

PHOTOSENSITIZED DEGRADATION OF TERBUTHYLAZINE IN WATER

SANLAVILLE Y., GUITTONNEAU S., MANSOUR M.*1, FEICHT E.A.*, MEALLIER P. and KETTRUP A.*

Laboratoire de Photochimie Industrielle - L.A.C.E. U.M. 9977 - Université Claude Bernard Lyon I - 43, boulevard du 11 novembre 1918, F-69622 Villeurbanne Cedex, France

* GSF - Institut für Ökologische Chemie, Ingolstädter Landstr. 1, D-85764 Oberschleißheim, Germany

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ABSTRACT

We investigated the photodegradation of terbuthylazine, an s-triazine herbicide, in the presence of hydrogen peroxide (H₂O₂), titanium dioxide (TiO₂), acetone or humic substances. In the presence of H₂O₂ and UV light, the degradation of terbuthylazine quickly leads to the formation of ammeline. The degradation pathway consists of dealkylation reactions giving 2-chloro-4,6-diamino-1,3,5-triazine, and then ammeline through hydroxylation. Irradiation of terbuthylazine with simulated solar light in the presence of titanium dioxide gives also dealkylation products in the first stage of degradation. Acetone at 1 % (v/v) produces a 7-fold enhancement of the degradation rate. In the presence of humic substances, different results were obtained, depending on the origin of the substances tested. The humic acids isolated from a soil accelerate the degradation speed, whereas the fulvic acids from a small stream reduce it. Copyright © 1996 Elsevier Science Ltd

Keywords : Terbuthylazine / Photodegradation / Hydrogen Peroxide / Titanium Dioxide / Acetone / Humic Substances

INTRODUCTION

Triazine herbicides are among the most used pesticides in the world. The main compound of this family, atrazine (2-chloro-4-ethylamino-6-isopropylamino-1,3,5-triazine) is now found in many environmental compartments, contaminating soils and water reserves. This has lead to a severe restriction of its use or to its interdiction, as in Germany [1]. Terbuthylazine (2-tert-butylamino-4-chloro-6-ethylamino-1,3,5-triazine) is presented as a substitute for atrazine, so that it becomes interesting to determine its behaviour during oxidation processes or in the presence of natural compounds such as humic substances.

Advanced Oxidation Processes (AOP's) have been developed to degrade the contaminants of drinking water and industrial effluents. Among them, hydrogen peroxide (H_2O_2) combined with UV-light ($\lambda = 254$ nm) represents an interesting degradation system. The photolysis of H_2O_2 gives hydroxyl radicals (OH) that can react with contaminants in solution. Its efficiency on atrazine has been previously demonstrated [2, 3]. Titanium dioxide, when irradiated, generates OH , and is also an interesting AOP for the degradation of triazines [4]. These two processes will be studied on terbuthylazine, in order to determine the kinetics of photodegradation and the products obtained.

^{*1} To whom all Correspondance should be addressed

Photodegradation of triazine herbicides under simulated solar light occurs very slowly [5]. Thus, the influence of natural substances such as humic substances on the photodegradation becomes of great interest. Humic substances have been found to act as photosensitizers when irradiated at a wavelength greater than 290 nm [6], in particular for atrazine [5, 7]. In our experiments, we have studied the influence of two extracted humic substances on the photodegradation of terbuthylazine.

EXPERIMENTAL SECTION

Terbuthylazine and its standard degradation products were purchased from Laboratory Dr. Ehrenstorfer at a purity greater than 99%. Hydrogen peroxide (35%) was supplied by Merck, titanium dioxide P 25 by Degussa, acetone and acetonitrile, both chromatographic grade, by Riedel de Haen.

The concentrations of terbuthylazine and of its photoproducts A, B, C and D (see figure 2) were determined by HPLC (HP series 1050) using a 20 cm 0.4 cm i.d. C18 hypersyl column. The mobile phase was a mixture of water and acetonitrile (50/50 v/v), and the detection was realised at 223 nm. The calibration was made with commercial standards.

The concentrations of ammeline (2-hydroxy-2,4 diamino-1,3,5 triazine) (H) and hydroxy-photoproducts (E, F, G) were determined by free zone capillary electrophoresis as described elsewhere [7]. The detection limit, for a signal/noise ratio of 3, was about 50 ppb of pesticide.

Confirmation of the nature of the photoproducts was obtained by GC-MS (EI) analysis with a Hewlett-Packard 5890 series II GC and HP 5989 mass detector. The samples were injected in a HP5 25 m \times 0.2 mm capillary column, using the following temperature programm : isotherm at 100°C for 5 min, from 100°C to 170°C at 5°C min⁻¹, isotherm at 170°C for 10 min. The polar products were derivated with bis (trimethylsilyl) trifluoroacetamide (Merck) after lyophilisation and dissolution in acetonitrile.

Photolysis experiments were carried out in a 100 ml UV-reactor, equipped with a diving Philips HPK 125 W high pressure mercury lamp. For the irradiation experiments at wavelength greater than 290 nm, the quartz envelope was replaced by a pyrex filter.

A suntest (Heraeus) apparatus was also used, which provides a good simulation of solar light. The irradiation source was a 1100 W Xenon lamp (Osram) with a filter that eliminates the wavelengths shorter than 290 nm.

The quantum yields of photooxidation were obtained with an optical bench (Amko) composed of a 450 W xenon lamp, a monochromator, a stirred sample cuvette (3 ml) and a reference cuvette, and an electronic counter. The calibration was realised with heterocoerdianthrone at 10^{-2} mol l^{-1} in dichloromethane [8]. The temperature of reference and sample cuvette was kept constant at 25°C.

RESULTS AND DISCUSSION

Photodegradation of terbuthylazine in the presence of hydrogen peroxide

A - Photooxydation by-product study

In order to determine the nature of the products appearing during the photodegradation study, an experiment at relatively high concentration in herbicide (5 ppm (2.18 10^{-5} mol 1^{-1}) which is near the solubility limit of 8.5 ppm in water) and 2.18 10^{-5} mol 1^{-1} in H₂O₂ was performed using the UV reactor. Results, reported in

figure 1, show that terbuthylazine is rapidly eliminated from the medium. A total degradation is observed after 5 minutes of irradiation.



Figure 1: Ammeline formation during UV irradiation of terbuthylazine (2.18 10⁻⁵ mol l⁻¹) with hydrogen peroxide (2.18 10⁻⁵ mol l⁻¹)

During the HPLC analysis, the products desethylterbutyhlazine (Fig.2, A), detertisobutylterbuthylazine (B), acetamidoterbuthylazine (C) (2-chloro-4-acetamido-6-tertiobutylamino-1,3,5 triazine) and 2-chloro-4,6-diamino-1,3,5 triazine (D) were also detected. These intermediates are then decomposed in ammeline (H) as the final compound. Ammeline appears after 8 minutes of irradiation and represents 72 % of the initial compound after 60 minutes. After 60 minutes, H_2O_2 is probably totally removed from the medium, which can explain that the concentration of ammeline stays constant. Actually, the oxydation of ammeline with OH leads to the cyanuric acid [9]. Hydroxyterbuthylazine (E), hydroxydetertisobutylterbuthylazine (F) or hydroxydesethylterbuthylazine (G) were not detected in the capillary electrophoresis analysis at any time of the irradiation. Nevertheless, this does not mean that these intermediate by-products are not formed, because they can be quickly decomposed by OH to give ammeline. According to these results, a degradation pathway of terbuthylazine by a H_2O_2 / UV system is proposed in figure 2.

This reaction scheme indicates that the radical attack of terbuthylazine favours the dealkylation of the lateral chains and then the dechlorination. This mechanism is different to the one observed by UV photolysis alone. In a previous work, the degradation under UV light alone, the hydroxylation of terbuthylazine has been found to be the primary degradation stage [10]. By the hydroxylation pathway 90 % of the initial amount of terbuthylazine in solution is decomposed, and by the dealkylation pathway 10%. This is the same for the direct photodegradation of atrazine [11].





B - Kinetic study of the photodegradation of terbuthylazine in the presence of H₂O₂

The efficiency of hydrogen peroxide on the degradation of pesticides can also be evaluated by the quantum yield of photooxidation (ϕ), that is defined as follows :

$$\dot{\phi} = \frac{D}{N}$$

where D is the number of molecules degraded and N the number of photon absorbed by the solution.

Without hydrogen peroxide, the quantum yield of photodegradation at 254 nm has been found to be 0.09 [10]. After the adjonction of 2.18 10^{-3} mol 1^{-1} of hydrogen peroxide, a value of 0.26 was obtained at the same wavelength. This represents a 2.9-fold increase of the efficiency of the incident radiation, due to the presence of OH radicals formed during H₂O₂ hydrolysis.

In order to determine the influence of the hydrogen peroxide concentration on the degradation rate of terbuthylazine, experiments were carried out in the UV reactor with solutions at an initial terbuthylazine concentration of 2.18 10^{-6} mol 1^{-1} and with various concentrations of hydrogen peroxide, ranging from 2.18 10^{-5} to 2.18 10^{-3} mol 1^{-1} . For diluted solutions, the rate of photodegradation follows a first order kinetic law. It can be concluded from the results shown in table 1 that the initial hydrogen peroxide concentration of 2.18 10^{-5} mol 1^{-1}

is the concentration threshold below which hydrogen peroxide has no significant effect on the degradation of terbuthylazine. Above this limit, the lower limit, the rate constant increases with the H_2O_2 concentration.

Table 1: Variation of the first ord	r kinetic apparent constant v	with the initial hydrogen	peroxide concentration
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[H ₂ O ₂] (mol l ⁻¹)	k (min ⁻¹)			
0	0.45			
2.18 10-5	0.46			
2.18 10-4	0.55			
2.18 10-3	0.95			

The kinetics of photodegradation of terbuthylazine can be described, for our experiments, as the sum of two mechanisms, the direct photolysis and the photooxydation :

$$-\frac{d[C]}{dt} = k_1 [C] + k_2 [H_2O_2] [C]$$
(1)
with k₁ = 0.45 min⁻¹
and k₂ = 230 l mol⁻¹ min⁻¹

The formation of desethylterbuthylazine during the experiments (figure 3) confirms the previous dealkylation of terbuthylazine with hydrogen peroxide. The presence of 2.18 10^{-3} or 2.18 10^{-4} mol 1^{-1} of H_2O_2 increases and accelerates the formation of desethylterbuthylazine, whereas the curves obtained with 2.18 10^{-5} mol 1^{-1} of H_2O_2 and without H_2O_2 are of a similar shape.





- $\blacksquare [H_2O_2] = 2.18 \ 10^{-4} \ \text{mol.l}^{-1}$
- [H₂O₂]= 2.18 10⁻⁵ mol.l⁻¹
- without H₂O₂

Figure 3 : Formation and depletion of desethylterbuthylazine according to the initial hydrogen peroxide concentration

Photodegradation of terbuthylazine in the presence of titanium dioxide

The first stages of the degradation of terbuthylazine were investigated in the presence of 72 mg l^{-1} titanium dioxide under simulated solar light (*suntest* apparatus) (figure 4). The degradation follows first order

kinetics. The apparent kinetic constant is 0.125 min⁻¹. Without titanium dioxide, the degradation occurred more than 600 times slower.



Figure 4 : Irradiation ($\lambda > 290$ nm) of terbuthylazine with titanium dioxide (72 mg l⁻¹)

The first reaction which takes place is the oxidation of the lateral chains. The main degradation products detected are desethylterbuthylazine and acetamidoterbuthylazine. They represent 30 percent of the terbuthylazine initially in the solution after 10 minutes of irradiation, and are fully decomposed after 30 minutes. In the *suntest* apparatus, the direct photodegradation is negligible, so that the degradation of terbuthylazine is only due to the reactive species formed during the irradiation of TiO_2 . This confirms that the OH radicals react preferentially with the alkyl groups, then they hydroxylate the molecule in position 2. The oxidation of terbuthylazine for longer irradiation times was not investigated in this study, so we have not seen the formation of advanced oxydation products such as ammeline or cyanuric acid.

Photodegradation of terbuthylazine in the presence of acetone.

Acetone can be used as a photosensitizer in order to degrade molecules. When irradiated under simulated solar light, acetone can absorb energy and then react with molecules in solution [12]. In the case of terbuthylazine irradiated in the *suntest*, the addition of 1 % (v/v) to an aqueous solution increases the degradation rate dramatically (figure 5).



Figure 5: Photosensibilisation of terbuthylazine with acetone

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The calculated half lives, according to a first order kinetic law, show a 7-fold enhancement of the degradation rate in the presence of acetone. Similar results have been previously found with atrazine, with a 5-fold enhancement of the degradation rate with 1% (v/v) of acetone under simulated solar light [13].

Photodegradation of terbuthylazine in the presence of humic substances

The effects of two humic substances, extracted from natural media following the IHSS procedure [14], on the photodegradation rate of the terbuthylazine have been studied. Humic acids (HA) have been isolated from the A_0 horizon of a cultivated brown soil (Scheyern, Germany), and the fulvic acids (FA) have been isolated from a small stream of the Munich region. The characteristics of the humic substances are given in table 2. The adsorption of the pesticides on the humic substances represents, in all cases, less than 5 percent of the amount in the solution.

Solutions with different doses of dissolved humic acids (0, 5 or 50 ppm) were irradiated with the HPK lamp with a pyrex filter (λ >290 nm). In order to determine the kind of mechanism involved in the photodegradation of the terbuthylazine, the solutions were kept saturated in O₂ or N₂. The gas was bubbling through a sintered glass located at the bottom of the reactor. The kinetics of photodegradation follow, in all cases, a first order kinetic law (figure 6, table 3) and the photodegradation rate is accelerated by the presence of the humic acids.

Table 2 : Elemental analysis of the humic substances used in the study

	C%	H%	N%	0%	Ashes %	Iron %	C/N	H/C (at.)	O/C (at.)
HA soil	48.3	4.04	4.44	39.52	3.7	0.18	10.88	1.01	0.61
FA stream	43.14	3.80	2.74	45.42	4.9	none	15.75	1.06	0.79

At similar humic acid concentrations, oxygen, which is a triplet-triplet energy transfer quencher, has no effect in the removal of terbuthylazine. The acceleration of the photodegradation rate in the presence of the humic acids is therefore probably due to a radical mechanism rather than a triplet-triplet energy transfer.

The analysis of the photoproducts formed during the irradiation shows that the presence of humic substances enhanced the formation of oxidation products of lateral chains, such as desethylterbuthylazine.

Table 3 : Kinetic constants of terbuthylazine degradation in the presence of humic acids

		under O ₂		under N ₂			
	without HA	HA 5 ppm	HA 50 ppm	without HA	HA 5 ppm	HA 50 ppm	
kinetic apparent constant (h ⁻¹)	0.021	0.040	0.11	0.022	0.035	0.10	



(°) under O_2 (•) under N_2 (□) under O_2 + 5 ppm HA (▲) under N_2 + 5 ppm HA (×) under O_2 + 50 ppm HA (■) under N_2 + 50 ppm HA



In the case of fulvic acids extracted from water, the irradiation experiments were carried out in the suntest apparatus (λ >290 nm). The initial concentration of terbuthylazine is 2.18 10⁻⁵ mol l⁻¹, and the fulvic acids are at a concentration of 5 ppm. The results show that these fulvic acids decrease the photodegradation rate of terbuthylazine (figure 7).



Figure 7: Photodegradation of terbuthylazine (2.18 10⁻⁵ mol l⁻¹) with fulvic acids of a stream in the *suntest* apparatus

This study shows two contradictory effects of the two humic substances studied on the photodegradation of terbuthylazine in solution. As humic substances are very complex, it is difficult to explain their role in the photodegradation pathway. Nevertheless, the presence of iron in the humic acids extracted from this soil, even in a small amount, could catalyse the formation of reactive oxygen species through a photo-fenton type mechanism [15]. This could explain the enhancement of the amount of dealkylated by-products observed with the humic substances.

CONCLUSIONS

The photodegradation of terbuthylazine has been found to be efficiently improved by H_2O_2 , TiO₂ and acetone. In the presence of hydrogen peroxide (2.18 10⁻³ mol⁻¹) and UV light, the mechanism of direct photodegradation, with hydroxylation as the first step, is in competition with a primary oxidation of the lateral chains. The humic substances that have been tested, have different effects on the photodegradation of terbuthylazine. The humic acids extracted from a soil act as a sensitiser, in promoting the dealkylation of the lateral chains.

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