

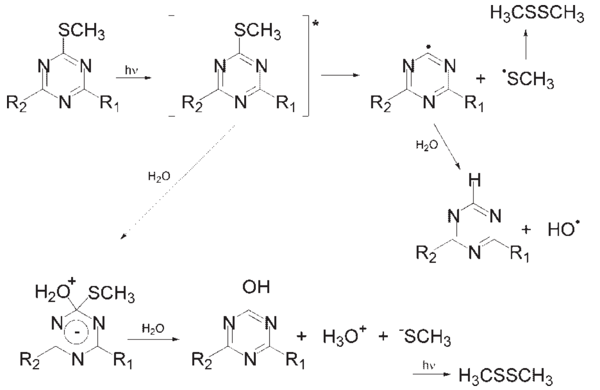
The rates of photodegradation of atrazine, cyanazine, terbutylazine and terbutryne have been measured and appropriate mechanisms outlined. The most significant processes observed are the partial or complete loss of side-chains, or rather the substitution of the heteroatom-containing side-chain with a hydroxyl group. Different products are formed, with mixed side-chains, until cyanuric acid and 2-amino-4,6-dihydroxy-1,3,5-triazine are formed with loss of all side-chains. The presence of dimeric products upon photodegradation of all triazines proves the radical character of the processes taking place. Different light intensities (of the same spectral range) were used to elucidate the effect of excitation energy on the process: increasing the nominal power input of the lamps used from 15 to 125 W (it would have been best, however, if the authors had performed an actinometric procedure for both irradiation sources) led to an increase of 2–5-fold in the degradation rate, and the Cl-containing metabolites, present in the completely degraded mixture of the low-energy experiments, completely disappeared from the mixture in the high-energy experiments. Hence an increased degradation energy favours the formation of less environmentally dangerous metabolites.[14]

A 193 nm laser flash photolysis study of the photodegradation of *s*-triazine, ametryne, desmetryne, prometryne and terbutryne showed for all the compounds monophotonic photoionization, with $\Phi < 0.10$, evidencing the existence of relevant relaxation pathways other than photoionization. No significant monophotonic photoionization was observed on irradiating with longer wavelength laser light.[15]

s-Triazine, 2-chloro-4,6-dimethoxytriazine, atrazine, 2-hydroxyatrazine, atraton and ametryne undergo aqueous one-electron oxidation by $(UO_2^{2+})^*$ and $SO_4^{\bullet -}$, but not by Tl^{2+}, which allows the estimation of the standard reduction potential of triazines as $E^\circ(T^{\bullet +}/T) = 2.3 \pm 0.1\,\mathrm{V}$ vs NHE, consistent with PM3 semiempirical calculations. This result implies that inhibition of photosynthesis by triazines must take place on the reductive part of the electron transport chain. The radical cation $T^{\bullet +}$ is not detected on time-scales larger than 500 ps. The results obtained allow, both by consideration of the photon energies used and by use of a correlation between known E° and vertical ionization potential values, the estimation of an aqueous ionization threshold between 8.17 and 8.38 eV for triazines. Dynamic quenching of fluorescence of $(UO_2^{2+})^*$ by triazines takes place. Reaction with $HO^{\bullet}$ proceeds almost quantitatively by addition to the aromatic ring, rather than one-electron oxidation.[16]



Scheme 1. Mechanism of photohydrolysis of 2-halo- and 2-methoxytriazines



Scheme 2. Mechanism of photohydrolysis and photohomolysis of 2-methylthiotriazines

Radiation of 254 nm induces photodegradation of atrazine, atraton and ametryne. The photoproducts formed, identified by high-performance liquid chromatography and gas chromatography–mass spectrometry by comparison with authentic samples, are 2-hydroxyatrazine, side-chain dealkylation products, and the corresponding 2-*H* triazine as a photoproduct of ametryne. The main pathway is proposed to be an addition–elimination (photosolvolysis, Scheme 1) process, yielding 2-OH in water and atraton in MeOH, which could further photodegrade. The observations for ametryne are rationalized in terms of concurrent addition–elimination and C—S homolysis processes, as shown in Scheme 2.[17] These mechanisms are supported by the changes found in the photoproducts on going from an oxidizing to an inert atmosphere, suggesting the involvement of both singlet and triplet states, which has been computationally confirmed at the CASPT2/CASSCF, and TD-DFT levels of calculation: the photohydrolysis mechanisms seems to originate from the triplet state, with the photohomolysis arising from the singlet state.[18]

One-electron reduction of triazines with e^-_{aq} yields the radical anion $T^{\bullet -}$, which can also be generated by one-electron reduction with $[(1,10\text{-phenanthroline})_3Ru^{2+}]^*$, as observed by decay of the fluorescence of the latter. This allows estimation of $E^\circ(T/T^{\bullet -}) \approx 1.1$ V vs NHE, in agreement with inhibition of photosynthesis by triazines taking place on the reductive part the e^- transport chain.[19] Theoretical structural characterization of these radical anion species, $T^{\bullet -}$, show an interesting Jahn–Teller effect, as a consequence of which $T^{\bullet -}$ is geometrically distorted relative to the parent triazines, T, in order to destroy the orbital degeneracy and therefore lower its energy.

Different aspects of the first stages of aqueous photodegradation of triazine-based herbicides have been studied by laser flash photolysis and pulse radiolysis. The rate constants for the one-electron oxidation of the triazines with $SO_4^{\bullet -}$ and one-electron reduction with e^-_{aq} were measured and the influence of structural parameters was discussed. In general, all the processes were below the diffusion control limit, with rate constants of the order of $10^9\ \text{M}^{-1}\cdot\text{s}^{-1}$.[20,21]

Photosensitized photodegradation of triazine herbicides

The photosensitized degradation of atrazine, atraton and ametryne was studied using 1% acetone and UV radiation from a medium-pressure mercury lamp ($\lambda > 290$ nm). The relative photostability observed was ametryne < atrazine < atraton. Dealkylated, doubly dealkylated and 2-hydroxytriazines were found as photoproducts. The corresponding 2-*H* derivative was also found for Ametryne. Deethylation was found to be easier than deisopropylation. The presence of two kinds of dealkylated products suggest a two-step mechanism. Acetone strongly sensitized the reaction. Dark experiments showed that all products arise from photodegradation.[22]

Aqueous, aerated solutions of ametryne, atraton and atrazine containing riboflavin as a photosensitizer were exposed to sunlight irradiation for several hours. The primary photodegradation products observed were the deethylated *s*-triazines, with 55, 62 and 70% yield, respectively, and the oxidized product. Photohydrolysis, with formation of 2-OH derivatives, was not observed. The photoreactions were affected by the electronegativity of the substituent at C-2, which might explain the relative rates observed: $SCH_3 > OCH_3 > Cl$. The reaction rate increased with decreasing pH. However, the photodegradation products are independent of pH. In all cases the *N*-Et group was photolyzed prior to *N*-iPr, which is explained in terms of the relative stabilities of the corresponding *N*-Et and *N*-iPr radicals. The mechanism of photosensitized degradation of triazines is described in terms of H abstraction from the amino group by the excited sensitizer, followed by a second H abstraction by a second molecule of sensitizer, with formation of an aldimine, readily hydrolyzed to the *N*-deethylated products and acetaldehyde. O_2 was found essential for the photodecomposition reaction, only minute amounts of *N*-deethylated product being found in its absence. Accordingly, the authors hypothesized the participation of hydroperoxyl radicals, $HO_2^{\bullet}$, in the mechanism.[23]

The photosensitized photocatalytic oxidation of terbutryne with $(bipyridyl)_3Ru^{2+}$ complexes and TiO_2 as semiconductor was investigated. The sensitizer molecule, adsorbed on the surface, absorbs visible light, and injects an electron into the conduction band of TiO_2, with subsequent reduction of dissolved O_2 to $O_2^{\cdot -}$ and oxidation of H_2O/HO^- to $HO^{\cdot}$ radicals, which rapidly react with organic compounds.[24]

The photochemistry of a two-component [merocyanine dye–4-(4-methoxycarbonylphenyl)-2,6-bis(trichloromethyl)-1,3,5-triazine] system that could be used as a visible-light radical generator in photopolymerization was investigated. Electron transfer from the excited merocyanine to the triazine, yielding a reactive photoinitiating radical, is proposed on the basis of fluorescence quenching studies and product analysis. The results obtained, with fluorescence lifetimes of the same order (ca 0.4 ns) in the presence and absence of triazine, support static quenching.[25] Hence the triazine used by the authors effectively undergoes a one-electron reduction to yield the corresponding radical anion, a result that is in agreement with our findings.

Recent studies have been performed on the use of porphyrin complexes for the photosensitized visible-light photodegradation of atrazine. The reaction is not sensitive to O_2, which suggests that $^1O_2$ is not involved. The photodegradation process seems to be more effective in the presence of porphyrin complexes. The reaction with low porphyrin:triazine ratios seems to be hardly effective.[26]

Photodegradation by photocatalysis

The TiO_2-photocatalyzed degradation of atrazine, simazine, triethazine, prometon and prometryne, simulating solar light with a xenon lamp, followed first-order kinetics only in the early part of the process. Several intermediates were identified, cyanuric acid being the final photoproduct in all cases. Thus, complete photomineralization was not achieved.[27] The same authors used a similar approach with simazine, propazine and atrazine, concluding that in the early stages the degradation takes place through competitive oxidation of the alkyl side-chains and substitution of Cl by OH at C-2. Further oxidative processes give rise to dealkylated products.[28] The authors also found atrazine to be efficiently degraded in a large modular flow-through system under solar light. Full mineralization products of the alkyl side-chains and cyanuric acid were obtained as photoproducts. The presence of $S_2O_8^{2-}$ was found to be highly advantageous in increasing the photodegradation rate. A complex mechanism is hypothesized to account for the observed products.[29]

Photodegradation of prometryne and prometon in aqueous solution using H_2O_2 as oxygen supplier on photocatalytic membranes involves a first step that follows apparent first-order kinetics. Based on product analysis and observations of the membrane during the photocatalysis experiments, the authors hypothesize that an S-containing intermediate is formed during the photodegradation of prometryne from the very beginning or irradiation, sulfones and sulfoxides being the most probable ones. A sulfoxide intermediate opens two routes: (i) cleavage of the S-group from the triazine ring, with formation of a hydroxylated compound and subsequent oxidation of alkyl side-chains attached to the N atoms at positions C-4 and C-6; (ii) cleavage of the $S—CH_3$ bond to yield a sulfonic acid or its sulfonate, plus the corresponding hydroxylated triazine. Two mechanistic routes are also proposed for the photodegradation of prometon: (i) primary oxidation of the alkyl side-chains attached to N atoms at positions C-4 and C-6; (ii) substitution of the MeO at the C-2 position by a OH, followed by stepwise oxidation of the side-chains. The presence of cyanuric acid after prolonged irradiation proves the demethoxylation.[30]

The homogeneous photocatalyst sodium decatungstate, $Na_4W_{10}O_{32}$, was used for the solar photocatalysed degradation of atrazine. The heterogeneous photocatalyst TiO_2 appeared to be more efficient for degradation of the pure substrates, but when the pesticides were used as formulated solutions, the added organic products had a small effect in the presence of $Na_4W_{10}O_{32}$, whereas the rate of degradation was lowered in the presence of TiO_2. Such a difference of reactivity is interpreted by the authors in terms of the different nature of the active species during both photodegradation processes: $HO^{\cdot}$ radicals in the case of TiO_2, but the excited state of the polyoxometalate, $(W_{10}O_{32}^{4-})^*$ in the presence of $Na_4W_{10}O_{32}$.[31]

Iron porphyrins and phthalocyanine complexes have been used as photocatalysts for the degradation of atrazine using a medium-pressure mercury lamp. The observed by-products suggest similar degradation routes for both the iron porphyrins and the phthalocyanines. The main intermediates found are desisopropylatrazine and, in the same proportion, 2-hydroxyatrazine. Dehalogenation and dealkylation mechanisms are suggested to be involved in parallel. Both complexes showed able to degrade atrazine efficiently, with half-lives of ca 220 and 640 min for phthalocyanine and porphyrin, respectively. These catalysts are able to induce cleavage of the triazine ring, which was not achieved with TiO_2.[32] The same authors analysed the efficiency of a photocatalytic system using TiO_2 and light with $\lambda > 290$ nm for atrazine degradation. The process showed a half-life of ca 20 min and the main by-products observed were dealkylated compounds, the ultimate product being cyanuric acid. Neither the pH nor the nature of the aqueous medium influences the degradation process.[9]

The photocatalytic degradation of atrazine, cyanazine, irgarol, prometryne and propazine using aqueous suspensions and simulated solar light shows degradation kinetics following apparent first-order kinetics consistent with a Langmuir–Hinshelwood model. The kinetics of photodegradation were followed by gas chromatography. The photodegradation in the absence of TiO_2 also follows first-order kinetics. The rate constants for photocatalytic oxidation, $3.57 \times 10^{-2}\,min^{-1}$ (atrazine), $1.80 \times 10^{-2}\,min^{-1}$ (cyanazine), $1.61 \times 10^{-2}\,min^{-1}$ (irgarol), $4.87 \times 10^{-2}\,min^{-1}$ (prometryne) and $6.24 \times 10^{-2}\,min^{-1}$ (propazine), were calculated from the apparent degradation constants by subtraction of the rate constants due to direct photodegradation, $1.60 \times 10^{-3}\,min^{-1}$ (atrazine), $6.40 \times 10^{-3}\,min^{-1}$ (cyanazine), $2.00 \times 10^{-3}\,min^{-1}$ (irgarol), $2.30 \times 10^{-3}\,min^{-1}$ (prometryne) and $1.80 \times 10^{-3}\,min^{-1}$ (propazine). The photocatalytic oxidation rate constants depend on the structure of the tested pesticides. The authors claim that the photodegradation starts with oxidation of the lateral chains, the main degradation products being acetamide and dealkylated derivatives. Subsequently, photohydrolysis of the substituent at C-2 and replacement of the amino groups by hydroxyl groups take place. The rate constants observed for the 2-chlorotriazines follow the order propazine > atrazine > cyanazine, which the authors interpret in terms of the difference in ionization potentials of the amines at the C-4 and C-6 positions, and of the stability of the different possible *N*-Et and *N*-iPr radicals that could take part in the reaction. A similar ordering is observed for the two 2-MeS-triazines (prometryne > irgarol). Comparison of 2-MeS-triazines with 2-Cl-triazines shows that the rate of photodegradation is affected by the electronegativity of the substituent at C-2, which influences the amino groups at C-4 and C-6.[33]

The improved photocatalytic oxidation of organic contaminants of water is explained in terms of acceleration by oxidants and photo-enhancement by dyes. The effects of O_2 and H_2O_2 indicate different reaction patterns of photo-oxidation of the herbicides. With metribuzine, O_2 has an important rate effect, whereas the influence of H_2O_2 is moderate. The authors hypothesize a mechanism involving a combination of oxidation by photocatalytically generated $HO^{\cdot}$ radicals and subsequent oxidation of photo-intermediates by $^1O_2$ formed by dye sensitization.[34]

The photocatalytic degradation of atrazine by TiO_2 (Degussa-P25 and anatase), ZnO, $SrTiO_3$, ZnS, Fe_2O_3 and $FeTiO_3$ and by five kinds of environmental particles (sand, soot, dust, volcanic ash and fly ash) was studied. Particle suspensions were irradiated in a sun simulator containing dissolved atrazine. The photodegradation follows first-order kinetics, in agreement with the Langmuir–Hinshelwood model. The photocatalytic rate constant for TiO_2 and the corresponding adsorption equilibrium constant are given by the authors (in unusual units) as $0.416\,\mu g\,l^{-1}\,min^{-1}$ and $1.88\,\mu g^{-1}$, respectively. TiO_2 and ZnO induce a fast photocatalytic degradation of atrazine, with $k = (27–327) \times 10^{-3}\,min^{-1}$. The degradation rates detected upon irradiation of other Ti-, Zn- or Fe-containing minerals were orders of magnitude lower, with $k = (0.15–0.70) \times 10^{-3}\,min^{-1}$, but faster than direct photolysis without particles, which showed $k = 0.10 \times 10^{-3}\,min^{-1}$. Environmental particle samples showed no photocatalytic activity, with $k = (0.07–0.16) \times 10^{-3}\,min^{-1}$. The rate of direct photodegradation of atrazine is affected by the pH of the medium, $k = (1.3 \pm 0.1) \times 10^{-3}\,min^{-1}$ at pH 5.5, one order of magnitude slower at pH 7.6. It is not clear, however, whether the observed rate enhancement of the photolysis rate may be due to the pH or just to ionic strength effects. Since the degradation of atrazine by irradiated particles was faster in unbuffered than in buffered suspensions (pH 7.6), the authors hypothesize that atrazine competes with buffer components for active adsorption sites of the particles. However, the effect of pH on the overall charge of the catalyst was not taken into account, although it significantly affects the adsorption equilibria.[35]

The photodegradation of atrazine in homogeneous solutions of $Fe(ClO_4)_3$ and heterogeneous suspensions of TiO_2 was investigated, in both cases under various conditions of acidity and ageing of the solutions. Hydrolysis and oligomerization in aqueous solutions of $Fe(ClO_4)_3$ strongly affect the kinetics of photodegradation, the initial reaction rates decreasing with time, which is interpreted in terms of reduction in the content of the photoactive complex $[Fe(OH)(H_2O)_5]^{2+}$. The observed rates of photodegradation with fresh $Fe(ClO_4)_3$ solutions and aqueous TiO_2 slurries were similar. The rates of photodegradation of intermediate 2-chloro-4-ethylamino-6-aminotriazine and 2-chloro-4-isopropylamino-6-aminotriazine are similar to that for atrazine.[36]

The photocatalytic degradation of two triazine-containing azo dyes, Procion Red MX-5B and Reactive Brilliant Red K-2G, in aqueous TiO_2 dispersions verified decolorization and desulfuration at almost the same rate in the first step of photo-oxidation. The substituents attached to the naphthalene of the dye were hydroxylated more easily than those linked to the triazine. Cyanuric acid was characterized as one of the final products for both azo dyes, and it was not further decomposed.[37]

Degradation by reaction with photochemically produced hydroxyl radical ($HO^{\bullet}$)

The aqueous photodegradation rates of atrazine, ametryne, prometon and prometryne are enhanced on addition of ferric perchlorate or ferric sulphate. $HO^{\bullet}$, derived from the photoreaction of the complex $Fe(OH)^{2+}$, is suggested as the active reactant. The reaction rate decreases in the absence of O_2. It increases with added iron and decreases in natural water, implying that some dissolved constituents of natural waters have a retarding effect on the photodegradation, possibly by competition for the $HO^{\cdot}$ radicals.[38]

Atrazine photodegradation has been studied by both direct photolysis and nitrate-mediated ($\lambda = 290\,\text{nm}$) $HO^\bullet$ radical processes. The observed first-order rate constants are $(4.0 \pm 0.6) \times 10^{-3}$ and $(2.9 \pm 0.2) \times 10^{-2}\,\text{h}^{-1}$ for direct and indirect photolysis, respectively. The ratio of products formed on direct and indirect irradiation suggest that 2-hydroxyatrazine is not formed through a radical process, but rather owing to the absorption of light by atrazine itself (direct photolysis), the rate-determining step being the dechlorination.[39]

The degradation of atrazine was studied using a Fenton electrochemical system. The degradation takes place by attack of $HO^\bullet$ radicals, produced from reaction of H_2O_2 with electrochemically generated Fe^{2+}. *N*-Dealkylation and dechlorination are suggested as the major pathways of degradation for atrazine.[40]

The rate constants for $HO^\bullet$ addition (ca $10^9\,\text{M}^{-1}\,\text{s}^{-1}$) were below the diffusion control limit, and the influence of structural parameters was discussed. A $\text{p}K_\text{a} \approx 11$ has been estimated for the $HO^\bullet$ adducts of triazines.[20,21]

$HO^\bullet$ radicals generated by anodic Fenton treatment were used to study the degradation of atrazine and seven of its degradation products: deethylatrazine, deisopropylatrazine, diaminochlorotriazine, hydroxyatrazine, desethylhydroxyatrazine, desisopropylatrazine and ammeline. The degradation of atrazine follows pseudo-first-order kinetics with a rate constant of $1.95\,\text{min}^{-1}$. Dealkylation of atrazine is suggested as the preferred degradation pathway over hydroxylation at C-2 (dechlorination). The ultimate product found is ammeline. Ring cleavage and mineralization are not detectable.[41]

The degradation of atrazine using Fenton's reagent showed that the oxidation capabilities of the Fenton reagent depends on the concentrations of H_2O_2 and Fe^{2+}. The kinetics show a rapid initial decay, followed by a much slower one. After 5–10 min, the reactions ceased because the Fe^{2+} and H_2O_2 had been consumed.[42]

Acknowledgements

Financial support was provided through research projects PPQ2000-0449-C02-01 of the Ministerio de Ciencia y Tecnología and PGIDT01PX110306PN of the Xunta de Galicia. M.I.F. works under contract for the latter project.

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