

Photochemical behavior of the fungicide carbendazim in dilute aqueous solution

Patrick Mazellier*, Émilie Leroy, Bernard Legube

*Laboratoire de Chimie de l'Eau et de l'Environnement, UMR CNRS, Université de Poitiers No. 6008, ESIP
40, Avenue du Recteur Pineau, 86022 Poitiers Cedex, France*

Received 26 February 2002; received in revised form 19 July 2002; accepted 22 July 2002

Abstract

The direct phototransformation of the fungicide carbendazim has been studied upon monochromatic irradiation at 254 nm. In aqueous solution, carbendazim presents the properties of weak base. The pK_a of carbendazim has been determined equal to 4.53 ± 0.07 (by UV-Vis spectrophotometric measurements). Both forms of carbendazim present an emission of fluorescence. The wavelength for the maximum of emission are 393 and 305 nm for the protonated and the neutral form respectively. The fluorescence quantum yields have been measured and values equal to 5×10^{-3} and 9×10^{-3} have, respectively been obtained for the NH^+ and N form ($\lambda_{exc} = 254$ nm). Upon irradiation at 254 nm, the quantum yield of carbendazim phototransformation has been determined. It is respectively equal to 2.9×10^{-3} and 2.3×10^{-3} for the protonated and the neutral form. The increase of oxygen concentration leads to an increase of the phototransformation rate at pH 8.4. On the contrary, the addition of bicarbonate ions inhibits the phototransformation process. This inhibition is consistent with a hypothesis of a Stern–Volmer quenching. The Stern–Volmer quenching constant has been evaluated to $400 M^{-1}$. Degradation products have been identified by liquid chromatography coupled with mass spectrometry. The major one was aminobenzimidazole and its formation could be explained by a photohydrolysis mechanism.

© 2002 Elsevier Science B.V. All rights reserved.

Keywords: Carbendazim; Fungicide; UV; Photochemical transformation

1. Introduction

Benzimidazole fungicides have been introduced in the 1960s and their use has considerably increased. Actually, they are efficient at low doses and they inhibit the development of a wide variety of fungi. Among these fungicides, the most used are thiabendazole, fuberidazole, benomyl, thiophanate-methyl [1]. Carbendazim is also among the most important systemic fungicides. Studies have shown that carbendazim appears as the active substance of benomyl and thiophanate-methyl and moreover it is the main degradation product of these two compounds [1]. Carbendazim is a toxic substance [2]. Because of its extensive use, carbendazim can be found as a pollutant of water resources where it can accumulate and it is of great interest to investigate to process leading to its elimination.

Little is known on the photochemical behavior of carbendazim or of molecule of similar structure. Some studies on the phototransformation of carbendazim have already been published. However, they were performed in the presence

of an organic co-solvent (methanol) or hydrochloric acid to improve the solubility of carbendazim or a photosensitizer (dye, acetone) leading to the production of singlet oxygen or to energy transfer [3–6]. The addition of these external compounds allows different photodegradation pathways to occur. In addition, these studies have been performed in relatively concentrated solution [3–6]. The most recent study dealing with carbendazim photolysis was conducted by Panades et al. [7] but here again methanol was added as co-solvent. These authors recorded the UV-Vis spectra of carbendazim in aqueous solution at different pH and performed polychromatic irradiation of carbendazim in dilute aqueous solutions containing methanol. In view of their results, they assessed that the protonated form of carbendazim (at $pH < pK_a$) was stable towards UV whereas the neutral form ($pH > pK_a$) was easily photolyzed. The rate of carbendazim photolysis increased when the oxygen concentration increased. No information was given about the degradation products.

With regards to the extensive use of carbendazim as fungicide and because this compound is often detected in natural waters [8,9], we undertake a complete study of carbendazim photolysis at 254 nm to have a better understanding of the

* Corresponding author.

E-mail address: patrick.mazellier@univ-poitiers.fr (P. Mazellier).

mechanism of phototransformation. The 254 nm wavelength was chosen because it is often to be used for disinfection process in drinking water treatment plants.

2. Experimental

Carbendazim, aminobenzimidazole, phenol, sodium hydroxide, sodium perchlorate, sodium acetate, sodium bicarbonate, sodium dihydrogenophosphate, disodium hydrogenophosphate, perchloric acid and methanol were commercial products of the purest grade available.

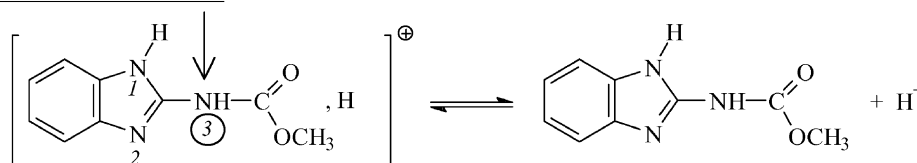
All solutions were prepared with water obtained with a Millipore Milli-Q system. The pH measurements were carried out with a Tacussel PHM 240 pH-meter. The ionic strength was adjusted either with NaClO_4 , NaH_2PO_4 – Na_2HPO_4 or NaHCO_3 according to the experiments. Oxygen concentration was measured with a Consort Z621 oxymeter.

The irradiation set-up was a batch annular photoreactor (internal diameter = 100 mm). The lamp (Heraeus low pres-

3. Study on carbendazim in aqueous solution

Carbendazim is poorly soluble in water (5 mg l^{-1} at 25°C at pH 8 [2]). Saturated solutions were prepared by stirring carbendazim under dark conditions in 5 l flask. After filtration to remove the undissolved carbendazim, the concentration of the aqueous solution was determined by HPLC after calibration with methanolic solution of carbendazim (carbendazim is fully soluble in this organic solvent), diluted with Milli-Q water. The aqueous solutions of carbendazim were prepared weekly, kept in the dark and no change in carbendazim concentration was observed within a week whatever the value of pH between 2 and 10. Panades et al. [7] reported that carbendazim was rapidly transformed in aminobenzimidazole at pH around 10 but we could not confirm this result. Actually, our results showed that carbendazim was a very stable compound in this range of pH, in agreement with the previous studies of Singh and Chiba [11] and Gauthier et al. [12].

Carbendazim in aqueous solution presents the properties of a weak base according to the following equilibrium:



sure mercury lamp NN 40/20) was located at the axis of the reactor, in a quartz sleeve (external diameter = 28 mm). The height of the lamp arc was 200 mm. The volume of the irradiated solution was 2 l, exactly overlapping the arc of the lamp. The flux of the lamp was evaluated using hydrogen peroxide as an actinometer as described elsewhere [10]. Actinometries were performed weekly. Typical values equal to $6.0 \pm 0.5 \times 10^{-6} \text{ E l}^{-1} \text{ s}^{-1}$ were measured during the period of experiments. UV-Vis spectra were recorded on a Safas double-beam spectrometer, fluorescence spectra with a Jobin–Yvon Spex-Fluoromax 2 spectrofluorimeter (excitation wavelength at 254 nm emission slit: 3 mm, excitation slit: 5 mm). Carbendazim disappearance and transformation products formation were quantified using high performance liquid chromatography (HPLC) experiments performed with a Waters system equipped with a Waters 600 pump, a Waters 717 autosampler and a Waters 996 photodiode array detector (HPLC/PDA) giving the UV-Vis spectrum corresponding to each peak. The column was purchased from Alltech (Kromasil C18 250 mm \times 4.6 mm) and the eluent was a mixture of methanol/water (60/40) with or without addition of phosphate buffer (pH 7.2). HPLC/mass spectrometry (HPLC/MS) experiments have been performed at the “Service Central d’Analyses” of CNRS (Lyon). The apparatus was a Hewlett-Packard HP1100-MSD system working in positive electrospray. The column was a Waters Xterra MSC18 (150 mm \times 2.1 mm) and the eluent was a mixture of methanol and H_3PO_4 -acidified water.

The compound exists as a protonated form ($\text{pH} < \text{p}K_a$) and a neutral form ($\text{pH} > \text{p}K_a$). As it can be seen according to the chemical formula of carbendazim, three nitrogen atoms are present leading thus to three possible sites of protonation. Calculations have been performed to obtain informations about the most probable protonation site using Hyperchem[®] software [13]. We tried to evaluate the participation of the electrons of the extra imidazole cycle nitrogen atom (labeled 3 and with an arrow in the above mentioned equilibrium) to the HOMO of carbendazim. Calculations performed by the software showed a strong participation of these electrons. Moreover, evaluation of molecular energies for the three different protonated forms showed that the organic cation of lowest energy was corresponding to a protonation of the nitrogen labelled 3 above.

The UV-Vis spectrum of an aqueous solution of carbendazim changes according to the pH of the solution (Fig. 1). Many isosbestic points can be observed at the following wavelengths: 218, 235, 256, 278, 284 nm.

Maxima can be noted at 224 nm ($\epsilon = 18600 \text{ M}^{-1} \text{ cm}^{-1}$), 274 and 281 nm ($\epsilon = 16150 \text{ M}^{-1} \text{ cm}^{-1}$) for the protonated form (pH 2.36) and 207 nm ($\epsilon = 24300 \text{ M}^{-1} \text{ cm}^{-1}$) and 285 nm ($\epsilon = 14740 \text{ M}^{-1} \text{ cm}^{-1}$) for the molecular form (pH 7.47). The first $\text{p}K_a$ has been determined using the UV-Vis characteristics of both the protonated and the molecular form. Experiments have been performed in aqueous solution at ionic strength equal to $5.0 \times 10^{-3} \text{ M}$. After corrections to reach zero-ionic strength solutions (the activity coefficients

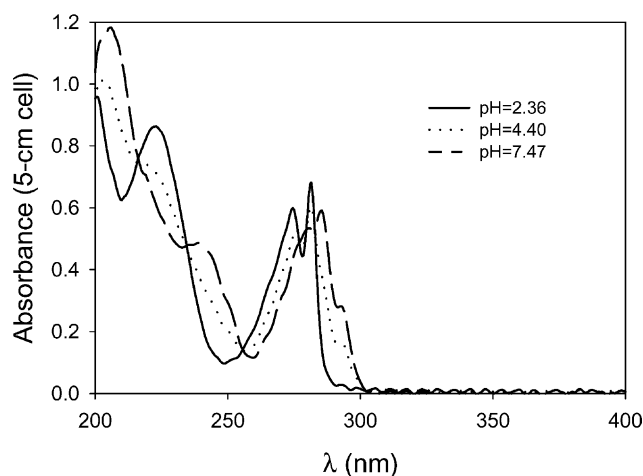


Fig. 1. Evolution of the UV-Vis spectrum of an aqueous solution of carbendazim at different pH (ionic strength was not controlled).

for the H^+ and NH^+ form have been calculated according to the Debye–Hückel formula [14], we obtained a value of 4.53 ± 0.07 . Two values were reported in the literature: 4.2 [12] and 4.48 [15]. Our determination is in good agreement with the one reported in the Merck index [15]. The value of the pK_a equal to 4.2, recently obtained by Gauthier et al. [12], may be slightly different because of the absence of control of the ionic strength during their measurements.

The molar absorption coefficients of the two forms have also been determined at 254 nm, the irradiation wavelength chosen for the phototransformation experiments: $\varepsilon_{254,NH^+} = 2330 \text{ M}^{-1} \text{ cm}^{-1}$ and $\varepsilon_{254,N} = 4470 \text{ M}^{-1} \text{ cm}^{-1}$, respectively for the protonated and the neutral compounds. We have to mention that the value determined for ε_{254,NH^+} is significantly different from the one determined by Panades et al. [7] (reported value for ε_{254,NH^+} is $3470 \text{ M}^{-1} \text{ cm}^{-1}$) whereas a

good agreement exists for $\varepsilon_{254,N}$. Solutions used by these authors contained methanol (the percentage was not specified). We compared UV-Vis spectrum of carbendazim acid aqueous solutions containing 0, 5 and 10% (v/v) of methanol. Even if we observed a slight increase of the absorbance at 254 nm (20% when the percentage of MeOH is 10%), we did not reach such a high value as the one reported by Panades et al. [7].

4. Fluorescence of carbendazim in aqueous solution

As previously mentioned, protonated (NH^+) and neutral form (N) of carbendazim are fluorescent. Their fluorescence spectra have been recorded. The maximum of fluorescence are 391 nm for NH^+ and 305 nm for N indicating that the first singlet excited state of NH^+ form was of the lower energy than the first excited state of N. The quantum yields of fluorescence of the NH^+ and N forms have been determined upon excitation at 254 nm (the quantum yield of phenol fluorescence in aqueous solution equal to 0.07 [16,17] has been taken as reference). The fluorescence intensity increased with increasing the light absorbed by the solutions as presented in Fig. 2. Straight lines were observed in good agreement with the relation:

$$I_f = \phi_f I_0 (1 - 10^{-O.D.})$$

where I_f is the integrated fluorescence, ϕ_f the quantum yield of fluorescence, I_0 the intensity of incident light and O.D. the absorbance.

The calculations led to the following results: $\phi_f = 0.009$ and 0.005, respectively for the NH^+ and the N forms. The values are not high ones indicating that fluorescence is not the main deactivation process.

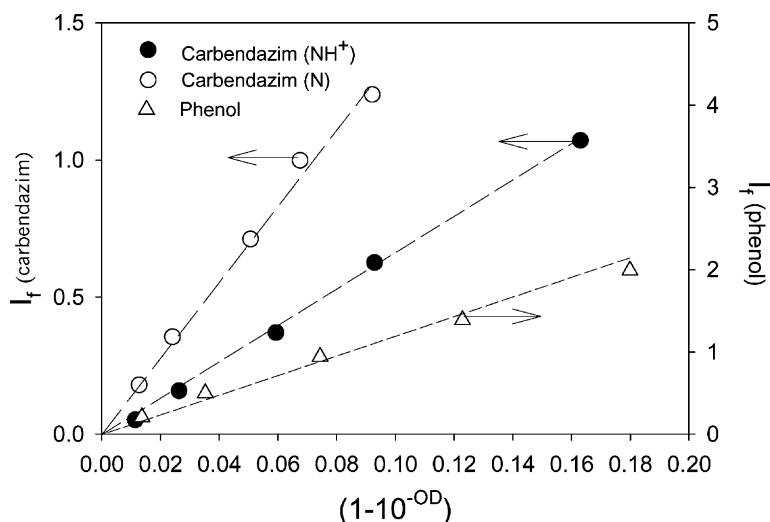


Fig. 2. Determination of the quantum yield of carbendazim fluorescence. Comparison with respect with phenol fluorescence. ($\lambda_{exc} = 254 \text{ nm}$).

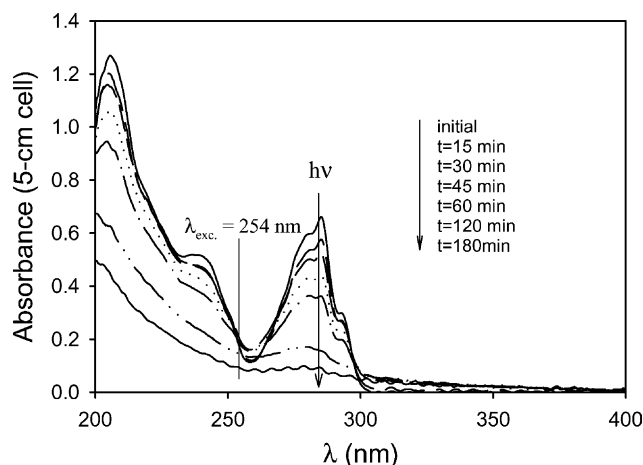


Fig. 3. Evolution of the UV-Vis spectrum of an aqueous solution of carbendazim upon irradiation at $\lambda_{\text{exc}} = 254$ nm. $[C]_0 \approx 10 \mu\text{M}$, pH 5.6.

5. Direct photolysis

5.1. General aspects

The photolysis of carbendazim has been studied in pure aerated aqueous solution at 254 nm. No organic co-solvent was added in the solutions.

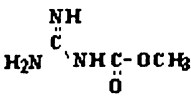
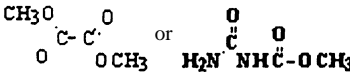
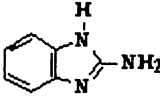
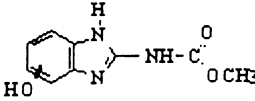
In Fig. 3 is reported the evolution of the UV-Vis spectrum of an aerated aqueous solution of carbendazim ($10 \mu\text{M}$) upon irradiation at 254 nm at pH 5.5 (almost 10% of carbendazim is protonated). We observed a continuous decrease of the absorbance between 200 and 320 nm. More particularly, there is a strong decrease in absorbance at 207 and 285 nm, the two maxima of the N form of carbendazim. This indicates that the primary photoproducts did not absorb light around 280 nm or that eventually-formed photoproducts were photolyzed more rapidly than carbendazim itself. Note that the absorbance at 254 nm increased in the early stages of the irradiation and then decreased. It did not fit with the decrease in carbendazim concentration measured by HPLC. This observation is strongly in the favour of the formation of photoproducts absorbing at 254 nm which are further degraded.

5.2. Identification of photoproducts

Analyses of irradiated solutions of carbendazim at pH 5.6 ($[C]_0 \approx 10 \mu\text{M}$) by liquid chromatography coupled with mass spectrometry allows the identification of the degradation products. The attributed structure and the corresponding molecular weight are gathered in Table 1. It was evidenced both by HPLC/PDA and HPLC/MS that only one degradation product presented a similar structure than carbendazim (i.e. aminobenzimidazole). It appears that the formation of the products **1** or **2** and of aminobenzimidazole **3** certainly do not proceed via the same photochemical pathway. Even if the literature experiments were performed in different conditions than us, many other degradation products were men-

Table 1

Possible structure of phototransformation products of carbendazim in aqueous solution

| Mass (g mol ⁻¹) | Structure | Compound no. |
|--------------------------------|-------------------------------------------------------------------------------------|-----------------|
| 117 |  | 1 |
| 118 |  | 2 |
| 133 (major) |  | 3 |
| 207 (very weak) |  | |

tioned in the literature [3–7]. We did not observe any dimer formation (at least four were mentioned by Abdou et al. [5,6]) in our experimental conditions certainly because we worked in strongly diluted solutions. Additionally, we did not observe the formation of the following products: benzene, benzimidazole, phenol, aniline or 1,2-diaminobenzene. These commercially available products have been injected in LC/PDA and they were not present in the chromatograms of irradiated aqueous solutions of carbendazim.

Because aminobenzimidazole (Am) was a commercially available product, it has been possible to quantify its formation. It represents about 30% of carbendazim disappearance in the early stages of the photoreaction but it does not accumulate in the irradiated solutions because it is efficiently photolyzed (see later).

5.3. Quantum yields

The general equation of the degradation of a photolyzed compound (C) is given by:

$$\frac{dC}{dt} = -\phi_C \times I_a = -\phi_C \times I_0 \times (1 - e^{-(2.3\epsilon_C \ell C)})$$

where ϕ_C , ϵ_C and C are, respectively the quantum yield of compound disappearance, the molar absorption coefficient at 254 nm, and its concentration. I_a , I_0 and ℓ are, respectively the light absorbed by C, the light intensity determined by hydrogen peroxide actinometry and the optical pathway.

If the concentration of the absorbing compound C is low enough, we can do the following approximation:

$$1 - e^{-(2.3\epsilon_C \ell C)} \approx 2.3\epsilon_C \ell C$$

which leads to

$$\frac{dC}{dt} = -\phi_C \times I_0 \times (2.3\epsilon_C \ell C) = k_{\text{app}} C$$

with

$$k_{\text{app}} = -2.3\phi_{\text{C}}\varepsilon_{\text{C}}I_0\ell$$

Accordingly, the disappearance of carbendazim should obey an apparent first-order kinetic law.

In our irradiation set-up, some uncertainties remain for the measurements of the optical pathway. So, actinometries were performed under the same experimental conditions than the irradiation experiments themselves (i.e. low or high light absorption conditions). Moreover, irradiations have been performed with a test compound: 2,6-dimethylphenol, the phototransformation quantum yield of which is well known [18]. Actually, the value of 2,6-dimethylphenol direct phototransformation in aqueous solution was evaluated equal to 0.06 in this system. In the case of our annular photoreactor, we obtain values ranging from 0.065 to 0.05, respectively in diluted and concentrated solutions using an average optical pathway equal to 3.6 cm.

These experiments are showing that using an average optical pathway equal to the radius of the photoreactor leads to similar results as those obtained using a system with a parallel beam.

The quantum yield of carbendazim disappearance is proportional to the slope of the straight line ($\ln C_0/C_t$) as a function of irradiation time (see Fig. 4).

The quantum yield of carbendazim disappearance has been determined for both the protonated (NH^+) and the neutral form (N). The values obtained for the quantum yields are:

- $\phi_{\text{NH}^+} = 2.9 \times 10^{-3}$ at pH 2.3 (pH adjusted with HClO_4),
- $\phi_{\text{N}} = 2.3 \times 10^{-3}$ at pH 8.4 (pH adjusted with NaOH).

The two values are quite similar indicating a quite similar photostability. Note that the pH value remained roughly constant within the time scale of our experiments.

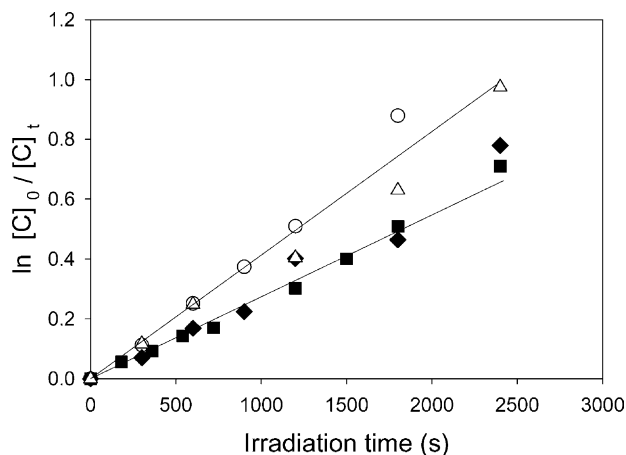


Fig. 4. Determination of the quantum yield of carbendazim phototransformation upon irradiation at $\lambda_{\text{exc}} = 254 \text{ nm}$ at pH 2.36: (■) $[C]_0 = 0.94 \mu\text{M}$; (◆) $[C]_0 = 1.07 \mu\text{M}$ and at pH 8.40: (Δ) $[C]_0 = 1.12 \mu\text{M}$; (○) $[C]_0 = 1.18 \mu\text{M}$ in aerated dilute aqueous solution.

Table 2

Quantum yields of carbendazim phototransformation at pH 8.4

| | ϕ_{N} |
|---------------------------------------------------------------|----------------------|
| Deaerated solutions, $[\text{O}_2] < 30 \mu\text{M}$ | 1.1×10^{-3} |
| Aerated solutions, $[\text{O}_2] = 275 \mu\text{M}$ | 2.3×10^{-3} |
| Oxygen saturated solutions, $[\text{O}_2] = 1225 \mu\text{M}$ | 4.8×10^{-3} |

Because aminobenzimidazole (Am) was the major photoproduct, we determined its phototransformation quantum yield. The molar absorption coefficient of Am in aqueous solution at pH 6.0 (neutral form) was equal to $2880 \text{ M}^{-1} \text{ cm}^{-1}$. The quantum yield of Am direct phototransformation upon irradiation at 254 nm (low concentration, pH 6.0) has been evaluated equal to 3.7×10^{-3} , which is a value about 1.5 times higher than carbendazim phototransformation quantum yield. This is the reason why Am did not accumulate a lot upon irradiation of carbendazim in aqueous solution.

5.4. Influence of oxygen

Carbendazim aqueous solutions ($\approx 1 \mu\text{M}$) have been irradiated in oxygen saturated, aerated or deoxygenated solutions (the bubbling for oxygen or nitrogen was maintained during the experiments). No change in carbendazim concentration was observed in the absence of light but in the presence of either nitrogen or oxygen bubbling. Oxygen concentration (see Table 2) was stable within the time scale of the experiments. The kinetics of carbendazim disappearance are presented in Fig. 5. We evidenced a strong effect of the oxygen concentration. The quantum yields of carbendazim phototransformation are gathered in Table 2. A similar effect of oxygen on carbendazim phototransformation has already been described by Panades et al. [7]. No explanation was given by these authors concerning this increase of the rate of carbendazim transformation.

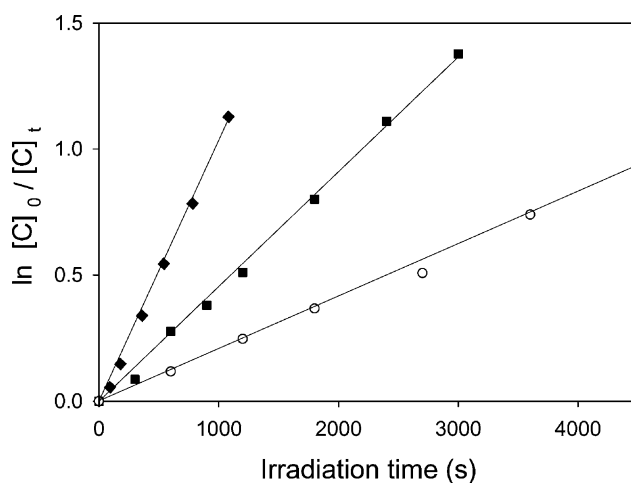


Fig. 5. Influence of the oxygen on the rate of carbendazim phototransformation. $[C]_0 \approx 1 \mu\text{M}$; pH 8.4 (◆) oxygen bubbling, (■) air, (○) nitrogen bubbling.

Table 3
Quantum yields of carbendazim phototransformation in the presence of HCO_3^-

| $[\text{HCO}_3^-]$ (mM) | ϕ_N (R^2) |
|-------------------------|-------------------------------|
| 0 | 2.30×10^{-3} (0.959) |
| 1 | 1.26×10^{-3} (0.986) |
| 2.5 | 0.82×10^{-3} (0.990) |
| 5 | 0.61×10^{-3} (0.991) |
| 7.5 | 0.59×10^{-3} (0.968) |
| 10 | 0.37×10^{-3} (0.970) |

5.5. Inhibition by bicarbonate ions

Because of the presence of bicarbonate ions in natural waters, we study the phototransformation of carbendazim in aqueous solution in the presence of various amount of bicarbonate. We checked that no detectable interaction was occurring in the ground state between carbendazim and HCO_3^- ion: the UV-Vis spectrum of carbendazim does not change with the presence of HCO_3^- . Moreover, the fluorescence of carbendazim (N form) was not influenced by the presence of bicarbonate ions. The pH of the irradiated solutions was equal to 8.4 and we varied the HCO_3^- concentration in the range 0–10 mM. The starting concentration of carbendazim was around 1 μM . The photochemical transformation is inhibited by the presence of bicarbonate ions: the highest the concentration of HCO_3^- , the lowest the rate of carbendazim transformation (see Table 3). HCO_3^- anions did not absorb light at 254 nm. Hence, the decrease in the carbendazim disappearance rate was not due to an absorption of light by bicarbonate ions. In the presence of NaClO_4 at pH adjusted to 8.2 with NaOH , this effect was not observed which means that the inhibition was not connected neither to the ionic strength of the solution nor to the presence of sodium cation. Inhibition of pesticide phototransformation by HCO_3^- had already been observed by Kochany [19] who studied the influence of these anions on the photochemical transformation of bromoxynil, a phenol derivative. The explanation given for the observed phenomenon involved a reaction between the initially photo-ejected electron from the phenol and carbonate ions which prevent the trapping of the above mentioned electron with the phenol. However, the second-order rate constant of reaction of the hydrated electron and bicarbonate or carbonate ions is low ($<10^6 \text{ M}^{-1} \text{ s}^{-1}$ [20]) whereas the reaction with oxygen processes with a very high second-order rate constant ($1.9 \times 10^{10} \text{ M}^{-1} \text{ s}^{-1}$ [20]). So, this explanation may be subject to controversy and must not be used in our system.

Quenching of photochemical reaction or fluorescence emission are often rationalised by the well-known Stern–Volmer formalism. In Fig. 6 is represented the Stern–Volmer dependence of the quantum yield of carbendazim transformation as a function of the bicarbonate concentration. The calculated Stern–Volmer constant is equal to $K_{\text{SV}} = 400 \text{ M}^{-1}$ indicated that the quenching exists but

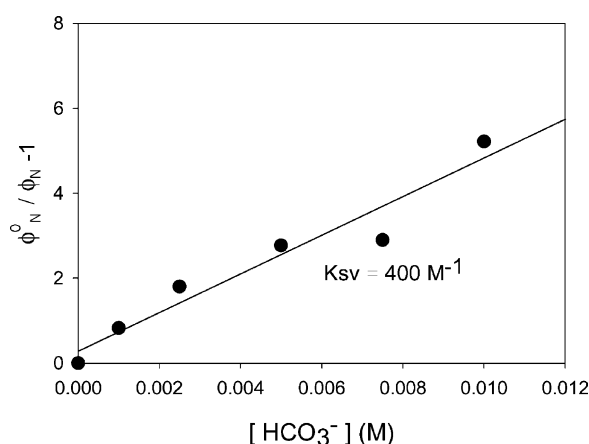


Fig. 6. Inhibition of carbendazim phototransformation by HCO_3^- . Stern–Volmer representation. $[\text{C}]_0 \approx 1 \mu\text{M}$, pH 8.4 ± 0.1 .

process with a low efficiency. If we assume that the combination between the excited state and the HCO_3^- anions is diffusion controlled rate, an estimation of the excited state lifetime by be done using $K_{\text{SV}} = k_d \tau$. The calculations lead to $\tau > 50 \text{ ns}$ using $k_d = k_{\text{diff}} = 7.4 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ [21]. This value does not indicate if the singlet state or the triplet state is involved for the quenching process.

6. Discussion

The phototransformation of carbendazim has been studied in dilute aqueous solution upon irradiation at 254 nm. In aerated solutions, the protonated form and the neutral form of carbendazim present similar quantum yield of phototransformation ($\phi_{\text{NH}^+} = 2.9 \times 10^{-3}$ at pH 2.3, $\phi_N = 2.3 \times 10^{-3}$ at pH 8.4). The photoproducts which were formed indicated the existence of different pathways of degradation. The phototransformation of carbendazim at 254 nm is a process which is relatively slow (quantum yields lower than 1%) so the molecule can be consider as a quite stable compound towards UV. The quantum yields of carbendazim fluorescence in acid and weakly basic solution are also weak. These two experimental results indicate either that deactivation via non radiative process giving back the fundamental state is predominant (the quantum yield of the inter-system crossing leading to the formation of triplet state being certainly low in agreement with the experimental results for the oxygen effect). The fluorescence of carbendazim was not influenced by the presence of HCO_3^- or the concentration of oxygen but the results are different for the phototransformation of carbendazim. As above presented, the rate of carbendazim degradation increases when the oxygen concentration increases whereas it decreases when the concentration in bicarbonate ions increases. The first effect had already been observed by Panades et al. [7]. The positive influence of the concentration of oxygen may be an indication of the occurrence of an electron photoejection process as already described

for substituted phenol [18]. Electron acceptors such as oxygen promote the process because they prevent the recombination of the electron with the organic radical formed. The presence of electron donors should play the opposite role and this may be the explanation for the negative effect of bicarbonate ion. However, the nature of the identified photoproducts is showing that a photochemical transformation of carbendazim is not processing via a simple pathway. This assumption is also supported by the fact that we only obtain a factor of 2 between the quantum yield of carbendazim disappearance in aerated and oxygen-saturated solutions and again a factor of 2 between the quantum yield of carbendazim disappearance in oxygen-free and aerated solutions. Hence, we could expect a very much higher difference between oxygen-free and oxygen-saturated irradiated solutions if only one photochemical process was present (the photoejection of electron). Photoejection of electron is a rapid process that is always coming from the singlet state. The involvement of triplet state of excited carbendazim can be an additional process. Concerning the influence of bicarbonate ions, another possibility would involve a quenching of the other photochemical degradation pathway arising from triplet state, in agreement with the Stern–Volmer equation. Maybe experiments performed with laser-flash photolysis apparatus would allow the elucidation of the primary photochemical mechanism even if the low solubility of carbendazim in aqueous solution could limit the use of this technique.

According to our results, essentially monomolecular pathways are involved in the phototransformation of carbendazim. We did not detect any dimer formation in our irradiated samples. The chemical formula indicated in Table 1 for the degradation product do not allow us to propose a complete mechanism for the degradation of carbendazim. However, the formation of aminobenzimidazole could involve a photohydrolysis process beside the electron photoejection which could lead to the formation of products **1** and **2** lead to the break down of the benzimidazole ring. Further experiments performed with laser-flash photolysis apparatus would be useful to fully explain the photochemical behavior of carbendazim.

7. Conclusion

Carbendazim in aqueous solution absorbs light in the range 200–300 nm. Carbendazim is a quite stable molecule toward UV, with low quantum yield of fluorescence. The quantum yield of carbendazim phototransformation was determined equal to 2.3×10^{-3} at pH 8.4. A significant effect

of oxygen is observed leading to an increase of the quantum yield when the concentration of oxygen increases. On the other hand, the addition of bicarbonate ions in the irradiated solutions decreases the efficiency of the phototransformation process according to a Stern–Volmer plot. Aminobenzimidazole is the unique degradation product that keeps the structure of benzimidazole cycle and it can be formed according to a photohydrolysis process. The other degradation product may be formed after a photoejection of an electron of the benzimidazole structure leading to the break down of the imidazole part.

Acknowledgements

The authors would like to thank Dr. Ludovic Lopes for performing calculations with Hyperchem[®] software and Prof. Joseph De Laat for helpful discussions.

References

- [1] C.J. Delp, in: H. Lyr (Ed.), *Modern Selective Fungicides*, Wiley, New York, 1987, pp. 233–244.
- [2] C. Tomlin, *The Pesticide Manual*, 10th ed., British Crop Protection Council, Bracknell, London, 1994.
- [3] D. Watkins, *Chemosphere* 38 (1974) 239–240.
- [4] J.R. Fleeker, H.M. Lacy, *J. Agric. Food Chem.* 25 (1977) 1.
- [5] W.M. Abdou, M.R. Mahran, M.M. Sidky, H. Wamhoff, *Chemosphere* 14 (1985) 1343–1353.
- [6] W.M. Abdou, M.R. Mahran, M.M. Sidky, H. Wamhoff, *Chemosphere* 15 (1986) 1063–1071.
- [7] R. Panades, A. Ibarz, S. Esplugas, *Water Res.* 34 (2000) 2951–2954.
- [8] A. Oubina, E. Martinez, J. Gascon, D. Barcelo, I.B. De Alleluia, *Int. J. Environ. Anal. Chem.* 70 (1998) 75–91.
- [9] M. Loewy, V. Kirs, G. Carvajal, A. Venturino, A.M. Pechen De d'Angelo, *Sci. Total Environ.* 255 (1999) 211–218.
- [10] I. Nicole, J. De Laat, M. Doré, J.P. Duguet, C. Bonnel, *Water Res.* 24 (1990) 157–168.
- [11] R.P. Singh, M. Chiba, *J. Chromatogr.* 643 (1993) 249–260.
- [12] G. Gauthier, J. Ayele, G. Guibaud, *J. Eur. Hydr.* 31 (2000) 65–84.
- [13] Hyperchem Package, Hypercube Inc., Waterloo, Canada, 1996.
- [14] W. Stumm, J.J. Morgan, *Aquatic Chemistry*, 3rd ed., Wiley/Interscience, New York, 1996, p. 101.
- [15] *The Merck Index B*, 20th ed., Merck and Co., 1983.
- [16] A. Gilbert, J. Baggott, *Essentials of Molecular Photochemistry*, Blackwell Scientific Publications, Oxford, 1991, p. 103.
- [17] S.L. Murov, I. Carmichael, G.L. Hug, *Handbook of Photochemistry*, 2nd ed., Marcel-Dekker, New York, 1993, p. 53.
- [18] P. Mazellier, M. Sarakha, A. Rossi, M. Bolte, *J. Photochem. Photobiol. A: Chem.* 115 (1998) 117–121.
- [19] J. Kochany, *Chemosphere* 24 (1992) 1119–1126.
- [20] G.V. Buxton, C.L. Greenstock, W.P. Helman, A.B. Ross, *J. Phys. Chem. Ref. Data* 17 (1988) 536–635.
- [21] S.L. Murov, I. Carmichael, G.L. Hug, *Handbook of Photochemistry*, 2nd ed., Marcel-Dekker, New York, 1993, p. 208.