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Photocatalysed degradation of cyromazine in aqueous titanium dioxide suspensions: comparison with photolysis

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Abstract

The fate of cyromazine (*N*-cyclopropyl-1,3,5-triazine-2,4,6-triamine), an insect growth regulator, has been studied upon irradiation as well as its photocatalytic treatment (advanced oxidation technology). Most of the organic compounds occurring during the photodegradation have been identified by means of liquid chromatography and mass spectrometry coupled techniques (LC–MS). The main photoproducts of the first degradation steps are amide-triazines and melamine. Simultaneously, carboxylic acids, such as acrylic, pyruvic and glycolic acids have been identified by LC–UV. These acids are resulting from the cyclopropyl degradation. The melamine (1,3,5-triazine-2,4,6-triamine) is transformed into cyanuric acid (2,4,6-trihydroxy-1,3,5-triazine) by means of three successive deaminations. This compound remains very stable in aqueous solution. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Cyromazine; Titanium dioxide; Photolysis; Photodegradation; Photocatalysis

1. Introduction

Symmetric triazines (1,3,5-triazines or s-triazines) derivatives are among the most widely used pesticides. In soils, or by photolytic reactions, degradation products are formed as a result of dealkylation and deamination of the substituents of the triazine ring. The resulting product is the cyanuric acid [1–3] which cannot be degraded nowadays by any oxidative method but by bacteria. The s-triazine degrading bacteria included two distinct *Pseudomonas* species and a strain of *Klebsiella pneumoniae* [4]. The cyanuric acid is thus transformed into biuret which is converted into urea and finally yields carbon dioxide and ammonia [4–7].

Cyromazine (*N*-cyclopropyl-1,3,5-triazine-2,4,6-triamine) is an insect growth regulator effective as a feed-through larvicide in poultry to control flies in manure and as a foliar spray to control leafminers on flowers and vegetables. Thus, its metabolism has been studied in tomatoes [8]. Tomatoes analysis has shown cyromazine and melamine residues, and two other compounds which were not identified. The melamine residue has also been detected in Chinese cabbages [9] and other vegetables [10] and is present in some locations in the soil of California [11].

Studies of s-triazines are essentially related to atrazine and to the three main classes of s-triazines: the 2-chloro-s-triazines, 2-methoxy-s-triazines and 2-methylthio-s-triazines. Their photocatalytic degradations have been examined under simulated solar light irradiation by means of semiconductor powders, such as TiO_2 aqueous suspensions [12–14].

The present study deals with one of the atypical substituted s-triazine [15], the cyromazine, which is representative of the most highly aminated group of mono-*N*-alkylated-s-triazines [16]. The aim was to establish the photolysis mechanism of cyromazine. Nevertheless, direct photolysis of triazine derivatives seems difficult due to their weak absorption of light with wavelengths greater than 260 nm. Thus, TiO_2 has been used as semiconductor in order to determine the capacity of photocatalysis to degrade this molecule. The mineralisation into nitrate and ammonium ions has also been studied.

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2. Experimental

2.1. Materials

Cyromazine (purity >95%) was obtained from Ciba-Geigy (Novartis). For all the experiments, the initial cyromazine concentration was $10\,\mathrm{mg\,l^{-1}}$. Melamine (1,3,5-triazine-2,4,6-triamine) with a purity >99% was purchased from Fluka Chemika. The photocatalyst compound was the titanium dioxide 'Degussa P25' which is predominantly anatase (80% anatase, 20% rutile). It is non-porous and offers a specific surface area of about $55\,\mathrm{m^2\,g^{-1}}$ and a density of $3.85\,\mathrm{g\,cm^{-3}}$.

2.2. Methods

Irradiation was carried out with a HPK 125 W Philips mercury lamp, emitting in the wavelength range 250–600 nm, with a maximum emission at 360 nm. The lamp was irradiating the reactor (85 ml) through pyrex-glass cutting the radiation shorter than 290 nm to simulate a part of the solar radiation. Between the lamp and the reactor, a circulating water pyrex-glass tank cooler was positioned. The solution was homogenised by a magnetic stirrer and remained in contact with air. The initial volume was of 70 ml. The advance of the reaction was followed by sampling (500 μl). A series of four or five runs was necessary to observe the whole degradation process. When TiO_2 was used the mixture was stirred during 90 min in the dark before the beginning of the irradiation in order to reach the adsorption equilibrium. Before analysis each sample was filtered on a 0.45 μm Whatman filter to eliminate the TiO_2 particles.

The cyromazine degradation was followed by liquid chromatography (Shimadzu LC-10AS) using a Chrompack Omnispher C18 column (5 μm, 250 × 4.6 mm i.d.). The mobile phase was a mixture of aqueous pH 7 phosphate buffer ($10^{-3}\,\mathrm{mol\,l^{-1}}$) solution and acetonitrile (95/5, v/v). The detection was monitored at 220 nm corresponding to the highest absorption wavelength of the cyromazine.

The intermediate products were separated and identified by means of LC–MS (HP 1100 series LC MSD) with a Chrompack C18 Inertsil ODS 3 column (5 μm, 150 × 3 mm i.d.). The mobile phase was a mixture of aqueous pH 4.3 formate buffer ($10^{-3}\,\mathrm{mol\,l^{-1}}$) and methanol (95/5, v/v). The UV detection was monitored from 210 to 300 nm with a photodiode array. In order to improve the chemical ionisation, a post column addition of a mixture of isopropanol and ammonium formate solution ($10^{-3}\,\mathrm{mol\,l^{-1}}$, adjusted to pH 7.8 by means of diluted ammonia) was performed using an external pump. Mass spectrometry detection was carried out in positive and negative electrospray modes.

The carboxylic acids were detected by LC using a Waters 600 pump and a Waters 486 UV detector fixed at 210 nm. The column was a Sarasep Car-H (300 × 7.8 mm i.d.) and the mobile phase was a sulphuric acid aqueous solution ($5 \times 10^{-3}\,\mathrm{mol\,l^{-1}}$).

Inorganic ions (NO_3^- and NH_4^+) were analysed by means of LC using a Waters 501 pump and a Waters 431 conductivity detector. The NO_3^- ions were separated with a Sarasep AN1 (250 × 4.6 mm i.d.) column with a $NaHCO_3$ 1.7×10^{-3}/Na_2CO_3 $1.8 \times 10^{-3}\,\mathrm{mol\,l^{-1}}$ mobile phase. For the NH_4^+ ions the column was a Chrompack Vydac IC 400 (50 × 4.6 mm) and the eluent was a HNO_3 $2.5 \times 10^{-3}\,\mathrm{mol\,l^{-1}}$ aqueous solution.

3. Results and discussion

3.1. Photolysis

Despite the weak absorption of cyromazine at the wavelengths of the irradiation (Fig. 1), the photolysis of a 10 ppm cyromazine (**1**) solution shows after 30 h of irradiation a degradation of 59% of the initial cyromazine (Fig. 2).

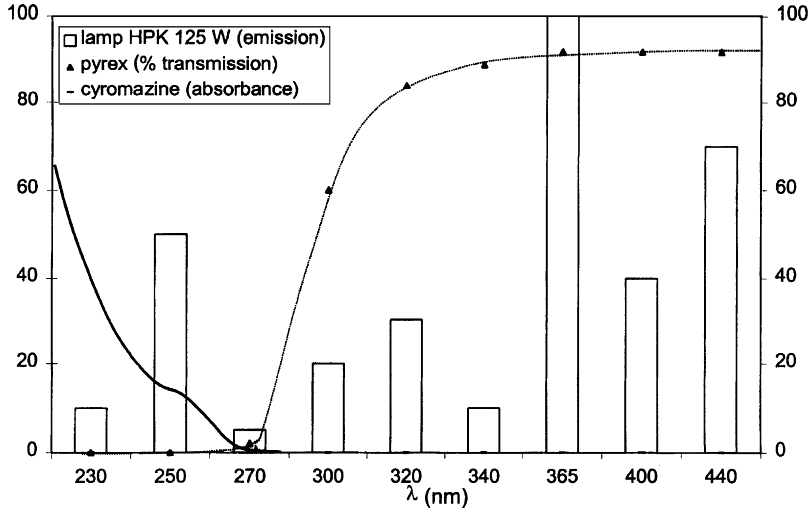


Fig. 1. UV spectra of cyromazine, pyrex-glass and mercury lamp.

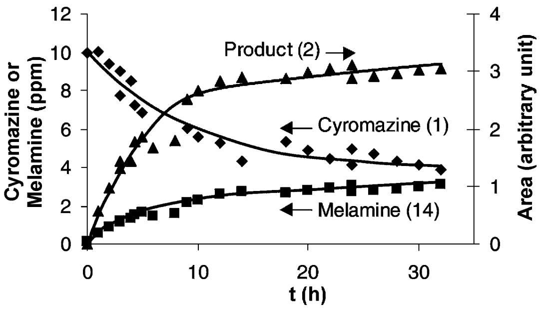


Fig. 2. Photolysis of cyromazine (LC–MS).

Melamine (2,4,6-triamino-1,3,5-triazine) ($t_R = 2.9$ min) (**14**), which was identified by LC–MS and measured from a calibration curve, represents 67% of the photoproducts formed. Among other compounds (33%) the main one was identified by LC–MS ($t_R = 6.8$ min, $m/z = 199$ [M + H], $m/z = 221$ [M + Na]) as 3-amino-*N*-(4,6-diamino-1,3,5-triazine)-3-ol-propionaldehyde (**2**). This compound resulting from the opening cyclopropyl oxidation has not been quantified as it is not commercially available. The non-nil initial slope of the curve representing photoproduct (**2**) leads to consider it as the first step of the degradation process. It can be noted that the concentrations of the three compounds **1**, **2** and **14** tend to stabilise after around 30 h of irradiation.

The photo-oxidation of product (**2**) gives through a series of oxidation and decarboxylation processes the *N*-(4,6-diamino-1,3,5-triazine)-formamide (**11**) which was identified by LC–MS ($t_R = 8.5$ min, $m/z = 155$ [M + H]). This compound (**11**) leads to melamine (**14**) by one oxidation step and a further decarboxylation process. The opening of the cyclopropyl ring gives simultaneously a series of carboxylic acids. Three acids (acrylic, $t_R = 18.0$ min; pyruvic, $t_R = 8.4$ min and glycolic, $t_R = 11.4$ min) have been detected by LC–UV with the Sarasep Car-H column.

The melamine (**14**) is very stable to photolysis. The NO_3^- and NH_4^+ species, resulting from deamination, appear only after 60 h of irradiation. The concentration sum $[NO_3^-] + [NH_4^+]$ is in the ratio $[NH_4^+] + [NO_3^-]/[\text{cyromazine}]_{\text{initial}} = 1$ and 1.5 after a time exposure of 120 and 200 h, respectively. Such a deamination process, leading step-by-step to ammeline (**15**), ammelide (**16**) and finally cyanuric acid (**17**), has been already detected in the degradation of the atrazine [12,13] and other s-triazines.

In addition, we have tested the influence of the irradiation power on the pesticide disappearance (Fig. 3).

The initial decrease of cyromazine concentration is proportional to the radiation power (Fig. 4). Considering that the mean solar power is 4 mW cm^{-2} [17], it can be estimated that the initial decrease of a 10 ppm cyromazine solution in the environment would be about 0.035 ppm h^{-1}. However this must be carefully extrapolated. Firstly the device used emits from 290 nm, whereas solar emission starts around 295 nm. Secondly, natural water is not pure water but contains chromophores capable of affecting the reaction in many ways.

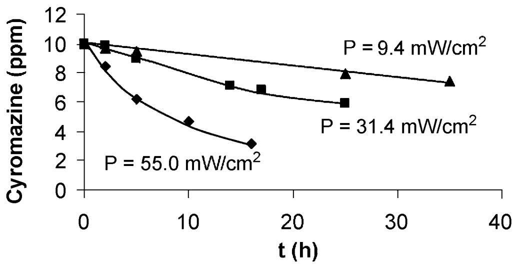


Fig. 3. Cyromazine concentration decrease versus irradiation power.

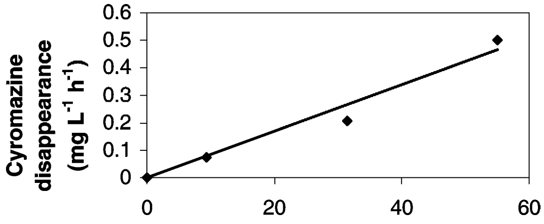


Fig. 4. Influence of the irradiation power on the cyromazine disappearance.

3.2. Photocatalysis

3.2.1. Kinetics of cyromazine disappearance

The complete disappearance of a 10 ppm solution of cyromazine was obtained upon irradiation at $\lambda > 290$ nm within 45 min in the presence of TiO_2 (Fig. 5). A first-order decay of cyromazine was observed.

The comparison of the cyromazine disappearance with and without the photocatalyst shows clearly the increase of the degradation rate in presence of TiO_2. The initial rate of disappearance was 30 times higher by photocatalysis (24 mg l^{-1} h^{-1}) than by photolysis (0.8 mg l^{-1} h^{-1}).

3.2.2. Nature and evolution of intermediates

Photocatalytic degradation of cyromazine was monitored with the optimum concentration of TiO_2 (700 mg l^{-1}) (Fig. 6). A typical LC–MS chromatogram is presented in Fig. 7. Like in photolysis we observe the formation of the photoproducts (**2**) and (**11**) resulting from the successive opening and oxidation of the cyclopropyl ring. By

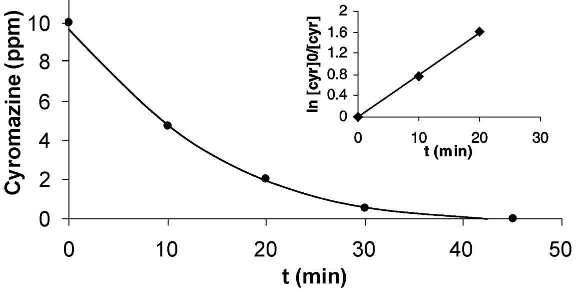


Fig. 5. Cyromazine photocatalysed degradation with optimal TiO_2 concentration (700 mg l^{-1}).

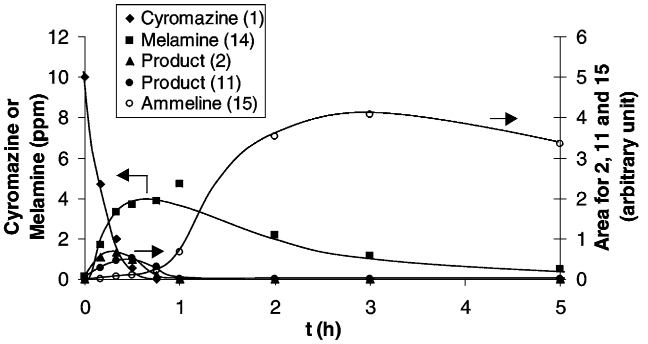


Fig. 6. Photocatalysis of cyromazine (700 mg l^{-1} TiO$_2$).

photocatalysis the 3-amino-*N*-(4,6-diamino-1,3,5-triazine)-3-ol-propionaldehyde (**2**) leads within 1 h to *N*-(4,6-diamino-1,3,5-triazine)-formamide (**11**) by successive oxidative reactions and melamine is oxidised into ammeline (**15**). In Fig. 6 we can notice that the formation of ammeline occurs when the degradation of melamine starts.

After 10 min of irradiation the melamine represents 22% of the initial cyromazine and corresponds to 42% of the photoproducts formed. By photolysis, 30 h of irradiation were necessary to form melamine in such yield.

The analysis of a sample irradiated during 7.5 h displays the presence of ammeline (**15**) and ammelide (**16**). Ammelide appears when the degradation of ammeline begins as in the sample illuminated 3 h we saw trivial quantity of ammelide. A sample irradiated 22 h reveals by LC–MS the presence of ammelide and some traces of cyanuric acid (**17**). We can consider that the formation of cyanuric acid begins at 22 h of photocatalysis when ammelide starts to photodegrade.

3.2.3. Mineralisation

Mineralisation of cyromazine under irradiation over TiO$_2$ yields essentially nitrate ions (Fig. 8). Ammonium ions are detected in negligible quantity. This result is correlated with the one obtained in nitrobenzene study [13]. On the other hand, the study of the mineralisation of aniline [18] shows the preferential formation of ammonium ions. This discrepancy with our results implies a role played by the s-triazinic ring. In our case, it could be suggested that oxidation of the amino group happens first and only after the cleavage with the s-triazinic ring occurs.

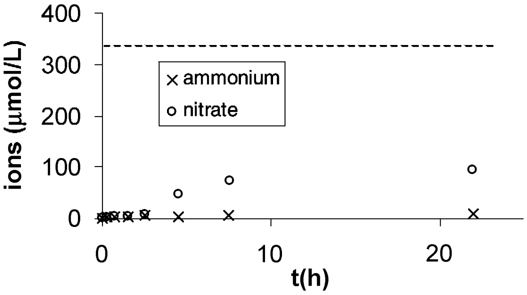


Fig. 8. Mineralisation of cyromazine.

Mineralisation is not complete because the last photoproduct is cyanuric acid that could only be degraded by bacteria [4–7]. This latter appears after 22 h of irradiation as ammelide (**16**) starts to be photodegraded. Ammelide contains four nitrogen atoms and thus the maximum quantity of ions nitrate and ammonium that can be formed is achieved.

3.3. Proposed degradation pathway

Scheme 1 is a proposed pathway for the cyromazine degradation. It results from the identified photoproducts LC–MS data during the photocatalytic degradation. Nevertheless some of them have also been detected during the photolysis process. These compounds are starred on Scheme 1. The first step is initiated by an oxidative opening of the cyclopropyl ring leading to an aldehyde (**2**). This

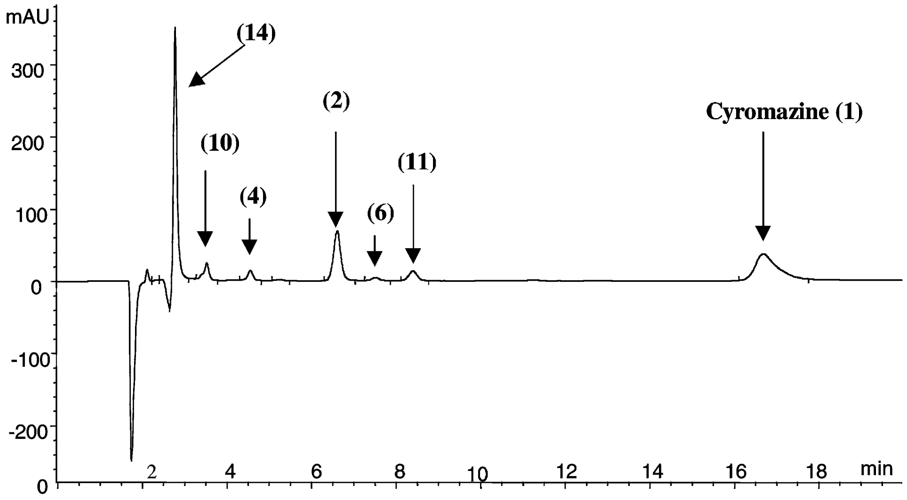
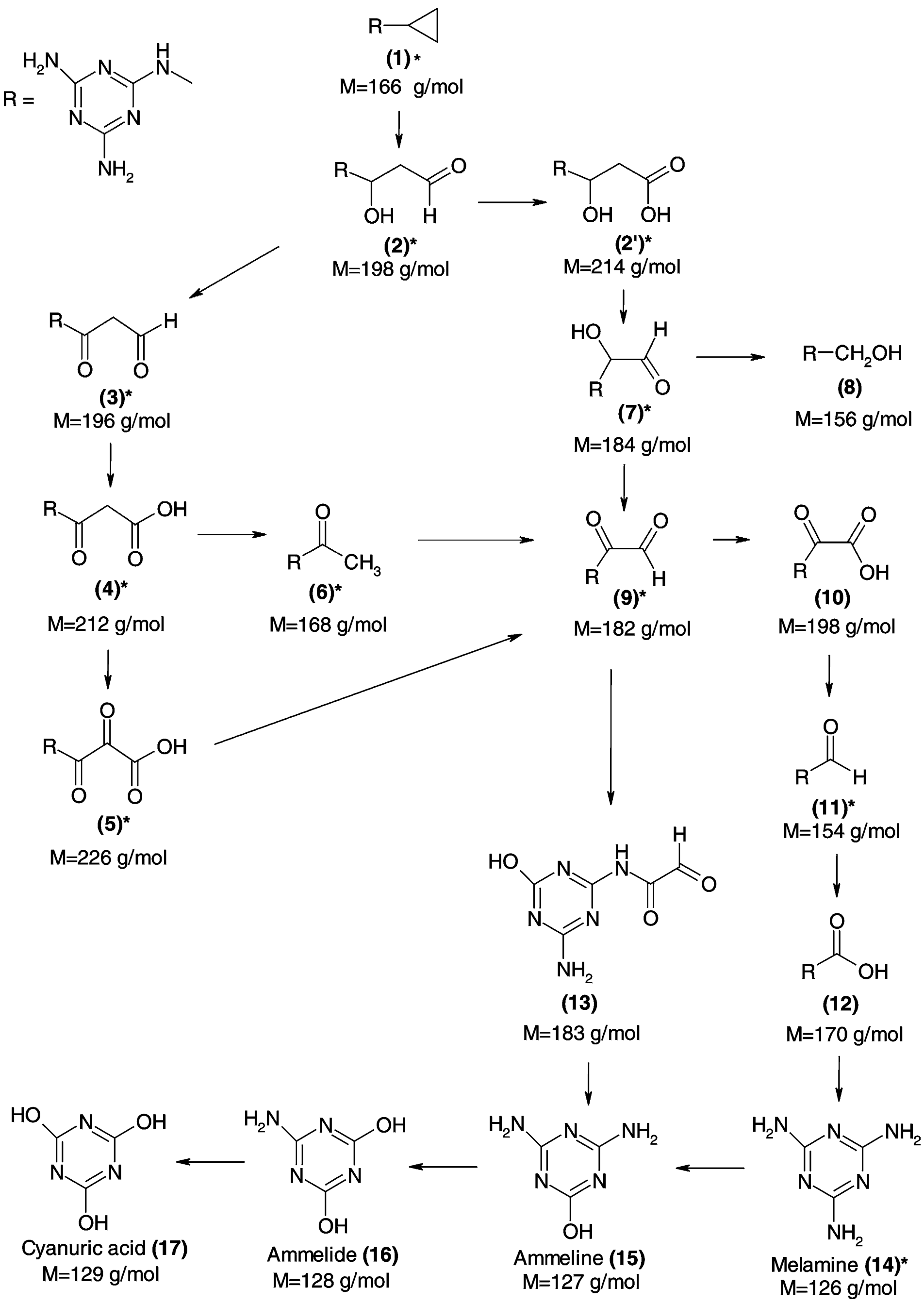


Fig. 7. Typical LC–MS chromatogram obtained during the photocatalytic degradation of cyromazine. Numbers in parenthesis refer to Scheme 1.

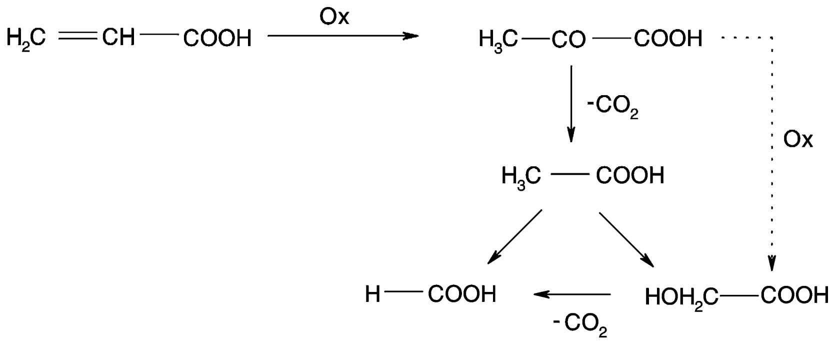


Scheme 1. Intermediates in the photocatalytic degradation of the cyromazine, (*) Compounds observed both by photolysis and photocatalysis.

opening can be due, in photocatalysis, to an attack by OH° radicals, while in direct photolysis it can result either from a photoassisted hydrolysis or from the participation of singlet oxygen.

Next step of the process involves a series of oxidation and decarboxylation processes. The latter occur by photocatalysis via reaction with the holes resulting from the excitation of the TiO_2 semiconductor. By photolysis the decarboxylation process arises from the formation of unstable acids which exist in the ceto-enolic form and can absorb the ultraviolet radiation to be degraded. For example the pyruvic acid, which has a structure similar to compounds (**10**) and (**5**), absorb at 321 nm due to its conjugation [19].

On one hand, the photoproduct (**2**) is oxidised into the β-ketoaldehyde (**3**) (t_R = 3.3 min, m/z = 197 [M + H], m/z = 219 [M + Na]) and further into a β-ketoacid (**4**) (t_R = 4.7 min, m/z = 213 [M + H], m/z = 235 [M + Na]) and an α–β-diketoacid (**5**) (t_R = 1.7 min, m/z = 227 [M + H]). The decarboxylation of (**4**) gives the methylketone (**6**) (t_R = 2.6 min, m/z = 169 [M + H]).



Scheme 2. Suggested degradation pathway for acrylic acid.

On the other hand the photoproduct (**2**) is converted into the α-alcoholformaldehyde (**7**) ($t_R = 5.4$ min, $m/z = 185$ [M+H], $m/z = 207$ [M+Na]) which leads either to the primary alcohol (**8**) ($t_R = 11.0$ min, $m/z = 157$ [M + H]) or to the α-ketoaldehyde (**9**) ($t_R = 2.8$ min, $m/z = 183$ [M + H]). Two different oxidation processes can occur for compound (**9**): (i) oxidation to an α-ketoacid (**10**) ($t_R = 3.5$ min, $m/z = 199$ [M + H]) which gives melamine (**14**) after one oxidation and two decarboxylation steps; (ii) substitution of an amino group of the triazine ring by a hydroxyl group to afford (**13**) ($t_R = 24.9$ min, $m/z = 184$ [M + H]). The formation of (**13**) is confirmed by the appearance of nitrate ions after 3 h of photocatalysis. Ammeline (**15**) could be obtained from (**13**) and (**14**) by cleavage of N–C amido bond or the oxidation of one amino group in hydroxyl group, respectively. Compounds (**16**) and (**17**) result from further replacement of NH_2 groups by OH groups. However the amine function may first be oxidised because in solution we have only observed the appearance of nitrate ions. Nevertheless we have not detected any triazinic ring substituted by NH_2OH or NO_2.

The compound (**17**) remains very stable in aqueous solution, even in presence of a photocatalyst such as TiO_2, and does not decompose before 100 h of irradiation [14]. The detection of acrylic acid shows that compound (**2′**) can also directly form melamine (**14**) without oxidation and decarboxylation of aliphatic part. Acrylic acid is formed by photoassisted dehydroxylation and decarboxylation of (**2′**) on TiO_2 as previously mentioned by one of us [20]. Scheme 2 proposes a degradation pathway of acrylic acid. Acrylic acid is oxidised into pyruvic acid which can be either decarboxylated to form acetic acid or oxidised. The oxidation of the acetic acid can give glycolic acid and formic acid.

4. Conclusion

The use of LC–MS and LC–UV allowed to put in evidence the degradation pathway of cyromazine under irradiation with or without TiO_2. This study shows the fate of this insecticide in environment in presence of UV and the efficiency of photocatalysis to degrade aliphatic chains. The formation of cyanuric acid prevents the obtaining of complete mineralisation of cyromazine as previously observed for atrazine and other s-triazines by any oxidative methods. However it can be noticed that the degradation can be achieved by means of bacteria.

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