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Aqueous photochemistry of pesticides triadimefon and triadimenol

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Abstract

The photochemistry of pesticides triadimefon and triadimenol was studied in aqueous solution and in methanol/water mixtures, in controlled and natural conditions. The photodegradation kinetics and product distribution are strongly dependent on the solvent and on the irradiation wavelength. The degradation rates are faster at 254 nm than at 313 nm. The kinetics is faster in water than methanol. Direct photoreaction is an important dissipation pathway of triadimefon in natural water systems while triadimenol is stable in these conditions. 1,2,4-Triazole and 4-chlorophenol are two of the major photodegradation products. The formation of the 4-chlorophenoxyl radical was detected for both pesticides in methanol and methanol/water mixtures. In methanol/water mixtures the reaction of both pesticides also occurs with 4-chlorophenolate formation, which increases with the water content. The photochemical studies of pesticides and other pollutants should be made in conditions as similar as possible to those observed in environmental systems.

Keywords: Triadimefon; Triadimenol; Laser flash photolysis; 4-Chlorophenoxyl radicals; Chlorophenolate; 4-Chlorophenol; 1,2,4-Triazole

1. Introduction

Pesticides enter into natural water bodies by direct application and by leaching from soil and vegetation. Many of these chemicals present in aqueous media can undergo photochemical transformation with sunlight via direct or indirect photoreaction. To assess the role of these processes on the behavior and fate of pesticides in natural water systems, photochemical studies in aqueous solution over a wide range of environmental conditions are needed [1].

Triadimefon, 1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl) butanone, **I**, and triadimenol, 1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl) butan-2-ol, **II** (Fig. 1) are two related systemic fungicides [2] that have been studied by us as model pesticides [3–6]. The photochemistry and photophysics of these compounds is well documented in organic solvents [6–9]. The photodegradation of triadimefon follows a first order kinetics and the rate constant is higher in acetone than methanol and hexane. The homolytic cleavage of the bonds to the C_1 carbon was proposed [7]. Laser flash photolysis studies of triadimefon and triadimenol in cyclohexane revealed the formation of the 4-chlorophenoxyl radical [6]. This result confirmed the homolytic cleavage of the C–O bond to the C_1 carbon and indicated that triadimenol undergoes the same degradation path.

The photodegradation kinetics of triadimefon and its photoproducts were also studied in water [10]. The degradation followed first order and the presence of humic and fulvic acids have little effect on the rate constant. 4-Chlorophenol and dechlorinated triadimefon were identified in all studied aqueous systems. However, little is known about the degradation quantum yields and photodegradation mechanism of these pesticides in aqueous solution. This paper reports the photodegradation quantum yields of triadimefon and triadimenol in aqueous solution. The main photodegradation pathways and primary products were additionally studied. Transient absorption results are also presented.

2. Experimental

2.1. Reagents

Water was deionized and distilled. Triadimefon (offered by Bayer Portugal in its highest purity grade), triadimenol (Riedel-de-Haën), 4-chlorophenol (Aldrich), 1,2,4-triazole (Fluka,), *o*-phenanthroline (Merck), hydrochloric acid (Merck), potassium hydroxide (Merck), potassium chromate (Merck), potassium carbonate (Merck), potassium

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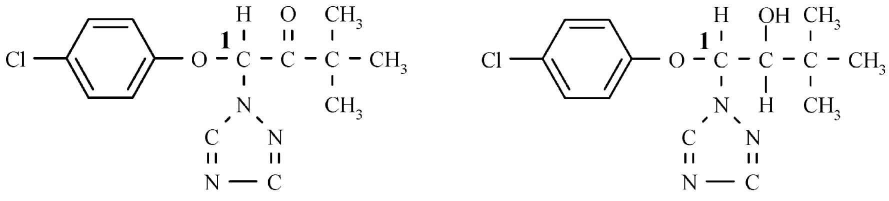

I **II**

Fig. 1. Triadimefon (**I**) and triadimenol (**II**).

oxalate (Merck), ferric chloride (Merck) and organic solvents (Merck LiChrosolv) were used without further purification. Potassium ferrioxalate, obtained by reaction of potassium oxalate with ferric chloride, was crystallized three times and kept in the dark.

2.2. *Equipment*

Photodegradation studies were conducted in a reactor previously used to study the photochemistry of pesticides [6], employing a merry-go-round and an immersion-well photochemical reactor (Applied Photophysics) immersed in water for cooling. The water temperature was kept constant (22 °C) using external circulation through a cooling bath. The 313 nm radiation was obtained using a medium-pressure 400 W mercury lamp (Applied Photophysics) and a filter solution of potassium chromate and sodium carbonate [11] circulated inside the double-walled well. The 254 nm radiation was obtained using a 16 W low-pressure mercury lamp (Applied Photophysics) without filters and refrigeration. Pesticide samples were irradiated in 1 cm quartz cells and actinometry was performed using potassium ferrioxalate [11], irradiated in the same way. Quantum yields were determined in air-equilibrated and argon-purged solutions, upon irradiation at 313 nm and at 254 nm. Photolysis was followed by HPLC using a Merck-Hitachi 655A-11 chromatograph with a 655A-22 UV detector and by GC–MS using a Hewlett Packard 5890 Series II gas chromatograph with a 5971 series mass selective detector (E.I. 70 eV). Analysis were conducted on irradiated samples and on control solutions, kept in the dark during irradiation. Controls showed no sign of pesticide degradation.

Laser flash photolysis experiments were carried out with the fourth harmonic of a YAG laser (266 nm, 6 ns FWHM, 10–30 mJ/pulse) from B.M. Industries (Thomson-CSF), model Saga 12–10, in the transmission mode. A schematic diagram of the system is presented in reference [12]. The probe beam passing through the sample excited by the laser pulse is collected by a beam collimator coupled to an optical fiber (fused silica) and detected by a gated intensified charge coupled device (ICCD, Oriel model Instaspec V) after passing via a compact fixed imaging spectrograph (Oriel, model FICS 77440). The ICCD has high speed gating electronics (2.2 ns) and intensifier, and works in the 200–900 nm wavelength range. Experiments were conducted in hexane, methanol and methanolic solutions containing 100, 200, 300 and 400 g l^{-1} of deionized and distilled water (air equilibrated and argon-purged) with O.D. ∼ 1.5 at the excitation wavelength.

3. Results and discussion

3.1. *Photodegradation quantum yields*

The average photodegradation rate of a given compound C is proportional to the absorbed radiation and to its reaction quantum yield. If the absorption is lower than 0.02 at the excitation wavelength λ, the integration of the rate equation leads to [1]

$$\ln\left(\frac{[C]}{[C]_0}\right)_\lambda = -2.303\phi_\lambda I_{0\lambda}\varepsilon_{C\lambda}bt, \qquad (1)$$

where $[C]_0$ is the initial concentration, $[C]$ the concentration at time t, ϕ_λ the photodegradation quantum yield, $I_{0\lambda}$ the intensity of the incident radiation, $\varepsilon_{C\lambda}$ the absorption coefficient and b the optical path. Thus, ϕ_λ can be easily obtained from a plot of $\ln([C]/[C]_0)_\lambda$ on time, provided $\varepsilon_{C\lambda}$ and $I_{0\lambda}$ are known. The concentrations were measured by HPLC and $I_{0\lambda}$ was determined using the ferrioxalate actinometer.

The results of the photodegradation of triadimefon in water and methanol, upon 313 nm irradiation, are given in Fig. 2. The linear relationship of $\ln([C]/[C]_0)_\lambda$ versus time indicates that the approximations leading to Eq. (1) are fulfilled. Table 1 gives the degradation quantum yields in the studied systems. The degradation quantum yield in water (air equilibrated) is the average of five measurements. The other quantum yield results were obtained using triadimefon as actinometer.

Table 1
Photodegradation quantum yields of triadimefon at 313 nm

Conditions	Quantum yield
Water, air-equilibrated	0.13 ± 0.01
Hexane, air-equilibrated	0.02
Methanol, air-equilibrated	0.03
Aqueous solution, 0.5 M 1,2,4-triazole	0.13
Water, O_2 free	0.13
Aqueous solution, pH = 3	0.13
Aqueous solution, pH = 11	0.13

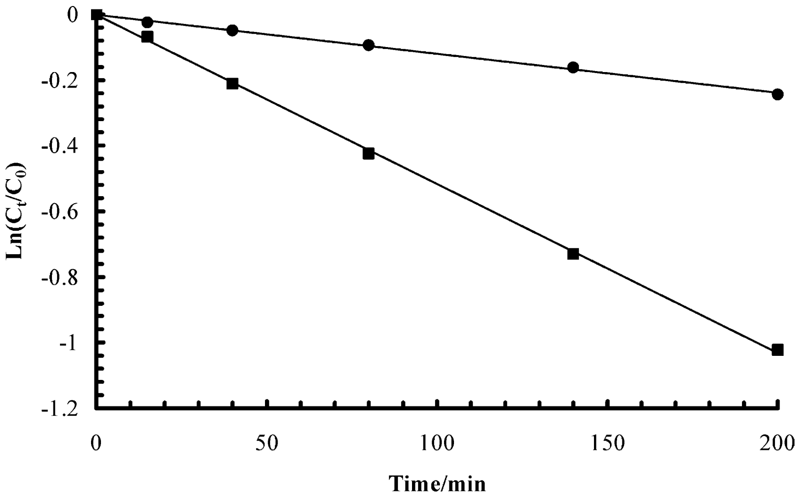

Fig. 2. Results of the photodegradation of triadimefon (313 nm) in water (■) and methanol (●).

The degradation quantum yields are independent (within the experimental error) of the studied additives (in water) but depend on the solvent. In hexane ϕ_λ is similar to the value found in cyclohexane [6]. This is expected since both solvents provide a similar environment to the molecule. In methanol, ϕ_λ is somewhat higher and the largest value was obtained for water. This result suggests that other reaction pathways are available in aqueous solution and indicates that the photochemical studies in organic solvents cannot be used to access the photochemical behavior in natural aquatic systems.

The reaction quantum yield does not depend on the presence of 1,2,4-triazole, although, as we will see later, this is one of the main reaction products. Upon excitation at 313 nm the n,π^* state of triadimefon, localized on the carbonyl group, is formed [6]. Therefore, the triazole group does not directly interact with the n,π^* excited state of triadimefon and the formation of 1,2,4-triazole is simply a consequence of the reaction process.

Several other parameters such as the pH (which was varied between 3 and 11), the presence of Na^+ and Cl^- (added when adjusting the pH) in concentrations up to 10^{-3} M and also the presence of oxygen (air equilibrated solutions) were studied. We verified that they do not significantly affect ϕ_λ. It was also verified that the presence of humic and fulvic acids have little effect on the photodegradation rate constant of triadimefon [10]. This range of conditions simulates most part of the spring water natural systems and the results indicate that direct photodegradation of triadimefon predominates in these systems. Zeep and Cline [13,14] proposed a model to estimate the direct photodegradation rate constants and half lives of pollutants in natural aqueous systems. The rate constant (k_d) can be calculated using the relation

$$k_d = \phi_d \sum_\lambda \varepsilon_\lambda L_\lambda, \qquad (2)$$

where ϕ_d is the direct photodegradation quantum yield, ε_λ the absorption coefficient and L_λ the daily average of solar irradiance at the wavelength λ. This last quantity is tabulated [1]. The half lives of triadimefon for the different seasons of the year (40°N latitude) were calculated using Eq. (2) and the obtained degradation quantum yield at 313 nm. The results are presented in Table 2. Its clear that photodegradation is an important dissipation process of triadimefon in natural conditions.

Triadimenol is stable at 313 nm. This was expected (the pesticide does not significantly absorb at this wavelength [6]) and indicates that triadimenol is stable to direct photoreaction in natural conditions. This result justifies the use of ϕ_λ at 313 nm for the half life estimation (of triadimefon) using Eq. (2) and indicates that the photochemical processes of this pesticide in natural conditions occur from the carbonyl group.

The degradation quantum yields of triadimefon and triadimenol in deionized and distilled water (air equilibrated samples) at 254 nm were 0.24 ± 0.02 and 0.41 ± 0.02, respectively. The results are markedly different form those obtained at 313 nm. This indicates that photochemical studies simulating natural conditions should be made using solar radiation or a wavelength interval of the solar spectrum at the ground level.

Triadimefon can be considered a bichromophoric molecule composed of non-conjugated carbonyl and chlorophenoxy groups. By excitation of the π,π^* state of the

Table 2
Half-lives of triadimefon estimated using the model of Zeep and Cline

Season	Half life (days)
Spring	1.6
Summer	1.2
Fall	2.9
Winter	5.9

chlorophenoxy group a very efficient energy transfer process ($\phi_{ET} \sim 1$) to the low-lying n,π^* state of the carbonyl occurs in cyclohexane [6]. If the same efficiency is effective in water one can expect similar degradation quantum yields at 313 and 254 nm. However, ϕ_λ almost duplicates at 254 nm, suggesting that the degradation from π,π^* state competes with the energy transfer process. The energy transfer was not investigated in polar solvents using fluorescence techniques due to the formation of fluorescent products during the analysis.

3.2. *Degradation products*

Two of the major degradation products were 4-chlorophenol and 1,2,4-triazole. The identification was based on the analysis of authentic samples. These products were already found as resulting from the photolysis of triadimefon and triadimenol in organic solvents [6,7,9]. 4-Chlorophenol has also been proposed as a photodegradation product of triadimefon in water [10]. We found that 1,2,4-triazole is one of the major photodegradation products of triadimefon and triadimenol in water. Fig. 3 shows the time evolution of triadimefon and its degradation products in methanol, upon irradiation at 254 nm. 1,2,4-Triazole is the main degradation product in this solvent. Although 4-chlorophenol undergoes photodegradation in these conditions [15], its formation is a minor pathway of reaction. The addition of water has little effect on the initial reaction rates of triadimefon upon irradiation at 254 nm. However, the product distribution indicates an increase in the formation of 4-chlorophenol and a decrease in the production of 1,2,4-triazole.

The initial rates and the photoproducts were also studied under solar radiation. The study was performed in Algarve (south Portugal) in July. The initial rate increases in the presence of water, going from $2 \times 10^{-5}\,\mathrm{M\,h^{-1}}$ in methanol to $4\times 10^{-5}\,\mathrm{M\,h^{-1}}$ in a methanolic solution containing $200\,\mathrm{g\,l^{-1}}$ of water. This result was expected since at 313 nm (a wavelength of the solar spectrum at ground level) the quantum yield is about five times higher in water then methanol. The product distribution indicates that 4-chlorophenol accounts for 50% of triadimefon degradation and is slight dependent on the water content of the mixtures. No sign of triadimenol degradation was found (within the experimental error) for a 5 h exposure time. The results indicate that both the degradation kinetics and product distribution are strongly dependent on the solvent and on the irradiation wavelength, indicating that the photochemical studies of pollutants should be made in conditions as similar as possible to those observed in environmental systems.

3.3. *Transient absorption*

The detection of transients in aqueous solution was limited by the low solubility of the pesticides under study. We determined the aqueous solubility of triadimefon and it was found to be $(2.4 \pm 0.1)\ 10^{-4}$ M at $20 \pm 0.5\,^\circ$C. Transient absorption studies were therefore conducted in methanol and methanol/water mixtures. Fig. 4 shows the transient absorption of triadimefon and triadimenol in different conditions. The transient absorption of triadimefon in methanol (spectrum A) is easily attributed to the 4-chlorophenoxy radical by comparison with its known spectrum [6,15,16]. The band centered at 310 nm can also be attributed to the 4-chlorophenoxyl radical [17]. This is in accordance with the photodegradation products study since 4-chlorophenoxyl radical can lead to 4-chlorophenol by hydrogen abstraction [18]. Similar spectra were obtained in air-equilibrated and argon-degassed samples. This is to be expected, since molecular oxygen has little influence on oxygen-centered radicals [19] and also agrees with the poor oxygen effect on the degradation quantum yields.

The presence of water increases the formation of the 4-chlorophenoxyl radical and originates a new absorption band centered at 300 nm, but only the later significantly grows with the water content. Compare spectrum B of Fig. 4 ($100\,\mathrm{g\,l^{-1}}$ of water) with spectrum A of Fig. 5 ($300\,\mathrm{g\,l^{-1}}$ of

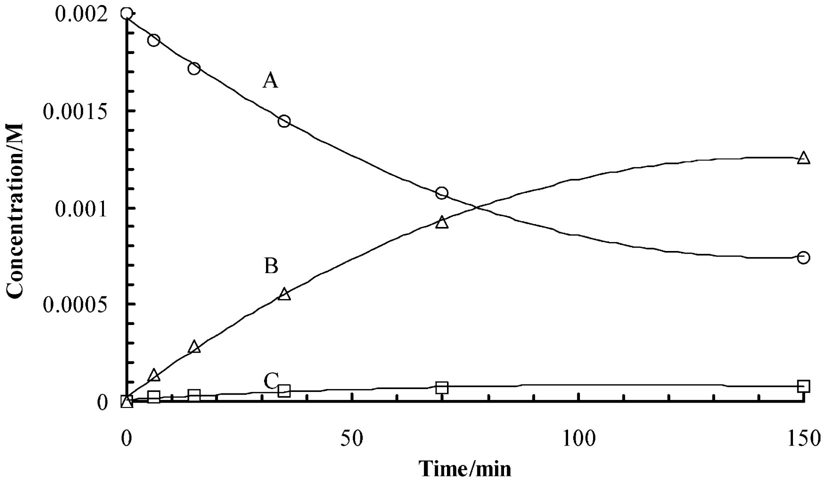

Fig. 3. Concentration of triadimefon (A), 1,2,4-triazole (B) and 4-chlorophenol (C) as function of the irradiation time, in methanol (254 nm).

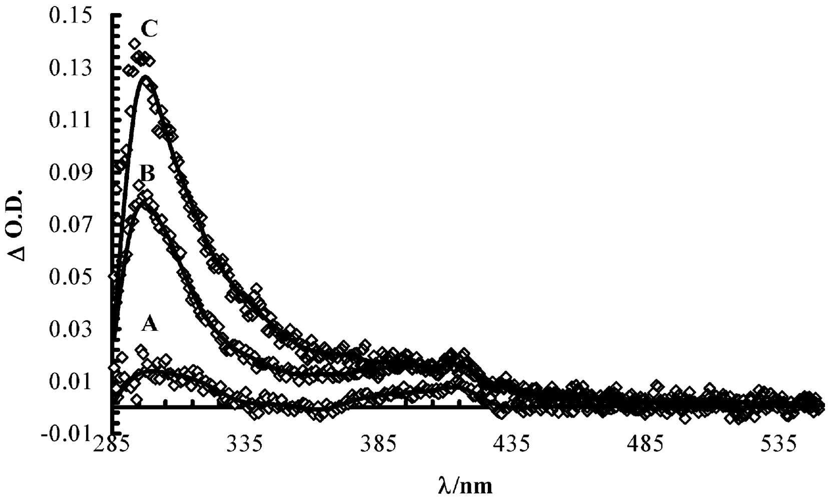

Fig. 4. Transient absorption of triadimefon and triadimenol at pulse end (excitation at 266 nm, ~20 mJ/pulse). (A) Triadimefon in methanol, (B) triadimefon in a methanolic solution containing 100 g l^{-1} of water and (C) triadimenol in a methanolic solution containing 400 g l^{-1} of water.

water). The results agree with the higher degradation quantum yields of triadimefon obtained in aqueous solution and confirm that the main degradation pathways are solvent dependent. The similar absorption bands observed for triadimenol suggest that this pesticide follows similar reaction pathways.

Fig. 5 shows the absorption spectra of triadimefon in a methanolic solution containing 300 g l^{-1} of water, at pulse end and at 5 and 20 μs after the laser pulse. The new absorption and the 4-chlorophenoxyl radical absorption decay within the same time scale. Photoproduct distribution indicates the increase of 4-chlorophenol formation with the water content of the mixture, upon irradiation at 254 nm. The comparison of transient absorption spectra obtained with different water concentrations indicates the increase of the absorption band located at 300 nm. The observation of any transient absorption from the 1,2,4-triazole group is not expected since triazole itself does not absorb to any appreciable extent above 200 nm [6,20]. Therefore, the new transient must have its origin in the chlorophenoxy group. Since high polarity solvents favor heterolytic bond dissociations [21] the new band can be due to 4-chlorophenolate formation. For comparison purposes we obtained the ground state absorption spectra 4-chlorophenolate in a methanolic solution containing 300 g l^{-1} of water. The spectrum was run before and after adding a few drops of NaOH 1N to a 4-chlorophenol solution with this water content. The inset of Fig. 5 shows the normalized ground state absorption spectra of chlorophenolate and the normalized transient absorption band observed at 300 nm. The spectra have the same maximum and spectral distribution around this wavelength. We, therefore, assign the new band to the absorption of 4-chlorophenolate.

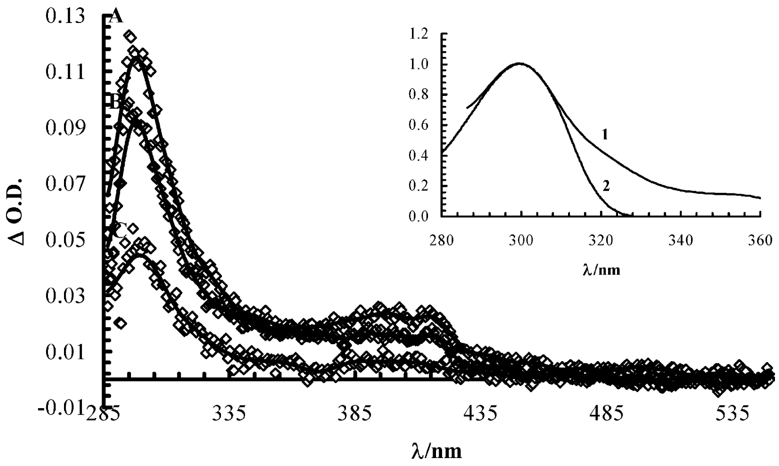

Fig. 5. Transient absorption of triadimefon in a methanolic solution containing 300 g l^{-1} of water (excitation at 266 nm, ~20 mJ/pulse) at pulse end (A), 5 μs (B) and 20 μs (C) after de laser pulse. The inset shows the normalized transient absorption spectra of triadimefon (1) and the normalized ground state absorption spectra of 4-chlorophenolate (2) in a methanolic solution containing 300 g l^{-1} of water.

The homolytic cleavage of the C–N and C–O bonds to the C_1 carbon of triadimefon were already proposed in methanol [7]. The C–O homolytic cleavage was also proposed for both pesticides in cyclohexane [6]. We confirm this degradation pathway for triadimefon in methanol and propose the same for triadimenol in this solvent. We also propose the same degradation pathway for triadimefon and triadimenol in aqueous solution. However, in the presence of water, the heterolytic cleavage of the C–O bond (and probably the C–N) to the C_1 carbon also becomes important.

4. Conclusion

The photochemistry of triadimefon and triadimenol is strongly dependent on the solvent and on the irradiation conditions. Direct photoreaction is an important dissipation pathway of triadimefon in natural water systems while triadimenol is stable in these conditions. Photodegradation kinetics of these pesticides is faster at 254 nm than at 313 nm. Water increases the photodegradation rates. 1,2,4-Triazole and 4-chlorophenol were two of the major degradation products. The formation of the 4-chlorophenoxyl radical was detected for both pesticides in methanol and methanol/water mixtures. In methanol/water mixtures the reaction of both pesticides also proceeds by 4-chlorophenolate formation, which increases with the water content. Photochemical studies simulating natural conditions should be made using solar radiation or a wavelength interval of solar spectrum at the ground level. The studied systems should also be as similar as possible to those found in natural water bodies.

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