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# Singlet molecular oxygen-mediated photooxidation of 2-substituted 3-hydroxypyridines

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## Abstract

The kinetics of the Rose Bengal sensitised photooxidation of six 2-substituted 3-hydroxypyridines and the parent compound 3-hydroxypyridine (3-OHP), all with the basic molecular structure of known pesticides, have been studied in solution in neutral or alkalinised water or acetonitrile-water 4 : 1. The kinetic constants of the involved chemical ($k_r$) and overall ($k_t$) singlet molecular oxygen [$O_2$ ($^1\Delta_g$)] quenching processes have been determined by comparative methods based on absorbance changes, oxygen uptake, or time-resolved phosphorescence detection. The results indicate that both rate constants are in the order range $10^5$–$10^8$ $M^{-1}$ $s^{-1}$, except in the case of 2-carboxy-3-hydroxypyridine in water, where no chemical reaction was detected. The $k_t$ value increases with electron-releasing substituents at position 2, as well as in water or alkaline media, pointing to a quenching process through a polar complex [$O_2$ ($^1\Delta_g$)-substrate]. All 3-hydroxypyridines are photooxidised, with quantum efficiencies as high as 0.66 for 2-methyl-3-hydroxypyridine. The photooxidation products from 3-OHP in water have been analysed by GC/MS. Products from the pyridine ring cleavage, as well as 2,3-dihydroxypyridine, have been detected. All can be derived from a 1,2-dioxetane intermediate formed by $O_2$ ($^1\Delta_g$) addition to the 2,3-positions of the pyridine ring. ©1999 Elsevier Science S.A. All rights reserved.

*Keywords:* Photo-oxidation; Singlet molecular oxygen; 3-Hydroxypyridines

## 1. Introduction

Hydroxylated aromatic contaminants, including nitrogen-containing aromatic heterocycles, are widely present at waters and soils. Among the possible pathways for their natural degradation to non-toxic products, the photochemical decay can became the most important one under favourable environmental conditions, in special in sunny countries. When the aromatic contaminant absorbs light in the near-UV zone, it can be degraded in an aqueous environment through the direct oxidation of its electronically excited state with the dissolved oxygen, or through the reaction of the contaminant with singlet molecular oxygen [$O_2(^1\Delta_g)$] generated by energy transfer from the excited contaminant to ground state oxygen. On the other hand, when the contaminant does not absorb any wavelength of the sunlight, the degradation can also be carried out through the $O_2(^1\Delta_g)$ pathway if a coloured compound, able to generate this excited oxygen species, is present in the medium. In the particular case of hydroxylated aromatic *N*-heterocycles, this pathway can be very efficient, because it has been demonstrated that many of these compounds are easily oxidised with $O_2(^1\Delta_g)$ [1].

In order to know more about the natural photochemical decay of the former *N*-heterocycles, in a recent paper [2] we have reported the kinetics of the dye-sensitised photooxygenation of several hydroxypyridines, hydroxyquinolines and hydroxypyrimidines with the basic molecular structures of known *N*-heteroaromatic pesticides [3] searching the conditions that maximise the dye-promoted photooxidation of the related contaminants. With the dye Rose Bengal as sensitiser, a $O_2(^1\Delta_g)$-mediated mechanism operates, with photooxidation quantum efficiencies in the range 0.01–0.85 for the reactive compounds, being hydroxypyridines in general, and 3-hydroxypyridine (3-OHP) in particular, the most susceptible derivatives towards photooxidation. Following

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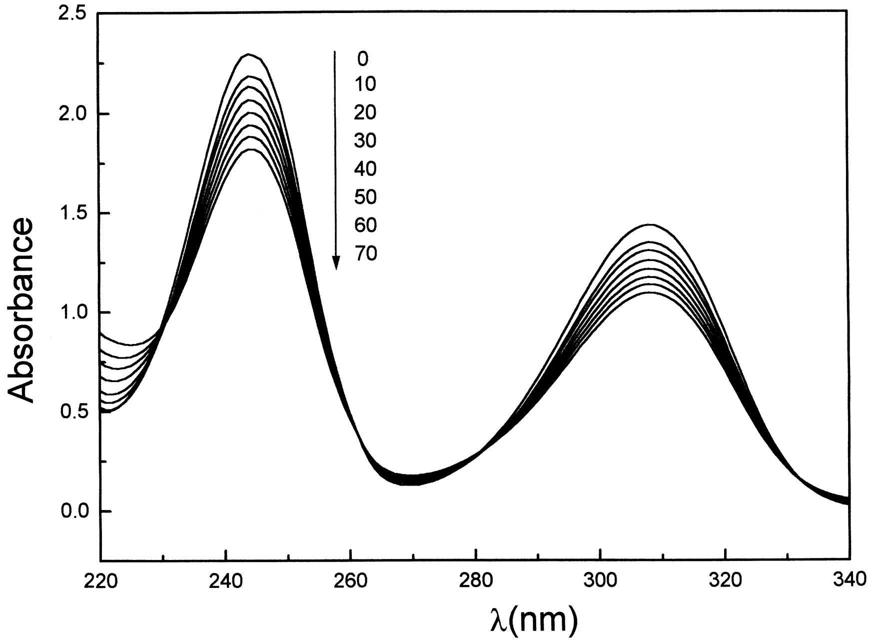


Fig. 1. Spectral changes in the Rose Bengal-sensitised irradiation of 2-amino-3-hydroxypyridine in pH 11 $H_2O$. Numbers are irradiation times in seconds.

this line, in the present work we report on the kinetics of the Rose Bengal-sensitised photooxidation of six 2-substituted 3-hydroxypyridines (see structures in Table 1), as well as the parent compound 3-OHP. As the full understanding of the photodegradation process requires the identification of the resulting compounds, the analysis of the products obtained in the sensitised photooxidation of 3-OHP is also reported.

## 2. Experimental

### 2.1. Materials

3-Hydroxypyridine (3-OHP), 2-methyl-3-hydroxypyridine (2-Me-3-OHP), 2-amino-3-hydroxypyridine (2-Am-3-OHP), 2-chloro-3-hydroxypyridine (2-Cl-3-OHP), 2-bromo-3-hydroxypyridine (2-Br-3-OHP), 2-carboxy-3-hydroxypyridine (2-C-3-OHP) and 2-carboxamide-3-hydroxypyridine (2-CA-3-OHP), as well as Rose Bengal and 9,10-dimethylanthracene (DMA), were from Aldrich and were used without further purification. Furfuryl alcohol (FFA) was from Riedel-de Haën. The following solvents were employed for kinetic determinations: acetonitrile (MeCN, HPLC quality) from Sintorgan, $D_2O$ (99.9% D) from Sigma, and triply distilled water. pH 11 and pD 11 solutions were obtained by the addition of NaOH to $H_2O$ or $D_2O$, respectively, measuring with a pH-meter. The pD values were estimated by adding 0.4 units to the observed pH values [4]. The solvent mixtures MeCN-$H_2O$ and MeCN-$D_2O$, both 4 : 1 v/v, were made alkaline (10 mM in NaOH) by preparing the mixtures with the corresponding 50 mM NaOH solution in $H_2O$ or $D_2O$.

### 2.2. Determination of photooxidation rate constants, $k_r$

The rate constant of the chemical reaction of each 3-hydroxypiridine with $O_2(^1\Delta_g)$, generated through Rose Bengal sensitisation ($Abs_{560} = 0.5$), was determined by the method of Foote and Ching [5] assuming that this reaction is the only way for substrate consumption, with a 1 : 1 stoichiometry. The irradiation device has been described elsewhere [6]. Cut-off filters ensure that the light was only absorbed by the sensitiser. The substrate loss was monitored by absorption spectroscopy in a Hewlett Packard 8452A diode array spectrophotometer. Typical spectral changes are shown in Fig. 1. The ratio of the slope of the first-order plot for substrate consumption versus the irradiation time ($slope_Q$), and the slope of a similar plot for a reference compound ($slope_{Ref}$) of known $k_r$ value ($k_{rRef}$) (both at identical concentrations), is equal to the ratio $k_r/k_{rRef}$. MeCN-$H_2O$ 4 : 1 v/v and alkaline MeCN-$H_2O$ 4 : 1 v/v were used as solvents. As reference, DMA in MeCN-$H_2O$ 4 : 1 v/v ($k_{rRef} = 8.7 \times 10^7\ M^{-1}\ s^{-1}$, determined by time-resolved phosphorescence detection, TRPD) was employed.

The method for $k_r$ determination in $H_2O$ or pH 11 $H_2O$ was essentially the same, except that in this case the ratio of the first order slopes of oxygen uptake by substrate and reference (FFA in $H_2O$, $k_{rRef} = 1.2 \times 10^8\ M^{-1}\ s^{-1}$[1]), determined with an oxygen electrode (Orion 97-08) [6], was used. A typical plot is shown in Fig. 2. As before, the ratio $slope_Q/slope_{Ref}$ is equal to the ratio $\alpha k_r/k_{rRef}$, where $\alpha$ is the stoichiometric coefficient of oxygen consumption by the 3-hydroxypyridine. The same coefficient for FFA is the unity [1].

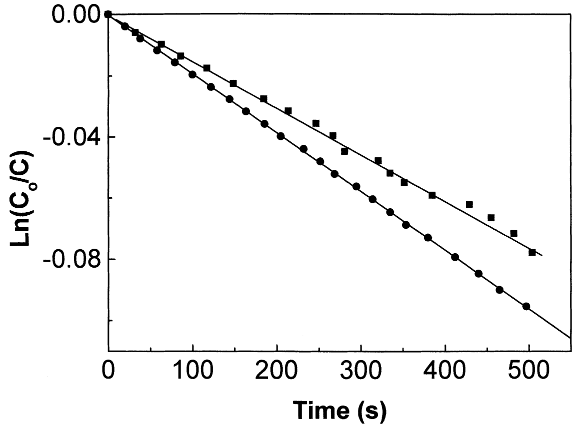


Fig. 2. First-order plots for the oxygen uptake by furfuryl alcohol (the reference, upper curve) and 2-amino-3-hydroxypyridine (lower curve) upon Rose Bengal-sensitised irradiation in pH 11 $H_2O$.

Oxygen consumption with time by FFA or the 3-hydroxypyridines was unambiguously first order, at least through three half-lives (not shown). The same was true for most of the experiments where the substrate disappearance (either the reference DMA or the pyridine derivative) was monitored by absorption spectroscopy. However, some tailing in the first order plots was observed for the less reactive 3-hydroxypiridines 2-C-3-OHP and 2-CA-3-OHP at high conversions, possibly as a consequence of the appearance of reaction products and/or the bleaching of the sensitiser due to prolonged irradiation. In order to avoid or minimise this tailing, only less than 15% absorption changes were considered.

### 2.3. Determination of overall rate constants, $k_t$

The rate constant of the overall $O_2(^1\Delta_g)$ quenching of each compound, $k_t$ (being $k_t = k_r + k_q$, where $k_q$ is the rate constant of the physical quenching), was determined by Stern–Volmer treatment, evaluating $O_2(^1\Delta_g)$ lifetimes by TRPD in the absence ($\tau_0$) and in the presence ($\tau$) of the quencher Q, and applying the expression $1/\tau = 1/\tau_0 + k_t[Q]$ (Fig. 3). As solvents, $D_2O$, pD 11 $D_2O$, MeCN-$D_2O$ 4 : 1 v/v and alkaline (10 mM NaOH) MeCN-$D_2O$ 4 : 1 v/v, were used. The sensitiser Rose Bengal ($Abs_{532}$ in the range 0.5–0.6) was excited with the frequency-doubled output (532 nm) of a Nd:YAG laser previously described [7]. The emitted radiation (mainly 1270 nm) was detected at right angles using an amplified Judson J16/8Sp germanium detector, after passing through appropriate filters. The output of the detector was coupled to a digital oscilloscope and to a computer for processing the signal. Sixteen shots were usually needed for averaging, in order to get a good signal-to-noise ratio, from which the lifetimes were calculated.

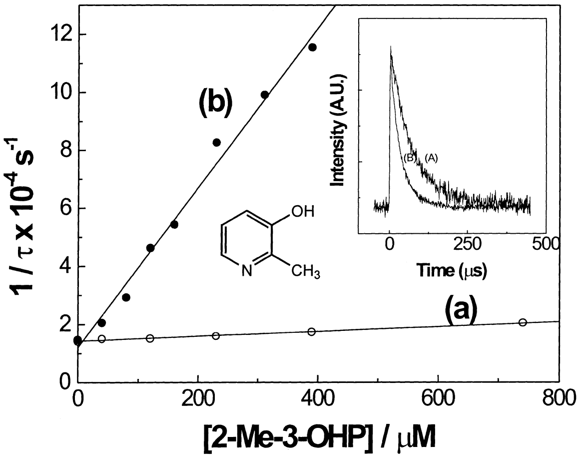


Fig. 3. Stern–Volmer plots for the quenching of the time resolved phosphorescence emission of $O_2(^1\Delta_g)$ by 2-methyl-3-hydroxypyridine in MeCN : $D_2O$ 4 : 1 v/v (a), and in alkaline MeCN : $D_2O$ 4 : 1 v/v (b). Inset: decay of the $O_2(^1\Delta_g)$ emission in alkaline MeCN : $D_2O$ 4 : 1 v/v in the absence (A) and in the presence (B) of $1.2 \times 10^{-4}$ M 2-methyl-3-hydroxypyridine. Rose Bengal as sensitiser, excitation at 532 nm.

### 2.4. Determination of photooxidation quantum efficiencies $\varphi_r$

They were calculated for each 3-hydroxypyridine (Q) with the expression $\varphi_r = k_r[Q]/(k_d + k_t[Q])$, were $k_d$ is the rate constant for $O_2(^1\Delta_g)$ deactivation by interaction with solvent molecules. The described $k_d$ values in $H_2O$ ($2.5 \times 10^5\ s^{-1}$ [8], and in MeCN-$H_2O$ 4 : 1 v/v ($3.0 \times 10^4\ s^{-1}$ [9], were used for $\varphi_r$ calculations in water or MeCN-water solutions, respectively.

### 2.5. Analysis of the photooxidation products of 3-hydroxypyridine (3-OHP)

Solutions in water (50 ml) or pH 11 water (50 ml, NaOH) of 3-OHP (20 mg, $4.2 \times 10^{-3}$ M) and Rose Bengal (1 mg) were externally irradiated in a pyrex flask with a 200 W tungsten lamp, while stirring and cooling with circulating air, and the reactions were followed by spectroscopy (1 : 10 dilution). After less than 50% UV change, each solution was lyophylized. In the case of the irradiated alkaline solution, this was previously neutralised, while cooling at 0°C, with acetic acid, and the lyophylized residue was extracted with chloroform, the extract was filtered and the solvent was vacuum evaporated. In both cases, an aliquot of the dry residue was treated in methanol (5 ml) at 0°C with excess of diazomethane in ether, and the solvent was eliminated. The isolated reaction mixtures, as such or in methylated form, were dissolved in chloroform and analysed by tandem GC/MS in a HP 5890 Series II gas chromatograph equipped with a HP 5971 mass detector in the electronic impact mode (ionisation energy 70 eV), scanning the range 38–450 amu; a laboratory made capillary column (20 m × 0.25 mm × 0.1 mm)

Table 1
Rate constants of the overall ($k_t$) and chemical ($k_r$) reactions of singlet molecular oxygen with 2-substituted 3-hydroxypyridines (R is the substituent at the 2-position), and the calculated photooxidation quantum efficiencies ($\varphi_r$) for 1 mM substrate concentration. Estimated relative error for rate constants: 10%

| Compound | R | Solvent | $k_t \times 10^{-8}$[a] ($M^{-1}\,s^{-1}$) | $k_r \times 10^{-8}$[b] ($M^{-1}\,s^{-1}$) | $\varphi_r$ |
|---|---|---|---|---|---|
| 3-OHP | H | water | 0.39[c] | 0.26[c] | 0.09[c] |
| | | water + NaOH | 2.6[c] | 2.6[c] | 0.50[c] |
| | | MeCN/water | 0.037 | 0.016 | 0.05 |
| | | MeCN/water + NaOH | 2.0 | 1.31 | 0.57 |
| 2-Me-3-OHP | Me | water | 0.52 | 0.52 | 0.17 |
| | | water + NaOH | 3.1 | 2.8 | 0.50 |
| | | MeCN/water | 0.08 | 0.033 | 0.09 |
| | | MeCN/water + NaOH | 2.80 | 2.05 | 0.66 |
| 2-Am-3-OHP | $NH_2$ | water | 3.9 | 1.35 | 0.21 |
| | | water + NaOH | 6.6 | 2.9 | 0.32 |
| | | MeCN/water | 0.99 | 0.29 | 0.22 |
| | | MeCN/water + NaOH | 3.20 | 1.1 | 0.31 |
| 2-Cl-3-OHP | Cl | water | 0.64 | 0.12 | 0.04 |
| | | water + NaOH | 2.9 | 1.7 | 0.31 |
| | | MeCN/water | 0.25 | 0.24 | 0.44 |
| | | MeCN/water + NaOH | 1.86 | 0.99 | 0.46 |
| 2-Br-3-OHP | Br | water | 1.49 | 0.21 | 0.05 |
| | | water + NaOH | 1.56 | 1.56 | 0.38 |
| | | MeCN/water | 0.33 | 0.23 | 0.37 |
| | | MeCN/water + NaOH | 2.36 | 0.60 | 0.22 |
| 2-C-3-OHP | $CO_2H$ | water | 0.014 | no reaction | – |
| | | water + NaOH | 0.65 | 0.60 | 0.19 |
| | | MeCN/water | 0.011 | 0.002 | 0.006 |
| | | MeCN/water + NaOH | 1.03 | 0.32 | 0.24 |
| 2-CA-3-OHP | $CONH_2$ | water | 0.073 | 0.039 | 0.01 |
| | | water + NaOH | 1.0 | 0.70 | 0.20 |
| | | MeCN/water | 0.012 | 0.007 | 0.02 |
| | | MeCN/water + NaOH | 1.16 | 0.44 | 0.30 |

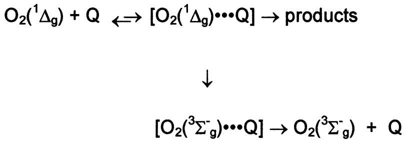
[a] $k_t$ determined in $D_2O$ or its mixtures.
[b] $k_r$ determined in $H_2O$ or its mixtures.
[c] Data from [2].

coated with silicone SE-54 was employed, using helium (23 cm $s^{-1}$) as carrier gas and an oven temperature program of 40°C for 1 min, then from 40 to 60°C at 4°C. $min^{-1}$, from 60 to 270°C at 6°C $min^{-1}$, and finally 15 min at 270°C; inlet block and detector at 275°C, splitless mode. Products were identified with the help of the Wiley mass spectral data library and by GC/MS comparison with pure samples.

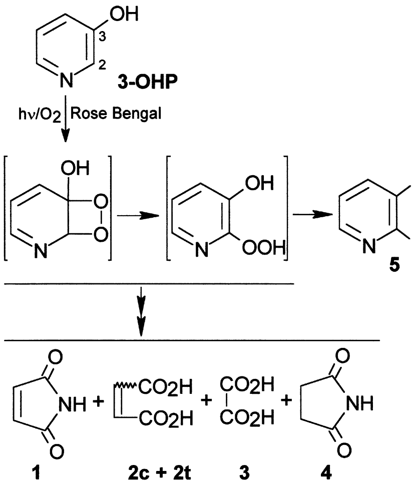
## 3. Results and discussion

Visible light irradiation of the 3-hydroxypyridine derivatives herein studied, in solution in any of the aqueous solvents used and in the presence of Rose Bengal as sensitiser, gave rise to spectral changes as those shown in Fig. 1 for a typical case. The changes were suppressed in the absence of oxygen (nitrogen atmosphere) or in the presence of 10 mM sodium azide. The initial photooxidation rates in $D_2O$ were 3–4 times as fast as in $H_2O$, depending on the particular hydroxypiridine derivative (results not shown). Although the lifetime of $O_2(^1\Delta)$ in $D_2O$ is ca. 15 times longer than in $H_2O$ [1], the relative increase of the photooxidation rate in the deuterated solvent, over that in $H_2O$, must maximise as the substrate concentration approaches to zero. Under our experimental conditions, a considerable fraction of the excited oxygen species must react with the substrate, so that deactivation by the solvent must not be the factor determining the value of $O_2(^1\Delta)$ lifetime. Although both the solvent isotope effect and the mentioned absence of reaction under nitrogen atmosphere constitute indirect evidences in favour of a $O_2(^1\Delta_g)$-mediated (Type II) photooxidation [10], this fact was unambiguously confirmed by TRPD of $O_2(^1\Delta_g)$-quenching.

Pyridine has a reported $k_t$ value of $2 \times 10^3\,M^{-1}s^{-1}$ in $CCl_4$ [1], i.e. practically does not interact with $O_2(^1\Delta_g)$. However, when the 3-position of the pyridine ring is substituted by an OH group, our results indicate that the $k_t$ value increases up to $(0.037–2.6) \times 10^8\,M^{-1}s^{-1}$, depending on the experimental conditions [2] (Table 1), with higher values in alkaline medium—where the OH group is ionised and, hence, has higher electron releasing ability than in non-ionised form—, or when an activating substituent, $CH_3$ or $NH_2$, is also present at the 2-position. On the contrary, $k_t$ decreases when the 2-substituent is a deactivating group, such as $CO_2H$ or $CONH_2$. These experimental findings, as well as the observed increase in rate constant values with



Scheme 1. Quenching of singlet molecular oxygen [$O_2(^1\Delta_g)$] by 3-hydroxypyridines (Q).



Scheme 2. Detected products, and possible mechanism for their formation, in the photooxidation of 3-hydroxypyridine.

the solvent polarity—specially for 3-OHP and its derivatives with electron releasing substituents in the 2 position—, suggest a quenching process through an encounter complex [$O_2(^1\Delta_g)\cdots Q$] (Scheme 1) with partial degree of charge-transfer character, as previously proposed for phenol derivatives [11]. For the latter pyridines, this solvent effect is clearly observed on going from water to MeCN/water. On the other hand, for all the studied compounds the rate constant values are higher in the presence of NaOH (Table 1), but the values obtained in water + NaOH tend to be similar to those in MeCN/water + NaOH, likely because the presence of alkali decreases the polarity difference between both media.

According to the former mechanism, both chemical reaction and physical quenching can operate, and the relative importance of each process is reflected by the values of the respective rate constants $k_r$ and $k_q$.

It must be pointed out that the $k_r$ values in $H_2O$ or pH 11 $H_2O$ shown in Table 1 have been determined by measuring the oxygen uptake and assuming 1 : 1 stoichiometry for the reaction of each 3-hydroxypyridine with $O_2(^1\Delta_g)$ ($\alpha = 1$, see Section 2). This would be the case if the primary reaction were 1,2-dioxetane formation, as shown in Scheme 2, and if this primary reaction were the only way for oxygen consumption in the first stages of the reactions herein studied, with less than 15% UV change.

Regarding the 3-hydroxypyridine derivatives with halogen or electron-withdrawing substituents in position 2, the effect due to the ionisation of the OH group is maintained: $k_t$ and $k_r$ values are higher in alkaline media. Nevertheless, both rate constant values do not obey to a definite reaction pattern involving a classical charge-transfer-mediated encounter complex. The photooxidation quantum efficiencies, $\varphi_r$, are definitively higher in the less polar solvent MeCN-water, a behaviour that differs from that observed in the derivatives with electron-releasing substituents, with not so different $\varphi_r$ values in water and in MeCN-water, with or without NaOH. These apparently intricate results could be interpreted in terms of the evolution of the suggested excited encounter complex. On the one hand, the overall quenching process is favoured, for all the studied compounds, with the increase of the solvent polarity, specially for compounds with electron releasing substituents. On the other hand, the reactive pathway is favoured in less polar media, and it appears to be an entropy-controlled process, as previously hypothesised for the phenolic compounds $\alpha$-tocopherol [12] and tyrosine-containing peptides [9]. The latter effect prevails in 3-hydroxypyridine derivatives with electron withdrawing substituents or halogens, where the reactivity is affected by the solvent polarity, as in processes where charges are neutralised along the reaction pathway.

The products of the Methylene Blue-sensitised photooxidation in ethanol solution of 3-OHP and its *N*-methyl and *N*-benzyl zwitterionic derivatives have been previously studied [13]. In three cases, the observed products were mainly derived from the cleavage of the pyridine ring, very probably via a 1,2-dioxetane intermediate formed by $O_2(^1\Delta_g)$ addition to the positions 2 and 3 of the heterocycle. Diethyl oxalate, diethyl maleate and ethyl oxamate were isolated with low yield from the photooxidation of 3-OHP in ethanol.

In our case, GC/MS analysis of the reaction products from photooxidations of 3-OHP in $H_2O$ or pH 11 $H_2O$, with less than 50% UV change, showed the presence of the starting 3-OHP (up to 80% on total ion current, found as such or partially converted to 3-methoxypyridine in the reaction mixtures treated with diazomethane), as well as several minor products (up to 20% total, less than 2% each), among which six compounds were unequivocally identified (Scheme 2): maleimide (**1**) (detected as such or in *N*-methylated form), maleic acid (**2c**), fumaric acid (**2t**) and oxalic acid (**3**) (all detected as the corresponding methyl esters), succinimide (**4**) (only found in the irradiated pH 11 $H_2O$ solution) and 2,3-dihydroxypyridine (**5**) (only detected in the irradiated plain $H_2O$ solution). Intractable unidentified material, probably with high molecular weight, was also detected during the work-up of the irradiated mixtures. Regarding the possible mechanism of appearance of the detected compounds, several plausible primary intermediates can be proposed. However, the dioxetane already suggested for the photooxidation of 3-OHP in ethanol [13] (Scheme 2) would yield the observed products, after subsequent thermal reactions such as heterocycle ring cleavage, dioxetane rearrangement, and further oxidations. Dihydroxypyridine (**5**) can also be readily formed from this dioxetane *via* a hydroperoxide derivative.

It seems that compound (**5)** is not an intermediate for the observed cleavage products, because any of them could be detected by GC/MS analysis of the irradiated mixture from **5** in $H_2O$, under the conditions used in the photooxidation of 3-OHP in the same solvent.

From the point of view of the elimination from the environment of 3-hydroxypyridines and related compounds, and ruling out the use of direct photoreactions with this purpose, the sensitised photooxidation appears as an interesting alternative pathway of degradation, in competence with other naturally-occurring photoprocesses, as the high photooxidation quantum efficiencies herein found indicate. In the case of a programmed oxidative photodegradation, alkaline media should be preferable.

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