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Photo-induced transformation of hexaconazole and dimethomorph over TiO_2 suspension

P. Calza*, C. Massolino, E. Pelizzetti

Dipartimento di Chimica Analitica, Università di Torino, via P. Giuria 5, 10125 Torino, Italy

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ABSTRACT

The photo-induced transformation in aqueous solution of hexaconazole and dimethomorph over irradiated titanium dioxide was studied. The investigation involved monitoring pesticides decomposition, identifying intermediate compounds, assessing mineralization, and evaluating toxicity of pesticides derivatives. HPLC/UV and HPLC/MS were used to follow the disappearance of the initial pesticides and the formation of intermediate products, while the acute toxicity was evaluated by using the *Vibrio fischeri* luminescent bacteria assay.

Hexaconazole photocatalytic transformation proceeds through the formation of highly persistent compounds. The formation of cyanuric acid, a non-toxic compound refractory to photocatalytic treatment, was recognized. Conversely, the toxicity assays prove that neither hexaconazole nor its intermediates exhibit acute toxicity.

Dimethomorph under photocatalytic treatment is completely mineralized within 14 h of irradiation. However, its transformation proceeds through the formation of toxic intermediates. A correlation exists between the evolution of the intermediate compounds and the toxicity profile, as the highest toxicity is measured when the intermediates with lower EC50 (hydroquinone and 4-chlorophenol) are formed.

1. Introduction

A combined use of morpholine and triazole fungicides had shown several advantages, above all when adopted for tea treatment [1]. Among them, we have chosen dimethomorph (a morpholine fungicide) and hexaconazole (triazole fungicide), whose structures are shown in Fig. 1. Dimethomorph (*EZ*)-4-[3-(4-chlorophenyl)-3-(3,4-dimethoxyphenyl) acryloyl] morpholine) is a systemic fungicide used to prevent the peronosporales germs disease and is widely used for vegetables and fruits treatment [2]. Hexaconazole [(*RS*)-2-(2,4-dichlorophenyl)-1-(1H-1,2,4-triazol-1-yl)hexan-2-ol] is a fungicide at broad spectrum of activity against ascomycetes and basidiomycetes [3]. Trace amount of hexaconazole (6 ng/L) was found in river water samples [4]. It is highly persistent and no degradation was apparent within 3 weeks. A study on soils shows that its degradation proceeded at similar rate in both sterilized and non-sterilized soils, so proving a minor role played by micro-organisms [5].

Besides, the employment of an appropriate technique for water decontamination is required. Photocatalytic degradation with irradiated semiconductors had shown to be effective in the abatement of numerous pollutants, as well as many pesticides [6–11]. Among semiconductor solids, TiO_2 is widely used because it is non-toxic, inexpensive, as well as a biologically and chemically inert photocatalyst. Light induces the formation of reactive species on the surface of the photocatalyst (i.e. h^+, e^- and •OH radicals), which produces degradation of a large variety of organic compounds. Such compounds are generally completely mineralized into non-toxic products like carbon dioxide, inorganic ions and water [12–14].

In contrast with the usual photocatalyzed transformations, that proceed through the formation of more simple compounds, some cases were reported where the formation of more complex compounds occurred. Alkyl ureas photocatalyzed transformation mainly proceeded through the formation of cyclic compounds [15]. Ring-expanded six-membered triazine were formed from triazole photodegradation [16]. These aspects emphasize the need to identify the intermediate species formed during the photomineralization process, in order to inspect the real ability of oxidation technology in reducing the toxicity of the treated matrix and to verify the possible formation of dangerous intermediates.

For this purpose, in the present paper we will go inside the transformation pathways followed by the selected fungicides under photocatalytic treatment through a combined evaluation of different aspects: (1) identification of the degradation compounds formed during the photocatalytic process; (2) assessment of total

* Corresponding author. Tel.: +39 0116707626; fax: +39 0116707615.
E-mail address: paola.calza@unito.it (P. Calza).

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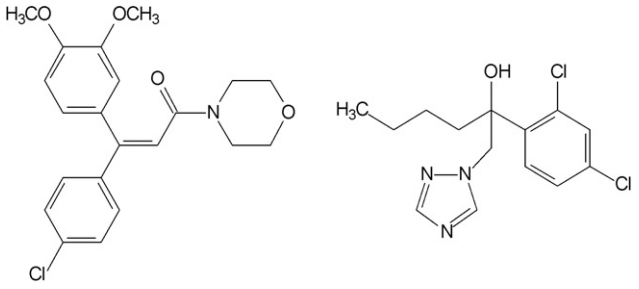


Fig. 1. Structure of hexaconazole (right) and dimethomorph (left).

mineralization during the process; (3) evaluation of the toxicity of the irradiated solutions.

The more suitable technique for detection of these pesticides and their transformation products is the liquid chromatography/tandem mass spectrometry [17–19]. A total of 13 hexaconazole degradation products and 9 dimethomorph degradation products were identified by HPLC tandem mass spectrometry.

2. Experimental

2.1. Material and reagents

Hexaconazole (purity 99.8%, solubility in water 18 mg/L) and dimethomorph (purity 99.0%, solubility in water >18 mg/L) were purchased from Dr. Ehrenstorfer. 3,5-Dichlorophenol, 4-chlorophenol, hydroquinone, morpholine, cyanuric acid, urea and 1,3,4-triazole were all purchased from Aldrich. HPLC grade water was obtained from MilliQ System Academic (Waters, Millipore). HPLC grade acetonitrile (BDH) was filtered through a 0.45-μm filter before use. Formic acid reagent grade was purchased from Carlo Erba. Experiments were carried out using TiO_2 Degussa P25 as the photocatalyst.

2.2. Irradiation procedures

The irradiation experiments were carried out in Pyrex glass cells, filled with 5 ml of a suspension containing the pesticide (15 mg/L) and TiO_2 (200 mg/L). The illumination was performed using a 1500 W Xenon lamp (CO.FO.MEGRA, Milan, Italy) equipped with a 340-nm cut-off filter simulating AM1 solar light. The temperature reached during the irradiation was 38 ± 2 °C. The entire content of each cell was filtered through a 0.45-μm filter and then analyzed by the appropriate technique.

2.3. Analytical procedures

2.3.1. Liquid chromatography

Pesticides and their transformation products were analyzed by HPLC/MS. The chromatographic separations followed by a MS analyzer were run on a C18 column Lichrosphere, 250 mm × 4.0 mm. Injection volume was 20 μL and flow rate 1000 μL/min. Gradient mobile phase composition was adopted: 80/20 to 20/80 in 10 min formic acid 0.05%/acetonitrile.

A surveyor mass spectrometer (Thermo Finnigan) equipped with an atmospheric pressure interface and an ESI ion source was used. The LC column effluent was delivered into the ion source using nitrogen as both sheath and auxiliary gas. The cone voltage was set at 50 V value. The heated capillary value was maintained at 300 °C. The acquisition method used was previously optimized in the tuning sections for the parent compound (capillary, magnetic lenses and collimating octapoles voltages) in order to achieve the maximum of sensitivity. The tuning parameters adopted for ESI source have been the following: capillary voltage 2.5 V, RF Lens Bios 0.3 V, ion energy 1 V mass spectra were collected in full scan positive mode in the range 60–700 *m*/*z*.

The chromatographic analysis for benzene derivatives were followed using a HPLC system (Merck Hitachi L-6200 pumps) equipped with a Rheodyne injector, a UV–vis detector (Merck Hitachi L-4200) and a RP C18 column (Lichrochart, Merck, 12.5 cm × 0.4 cm, 5 μm packing). Gradient mobile phase composition was adopted: 80/20 to 50/50 in 10 min phosphate buffer and acetonitrile.

2.3.2. Ion chromatography

A Dionex instrument was employed, equipped with a conductimeter detector. Determination of ammonium ions was achieved using a CS12A column and 25 mM metansulphonic acid as eluant, at a flow rate of 1 mL/min. In these conditions the retention time for ammonium ion was 4.7 min. The anions were analyzed using an AS9HC anionic column and 9 mM K_2CO_3 at a flow rate of 1 mL/min. In these experimental conditions the retention time of chloride and nitrate ions were 7.10 and 13.98 min, respectively.

2.3.3. Total organic carbon analyzer

Total organic carbon (TOC) was measured on filtered suspensions using a Shimadzu TOC-5000 analyzer (catalytic oxidation on Pt at 680 °C). The calibration was performed using standards of potassium phthalate.

2.3.4. Toxicity measurements

The toxicity of dimethomorph and hexaconazole solutions and of aqueous samples collected at different irradiation times was examined with a Microtox Model 500 Toxicity Analyzer. The toxicity was evaluated by monitoring changes in the natural emission of the luminescent bacteria *Vibrio fischeri* when challenged with toxic compounds. Freeze-dried bacteria, reconstitution solution, diluent (2% NaCl) and an adjustment solution (non-toxic 22% sodium chloride) were obtained from Azur. EC50 were estimated in medium containing 2% sodium chloride using five dilutions and luminescence was recorded after 5 and 15 min of incubation at 15 °C (basic test). The inhibition of the luminescence, compared with a toxic-free control to give the percentage of inhibition, was calculated following the established protocol using the Microtox calculation program. The toxicity of dimethomorph and hexaconazole solution collected at different irradiation times was measured after 5, 15 and 30 min of incubation by adopting the screening test.

3. Result and discussion

3.1. Hexaconazole

3.1.1. Hexaconazole photo-induced transformation

Dark experiments and direct photolysis experiments were preliminarily run, with the aim of assessing whether direct photolysis or thermal decomposition may contribute to the pesticide decomposition. Fig. 2 shows the disappearance of hexaconazole in the diverse experimental conditions as a function of the irradiation time. Experiments were run in the ESI positive mode, which appears to be more sensitive and suitable technique for both the parent compound and the most of the photogenerated products. Hexaconazole was found to be stable over the time interval considered (14 h). Conversely, the disappearance of hexaconazole under heterogeneous photocatalysis easily occurs and followed a pseudo first-order law. The calculated half-time is 11 min, while the complete disappearance occurs within 60 min of irradiation.

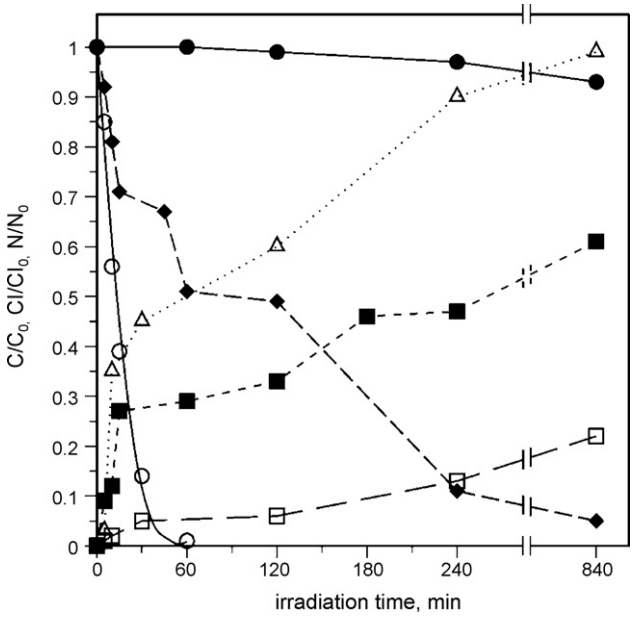


Fig. 2. Degradation of hexaconazole 15 mg L^{-1} on TiO_2 200 mg L^{-1}; disappearance of the initial compound (photolysis (●), TiO_2 (○)), TOC profile (♦) and evolution of chloride (△), nitrate (□) and ammonium (■) ions as a function of the irradiation time.

Fig. 2 also depicts the disappearance of organic carbon and the evolution of inorganic ions formed along with the photocatalyzed conversion of hexaconazole. Mineralization is a long process and even after 14 h of irradiation the organic carbon was not completely degraded. After 4 h of irradiation almost 10% of the organic carbon is still present. A small amount is still persistently observed after 14 h of irradiation (6%). It should be due to the formation of nondegradable organic intermediates produced under our experimental conditions (see below).

Looking closer to the fate of the nitrogen and chlorine atoms, at short irradiation time ammonium and chloride ions were formed at similar rates and, after 15 min of irradiation, approximately 27 and 35% of their stoichiometric amounts were released. For longer irradiation times, inorganic ions showed different formation rates. Chloride ions is easier released; after 1 h of irradiation almost 50% of the stoichiometric amount is formed, while up to 4 h is needed to obtain its stoichiometric release.

Conversely, the nitrogen is slowly released and, in the considered time (14 h), a lack of almost 20% in the nitrogen mineralization exists. It is consistent with the formation of partially de-nitrogenated intermediate compounds, in analogy with study performed on cyproconazole [20,21]. The nitrogen is mainly transformed into ammonium ions, while nitrate formation only occurs at long irradiation time (at 14 h of irradiation ratio NH_4^+/NO_3^- is 3).

3.1.2. Hexaconazole transformation pathways

Along with the hexaconazole degradation, several intermediates characterized by different *m*/*z* ratios were formed. A total of 13 intermediate compounds have been detected and identified by HPLC/MS/MS; they are summarized in Table 1 and Scheme 1. Fig. 3 shows typical bell-shaped profiles for the intermediates as a function of the irradiation time.

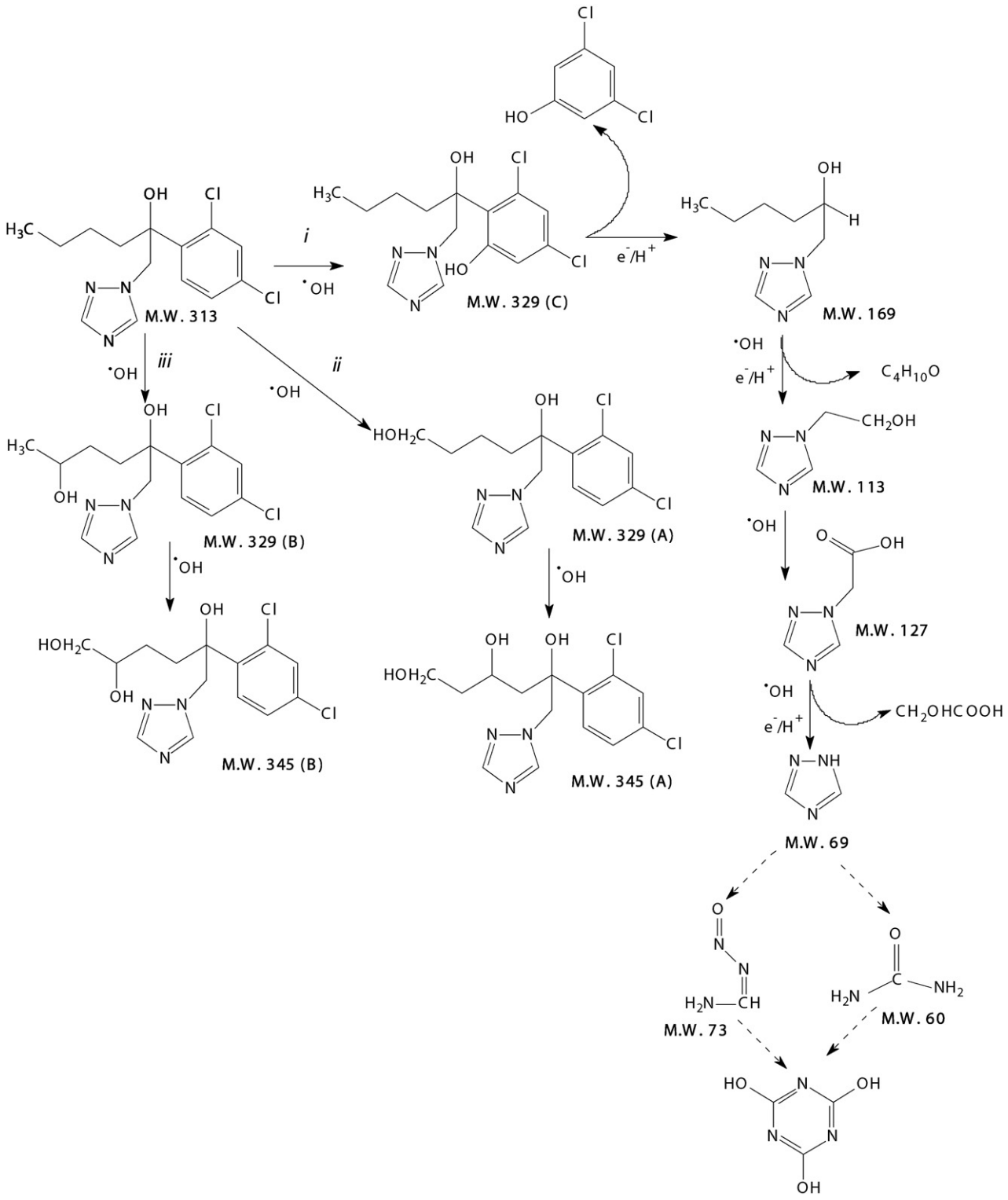
Three species at *m*/*z* 330 were detected, labelled A–C, formed through three concomitant pathways (i–iii), as shown in Scheme 1. A difference of 16 u with the parent compound permits to attribute them to the hexaconazole hydroxy derivatives. Through the analysis of their MS^2 spectra, it can be proposed the position for the OH group substitution. For the two isomers A and B, the hydroxyl group substitution occurs on the alkylic chain (both produce the ion at *m*/*z* 256 through the elimination of $C_4H_{10}O$). The species 330-B also eliminates methanol (product ion at *m*/*z* 300), thus suggesting the hydroxylation on C_6. The MS^2 spectrum for the isomer C shows several peculiar ions: (i) a product ion at *m*/*z* 207, originated from the elimination of $C_3H_3N_3$, that permits to exclude an attack on the triazolic ring; (ii) the product ions at *m*/*z* 314 (loss of methane) and 288 (loss of propene), that exclude the attack on the alkylic chain; (iii) the product ion at *m*/*z* 240 (loss of C_3H_3ClO) that involves the cleavage of the aromatic ring and supports the hydroxylation of the benzenic ring. The hydroxylation of the chloro aromatic ring during photocatalytic treatment is often reported [10,22]. This hypothesis is further supported by the formation of the species at *m*/*z* 170, through the detachment of the dichlorophenol moiety. The finding of the dechlorinated byproduct is consistent with the absence in its MS spectrum of the chlorine typical isotopic distribution. Besides, the contemporaneous formation of 3,5-dichlorophenol supports the breakage of the 330-C (see pathway i). Afterward, the opening of the aromatic ring could occur and aliphatic compounds, such as formic and acetic acid, should be formed [23,24].

Two isobaric species at *m*/*z* 346 were formed and identified as the hexaconazole bihydroxy derivatives. Their MS^2 spectra analysis shows for both isomers the formation of a product ion at *m*/*z* 256, due to the loss of $C_4H_{10}O_2$. It enables us to position both OH groups on the alkylic chain. Isomer B also eliminates ethylene glycol (*m*/*z* 284), so implying that the two OH groups are located on C_5 and C_6. These intermediates are formed at delayed time (see Fig. 3a) and may originate from the monohydroxylated species A and B, through the pathways ii and iii.

Several lower mass compounds were also detected and should derive from the transformation of the compound at *m*/*z* 170. The species at *m*/*z* 114 and 128 should be formed as a consequence of the breakage of the alkylic chain, with the formation of the ethanolic

Table 1
Hexaconazole and the identified transformation products: $[M+H]^+$, retention times and fragments coming from MS^2 spectra.

$[M+H]^+$	t_R (min)	MS^2
314	19.02	256 ($-CH_3CH_2CH_2CH_3$) 284 ($-CH_3CH_3$) 70 ($C_2H_3N_3^+$)
330 A	14.58	256 ($-CH_3CH_2CH_2CH_2OH$) 83 ($C_6H_{11}^+$) 70 ($C_2H_3N_3^+$)
330 B	14.93	256 ($-CH_3CH_2CH_2CH_2OH$) 70 ($C_2H_3N_3^+$) 300 ($-CH_3OH$) 268 ($-H_2O$, $-CHOHCH_2$)
330 C	16.10	240 ($-C_3H_3ClO$) 314 ($-CH_4$) 83 ($C_6H_{11}^+$) 207($-C_3H_3N_3$,$-C_3H_6$), 288 ($-C_3H_6$)
346 A	13.92	256 ($-HOCH_2CH_2CH_2CH_2OH$) 328 ($-H_2O$) 83 ($C_6H_{11}^+$)
346 B	14.50	256 ($HOCH_2CH_2CH_2CH_2OH$) 284 ($HOCH_2CH_2OH$) 328 ($-H_2O$) 83 ($C_6H_{11}^+$)
170	3.32	–
114	3.26	–
128	2.19	–
74	2.44	–
70	2.87	–
61	2.17	–



Scheme 1. Proposed transformation pathways followed by hexaconazole under TiO_2 treatment.

chain, then oxidized to the carboxylic derivative. Afterwards, their transformation leads to the detachment of the carboxylic/alcoholic chain, with the formation of the species at *m*/*z* 70, recognized as 1,2,4-triazole, whose identity was confirmed by injection of a standard solution. It accounts for the conversion of 22.5% of the triazolic moiety.

The triazole transformation is known to proceed through the formation of numerous species, even more complex than the triazole [16]. In our experimental condition we have detected the formation of a species at *m*/*z* 74 and 61, recognized as urea. Urea maximum concentration was 0.2 mg/L, which accounts for the transformation of 4% of the initial organic carbon. Urea is known to be slowly

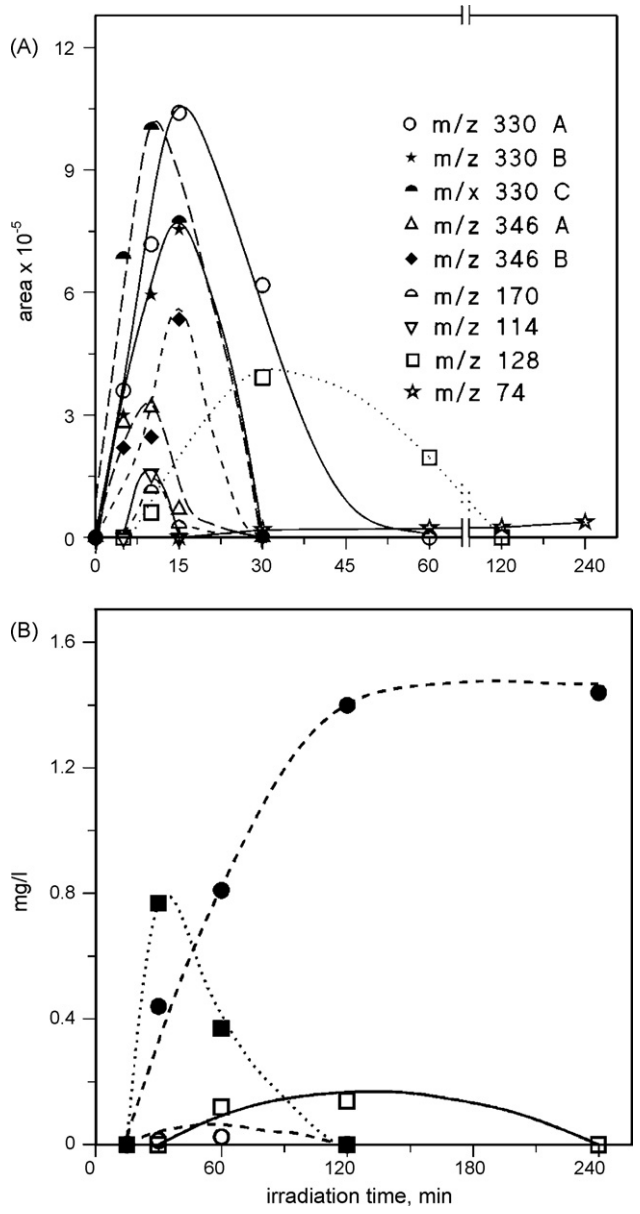


Fig. 3. Intermediates formed from hexaconazole degradation as a function of the irradiation time: (A) structures characterized by HPLC/MS/MS and (B) compounds identified by injection of standard solutions: urea (□, *m*/*z* 61), triazole (■, *m*/*z* 70), cyanuric acid (●), 3,5-dichlorophenol (○).

mineralized and to release the nitrogen mainly as nitrate ions [25]. Hence, its formation should account for the nitrate formation at long irradiation time. The formation of cyanuric acid occurred at longer irradiation time and is persistently observed in the investigated times (14 h). The formation of cyanuric acid was already detected during the triazole photocatalyzed transformation and seems to arise from a sequence of events involving the many fragments formed in the breakup of the triazole ring [16]. Cyanuric acid is known to be refractory to TiO_2 photocatalytic treatment [26]. Thus, its formation should justify the lack of carbon and nitrogen mineralization. The amount of organic carbon persistently measured after 14 h of irradiation (6%) approximates the organic carbon still bound in the cyanuric acid (5%). Also the extent of the remaining organic nitrogen (20%) approximates the amount of nitrogen still bound in the cyanuric acid (17%).

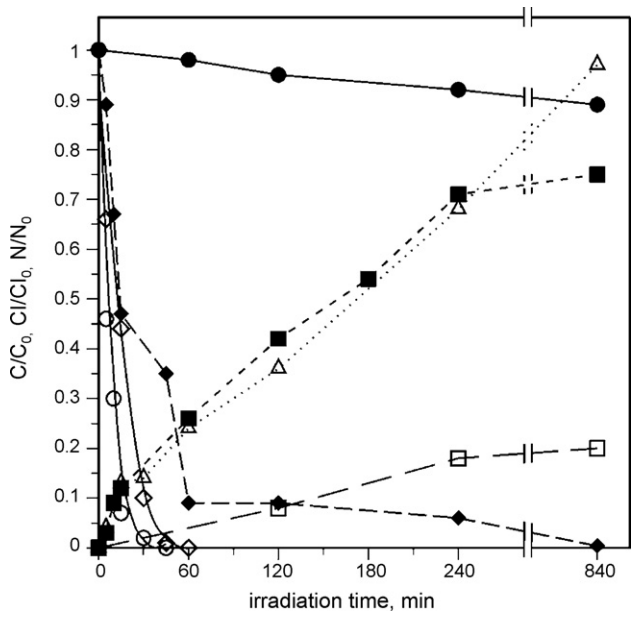


Fig. 4. Degradation of dimethomorph 15 mg L^{-1} on TiO_2 200 mg L^{-1}; disappearance of the initial compound (photolysis (●), TiO_2 (○)), TOC profile (♦) and evolution of chloride (△), nitrate (□) and ammonium (■) ions as a function of the irradiation time.

3.2. Dimethomorph

3.2.1. Dimethomorph photo-induced transformation

Dimethomorph shows two peaks with very closed retention times, corresponding to the *E* and *Z* geometrical isomers. Negligible degradation was observed in the dark at 25 ± 2 °C. Upon light exposure, dimethomorph did not undergo direct photolysis (10% lost after 14 h of irradiation), while in the presence of TiO_2 a fast photo-induced transformation occurs. Both isomers follow a pseudo-first order law decay, with a calculated half-life (from the fitting curve) of 5 min; they are then completely degraded within 30 min of irradiation (see Fig. 4). Organic carbon is easily degraded and after 1 h almost 90% of the organic carbon was mineralized. Besides, it underwent complete mineralization only after 14 h of irradiation, probably due to the formation of small oxidized molecules, slowly mineralized. Looking closer to the inorganic ions evolution, the nitrogen is easier released than chlorine. The nitrogen is predominantly transformed into ammonium ions, whose formation mainly occurs after the dimethomorph complete disappearance. The fate of the nitrogen, with the prevalent formation of ammonium ions, closely resemble the fate followed by morpholine [27]. After 14 h of irradiation the stoichiometric amount is achieved and the ratio NH_4^+/NO_3^- is 4.

3.2.2. Dimethomorph transformation pathways

Several intermediates were formed along with the fungicide degradation and are shown in Fig. 5. They were attributed to the structures summarized in Table 2 and Scheme 2. Two isobaric species at *m*/*z* 404 were detected and attributed to the dimethomorph hydroxy derivatives. Both have similar MS/MS spectra and retention times and were recognized as the *Z* and *E* geometric isomers of the structure shown in Scheme 2 (see pathway labelled i). MS^2 fragmentation shows morpholine elimination (product ion at *m*/*z* 317), then excluding an OH attack on the morpholinic moiety. Conversely, the absence of the methanol loss, evidenced in the dimethomorph MS/MS spectrum, is consistent with the entrance of an OH group on one (of the two) methoxy moiety. This compound is further transformed into the species at *m*/*z* 297, whose

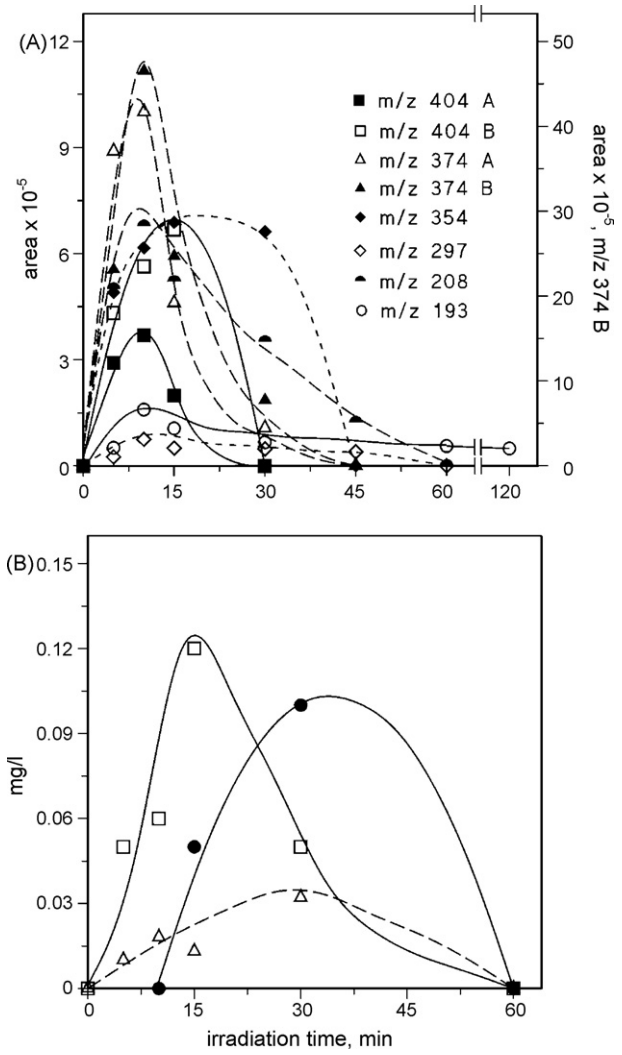


Fig. 5. Intermediates formed from dimethomorph degradation as a function of the irradiation time: (A) structures characterized by HPLC/MS/MS and (B) compounds identified by injection of standard solutions: morpholine (●, *m*/*z* 88), hydroquinone (□), 4-chlorophenol (△).

Table 2
Dimethomorph and the identified transformation products: $[M+H]^+$, retention times and fragments coming from MS^2 spectra and proposed structure.

$[M+H]^+$	t_R (min)	MS^2
388	15.93, 16.29	356 (–CH_3OH) 324 (–2CH_3OH) 301 ()
404	13.84, 14.34	386 (–H_2O) 317 ()
374	14.46, 14.94	287 () 338 (–HCl)
354	14.55	267 ()
297	3.29	–
208	3.38	–
193	3.30	–
88	3.27	–

formation was achieved through the combination of morpholine detachment, dechlorination and oxidation of the alcoholic group. A confirm about the proposed structure comes from the contemporaneous formation of morpholine (*m*/*z* 88), whose identity was confirmed by injection of a standard solution. Morpholine is a toxic, possibly mutagenic compound, used itself as a fungicide [28]. It is known to be photocatalytically degraded through the formation of numerous, also more complex compounds [27].

Two isobaric species at *m*/*z* 374 were formed. A difference of 14 u with dimethomorph is consistent with the formation of the demethylated derivatives. The proposed structure is shown in Scheme 2 and can be formed through the loss of a methyl group from one of the two methylesther groups (see pathway ii). Again, their similar MS^2 spectra and retention times suggest the formation of the *Z* and *E* isomers.

The contemporaneous formation of a species at *m*/*z* 354 occurs (pathway iii). It does not show the typical chlorine isotopic pattern and can be attributed to the dechlorinated derivative. The contemporaneous formation of chloride ions in solution (see Section 3.2.1) confirms the suggested structure.

Some other smaller molecules were then detected, whose formation involves the dimethomorph breakdown (see pathway iv). The two species at *m*/*z* 193 and 208 were formed through the detachment of chlorobenzene and breakage of the morpholine moiety. Their further degradation probably leads to the formation of dimethoxy derivatives [2]. The contemporaneous formation of 4-chlorophenol was evidenced.

Hydroquinone formation was also detected. Its maximum concentration was achieved before the 4-chlorophenol formation, so implying that its formation is a consequence of the hydroxylation one of the two benzenic ring rather than chlorophenol dechlorination.

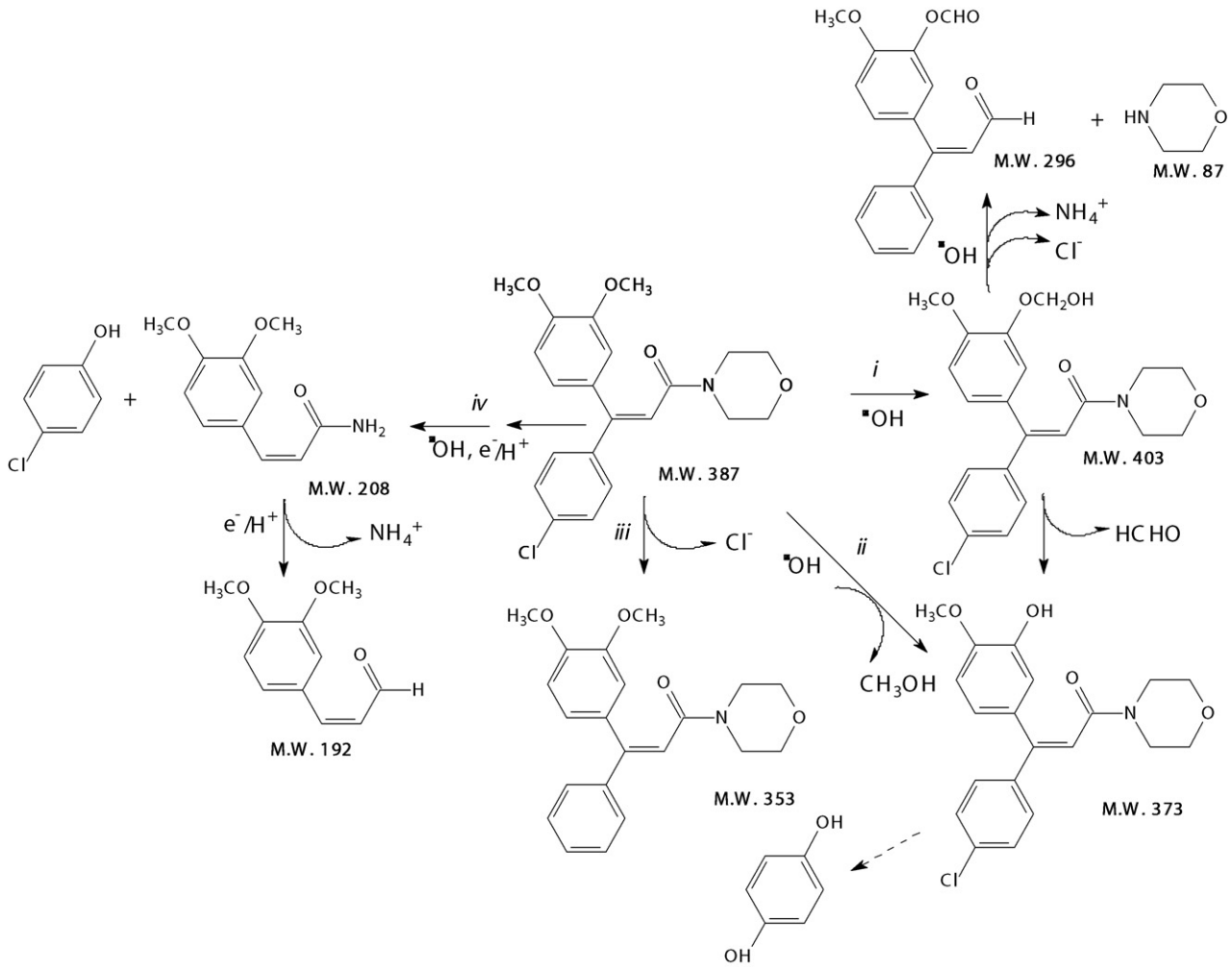
3.3. Toxicity assessments

The toxicity of the selected fungicides and their transformation products were evaluated using the *Vibrio fischeri* luminescent bacteria assay, a test appropriate for aquatic samples that shows a close correlation with other bioassays [29] and a good reproducibility [30]. Acute toxicity was evaluated by monitoring changes in the natural emission of the luminescent bacteria *Vibrio fischeri* when challenged with toxic compounds; it is expressed as the inhibition percentage of the bacteria's luminescence.

The solutions of the initial pesticides were not toxic (inhibition percentage value zero). In the case of dimethomorph, a biostimulation effect is observed, named hormesi. When dimetomorph was irradiated, illumination induced an increase in toxicity, caused by the formation of toxic intermediate compounds (see Fig. 6). Toxicity peaked after 15 min of irradiation (inhibition 45%). It is worth mentioning that the highest toxicity is observed at the irradiation times when hydroquinone, 4-chlorophenol and morpholine are formed. Their EC50 have been measured and are reported in Table 3. Hydroquinone and chlorophenol are toxic compound (EC50 0.08 and 8.49 mg/L, respectively), and the highest contribution to toxicity should come from hydroquinone. By considering

Table 3
EC50 measured for the identified intermediates in NaCl 2% solution.

	EC50, NaCl (mg/L)
4-Chlorophenol	8.49
3,5-Dichlorophenol	3.97
Hydroquinone	0.08
Urea	23914.3
Morpholine	116.1



Scheme 2. Transformation pathways followed by dimethomorph under TiO_2 treatment.

morpholine, even if is recognized as toxic/mutagenic compound, it does not significantly contribute to *Vibrio fischery* toxicity (EC50 116.10 mg/L). From 15 to 60 min of irradiation the percentage inhibition decreases, in a close analogy with these intermediates profiles, and reaches a final value of less than 1%, proving the efficiency of the photocatalytic process in detoxifying the irradiated solution.

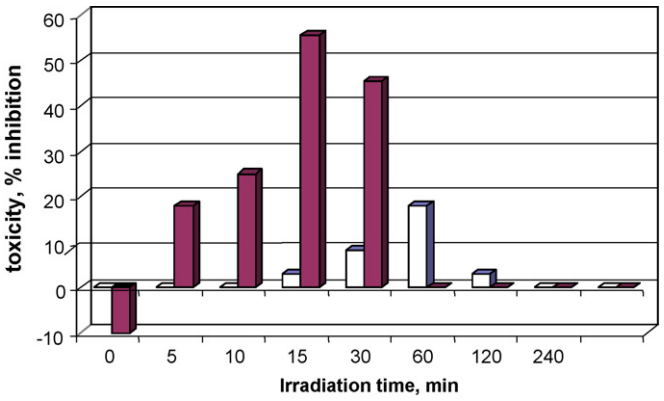


Fig. 6. Inhibition (%) of the luminescence of bacteria *Vibrio fischeri* as a function of the photocatalytic treatment time for dimethomorph (full bars) and hexaconazole (open bars).

On the contrary, hexaconazole degradation samples tested at different irradiation times were not toxic, so indicating that the transformation of this pesticide proceeds through the formation of non-toxic compounds. A little toxicity is only observed from 30 to 60 min of irradiation, probably due to the formation of 3,5-dichlorophenol (EC50 3.97 mg/L). Conversely, triazole, urea and cyanuric acid contribution to toxicity can be considered negligible, as triazole and cyanuric acid exhibit hormesi effect and for urea the EC50 is high (see Table 3).

4. Conclusions

Hexaconazole and dimethomorph were degraded in aqueous solution using titanium dioxide as photocatalyst. The results from this study have shown that both fungicides during the degradation process were transformed into numerous intermediate compounds. Hexaconazole gives finally rise to cyanuric acid, a product of triazine class herbicide transformation, while dimethomorph generates morpholine, used itself as fungicide.

Toxicity assays prove that neither hexaconazole nor dimethomorph are toxic compounds. However, while hexaconazole transformation proceeds through the formation of highly persistent, but non-toxic compounds, dimethomorph transformation proceeds through the formation of toxic intermediates. Among the identified intermediates, the toxicity seems to be due to hydroquinone and 4-chlorophenol.

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