ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 135 (2000) 207–212

Journal of Photochemistry and Photobiology A:Chemistry

www.elsevier.nl/locate/jphotochem

Kinetics of the dye sensitized photooxidation of 2-amino-4-hydroxy-6-methylpyrimidine, a model compound for some fungicides

A. Pajares [a], J. Gianotti [a], G. Stettler [a], E. Haggi [a], S. Miskoski [b], S. Criado [b], F. Amat-Guerri [c], N.A. García [b,*]

[a] *UARG, Universidad Nacional de la Patagonia Austral, 9400 Río Gallegos, Argentina*
[b] *Departamento de Química y Física, Universidad Nacional de Río Cuarto, 5800 Río Cuarto, Argentina*
[c] *Instituto de Química Orgánica, CSIC, Juan de la Cierva 3, 28006 Madrid, Spain*

Received 1 December 1999; received in revised form 15 March 2000; accepted 16 March 2000

Abstract

The kinetics of the dye-sensitized photooxidation of 2-amino-4-hydroxy-6-methyl-pyrimidine (AHMPD), a compound with the basic molecular structure of some systemic pyrimidine fungicides, has been studied in solution in water and in the mixture acetonitrile–water 4:1 v/v. Rate constants in the range 9×10^4–2.7×10^7 M^{-1} s^{-1} for both the overall and the reactive singlet molecular oxygen [$O_2(^1\Delta_g)$] quenching processes were determined by time-resolved $O_2(^1\Delta_g)$-phosphorescence detection and polarographic methods. Photooxidation quantum yields were in the range 0.005–0.41, with values significantly higher in alkalinized media. On the contrary, pyrimidine, 2-aminopyrimidine, 4-hydroxypyrimidine and 6-methylpyrimidine do not react with $O_2(^1\Delta_g)$, in neutral or alkalinized D_2O solutions. The presence of a 4-hydroxy group in pyrimidines plays a key role in the photooxidative process, because the formation of the tautomeric 4-oxo form, the predominant one in aqueous solution, diminishes or suppresses the interaction with $O_2(^1\Delta_g)$. However, in the presence of alkali the OH-ionization greatly enhances the photooxidation. The experimental evidence suggests a charge-transfer mediated mechanism involving an initial encounter excited complex. These results also show that the sensitized photooxidation is an alternative pathway for the environmental or programmed degradation of these colorless N-heteroaromatic compounds, in special in OH-ionized form.

Keywords: Photooxidation; Photosensitization; Pyrimidine fungicides

1. Introduction

Many agricultural pesticides of profuse use have molecular structures with a six-member nitrogen-containing aromatic heterocycle [1], and significant amounts of these compounds are contaminants of surface waters and soils. As a consequence, in the last decade both the thermal and the photochemical ways of degradation of such contaminants have been topics of growing interest [2,3]. In particular, their photoinduced degradation under natural conditions, i.e. in water solution and in the presence of air, has been tested with variable success, and the reactions involved have been studied in order to know more about the natural photochemical decay of all these substances [4]. In recent papers [5,6], we have reported on the kinetics of the dye-sensitized photooxygenation of several hydroxypyridines and hydroxyquinolines with basic molecular structures of known N-heteroaromatic pesticides [1], demonstrating that a singlet molecular oxygen [$O_2(^1\Delta_g)$]-mediated mechanism operates when employing the dye Rose Bengal as a sensitizer, with photooxidation quantum efficiencies in the range 0.01–0.85 for the reactive compounds, with higher values for hydroxypyridines [5]. Following this line, in the present work we show the results of the kinetic study of the Rose Bengal-sensitized photooxidation of 2-amino-4-hydroxy-6-methylpyrimidine (AHMPD), as a model compound for some systemic pyrimidine fungicides.

The photosensitization process for $O_2(^1\Delta_g)$ generation (Eqs. (1) and (2)) and its subsequent physical and chemical interactions with the pyrimidine substrate (PDS) can be depicted by the following kinetic scheme:

$$\text{Sens} + h\nu \rightarrow \text{Sens}^* \quad (1)$$

* Corresponding author.
E-mail address: ngarcia@exa.unrc.edu.ar (N.A. García)

1010-6030/00/$ – see front matter
PII: S1010-6030(00)00279-3

$$\text{Sens}^* + O_2(^3\Sigma_g^-) \xrightarrow{k_{ET}} O_2(^1\Delta_g) + \text{Sens} \quad (2)$$

$$O_2(^1\Delta_g) + \text{PDS} \xrightarrow{k_q} O_2(^3\Sigma_g^-) + \text{PDS} \quad (3)$$

$$O_2(^1\Delta_g) + \text{PDS} \xrightarrow{k_r} \text{oxidation products} \quad (4)$$

$$O_2(^1\Delta_g) \xrightarrow{k_d} O_2(^3\Sigma_g^-) \quad (5)$$

where $O_2(^3\Sigma_g^-)$ represents the ground state molecular oxygen, k_{ET}, k_q and k_r are the rate constants for energy transfer and for physical and reactive (or chemical) quenching processes (Eqs. (2)–(4), respectively), and k_d (Eq. (5)) is the rate constant for the $O_2(^1\Delta_g)$ decay by interaction with solvent molecules. The overall quenching rate constant k_t is defined as the sum (k_q+k_r).

The kinetics of the photosensitized oxidation of the pyrimidine fungicides ethirimol (5-*n*-butyl-2-diethylamino-4-hydroxy-6-methylpyrimidine), dimethirimol (5-*n*-butyl-2-dimethylamino-4-hydroxy-6-methylpyrimidine), and four analogous pyrimidines, all with structures closely related to that of AHMPD, has been previously studied, and the overall rate constants k_t have been evaluated in solution in water and in chloroform [7,8]. However, in terms of substrate photodegradation, these constants only provide limited kinetic information about the potential environmental relevance of the interaction $O_2(^1\Delta_g)$-PDS, because the actual significance of the photooxidation reaction cannot be straightforwardly judged neither by k_t nor by k_r independent values [2]. The adequate parameter to be evaluated is the photooxidation quantum efficiency (φ_r), as defined in Eq. (6):

$$\varphi_r = \frac{k_r(\text{PDS})}{k_d + k_t(\text{PDS})} \quad (6)$$

The aim of the present work was to study the influence of the substituents in AHMPD on the susceptibility of this compound to $O_2(^1\Delta_g)$ attack, looking for the experimental conditions that maximize the dye-promoted photodisappearance of this family of contaminants. With this purpose we have evaluated the photooxidation quantum efficiencies of said compound and of the related monosubstituted pyrimidines, 2-aminopyrimidine, 4-hydroxypyrimidine and 6-methylpyrimidine, as well as the disubstituted compound 2-amino-4-hydroxypyrimidine, under different experimental conditions of solvent polarity and medium pH. At the same time, we have also studied the influence of the medium on the physical (Eq. (3)) and reactive (Eq. (4)) quenching processes of $O_2(^1\Delta_g)$.

2. Materials and methods

2.1. Chemicals

Pyrimidine (PD), 2-aminopyrimidine (APD), 4-hydroxypyrimidine (HPD) (λ_{max} at pH 6 water solution, 224, 250 nm; at pH 11 water solution, 210, 226, 264 nm), 6-methylpyrimidine (MPD), 2-amino-4-hydroxypyrimidine (isocytosine) (AHPD) (λ_{max} at pH 6 water solution, 216, 268, 284 nm; at pH 11 water solution, 210, 228, 274 nm), 2-amino-4-hydroxy-6-methylpyrimidine (AHMPD) (λ_{max} at pH 6 water solution, 216, 268, 282 nm; at pH 11 water solution, 212, 226, 270 nm), Rose Bengal (RB), sodium azide and 9,10-dimethylanthracene (DMA) were commercial samples (Aldrich). Fluorescamine was purchased from Sigma, furfuryl alcohol (FFA) was from Riedel de Häen, acetonitrile (MeCN) was from Sintorgan (Argentina), D_2O (99.9%) was a gift from Nasa S.A. All the former products were used without further purification. H_2O was triply distilled.

The solvents employed in the kinetics measurements were water (H_2O or D_2O, depending on the particular experiment) and the mixture MeCN/water (H_2O or D_2O) 4:1 v/v, both in the absence and in the presence of KOH 0.01 M. Solutions in alkalinized media of HPD, AHPD and AHMPD show the characteristic UV spectra of the corresponding OH-ionized forms.

2.2. Kinetic determinations

The laser-kinetic spectrophotometer has been previously described [1]. Briefly, it consisted of a Nd:Yag laser (Spectron) as the excitation source. The frequency-doubled output at 532 nm was employed to excite RB. The emitted radiation ($O_2(^1\Delta_g)$ phosphorescence, mainly 1270 nm) was detected (using an amplified Judson J16/8Sp germanium detector) at right angles, after having passed through appropriate filters. The output of the detector was coupled to a digital oscilloscope and to a personal computer to carry out the signal processing. Sixteen shots were usually needed for averaging, in order to get a good signal/noise ratio, from which the decay times were calculated. Air-equilibrated solutions were employed in all the cases. The solutions with the sensitizer RB had an absorbance of ca. 0.3 at the lasing wavelength. All ground state absorption measurements were carried out with a Hewlett Packard 8452A diode array spectrophotometer. The $O_2(^1\Delta_g)$ lifetimes in MeCN/D_2O 4:1 and in D_2O were 55 and 60 μs, respectively. In the dynamic determinations, the solvent D_2O was employed, instead of H_2O, in order to enlarge the $O_2(^1\Delta_g)$ lifetime, as already discussed elsewhere [9], and the relatively long time-response (ca. 3 μs) for the employed IR detector was taken into account. Within the experimental error, the presence of alkali did not influence on the $O_2(^1\Delta_g)$ lifetimes.

The $O_2(^1\Delta_g)$ lifetimes were evaluated in the absence (τ^0) and in the presence (τ) of the quencher, and the data were plotted as a function of substrate concentration, according to a simple Stern–Volmer treatment (Eq. (7).

$$\frac{1}{\tau} = \frac{1}{\tau^0} + k_t(\text{PDS}) \quad (7)$$

The irradiation device for the kinetic determinations, including the specific oxygen electrode (Orion 97-08, polaro-

graphic detection), which can only be used in aqueous solutions, has been described elsewhere [10]. A cut-off filter for wavelengths of <450 nm was employed.

The reactive rate constants k_r (employing RB, $Abs_{530}=0.5$, as a dye-sensitizer) for the chemical reaction of each PDS with $O_2(^1\Delta_g)$ were determined by comparative methods. In all the cases, the knowledge of the k_r value for the photooxidation of a reference compound (Ref.) was required. In organic medium the reference was DMA, whose k_r value, determined by time resolved phosphorescence detection (TRPD), was $1.4\times10^8\,M^{-1}\,s^{-1}$. The k_r value of each substrate was determined by the method described by Scully and Hoigné [11], based on Eq. (8),

$$\frac{\text{slope}_{PDS}}{\text{slope}_{Ref.}} = \frac{k_{r\,PDS}}{k_{r\,Ref.}} \quad (8)$$

where slope_{PDS} and $\text{slope}_{Ref.}$ are the respective slopes of pseudo first order plots of PDS and reference consumption, respectively (determined by spectrophotometry in both cases, for conversions lower than 10%), upon RB sensitized irradiation. PDS and reference had identical concentrations. In water solution, oxygen consumption was monitored instead of PDS consumption. Assuming that the reaction of $O_2(^1\Delta_g)$ with the quencher is the only way for oxygen consumption, the ratio of the first order slopes of oxygen uptake by PDS and reference (slope-ox_{PDS}/slope-$ox_{Ref.}$), both determined at identical substrate concentrations, is equal to $\alpha k_{rPDS}/\beta k_{rRef.}$, where α and β represent the stoichiometric coefficients in the reactions (9) and (10), respectively:

$$PDS + \alpha O_2(^1\Delta_g) \rightarrow \text{Products from PDS} \quad (9)$$

$$Ref. + \beta O_2(^1\Delta_g) \rightarrow \text{Products from Ref.} \quad (10)$$

Employing this experimental technique it is necessary to know the values of the fractional consumption coefficients α and β, i.e. the number of moles of O_2 consumed per mol of PDS or of reference, upon sensitized irradiation. For PDS, the quotient α was determined by measuring the molar consumption of substrate (by absorption spectroscopy) and of oxygen (by means of the specific oxygen electrode) at the initial stages (with less than 10% consumption) in the same photoirradiated solution. In water the reference was FFA, with quotient β equals to the unity and a k_r value of $1.2\times10^8\,M^{-1}\,s^{-1}$ [12].

The rates of evolution (either loss or generation) of primary amine groups in substrates PDS (initial concentrations 2×10^{-4} M) upon RB-sensitized photooxidation were determined by the method described by Straight and Spikes [13]. Basically, the method employs an excess of the specific amino-complexing agent fluorescamine, which produces a fluorescent complex with compounds possessing primary amino groups, thus, allowing the spectrofluorimetric analysis of the evolution of the number of these groups in a given medium/substrate during the course of $O_2(^1\Delta_g)$-mediated photooxidations. The spectrofluorimeter employed was a Spex Fluoromax, and the excitation and emission wavelengths were 390 and 475 nm, respectively.

3. Results

The visible-light irradiation of air-equilibrated individual solutions of AHMPD in pH 6 and 11 aqueous solutions, and AHPD in pH 11 aqueous solution, in the presence of RB, strongly modifies their absorption spectra (Fig. 1). The same was true when similar experiments were run in the mixture MeCN/water for AHMPD. Under comparative conditions, the spectral modification depends on the pH value, being much higher in alkaline medium. These modifications were not observed in the absence of oxygen (argon bubbling), and comparative or higher irradiation times.

The rate of oxygen consumption upon irradiation of aerated RB–PDS systems was recorded, employing the already described specific oxygen electrode. Oxygen uptake was totally inhibited by 0.01 M NaN_3, a very known selective $O_2(^1\Delta_g)$ physical quencher [4]. The k_r values for PDS (Table 1) were graphically obtained through experiments of oxygen uptake (in water) or PDS consumption (in the mixture MeCN/water 4:1, <10% conversions). A typical example is shown in Fig. 2. The potential presence of UV-absorbing reaction products, in special at high conversions, could preclude the neat evaluation of substrate disappearance from UV data, but oxygen uptake unambiguously reflects the evolution of the photooxidation process, assuming known stoichiometry. The stoichiometric quotient for the reaction between $O_2(^1\Delta_g)$ and AHMPD in water (coefficient α, Eq. (9)) was 1.0±0.1 (data not shown). The same coefficient was assumed for AHPD in the calculation

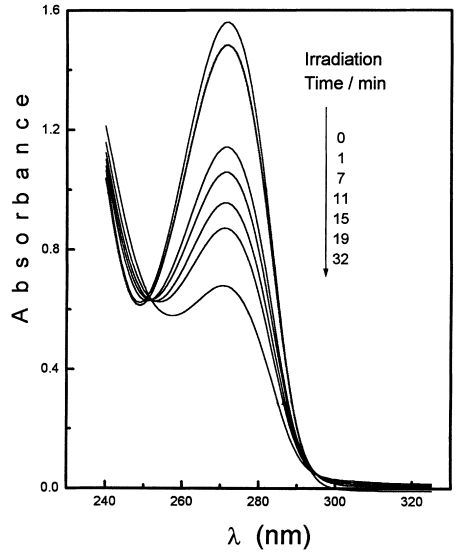
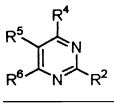


Fig. 1. Absorption spectrum evolution during the aerobic irradiation of 2-amino-4-hydroxy-6-methylpyrimidine in pH 11 H_2O in the presence of Rose Bengal. Numbers on the spectra are irradiation times in min.

Table 1
Overall (k_t) and reactive (k_r) rate constants, and quantum yields (φ_r) for the $O_2(^1\Delta_g)$-mediated photooxidation of 2-amino-4-hydroxy-6-methylpyrimidine (AHMPD) and related compounds in water or in MeCN/water 4:1[a]



	R^2	R^4	R^5	R^6	Solvent	$k_t/10^7$ ($M^{-1}\,s^{-1}$)	$k_r/10^7$ ($M^{-1}\,s^{-1}$)[b]	φ_r
PD	H	H	H	H	Benzene	<0.0001	nr	
APD	NH_2	H	H	H	D_2O	<0.0001	nr	
HPD[c]	H	OH	H	H	D_2O, pD 6	<0.0001	nr	
					D_2O, pD 11	<0.0001	nr	
MPD	H	H	H	Me	D_2O	<0.0001	nr	
					D_2O, pD 11	<0.0001	nr	
AHPD	NH_2	OH	H	H	D_2O, pD 6	<0.0001		
					H_2O, pH 6		nr	
					D_2O, pD 11	1.7±0.1		
					H_2O, pH 11		1.7±0.2	0.50
AHMPD	NH_2	OH	H	Me	D_2O, pD 6	0.057±0.004		
					H_2O, pH 6		0.018	0.01
					D_2O, pD 11	2.7±0.1		
					H_2O, pH 11		1.8	0.41
					MeCN/D_2O	0.025±0.002		
					MeCN/H_2O		0.009	0.005
					MeCN/D_2O+KOH	1.46±0.08		
					MeCN/H_2O+KOH		0.38	0.12
DEAHMPD[d]	NEt_2	OH	H	Me	$CHCl_3$	0.07	nd	
DMAHDMPD[e]	NMe_2	OH	Me	Me	$CHCl_3$	1.15	nd	
					H_2O, pH 7	8.07	nd	
					H_2O, pH 9	14.1	nd	

[a] For comparison, reported data for 4-hydroxypyrimidine (HPD), 2-diethylamino-4-hydroxy-6-methylpyrimidine (DEAHMPD) and 2-dimethylamino-4-hydroxy-3,6-dimethylpyrimidine (DMAHDMPD) have been included. φ_r values have been calculated employing (PDS)=1 mM.
[b] nr: no reaction was observed; nd: not determined.
[c] Data from Ref. [5].
[d] Data from Ref. [7].
[e] Data from Ref. [8].

of the k_r value in pH 11 aqueous solution.The data obtained for AHPD and AHMPD through the TRPD method were treated according to Eq. (7) (Fig. 3). Table 1 shows the k_t values in pD 6 and pD 11 D_2O solutions for AHPD and AHMPD, and in MeCN/D_2O 4:1, with or without KOH, for the last compound, as well as the respective φ_r values in H_2O or MeCN/H_2O 4:1. The latter values range between 0.005 and 0.50, depending on the solvent and the pH of the medium.

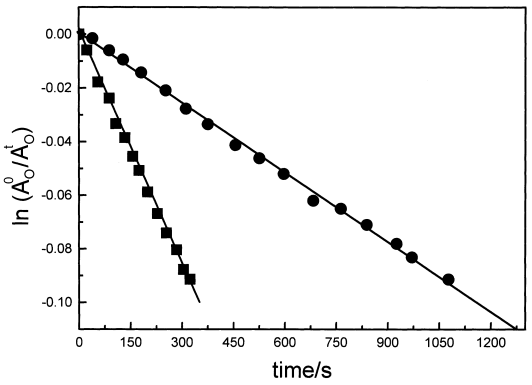


Fig. 2. First order plots for the oxygen uptake of 2-amino-4-hydroxy-6-methylpyrimidine (5.0×10^{-3} M) (●), and furfuryl alcohol (FFA) (5.0×10^{-3} M, the reference) (■), upon Rose Bengal sensitized irradiation in pH 11 H_2O solution. A_o^0 and A_o^t represent oxygen concentrations at time t=0 and t=t, respectively.

The evolution of the number of reactive NH_2 groups during the sensitized photooxidation of AHMPD in pH 11 water, determined by fluorimetric analysis (see Section 2), is shown in Fig. 4. The observed dependence was reproducible within a 3% dispersion. It can be observed as a continuous increase in the fluorescence signal as the photooxidation progresses, indicating the simultaneous generation of primary amino groups. Blank runs of the same solutions without irradiation did not produce fluorescence emission. This technique has been previously employed with success by the authors to demonstrate the evolution of peptide bonds upon sensitized photooxidation of polypeptides [14,15].

4. Discussion

All $O_2(^1\Delta_g)$-mediated photooxidations of compounds possessing aromatic OH groups have two common features [2]: (a) the overall $O_2(^1\Delta_g)$ quenching is favored (i.e. the

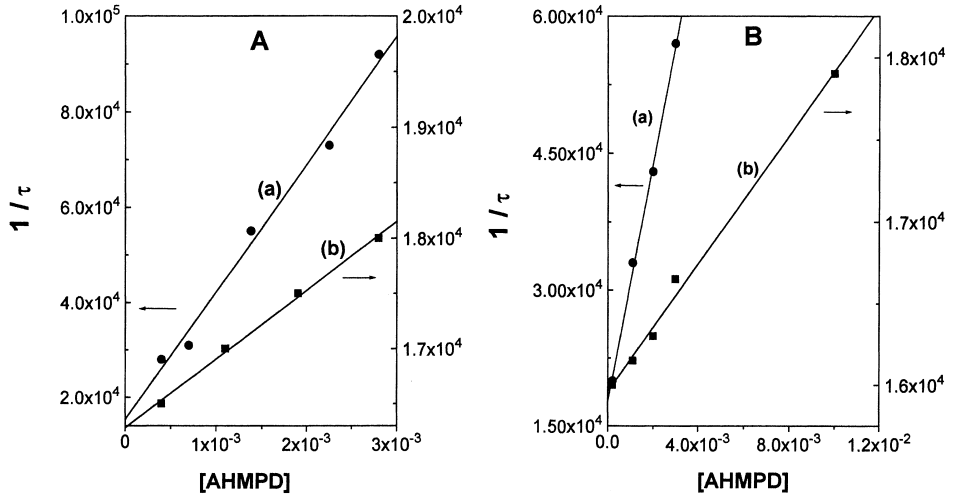


Fig. 3. Stern–Volmer plots for the overall quenching of $O_2(^1\Delta_g)$ by 2-amino-4-hydroxy-6-methylpyrimidine. Panel A: in pD 11 D_2O (a), and pD 6 D_2O (b). Panel B: in MeCN/D_2O 4:1 in the presence (a) and in the absence (b) of 0.01 M KOH.

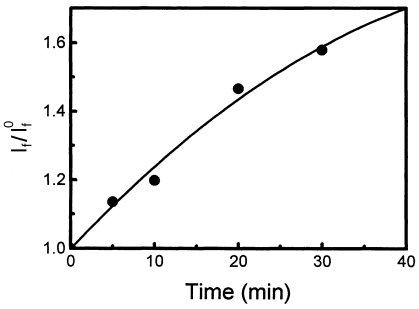


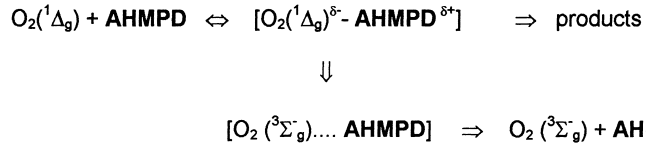
Fig. 4. Temporal evolution of the relative fluorescence intensity in the sensitized photooxidation of AHMPD in pH 11 water solution after addition of fluorescamine. I_f^0 and I_f are the fluorescence intensities in the absence and in the presence of this amine-complexing reagent.

k_t value increases) when the solvent polarity increases; and (b) k_t values are ca. two orders of magnitude higher for the species with the OH group in ionized form, while the reactive quenching of $O_2(^1\Delta_g)$ is hardly observed when the OH group is not ionized. These characteristics have been rationalized on the basis of a photooxidation mechanism involving an intermediate complex possessing partial charge-transfer character, in a similar fashion to the well known medium dependence of the kinetic photooxidation behavior of phenols [16–19] and other hydroxyaromatic compounds [5,6].

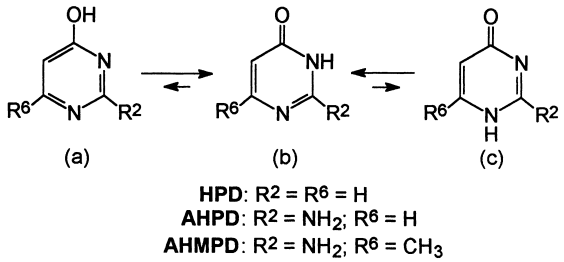
In the cases of AHPD and AHMPD, the same mechanism can be envisaged (Scheme 1), thus, explaining the higher values obtained for the rate constants k_t and k_r in alkaline media, where the electron releasing ability of the hydroxy group is enhanced by ionisation.

The φ_r values deduced in the present work for AHMPD indicates that in this compound the reactive quenching component is more important in pure water, either in the absence or in the presence of alkali, than in MeCN/water. In other words, in a higher polar environment a higher proportion of the $O_2(^1\Delta_g)$-quenching events results in AHMPD photodegradation.

Total absence of reactivity was observed in the simpler compounds PD, APD, HPD and MPD. In the particular case of HPD, its lack of reactivity, even in the presence of alkali, seems not in accord with the already commented effect of an OH group as such or in ionized form on the kinetics of PDS photooxidations, i.e. said group in a pyrimidine molecule constitutes a necessary, but not a sufficient condition for the interaction with $O_2(^1\Delta_g)$. This lack of reactivity in HPD is a consequence of the predominant, or exclusive, presence in water solution of the corresponding tautomeric 4-oxo forms (b) (major) and (c) (minor) (Scheme 2) [20,21], much less aromatic than the 4-hydroxy form (a) and, hence, much less reactive towards the well-known electrophilic reagent $O_2(^1\Delta_g)$ [4]. A similar equilibrium can be envisaged in the case of AHMPD, because it is known that in the related compound AHPD the corresponding 2-amino-4-oxo forms coexist in aqueous solution [21], and possible zwitterionic structures have been disregarded. In the presence of alkali,



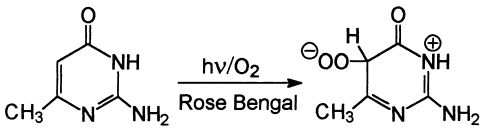
Scheme 1. Quenching of singlet molecular oxygen $[O_2(^1\Delta_g)]$ by 2-amino-4-hydroxy-6-methylpyrimidine (AHMPD).



Scheme 2. Possible tautomeric forms in 4-hydroxypyrimidines HPD, AHPD and AHMPD.

the OH-ionized form of structure (a) predominates, and the reaction with $O_2(^1\Delta_g)$ is favored, as the experimental evidence demonstrates for the case of AHPD, where a total absence of reactivity was observed in pH/pD 6 media. The pH effect on the reactive rate constant k_r is qualitatively similar to that observed for simple substituted phenols, although AHMPD is moderately reactive even under conditions in which the OH group is not ionized, because the presence of both the 2-amino and, specially, 6-methyl groups increases the electron donor ability of the substrate and, consequently, favors the generation of the charge transfer-mediated encounter complex postulated in Scheme 1.

We have not analyzed the products of the sensitized photooxidation of AHMPD. However, some information about the oxidative pathway can be extracted from the conjunctive analysis of the stoichiometric factor α (Eq. (9)), the presence of clear isosbestic points in the irradiated mixtures (Fig. 1), and the evolution of the primary amino groups (Fig. 4). The first two experimental facts are in agreement with the primary generation in the reaction AHMPD+O_2 of a zwitterionic intermediate such as that shown in Scheme 3, formerly proposed by Dixon and Wells [8] for the sensitized photooxidation of the 2-diethylamino analog DEAHMPD (Table 1). In addition, the kinetic fluorimetric analysis by fluorescamine complexation of primary amino groups points to the generation of at least one additional NH_2 group, obviously through ring cleavage in further reaction steps. Although for the moment we have not enough experimental evidence for suggesting a possible chemical pathway for the secondary processes, the cited zwitterionic intermediate can undergo plausible reactions that could account for these observations, such as subsequent rearrangement to 1,2-dioxetane, followed by cleavage to a dicarbonyl compound and further reactions yielding products of lower molecular weight, a mechanism likely similar to the one formerly suggested for the case of the photooxidation of 3-hydroxypyridine [6].



Scheme 3. Possible primary photoreaction in the Rose Bengal sensitized photooxidation of AHMPD.

From the results herein shown, it can be concluded that if $O_2(^1\Delta_g)$ were photogenerated under field conditions, photooxidation of pyrimidine-type fungicides related to AHMPD might be expected to occur, in competence with other naturally occurring photoprocesses. Ruling out the use of direct photoreactions, the sensitized photooxidation appears as an interesting alternative pathway of degradation, as the photooxidation quantum efficiencies herein found indicate.

Acknowledgements

Thanks are given to CONICOR, CONICET and SECyT UNRC and SECyT UNPA (Argentine), and to CSIC and the Ministerio de Educación y Cultura (Spain) for financial support.

References

[1] C. Tomlin (Ed.), The Pesticide Manual, British Crop Protection Council and The Royal Society of Chemistry, UK, 1994.
[2] N.A. García, J. Photochem. Photobiol. B: Biol. 22 (1994) 185–196.
[3] T. Alseberg, L. Balk, K. Nylund, C. de Wit, A. Bignert, M. Olson, T. Odsjö, Persistent Organic Pollutants and the Environment, AB Fälths Tryckeri, Värnamo, 1994, p. 125.
[4] F. Wilkinson, W.P. Helman, A.B. Ross, J. Phys. Chem. Ref. Data 22 (1993) 663–1021.
[5] A. Pajares, J. Gianotti, E. Haggi, G. Stettler, F. Amat-Guerri, S. Criado, S. Miskoski, N.A. García, J. Photochem. Photobiol. A: Chem. 119 (1998) 9–14.
[6] F. Amat-Guerri, A. Pajares, J. Gianotti, E. Haggi, G. Stettler, S. Bertolotti, S. Miskoski, N.A. García, J. Photochem. Photobiol. A: Chem. 126 (1999) 59–64.
[7] G.J. Harkness, C.H.J. Wells, Pesticide Sci. 12 (1981) 215–218.
[8] S.R. Dixon, C.H.J. Wells, Pesticide Sci. 14 (1983) 444–448.
[9] S. Nonell, L. Moncayo, F. Trull, F. Amat-Guerri, E.A. Lissi, A.T. Soltermann, S. Criado, N.A. García, J. Photochem. Photobiol. B: Biol. 29 (1995) 157–162.
[10] M.C. Palumbo, N.A. García, G. Argüello, J. Photochem. Photobiol. B: Biol. 7 (1990) 33–42.
[11] F.E. Scully, J. Hoigné, Chemosphere 16 (1987) 681–694.
[12] W.R. Hagg, J. Hoigné, Environ. Sci. Technol. 20 (1986) 341–348.
[13] R.C. Straight, J.D. Spikes, Photochem. Photobiol. 27 (1978) 565–569.
[14] S. Criado, A.T. Soltermann, N.A. García, Amino Acids 8 (1995) 367–377.
[15] S. Criado, A.T. Soltermann, J.M. Marioli, N.A. García, Photochem. Photobiol. 68 (1998) 453–458.
[16] C.S. Foote, in: Alan R. Liss (Ed.), Mechanisms of Photooxygenation in Porphyrin Localization and Treatment of Tumors, New York, 1984.
[17] M.J. Thomas, C.S. Foote, Photochem. Photobiol. 27 (1978) 683–693.
[18] M. Luiz, M.I. Gutiérrez, G. Bocco, N.A. García, Can. J. Chem. 71 (1993) 1247–1252.
[19] G. Bocco, M. Luiz, M.I. Gutiérrez, N.A. García, J. Prakt. Chem. 336 (1994) 243–246.
[20] D.J. Brown, S.F. Mason (Eds.), The Pyrimidines, Interscience, New York, 1962.
[21] J. Elguero, C. Marzin, A.R. Katritzky, P. Linda, The Tautomerism of Heterocycles (Advances in Heterocyclic Chemistry, Suppl. 1), A.R. Katritzky, A.J. Boulton (Eds.), Academic Press, New York, 1976.