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Journal of Photochemistry and Photobiology A: Chemistry 142 (2001) 31–37

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.com/locate/jphotochem

Photophysics and photochemistry of azole fungicides: triadimefon and triadimenol

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Received 30 March 2001; accepted 31 May 2001

Abstract

Photophysics and photochemistry of pesticides triadimefon {1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl) butanone} and triadimenol {1-(4-chlorophenoxy)-3,3-dimethyl-1-(1H-1,2,4-triazol-1-yl) butan-2-ol} were studied in the solution. The excited singlet states were identified by comparison with the absorption spectra of adequate model compounds, in several solvents. The first excited singlet state of triadimefon is an n, π^* state localized on the carbonyl group, while higher excited states are localized on the chlorophenoxy group and have a π, π^* character. The lowest singlet state of triadimenol is a π, π^* state, since a methoxyl group replaces the carbonyl group of triadimefon. Triadimefon shows a weak fluorescence from the n, π^* state, upon excitation at both 310 and 250 nm. This suggests a fast intramolecular energy transfer process from the localized π, π^* state of the chlorophenoxy group to the n, π^* state of the carbonyl group. The photodegradation quantum yield of triadimefon in cyclohexane at 313 nm is 0.022. Triadimenol is photostable under the same conditions. Two major photodegradation products of triadimefon and triadimenol were identified: 4-chlorophenol and 1,2,4-triazole. 4-Chlorophenoxyl radicals were detected by flash photolysis, suggesting a homolytic cleavage of the C–O bond of the asymmetric carbon.

Keywords: Triadimefon; Triadimenol; Energy transfer; Phenoxyl radicals; Chlorophenol

1. Introduction

The photodegradation of pesticides has great importance in agriculture and a large economical and environmental impact. The photophysical and photochemical parameters are fundamental for predicting the environmental behavior and fate of these xenobiotics in natural systems [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 the two powerful related systemic fungicides [2] against powdery mildew and rust fungi [3]. Triadimenol was found to be the major metabolite of **I** in plants in the presence of fungi [4–6]. The photoproducts of **I** were obtained in several solvents [7,8] and on the solid/gas interface [9]. The main reactions are supposed to involve the homolytic bond cleavage of the asymmetric carbon. The photodegradation follows a first-order kinetics and the rate constant is higher in acetone than in methanol or hexane. The main photolysis products of **II** were also identified in organic solvents [10]. Despite their information, photophysic and photodegradation quantum yields are not available. This paper reports the photophysic, photodegradation kinetics and reaction mechanisms of these pesticides.

2. Experimental

2.1. Reagents

Water was deionized and distilled. Triadimefon (offered by Bayer Portugal in its highest purity grade), triadimenol (Riedel-de-Haën, 98%), 4-chloroanisol (Sigma, 99%), 1,2,4-triazole (Fluka, 99%), pinacolone (Sigma, 99%) and organic solvents (Merck Uvasol) were used without further purification.

2.2. Equipment

UV–Vis absorption spectra were run in 1 and 10 cm quartz cells on a Shimadzu UV-260 spectrometer. Corrected fluorescence spectra were recorded at 21 ± 1°C on a Jasco FP777 spectrofluorimeter. Quantum yields were obtained by a comparative method [11], using acetone in cyclohexane as

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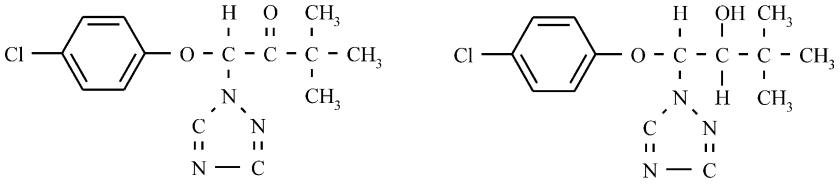
PII: S1010-6030(01)00489-0



I **II**

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

standard for **I** [12] and toluene in cyclohexane as standard for **II** and 4-chloroanisol [13]. The fluorescence quantum yields of **I** in cyclohexane were determined with excitation at both 310 and 250 nm, with the emission registered between 340 and 550 nm, and 280 and 480 nm, respectively. Fluorescence quantum yields of **II** and 4-chloroanisol were determined in cyclohexane, with excitation at 250 nm and the emission registered between 280 and 480 nm. The yields were calculated from fluorescence spectra of both air-equilibrated and degassed solutions. Degassing was done by the freeze-pump-thaw technique (3 cycles), with the cells sealed under vacuum of better than 10^{-4} Torr.

Fluorescence lifetimes were measured by the single photon timing technique using ps laser excitation. The apparatus [14] consisted of a mode-locked Coherent Innova 400-10 argon-ion laser that synchronously pumped a cavity-dumped Coherent 701-2 dye laser, delivering 5–6 ps pulses with 40 nJ/pulse at a frequency of 460 kHz. The excitation light was generated by frequency doubling the output of the rhodamine 6G dye laser. The emission was selected by a Jobin-Yvon HR320 monochromator with a 100 lines/mm grating. The detector used was a Hammamatsu 2809U-01 microchannel plate photomultiplier. The instrument response function had an effective full width at half maximum (FWHM) of 35 ps. A total of about 10 000 counts were accumulated in the channel of maximum counts of the multichannel analyzer operating with 1024 channels. The excitation of **I** was at 310 and 285 nm, and the emission observed at 410 nm. The excitation of **II** was at 285 nm and the emission was observed at 320 nm. Air-equilibrated solutions were used in time-resolved fluorescence measurements.

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 Ref. [15]. 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 cyclohexane using O.D. $\sim$ 1.5 in a 1 cm cell on the excitation wavelength, on air-equilibrated and argon purged solutions.

Photodegradation studies were conducted in a reactor previously used to study the photochemistry of pesticides [16], 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 [17] circulated inside the double-walled well. The 254 nm radiation was obtained using a 16 W low-pressure mercury lamp (Applied Photophysics) without filters, samples were irradiated in the same way although no refrigeration was required. Pesticide samples were irradiated in 1 cm quartz cells and actinometry was performed using potassium ferrioxalate [17], irradiated in the same way. Quantum yields were determined in air-equilibrated solutions, upon irradiation at 313 nm. Photolysis was followed by HPLC using a Merck-Hitachi 655A-11 chromatograph with a 655A-22 UV detector. Analysis were conducted on irradiated samples and on control solutions, kept in the dark during irradiation. Controls showed no sign of pesticide degradation.

Photoproducts were studied by irradiating **I** at 313 and 254 nm, and **II** at 254 nm. Analyses were conducted at 10–20% conversions. Mass spectra were obtained by GC–MS using a Hewlett Packard 5890 series II gas chromatograph with a 5971 series mass selective detector (E.I. 70 eV).

3. Results and discussion

3.1. Photophysics

The UV–Vis absorption spectra in solution were run in several solvents. The spectrum of **I** in acetonitrile (Fig. 2) shows three electronic bands: a low intensity band between 290 and 340 nm (**1**); a medium intensity absorption band between 250 and 290 nm (**2**); an intense band below 250 nm (**3**). Table 1 summarizes the wavelength maximum of bands **1** and **2**, obtained from the minimums of the second derivative of the absorption spectra.

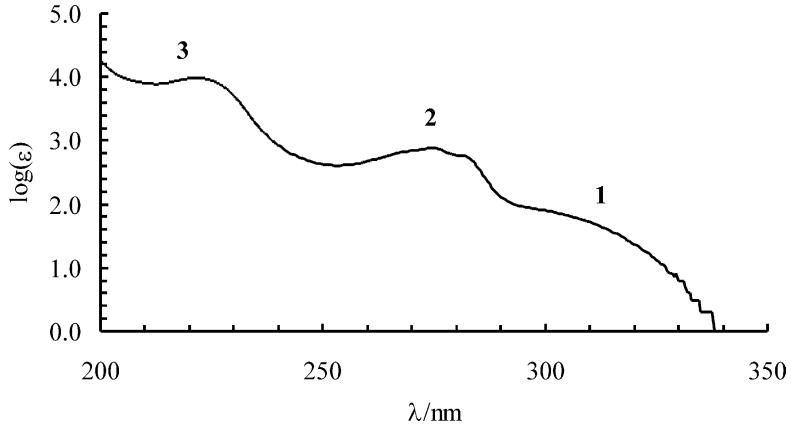


Fig. 2. Absorption spectrum of triadimefon in acetonitrile.

Table 1
Absorption maximums of bands **1** and **2** of triadimefon

Solvent	λ_{max} (nm)							
Water	[a]	[a]	[a]	282.5	274.9	267.4	260.2	253.0
Methanol	324.7	312.3	301.5	283.3	275.6	267.9	260.9	254.5
Acetonitrile	325.3	311.3	302.5	283.3	275.5	268.1	260.4	254.4
Cyclohexane	329.0	316.3	304.8	284.7	277.0	269.2	262.1	255.2

[a] Undetected in the conditions used.

Fig. 3 shows the absorption spectra of **I** and of the model compounds 4-chloroanisol and pinacolone. The model compound 1,2,4-triazole has an absorption coefficient lower than $1\,M^{-1}\,cm^{-1}$ above 250 nm. The band **1** was assigned to an $n \rightarrow \pi^*$ transition involving the non-bonding electrons of the carbonyl group. The band assignment is based on its intensity, spectral localization, blue shift with solvent polarity increase and average separation of the absorption maximums ($\cong 1200\,cm^{-1}$) [18]. The only model compound that absorbs in the 290–340 nm region (band **1**) is pinacolone which confirms the assignment. The band **2** was assigned to the first $\pi \rightarrow \pi^*$ transition localized on the chlorophenoxy group. This attribution is based on the intensity, spectral localization and average separation of the absorption maximums ($\cong 1000\,cm^{-1}$) of this band, which compares well with those of similar benzene derivatives [18]. The π, π^* band shows a hipsochromic shift with increasing solvent polarity, which is the opposite of the normally observed for polar aromatic molecules [19]. This result cannot be attributed to the interaction between 1,2,4-triazole and chlorophenoxy groups since similar solvathochromic shifts were observed for 4-chloroanisol. However, this interaction should exist since the π, π^* bands of **I** are less intense and shifted to higher wavelengths than the corresponding band of 4-chloroanisol (Fig. 3). The solvathochromic behavior should be attributed to a decrease of the polarity upon

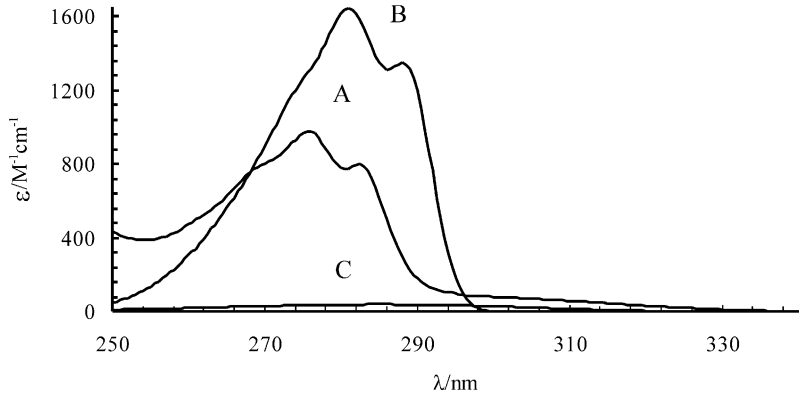


Fig. 3. Absorption spectra in acetonitrile: (**A**) triadimefon (2×10^{-4} M); (**B**) 4-chloroanisol (2×10^{-4} M); (**C**) pinacolone (1×10^{-3} M).

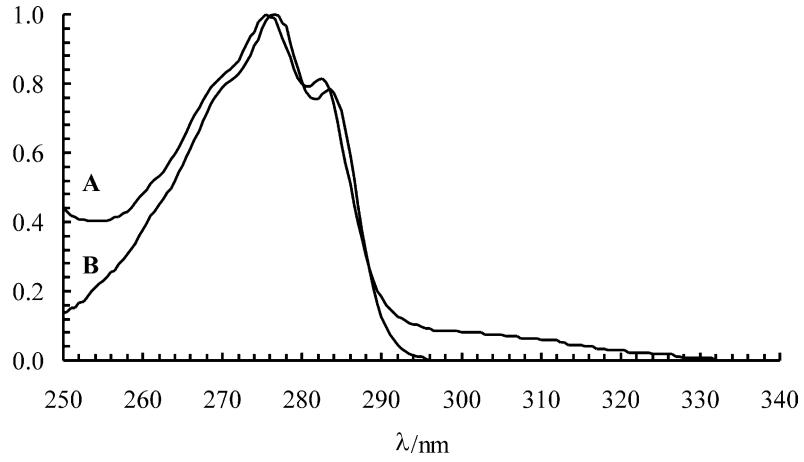


Fig. 4. Normalized absorption spectra of triadimefon, **A**, and triadimenol, **B**, in acetonitrile.

excitation as observed for 4-nitroaniline and related compounds [18]. The third band (**3**), below 250 nm, was assigned to a higher $\pi \rightarrow \pi^*$ transition of the chlorophenoxy group.

Fig. 4 shows normalized UV–Vis absorption spectra of **I** and **II**. The triadimenol spectrum does not have the band **1**, while bands **2** and **3** are similar in intensity and spectral shape to those of **I**. This is to be expected since a methoxyl group in **II** substitutes the carbonyl group of **I**, without electronic conjugation between the aromatic ring and these groups.

The normalized fluorescence spectra of **I** and pinacolone in cyclohexane, obtained by excitation at 310 nm, are presented in Fig. 5. Both spectra show a similar weak broad fluorescence band centered around 420 nm. Based on the intensity and spectral characteristics, the band was assigned to an $n \rightarrow \pi^*$ transition, localized in the carbonyl group. This is reasonable since at this excitation wavelength the absorbance of **I** is mainly due to the carbonyl group (see Figs. 2 and 3). Upon excitation at 250 nm the fluorescence spectrum of **I** shows weak emission centered at 310 nm besides the 420 nm band. The singlet state energies of **I** (330 kJ mol^{-1}, $\lambda \sim 360$ nm and 410 kJ mol^{-1}, $\lambda \sim 290$ nm) were estimated from the onset of the fluorescence spectrum.

Fig. 6 shows fluorescence spectra of **I**, **II** and 4-chloroanisol in cyclohexane upon excitation at 250 nm. Both **II** and 4-chloroanisol show an intense band centered at 310 nm due to a $\pi \rightarrow \pi^*$ transition localized in the chlorophenoxy group. However, the corresponding triadimefon band is very weak. Table 2 summarizes fluorescence quantum yields of the pesticides and 4-chloroanisol in cyclohexane. The fluorescence quantum yields of **I** are very low, in agreement with published values for aliphatic ketones [18]. The triadimenol quantum yields compare well with those published for related benzene derivatives [18]. The values for **II** and 4-chloroanisol are similar, suggesting that both the 1,2,4-triazole and the hydroxyl group do not perturb significantly the excited singlet state of the chlorophenoxy group.

The fluorescence quantum yields of **I** are equal within the experimental error in air-equilibrated and oxygen-free solutions. A small effect of oxygen in the quantum yields was observed for **II** and 4-chloroanisol, consequence of longer

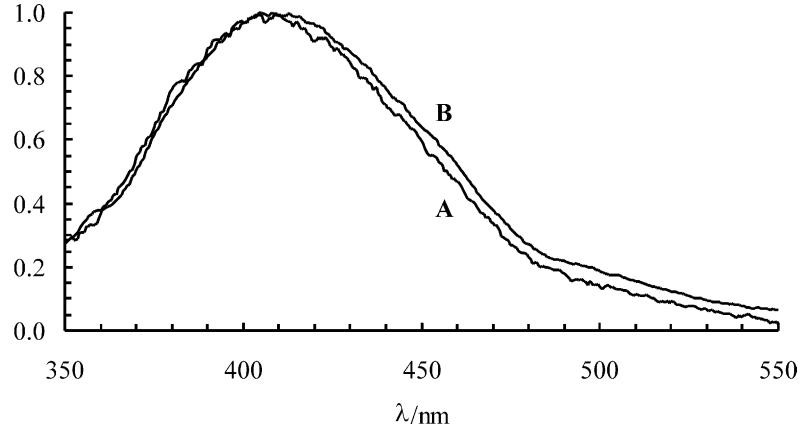


Fig. 5. Normalized fluorescence spectra of triadimefon, **A**, and pinacolone, **B**, in cyclohexane upon excitation at 310 nm.

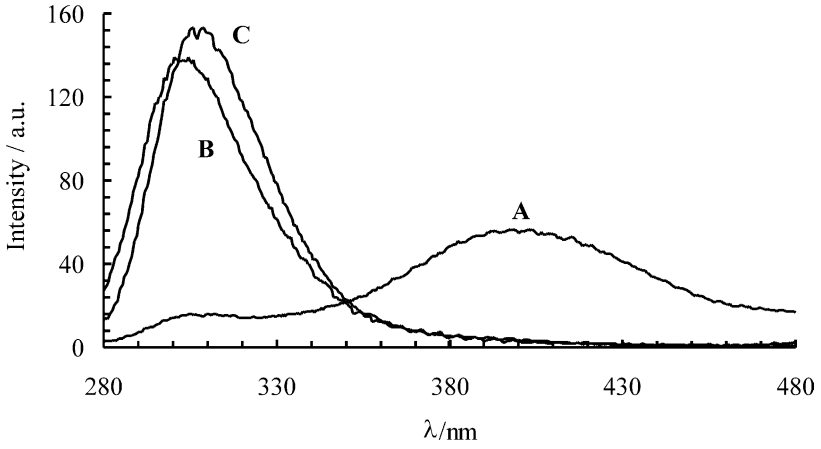


Fig. 6. Fluorescence spectra of triadimefon, **A** (1.0×10^{-3} M), triadimenol, **B** (5.0×10^{-6} M) and 4-chloroanisol, **C** (5.0×10^{-6} M), in cyclohexane. Excitation wavelength: 250 nm.

Table 2
Fluorescence quantum yields (Φ_f) and rate constants (k_f) for different compounds

Compound	λ_{exc} (nm)	Φ_f		k_f, O_2 (s^{-1})
		O_2	O_2 free	
Triadimefon	310	$3.2 \pm 1.5 \times 10^{-4}$		$1.3 \pm 0.6 \times 10^{6}$
Triadimefon	250	$2.1 \pm 1.6 \times 10^{-4}$		
Triadimenol	250	$1.17 \pm 0.09 \times 10^{-2}$	$1.28 \pm 0.07 \times 10^{-2}$	$1.6 \pm 0.1 \times 10^{7}$
4-Chloroanisol	250	$1.08 \pm 0.03 \times 10^{-2}$	$1.26 \pm 0.07 \times 10^{-2}$	

lifetimes and better accuracy in the quantum yields determination.

The fluorescence decays of **I** and **II** are single exponential with lifetimes summarized in Table 3. The lifetime of **I** at 410 nm (carbonyl group), is similar upon excitation at 285 and 310 nm. However, the lifetime in the emission range of the chlorophenoxy group (290–340 nm) is inferior to the time resolution of our single photon counting apparatus (~5 ps).

Fluorescence rate constants (k_f), calculated from the fluorescence quantum yields (Φ_f) and lifetimes (τ_f) using the relation $k_f = \Phi_f/\tau_f$, are presented in Table 2. Fluorescence rate constants were also estimated according to the relationship $k_f \approx 10^4 \varepsilon_{max}$ [18]. The values obtained are $k_f = 1 \times 10^6\ s^{-1}$ for the carbonyl group of **I** ($\varepsilon_{max} \sim 100\ M^{-1}\ cm^{-1}$) and $k_f = 1 \times 10^7\ s^{-1}$ for triadimenol ($\varepsilon_{max} \sim 1100\ M^{-1}\ cm^{-1}$). These values are in good agreement with the experiment, indicating that the same state is observed in absorption and fluorescence.

Table 3
Lifetimes and χ^2 of fits to a single exponential function of triadimefon and triadimenol fluorescence decay kinetics in cyclohexane

Compound	λ_{exc} (nm)	λ_{em} (nm)	τ (ps)	χ^2
Triadimefon	310	410	252	1.25
Triadimefon	285	410	258	1.06
Triadimenol	285	320	725	1.19

The fluorescence spectra of **I**, upon excitation of the chlorophenoxy group ($\lambda_{exc} = 250$ nm), reveal that the emission results almost exclusively from the carbonyl group (see Fig. 6). This implies a very fast conversion from the π, π^* state to the n, π^* state. As the electronic states are localized in non-conjugated choromophoric groups, we should invoke a singlet–singlet intramolecular energy transfer [20,21] process from the chlorophenoxy group (donor, S_2 state) to the carbonyl group (acceptor, S_1 state). The rate constant of the energy transfer is given by

$$k_{ET} = \frac{1}{\tau_D} - \frac{1}{\tau_D^0} \quad (1)$$

where τ_D, τ_D^0 are the donor lifetimes in the bichromophoric molecule and when isolated, respectively. On the other hand, the energy transfer quantum yield is given by

$$\Phi_{ET} = \frac{k_{ET}}{k_{ET} + (1/\tau_D^0)} = 1 - \frac{\Phi_{fD}}{\Phi_{fD}^0} = 1 - \frac{\tau_D}{\tau_D^0} \quad (2)$$

where Φ_{fD}^0, Φ_{fD} are the fluorescence quantum yields of the isolated donor and bichromophoric molecule, respectively.

Using triadimenol as a model for the isolated donor, one could in principle determine these two parameters. However, the low intensity of the chlorophenoxy group emission in **I** does not allow an accurate quantum yield measurement (Φ_{fD}), while the lifetime (τ_D) is too short to be accurately

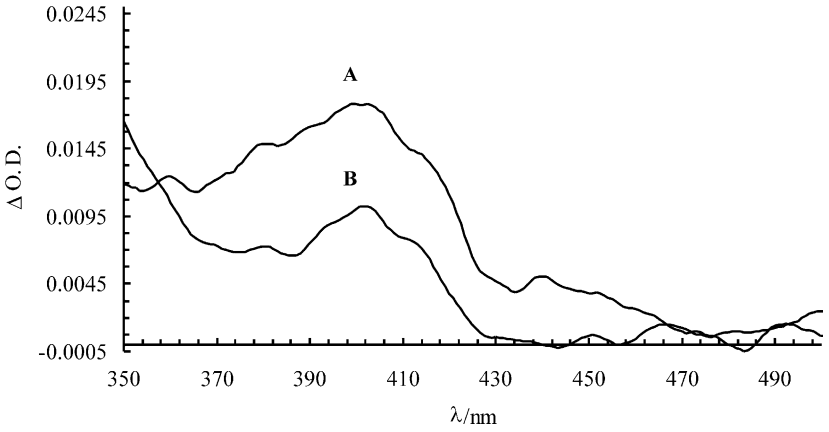


Fig. 7. Transient absorption in cyclohexane upon excitation at 266 nm: (**A**) triadimefon (∼30 mJ/pulse); (**B**) triadimenol (∼15 mJ/pulse).

determined with the equipment. Nevertheless, fluorescence intensity of the chlorophenoxy group in **II** is about three orders of magnitude higher than in **I** (see Fig. 6), showing that the energy transfer quantum yield is close to unity. The same result is achieved if the energy transfer quantum yield is calculated from the emission of the carbonyl excited directly or indirectly by way of the energy transfer from the chlorophenoxy group. Indeed, using selective excitation, it is possible to calculate the quantum yields of the carbonyl (acceptor) emission by direct excitation at 310 nm ($\Phi_{fA,310}$) or by indirect excitation via the donor group at 250 nm ($\Phi_{fA,250}$). Thus, the energy transfer efficiency can be calculated using the relation

$$\Phi_{ET} = \frac{\Phi_{fA,250}}{\Phi_{fA,310}} \quad (3)$$

The acceptor quantum yields are equal within the experimental errors (see Table 2) indicating that the energy transfer efficiency is close to unity. This implies an energy transfer rate constant of the order of $10^{12}\ s^{-1}$ and a lifetime of the chlorophenoxyl group of **I** in the sub-picosecond region. This is reasonable since the donor and acceptor groups are in close proximity thus the energy transfer must be very efficient by the exchange interaction mechanism.

3.2. Photochemistry

Photochemical studies simulating natural conditions should be made using solar radiation or a wavelength interval of solar spectrum at the ground level. Irradiating at 313 nm fulfils this condition, as the UV absorption spectrum of the compounds studied superimposes the solar radiation spectrum at ground level in this wavelength region. The direct photodegradation quantum yield of **I** at 313 nm was found to be 0.022, while **II** is photostable. This result was expected since the latter does not absorb at 313 nm (see Fig. 3).

The mass spectra of the photoproducts of both pesticides show that one of the major compounds is 4-chlorophenol. Time-resolved transient spectrums of **I** and **II**, registered 25 ns after the beginning of the laser pulse and using a temporal window of 250 ns, reveal a transient absorption band maximizing around 400 nm (Fig. 7). This absorption is attributed to the phenoxyl radical, based on the similarity between these absorption spectra and the known spectra of this radical [22,23]. 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 [24]. This assignment is supported by the product distribution since the 4-phenoxyl radical can lead to 4-chlorophenol by hydrogen abstraction [25]. The estimates made of the theoretical transient absorption amplitude taking into account the laser pulse energy, the sample geometry, experimental quantum yields of the products and the known radical absorbance also confirm the assignment.

Molar balance results indicate that the formation of 4-chlorophenol accounts for about 20% degradation of **I** irradiated at 313 nm, suggesting the existence of other photolysis pathways. A precipitate was detected in all irradiated samples, which was identified by its mass spectrum as being 1,2,4-triazole. This result suggests that 1,2,4-triazole results from another important photodegradation pathway. The mentioned photoproducts were already found for the two pesticides in solution [7,8,10]. These photodegradation products were found at both 313 and 254 nm irradiation of **I**. This result supports the intramolecular energy transfer process described above.

The importance of the C-1 bond stability in triazole is well recognized with respect to biological activity of these pesticides [8]. We observed that the cleavage of this bond does occur for **I** upon excitation at 313 nm, suggesting that solar radiation can lead to biological deactivation of this pesticide. A similarly behavior is not expected for **II**.

4. Conclusions

The photophysics and photochemistry of the pesticides triadimefon and triadimenol were studied in solution.

Triadimefon can be considered as a bichromophoric molecule composed of non-conjugated carbonyl and chlorophenoxy groups. By excitation of the π, π^* state of the chlorophenoxy group a fast energy transfer process occurs to the low lying n, π^* state of the carbonyl. The n, π^* state does not exist in triadimenol because the carbonyl group was replaced by a methoxyl group. However, the energy of the π, π^* states in both pesticides is similar indicating the bichromophoric nature of triadimefon. 4-Chlorophenol and 1,2,4-triazole are two of the major products of photodegradation. The reaction proceeds by 4-chlorophenoxy radical formation for both pesticides. Triadimenol is expected to be stable to direct photodegradation under natural conditions. Triadimefon can be deactivated upon solar irradiation.

Acknowledgements

We would like to thank Dr. Alexander Fedorov for his kind and helpful assistance with the fluorescence decay measurements. We are grateful to Bayer Portugal for the samples of triadimefon. This work was supported by Junta Nacional de Investigação Científica e Tecnológica, grant PRAXIS XXI/BD/3617/94.

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