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Kinetic study of the singlet molecular oxygen-mediated photodegradation of monohydroxylated *N*-heteroaromatic compounds

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Abstract

The kinetics of the dye-sensitized photooxygenation of the monohydroxylated *N*-heteroaromatic compounds, 2-hydroxypyridine, 3- hydroxypyridine, 4-hydroxypyridine, 4-hydroxyquinoline, 8-hydroxyquinoline, 2-hydroxypyrimidine and 4-hydroxypyrimidine, with the basic structures of some pesticides, has been studied. Rate constants in the range 10^6–10^8 M^{-1} s^{-1} for both the overall and the reactive singlet molecular oxygen [$O_2(^1\Delta_g)$] quenching were determined by time-resolved $O_2(^1\Delta_g)$ phosphorescence detection and polarographic methods. Photooxidation quantum yields were in the range of 0.01–0.50 in the cases where reaction was observed, with values significantly higher in aqueous media. The hydroxy substituent plays a key role in the photooxidative process. In 2- and 4-hydroxypyridines, 4-hydroxyquinoline and 4-hydroxypyrimidines the predominant, and almost exclusive, presence of the tautomeric oxo form drastically suppresses the interaction with $O_2(^1\Delta_g)$. In the case of 3-hydroxypyridine and 8-hydroxyquinoline, compounds with hydroxy form, the OH-ionization greatly enhances the photooxidative process. Experimental evidence suggests the participation of a charge-transfer mediated mechanism, involving an initial excited encounter complex. © 1998 Elsevier Science S.A. All rights reserved.

Keywords: Hydroxypyridines; Hydroxypyrimidines; Hydroxyquinolines; Pesticides; Photooxidation; Singlet molecular oxygen

1. Introduction

Herbicides and, in general, pesticides constitute one of the most frequent and powerful sources of environmental contamination because of their broad employment for agricultural purposes. Photodecomposition is known to be a determining factor that influences the natural chemical evolution of contaminants as well as the strategies of programmed decontamination. In this context, as most common contaminants are transparent to natural daylight, sensitized photooxidations and, in particular, singlet-molecular-oxygen [$O_2(^1\Delta_g)$] mediated processes appear as potential photochemical alternatives, because the only requirement is the coincidence of dissolved oxygen in the pesticide-polluted medium, day-light and a daylight-absorbing impurity. This scheme is very often fulfilled under natural environmental conditions.

Since many widely used pesticides have *N*-heteroaromatic groups in their molecular structure [1], the knowledge of the behavior of said groups in the environment is vitally important. Very few works [2–5] have been devoted to the study of these compounds as $O_2(^1\Delta_g)$ deactivators, possibly due to the low reactivity of these chemicals towards the excited oxygen species. Nevertheless, it is known that in some cases the photooxidative reactivity can be enhanced by adequate choice of experimental conditions such as solvent polarity, pH, presence of detergents, etc. In this paper we present a kinetic study of the interaction of the dye-promoted $O_2(^1\Delta_g)$ with some hydroxylated *N*-heteroaromatic derivatives (OH-ND): the three hydroxypyridines, two hydroxyquinolines and one hydroxypyrimidine. The research was mainly conducted to determine the experimental conditions that maximize the photodegradation quantum efficiency of OH-ND.

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2. Materials and methods

2.1. Chemicals

Rose Bengal (RB), 9,10-dimethylanthracene (DMA), furfuryl alcohol (FFA) and the OH-ND 2-hydroxypyridine (**1**), 3-hydroxypyridine (**2**), 4-hydroxypyridine (**3**), 4-hydroxyquinoline (**4**), 8-hydroxyquinoline (**5**) and 4-hydroxypyrimidine (**6**) were purchased from Sigma. For kinetic determinations the following solvents were employed: acetonitrile (MeCN), and methanol (MeOH), both from Sintorgan, Argentine, and D_2O (99.9% D) from Sigma. Water was triply distilled. The pD values were estimated by adding 0.4 units to the known pH values [6]. pH 11 and pD 11 solutions were obtained by the addition of KOH. The organic solvent mixture MeCN–MeOH 9 : 1 v/v was made alkaline by adding KOH in MeOH up to 10 mM.

2.2. Time resolved phosphorescence detection (TRPD)

The laser-kinetic spectrophotometer has been previously described [7]. Briefly, it consisted in 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 at right angles (using an amplified Judson J16/8Sp germanium detector) 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. Usually 16 shots were needed for averaging, in order to get a good signal/noise ratio, from which the decay time was calculated. Air-equilibrated solutions were employed in all cases.

The solutions containing the sensitizer (RB) had $\mathrm{Abs}_{532} = 0.2$–0.4.

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

$$1/\tau = 1/\tau^0 + k_t[\text{OH-ND}] \tag{1}$$

being k_t the overall rate constant for $O_2(^1\Delta_g)$ quenching (see the kinetic scheme (Eqs. (2)–(6)) in Section 3).

2.3. Static photolysis

The irradiation device, including the specific oxygen electrode, has been described elsewhere [8]. The $O_2(^1\Delta_g)$ was generated by irradiation of the solutions (containing the sensitizer plus the individual OH-ND) at wavelengths greater than 500 nm (cut-off filters ensure that the light was only absorbed by the sensitizer). Light of a 150 W quartz-halogen lamp was passed through a water filter and focused onto the reaction vessel (either the spectrophotometric cuvette or the hermetically sealed oxygen electrode reaction cell) containing the continuously stirred solutions.

2.4. Determination of photooxidation rate constants

The rate constants for chemical reaction with $O_2(^1\Delta_g)$ of OH-ND were determined by different comparative methods [9], depending on the solvent. In all the cases the reactive rate constant for the sensitized photooxidation of a reference compound (R) must be known. In organic-solvent media R was DMA, and in these cases the rates of disappearance of OH-ND and reference compound were compared. The k_{rR} values for DMA were 1.2×10^7 and $5.2 \times 10^7\ \mathrm{M^{-1}\,s^{-1}}$, evaluated from TRPD in MeCN–MeOH and MeCN–MeOH–10 mM KOH, respectively. The loss of DMA upon sensitized irradiation was monitored by spectrofluorimetry, employing 395 and 450 nm as excitation and emission wavelengths, respectively. The loss of each OH-ND (in concentrations in the order of 0.1 mM), for conversions lower than 10% was monitored by absorption spectroscopy. In both cases (R and OH-ND) the respective fluorescence and absorption spectra were recorded at different irradiation times.

Parallel experiments of substrate consumption vs. irradiation time in oxygen-saturated solutions containing the sensitizer (RB, $\mathrm{Abs}_{560} = 0.5$) plus either DMA or OH-ND were run. Assuming that the chemical reaction of $O_2(^1\Delta_g)$ with the quencher is the only way for substrate consumption, the ratio of the first order slopes of OH-ND and R disappearance (both at identical concentrations) yields k_r/k_{rR}.

In water the method for k_r determination was essentially the same as in MeCN–MeOH, except that in this case the ratio of the first order slopes of oxygen uptake, upon sensitized irradiation of individual air-saturated solutions containing OH-ND and FFA were compared, being their respective concentrations in the order of 5 mM. The reference was FFA [10] with $k_{rR} = 1.2 \times 10^8\ \mathrm{M^{-1}\,s^{-1}}$. The oxygen electrode (Orion 97–08) has a membrane which can only be used in media containing a high percentage of water (typically >95%).

Ground state absorption measurements were carried out with a Hewlett Packard 8452A diode array spectrophotometer. The spectrofluorometer employed was a Spex Fluoromax apparatus.

3. Results

When solutions of compounds **1**, **2**, **4** or **5**, in water or in the organic solvent mixture MeCN–MeOH 9 : 1, were irradiated in the presence of the well known $O_2(^1\Delta_g)$ sensitizer RB [11], important changes were observed in their respective absorption spectra (see representative changes for compounds **2** and **5** in Fig. 1(A) and (B), respectively). No photoreaction was observed in compounds **3** and **6**. It is clear that in the former case the compounds are being transformed into a single or a constant mixture of products (presence of isosbestic points) with less absorption at the analytical wavelength, at least at the conversions used in this

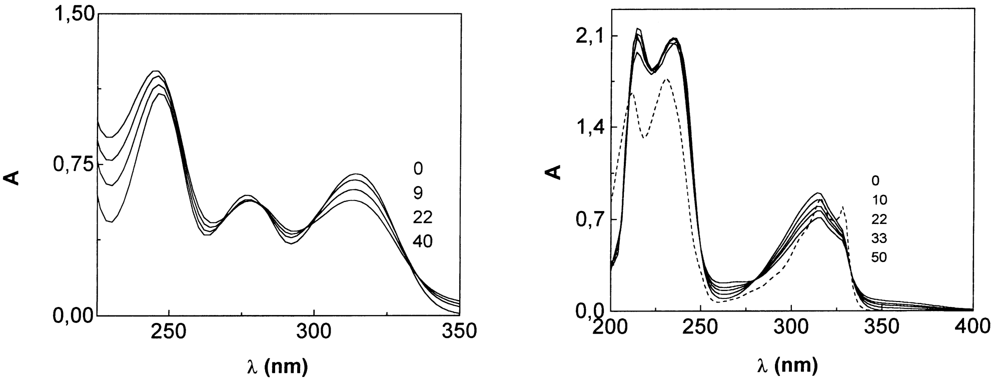


Fig. 1. Spectral evolution of 3-hydroxypyridine (**2**) in pH 6 water (panel A) and of 8-hydroxyquinoline (**5**) at pH 11 water (panel B, full lines); numbers on the spectra represent irradiation times in seconds. For comparison the spectrum of compound **5** at pH 6 is included (panel B, dashed line).

work, i.e. lower than 10%. As the absorption characteristics of these products are not known, photooxidation rate constant values obtained from these absorption decreases (Table 2) must be taken as lower, albeit fairly accurate limits. The reaction was totally suppressed in the absence of dissolved molecular oxygen, as well as in the presence of 10 mM NaN_3, a known selective $O_2(^1\Delta_g)$ quencher [2]. The spectral changes were comparatively faster, at the same irradiation fluences, when H_2O was replaced by D_2O. According to currently accepted criteria [12], the last three observations indicate that the photooxidation of OH-ND is largely an $O_2(^1\Delta_g)$-mediated (Type II) process. Furthermore, an unambiguous evidence for this interaction is given by the $O_2(^1\Delta_g)$ quenching experiments by TRPD (vide infra).

The following scheme (Eqs. (2)–(6)) summarizes the most important reactions, according to the preceding statements, where Sens represents a sensitizer, i.e. a species that absorbs radiation in a wavelength range (typically that of the visible light) where OH-ND are transparent:

$$\mathrm{Sens} + h\nu \rightarrow {}^*\mathrm{Sens} \qquad (2)$$

$$^*\mathrm{Sens} + O_2(^3\Sigma_g^-) \xrightarrow{k_{ET}} \mathrm{Sens} + O_2(^1\Delta_g) \qquad (3)$$

$$O_2(^1\Delta_g) \xrightarrow{k_d} O_2(^3\Sigma_g^-) \qquad (4)$$

$$O_2(^1\Delta_g) + \mathrm{OH\text{-}ND} \xrightarrow{k_q} O_2(^3\Sigma_g^-) + \mathrm{OH\text{-}ND} \qquad (5)$$

$$O_2(^1\Delta_g) + \mathrm{OH\text{-}ND} \xrightarrow{k_r} \mathrm{oxidized\ OH\text{-}ND} \qquad (6)$$

The incident light promotes Sens to electronically excited states (reaction [2]). From these states, an energy transfer reaction to the ground state-triplet molecular oxygen ($O_2(^3\Sigma_g^-)$), dissolved in the solution, can take place, yielding the excited state oxygen species $O_2(^1\Delta_g)$ (reaction [3]). This can decay either by collision with surrounding solvent molecules (reaction [4]) or by interaction with OH-ND through an exclusive physical processes (reaction [5]). Finally, reaction [6] represents the photooxidation pathway of OH-ND. The overall rate constant k_t represent the sum of the respective rate constants for physical and reactive processes ($k_t = k_q + k_r$).

From the $O_2(^1\Delta_g)$ decay analysis at several OH-ND concentrations, the values of k_t were determined (Tables 1 and 2) employing TRPD from linear Stern–Volmer plots (Fig. 2). No quenching of $O_2(^1\Delta_g)$ luminescence could be observed for compounds **3** and **6**, up to saturated solutions (ca. 5 mM). Hence, upper limits for k_t values in the order $\leq 5 \times 10^4\ M^{-1}\ s^{-1}$ can be assigned to these compounds.

The possible solvent-polarity effect on k_t (Tables 1 and 2) was analyzed by comparing the results obtained in water and MeCN–MeOH as solvents. The presence of alkali (see Tables) highly favors the OH-ND/$O_2(^1\Delta_g)$ interaction. Only compounds **2** and **5** gave positive $O_2(^1\Delta_g)$ quenching in non-alkaline solvents. For the determination of k_r, it was assumed that 1 : 1 stoichiometry holds for the chemical reaction $O_2(^1\Delta_g)$ + OH-ND (process [6]). The pseudo first order plots for compounds **1** and **2** in water are shown as typical examples in Fig. 3.

As we have already discussed [13,14], in $O_2(^1\Delta_g)$-mediated reactions the actual photooxidation can only be evaluated through the photooxidation quantum efficiency

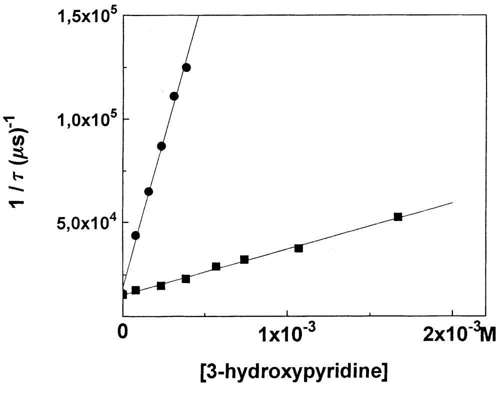
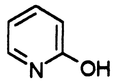
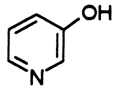
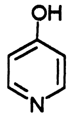
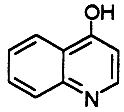
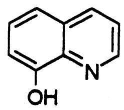
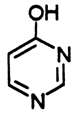


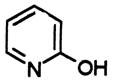
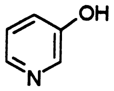
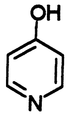
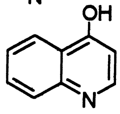
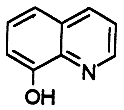
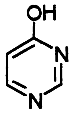
Fig. 2. Stern–Volmer plots for the singlet molecular oxygen quenching, determined by TRPD, of 3-hydroxypyridine (**2**) in D_2O, pD 6 (■), and pD 11 (●)

Table 1
Rate constants for overall (k_t, $M^{-1}\,s^{-1}$) and reactive (k_r, $M^{-1}\,s^{-1}$) quenching of $O_2(^1\Delta_g)$ by OH-ND, and photooxidation efficiencies (φ_r) in pH 6 or pH 11 aqueous media

Compound	Structure	pH	$k_t \times 10^{-8}$	$k_r \times 10^{-8}$	φ_r
1		6 11	NQ[a] 1.23	NQ[a] 0.20	 0.05
2		6 11	0.39 2.60	0.26 2.60	0.09 0.50
3		6 11	NQ[a] NQ[a]	NQ[a] NQ[a]	
4		6 11	NQ[a] 0.90	NQ[a] 0.26	 0.08
5		6 11	0.23 4.20	0.08 1.70	0.03 0.25
6		6 11	NQ[a] NQ[a]	NQ[a] NQ[a]	

[a]No quenching was observed up to concentrations ca. 0.005 M.

Table 2
Rate constants for overall (k_t, $M^{-1}\,s^{-1}$) and reactive (k_r, $M^{-1}\,s^{-1}$) quenching of $O_2(^1\Delta_g)$ by OH-ND, and photooxidation efficiencies (φ_r) in MeCN–MeOH 9 : 1 v/v with (yes) or without (no) 10 mM KOH

Compound	Structure	with 10 mM KOH	$k_t \times 10^{-8}$	$k_r \times 10^{-8}$	φ_r
1		no yes	NQ[a] 1.45	NQ[a] 0.03	 0.17
2		no yes	2.10 2.80	<0.001 0.81	<0.001 0.25
3		no yes	NQ[a] NQ[a]	NQ[a] NQ[a]	
4		no yes	NQ[a] 0.16	NQ[a] 0.030	 0.06
5		no yes	0.015 4.68	<0.001 0.052	<0.001 0.01
6		no yes	NQ[a] NQ[a]	NQ[a] NQ[a]	

[a]No quenching was observed up to concentrations ca. 0.005 M.

(φ_r) (Eq. (7))

$$\varphi_r = k_r[\text{OH-ND}]/(k_d + k_t[\text{OH-ND}]) \qquad (7)$$

The respective φ_r values were calculated from the kinetic data (Tables 1 and 2). The values employed in the calculations were $k_d = 2.5 \times 10^5\ s^{-1}$ [15], and $k_d = 3.3 \times 10^4\ s^{-1}$ (experimental result) in water and in MeCN–MeOH respectively, as well as an OH-ND concentration equals to 1 mM. As can be seen, the values of the photooxidation quantum efficiencies for the reactive OH-ND are in the range 0.01–0.50, with the highest values for compound **2**, that also exhibits a significantly high photodegradation efficiency: $\varphi_r = 0.48$ and 0.25 in aqueous and in organic alkaline media, respectively.

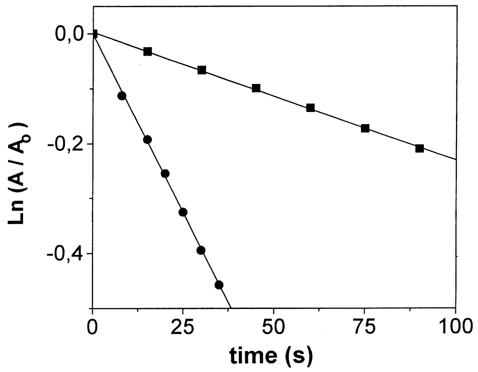


Fig. 3. Pseudo first order plots for the disappearance of 2-hydroxypyridine (**1**) (■), and 9,10-dimethylanthracene (●), in MeCN–MeOH–10 mM KOH, by reaction with $O_2(^1\Delta_g)$. A_o and A represent the respective maximum absorbances of the substrates at irradiation times $t = 0$ and $t = t$ respectively.

The increment in solvent polarity, on going from MeCN–MeOH to water, gave rise to pronounced increments in k_r values in the respective OH-ND.

4. Discussion

Phenols [16,17], polyhydroxybenzenes [18] and hydroxybiphenyls [19] are efficient physical and/or chemical scavengers of $O_2(^1\Delta_g)$. Nevertheless, the opposite can be said about their respective non-hydroxylated parent compounds [2]. Apparently, a similar phenomena has been here observed in the case of some OH-ND, if these derivatives are compared with the corresponding non-hydroxylated compounds. Literature reports indicate a k_t value of $2 \times 10^3\ M^{-1}\,s^{-1}$ for pyridine in CCl_4 [3], and no measurable effect as $O_2(^1\Delta_g)$ quenchers for quinoline [4] and pyrimidine [2]. In this context we can say from our results that the presence of an OH group as a nuclear substituent in pyridines and quinolines constitute a necessary condition for the $O_2(^1\Delta_g)$ quenching. The case of pyrimidines will be discussed later.

The comparison of the kinetic data in Tables 1 and 2 indicates a dramatic increase in the rate constants k_t and k_r in the presence of alkali, and the absence of a remarkable solvent polarity effect on k_t. These results and, particularly, the alkali effect on the rate constants are coincident with those already observed for bimolecular reactions between $O_2(^1\Delta_g)$ and phenols [13] through a mechanism involving an excited encounter complex (Eq. (8))

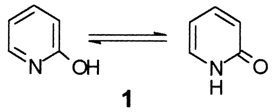
$$O_2(^1\Delta_g) + \text{OH-ND} \Leftrightarrow [O_2(^1\Delta_g)\cdots\text{OH-ND}] \Rightarrow \text{products} \qquad (8)$$

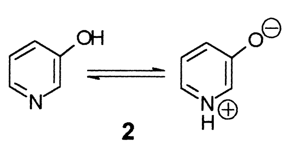
$$\Downarrow$$

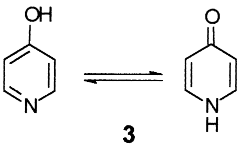
$$[O(^3\Sigma_g^-)\cdots\text{OH-ND}]2 \Rightarrow O_2(^3\Sigma_g^-) + \text{OH-ND}$$

According to this mechanism, both physical quenching and chemical reaction can operate, the relative importance of each process reflected by the respective k_q and k_r values (Eqs. (5) and (6)). The kinetics of the $O_2(^1\Delta_g)$-quenching process is mainly affected by the electron-donor ability of the substrate. This is in agreement with the higher values for the rate constants in alkaline media, accounting for the enhancement of the electron releasing ability of ionized hydroxy groups. Nevertheless, the defined solvent-polarity effect that often accompanies charge transfer-mediated mechanisms could be only observed on the reactive rate constant k_r. The global results definitively show higher φ_r values in water.

Relatively low or total absence of reactivity was observed in compounds **1**, **3**, **4**, and **6**, all of them with the OH group in *ortho* or *para* positions with regard to a heterocyclic nitrogen. This lack of reactivity is a consequence of the predominant, or exclusive, presence in both aqueous and organic media of the corresponding tautomeric oxo forms (shown for the hydroxypyridines **1** and **3** below), much less aromatic than the hydroxy forms [20,21] and, hence, much less reactive towards the well-known electrophilic reagent $O_2(^1\Delta_g)$ Eq. (3). On the contrary, the OH form in compound **2** is in equilibrium with the N-protonated zwitterionic tautomer (see below) [20,21], and the reaction with $O_2(^1\Delta_g)$ is much more efficient, as the experimental results confirm. No tautomeric equilibrium is possible in compound **5**.


1


2


3

As far as we know, no literature information exists on the kinetics of the interaction $O_2(^1\Delta_g)$-hydroxypyridines.

Regarding the OH-quinoline family, the only datum related to our present investigation is a k_t value of $1.1 \times 10^8\ M^{-1}\ s^{-1}$ for compound **5** in CCl_4 [5], i.e. two orders of magnitude higher than the one obtained in this work for the same derivative in the solvent mixture MeCN–MeOH. Since our k_t values have been determined by the TRPD method, in our opinion the published k_t value must likely be overestimated due to the use of the Carlsson method [22], which employs the polyaromatic compound rubrene with the double function of sensitizer and sacrificial substrate. In this indirect method, a frequent source of error is to ignore the possible interaction of excited singlet and/or triplet rubrene with the substrate [23].

Only some hydroxypyrimidine derivatives structurally related to compound **6** have been reported as $O_2(^1\Delta_g)$-quenchers. They form the series of systemic pyrimidine fungicides with the basic structure 3,5-dialkyl-2-amino-4-pyrimidinol. Overall rate constants in the order of 10^6–$10^7\ M^{-1}\ s^{-1}$ have been determined for these derivatives in chloroform [24] and in water [25]. This moderate reactivity, as compared with the total absence of reactivity found in our experiments on the parent hydroxy derivative, is justified by the presence in the molecule of activating nuclear alkyl groups that favor the interaction with the electrophilic $O_2(^1\Delta_g)$, and of the amino group, a well known moderate $O_2(^1\Delta_g)$-quencher [2].

5. Conclusion

The position of the hydroxy group in the monohydroxylated pyridines, quinolines and pyrimidines herein studied plays a key role in the efficiency of their interaction with $O_2(^1\Delta_g)$. In 2- and 4-hydroxypyridines and 2- and 4-hydroxypirimidines the exclusive presence of the tautomeric oxo form drastically suppresses the interaction with $O_2(^1\Delta_g)$. In hydroxylated *N*-heterocycles with hydroxy forms, the OH-ionization greatly enhances the photooxidative pathway, the enhancement greatly depending on the solvent polarity and, particularly, on the pH of the medium. In these compounds the experimental evidence suggests the participation of a charge-transfer mediated mechanism involving an initial encounter excited complex between $O_2(^1\Delta_g)$ and the hydroxylated *N*-heteroaromatic derivative.

From the point of view of the natural or programmed photodegradation of pesticides with structures related to these *N*-heteroaromatic compounds, the sensitized photooxidation through a $O_2(^1\Delta_g)$-mediated process appears as an interesting alternative, in special in the presence of alkali.

Work is in progress in order to determine the nature of the photooxidation products.

Acknowledgements

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