

Monosubstituted naphthalenes as quenchers and generators of singlet molecular oxygen

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Abstract

The monosubstituted naphthalenes (MSN) 1-hydroxynaphthalene (1-OHN), 2-hydroxynaphthalene (2-OHN), 1-methoxynaphthalene, 2-methoxynaphthalene, 1-aminonaphthalene (1-AN), 2-aminonaphthalene (2-AN), 1-methylnaphthalene, 1-fluoronaphthalene and 1-cyanonaphthalene, and the parent compound naphthalene have been evaluated as physical and chemical quenchers and as generators of singlet molecular oxygen, $[O_2(^1\Delta_g)]$, in water and in organic solvents. Rate constant values for the overall (k_t) and chemical (k_r) quenching of $O_2(^1\Delta_g)$, respectively, determined by time-resolved phosphorescence detection and by substrate or oxygen consumption- were from less than 10^4 – $3.92 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$, depending on the solvent polarity and the pH of the solution. The derivatives 1-OHN, 2-OHN, 1-AN and 2-AN react with $O_2(^1\Delta_g)$, generated with external sensitizers, with quantum efficiencies in the range 0.03–0.67. The photooxidation mechanism must include the formation of an encounter complex with partial charge-transfer character of the type $[O_2(^1\Delta_g)^{\delta-} \dots MSN^{\delta+}]$, in accordance with the observed variation of k_t with the global free energy change. All the herein studied MSN generate $O_2(^1\Delta_g)$ upon direct irradiation, with fair to good quantum yields.

The structure of the photooxidation products from 1-OHN and 2-OHN, two compounds with environmental interest, have been determined by combined GC/MS analysis. Benzoic acid, phthalic acid, 1,4-naphthoquinone and a dimer were identified in the reaction mixture from 1-OHN, while 2-OHN yielded phthalic acid and the dimer 2,2'-dihydroxy-1,1'-binaphthyl. ©1999 Elsevier Science S.A. All rights reserved.

Keywords: Monosubstituted naphthalenes; Singlet molecular oxygen quenching and generation; Photooxidation mechanism; Photooxidation products

1. Introduction

Substituted naphthalenes, in special monohydroxynaphthalenes and dihydroxynaphthalenes, are compounds of environmental interest because they are often released into natural aquatic media from diverse sources, with massive contributions from industrial wastes and petroleum spills [1,2]. Their natural (sun-light promoted) photochemical oxidation and, particularly, the singlet molecular oxygen $[O_2(^1\Delta_g)]$ -mediated process constitute an attractive and potential decontamination way, since it only needs the simultaneous presence in the medium of dissolved oxygen and a

light-absorbing compound. This possibility has attracted the attention of several research groups towards the study of the implied photochemical reactions. Thus, the dye-sensitised photooxidation in different media of 1-hydroxynaphthalene (1-OHN) and 2-hydroxynaphthalene (2-OHN) [3], of some other monosubstituted naphthalenes (MSN) [4], and of a series of dihydroxynaphthalenes [5,6,7] have been previously studied from the chemical and kinetic points of view, and some MSN have been proposed as $O_2(^1\Delta_g)$ carriers for biological media, through their corresponding 1,4-endoperoxides [8].

Looking for a complete picture of the interactions between MSN and $O_2(^1\Delta_g)$, in this work we show the results of a systematic study carried out on nine MSN and on the parent compound naphthalene. We report data on the kinetics and mechanism of the dye-sensitised photooxidation of all the compounds, and on the resulting products in the cases

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of 1-OHN and 2-OHN. In particular, attention has been paid to the influence of the naphthalene substituents and of the polarity and pH of the medium, in order to find the best experimental conditions for the photo-oxidative degradation of these substrates. As some of the herein studied MSN have been previously described as good $O_2(^1\Delta_g)$ -generator [9,10], we have also determined the efficiencies of the rest of the compounds for $O_2(^1\Delta_g)$ -production upon direct irradiation.

2. Experimental

2.1. Materials

Rose Bengal (RB, 90%), Eosine (EO, 90%) and Methylene Blue (MB, 82%) were from Sigma. Perinaphthenone (1*H*-phenalen-1-one, PN, 97%), 9,10-dimethylanthracene (DMA, 99%), furfuryl alcohol (FFA, 99%), naphthalene (NAP, 99%), 1-hydroxynaphthalene (1-OHN, 99%), 2-hydroxynaphthalene (2-OHN, 99%), 1-methoxynaphthalene (1-MeON, 98%), 2-methoxynaphthalene (2-MeON, 99%), 1-aminonaphthalene (1-AN, unknown purity), 2-aminonaphthalene (2-AN, 95%), 1-methylnaphthalene (1-MeN, 95%), 1-fluoronaphthalene (1-FN, 99%) and 1-cyanonaphthalene (1-CNN, 98%) were purchased from Aldrich. 1-OHN and 2-OHN were purified by sublimation. 1-AN and 2-AN were recrystallised three times from ethanol-water and then twice sublimed; their respective melting points, $50 \pm 0.2^\circ\text{C}$ and $112.8 \pm 0.2^\circ\text{C}$, were coincident with those reported for the pure compounds [11]. The other products were employed as received. Perinaphthenone-2-sulfonic acid (1*H*-phenalen-1-one-2-sulfonic acid, PNS) was obtained as described. Acetonitrile (MeCN) and methanol (MeOH) were from Sintorgan, and D_2O (99.9% D) was from Sigma. Water was triply distilled. For comparative purposes 2,2'-dihydroxy-1,1'-binaphthyl (Di-2-OHN) was obtained by solid phase oxidation of 2-OHN with $FeCl_3$; *ms* 286 (M^+ , 100%), 268 (9), 257 (21), 239 (23), 226 (14), 134 (18), 119 (56).

2.2. Determination of overall quenching rate constants, k_t

The overall constant for $O_2(^1\Delta_g)$ quenching (k_t) is defined as the sum of the rate constants of physical deactivation to ground-state molecular oxygen (k_q), and of chemical or reactive quenching (k_r). k_t values were determined by time resolved phosphorescence detection (TRPD) using a laser kinetic spectrophotometer with a laser optics nitrogen laser with pulses of 5 mJ and 7 ns half-width (337 nm) as the excitation source [14]. The emitted radiation (mainly 1270 nm) was detected at right angles with 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 that allowed the processing

of the signal. Sixteen shots were usually needed for averaging decay times, in order to get a good signal/noise ratio.

Solutions of PN in organic solvents and of PNS in D_2O were used as sensitizers, with absorptions at 336 nm in the range 0.4–0.5. $O_2(^1\Delta_g)$ lifetimes were evaluated in the absence (τ^0) and in the presence (τ) of each $O_2(^1\Delta_g)$ quencher, and $1/\tau$ was plotted as a function of MSN concentration, according to a simple Stern–Volmer treatment (Eq. (1)), using [MSN] in the range 10^{-4} – 10^{-5} M, or higher for compounds with $k_t \leq 10^4 \text{ M}^{-1} \text{ s}^{-1}$. The $O_2(^1\Delta_g)$ lifetimes in MeCN and D_2O were 40 and 64 μs , respectively. The value in MeCN is somewhat lower than other ones reported in the literature in the same solvent [15], possible due to different moisture content in the medium, but this is not significant for the reported results.

$$\frac{1}{\tau} = \left(\frac{1}{\tau^0} \right) + k_t [\text{MSN}] \quad (1)$$

2.3. Determination of photooxidation rate constants, k_r

The rate constant of the chemical reaction of each MSN with $O_2(^1\Delta_g)$, k_r , was determined by already described comparative methods [16] which are based on the comparison of the slopes of the time course (pseudo first order plots) of the sensitised photooxidations of the substrate and of a reference compound with known k_r value (k_{rR}), both at the same concentration. The ratio of the respective slopes is equal to the ratio k_r/k_{rR} . In water, rates of oxygen disappearance were compared, using FFA as a reference ($k_{rR} = 1.2 \times 10^8 \text{ M}^{-1} \text{ s}^{-1}$) [17] and assuming that the chemical reaction of $O_2(^1\Delta_g)$ with the quencher is the only way for oxygen consumption. Oxygen consumption was followed with a specific oxygen electrode (Orion 97-08) described elsewhere [18], employing an irradiation device with a set of cut-off filters that ensures that the light is only absorbed by the sensitizer. In organic media, rates of disappearance of substrate and reference compounds were compared, using DMA as a reference ($k_{rR} = 5.5 \times 10^7 \text{ M}^{-1} \text{ s}^{-1}$ in MeCN, as determined by TRPD). The disappearances of substrate and DMA were monitored by absorption spectroscopy and by spectrofluorimetry, respectively, at 450 nm (excitation at 395 nm). The physical contribution k_q to the overall $O_2(^1\Delta_g)$ -quenching rate constant k_t is negligible for the reference compounds FFA and DMA [4]. Ground state absorption measurements were carried out in a Hewlett–Packard 8452A diode array spectrophotometer.

2.4. Determination of quantum yields of singlet molecular oxygen generation, Φ_Δ

It was carried out by a comparative method already described [19]. Briefly, the dependence of $O_2(^1\Delta_g)$ -phosphorescence intensity (I_0) on the laser fluence (E_L), extrapolated to zero time, was measured for each air-equilibrated MSN solution, and for a reference solution, changing the

laser fluence with filters of neutral density. Φ_{Δ} values were calculated from the ratio of the respective slopes of the linear plots I_0 versus $(E_L \times \text{fraction of absorbed light})$. The references were PN in MeCN ($\Phi_{\Delta} = 0.95$) and PNS in D₂O ($\Phi_{\Delta} = 1.0$) [12]. Absorbances for MSN and reference solutions were ca. 0.1 at the laser emission wavelength, corresponding to concentrations lower than 3×10^{-5} M for 1-AN and 2-AN in benzene, and for 2-OH in MeCN. Since 1-OHN, 1-MeON and 2-MeON scantily absorb at 337 nm in MeCN, the respective concentrations employed were higher: 3×10^{-3} M, 6×10^{-3} M, and 5×10^{-4} M.

2.5. Analysis of the photooxidation products from 1-hydroxynaphthalene and 2-hydroxynaphthalene

A solution of 1-OHN (100 mg) or 2-OHN (100 mg) in pH 12 water (240 ml, NaOH) and MeOH (10 ml), containing RB (maximum visible absorbance 0.5 at 546 nm, concentration ca. 5×10^{-6} M) was externally irradiated in a pyrex flask with the light from a 200 W tungsten lamp, while bubbling air and with stirring. Flask and lamp were located in the focal points of an elliptical reflector [20]. The photooxidation reaction was followed by UV-Vis absorption spectroscopy after dilution with water, and by thin layer chromatography (TLC) (silicagel, 4:1 v/v CHCl₃-EtOH as eluent) of the ethyl acetate extracts of acidified samples. The photoproducts were analysed in irradiated mixtures with maximum absorption change of less than 20%. Each reaction mixture was acidified (HCl) and extracted (ethyl acetate); the extract was washed, dried, and the solvent was vacuum evaporated. The residue was analysed by TLC as before. The reaction mixture was also analysed by GC/MS in a Hewlett–Packard HP G1800A (GCD system) gas chromatograph equipped with a mass detector in the EI mode (ionisation energy 70 eV) [7], scanning between 40 and 425 amu, and controlled by an HP 3365 ChemStation software; a laboratory-made capillary column (25 m \times 0.32 mm \times 0.8 μ m) coated with methylsilicone OV-1 was employed, using helium (0.8 ml min⁻¹) as carrier gas; temperature program from 80 to 220°C at 5°C min⁻¹, inlet block and detector at 250°C, split mode. Percentages of products were based on the total area of the chromatographic peaks (total ion current, TIC). The products were identified by comparison of their retention times (t_R) and mass spectra with those of pure samples. Alkaline solutions of 1-OHN or 2-OHN are stable in the dark or when irradiated as before, but in the absence of sensitiser, at least during the irradiation times herein used.

3. Results and discussion

3.1. Photooxidation of monosubstituted naphthalenes

The kinetics of the dye sensitised photooxidation of MSN can be depicted by the simplified process shown below (in

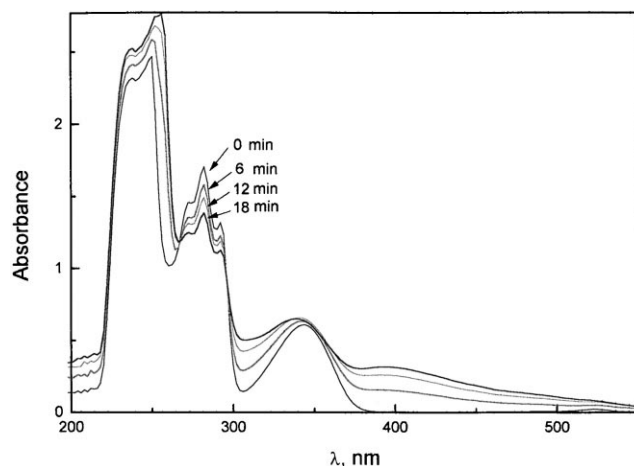
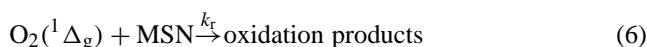
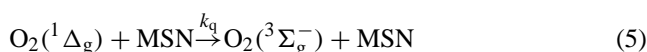
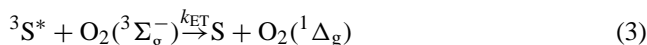


Fig. 1. Spectral evolution of 2-aminonaphthalene (2-AN) in MeCN-MeOH 3:1 v/v with KOH, upon Rose Bengal sensitised irradiation.

reactions 2 and 6). The absorption of light by the sensitiser (S) gives rise to the electronically excited singlet and triplet states (reaction 2), and an energy transfer from this triplet to ground state molecular oxygen generates the excited oxygen species $O_2(^1\Delta_g)$ reaction 3. This can decay by light emission (phosphorescence) and by collision with surrounding molecules (typically the solvent) reaction 4, or interact physically (reaction 5) or chemically (reaction 6) with a quencher, in this case a MSN.



As a consequence of reaction (6), irradiation of air-equilibrated solutions of 1-OHN, 2-OHN, 1-AN or 2-AN with visible light in the presence of the Dyes EO, RB or MB strongly modifies their absorption spectra. A typical change is shown in Fig. 1 for 2-AN. These changes were greatly inhibited in the absence of oxygen (nitrogen atmosphere) or in the presence of 10 mM sodium azide, a known selective $O_2(^1\Delta_g)$ quencher [4]. According to currently accepted criteria [21] these observations indicate that the photooxidation of MSN is mostly 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. Reactions (5) and (6) are responsible for the observed inhibition of the $O_2(^1\Delta_g)$ -TRPD signal by the former MSN (see representative Stern–Volmer plots in Fig. 2). 1-MeON and 2-MeON slightly quenched the singlet oxygen phosphorescence signal, whereas no alteration of the emission was

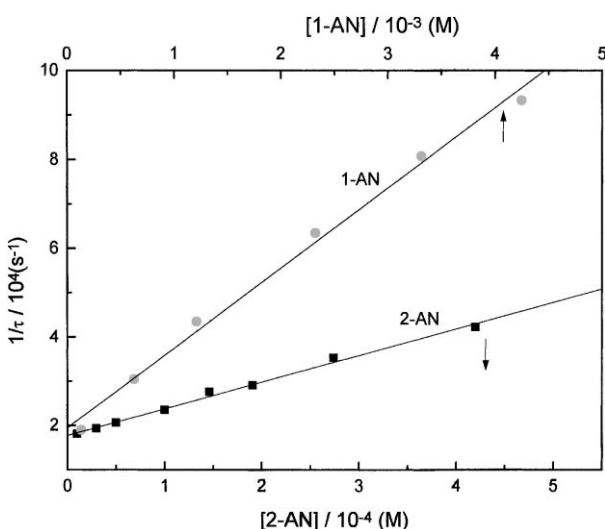


Fig. 2. Stern–Volmer plots for the overall quenching of $O_2(^1\Delta_g)$ by 1-aminonaphthalene (1-AN) and 2-aminonaphthalene (2-AN) in D_2O . Rose Bengal as sensitizer, $Abs_{532} = 0.22$.

detected in the presence of 1-MeN, 1-FN, 1-CNN and NAP in concentrations up to 0.05 M. The experimental k_t values are compiled in Table 1, together with some previously described data [9,10,22,23,24]. The only directly comparable k_t values, those of 2-OHN in MeCN, are similar.

The observed overall ability of each MSN to act as $O_2(^1\Delta_g)$ quenchers does not provide information about the nature of the quenching mechanism. However, distinction between chemical and physical contributions to the overall rate constant is possible employing comparative methods (see Section 2). Table 1 exhibits the k_r values found for MSN, and a typical result is shown in Fig. 3.

Nevertheless, as it has been stressed [25], the efficiency of the actual photodegradation cannot be deduced from these k_r data. This information is only provided by the photooxidation quantum efficiency (φ_r) (Eq. (7)) (Table 1):

$$\varphi_r = \frac{k_r [\text{MSN}]}{(k_d + k_t [\text{MSN}])} \quad (7)$$

Eq. (7) takes into account the simultaneous effects of the physical and chemical interactions, being the physical contribution usually interpreted in practical terms as a self-protection against $O_2(^1\Delta_g)$ -mediated photooxidations. In the particular case of 1-OHN and 2-OHN in ionised form, the similar values of k_t and k_r point to an almost exclusive chemical reaction of the respective anions with $O_2(^1\Delta_g)$. As the experimental results indicate, these chemical reactions proceed with high φ_r values.

3.2. Chemical structure, solvent effects and mechanism

The experimental results shown in Table 1 indicate that both k_t and k_r values increase when naphthalene is substituted by electron-releasing substituents, includ-

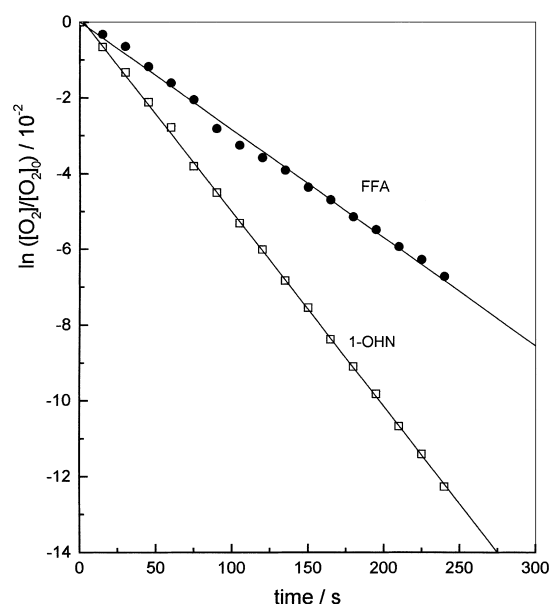
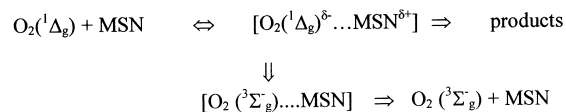


Fig. 3. First order plots for the oxygen uptake of 1-hydroxynaphthalene (1-OHN, $1.0 \text{ M} \times 10^{-4} \text{ M}$) and furfuryl alcohol (FFA) ($5.0 \times 10^{-4} \text{ M}$, the reference) upon Methylene Blue sensitised irradiation in pH 11 water solution.

ing the ionised OH group (pK_a values 9.2 and 9.52 for 1-OHN and 2, respectively [26]) and that the photooxidative chemical process predominates in the presence of OH and NH_2 groups. In the particular cases of 1-OHN and 2-OHN, their kinetic behaviour can be compared with that of the profusely studied family of phenol derivatives [25]. For unionised phenols, a moderate $O_2(^1\Delta_g)$ physical quenching has only been observed, whereas a dramatic increase in both k_t and k_r values was noted in alkaline medium, where the interacting species is the phenolate anion.

Our present results are coincident with those reported for bimolecular reactions between $O_2(^1\Delta_g)$ and sulfides, amines or anilines [4,25,27], or the already mentioned phenols [25], all reactions being explained through a mechanism involving an excited encounter complex $[O_2(^1\Delta_g)^{\delta-} \dots \text{substrate}^{\delta+}]$, represented for the MSN in Scheme 1, that can disappear



Scheme 1.

by both chemical reaction and physical quenching:

A defined solvent-polarity effect that often accompanies charge transfer-mediated mechanisms can also be observed.

If we assume partial or total charge transfer character for the encounter complex $[O_2(^1\Delta_g)^{\delta-} \dots \text{MSN}^{\delta+}]$, an inverse correspondence should be expected between the free energy of the process (ΔG) and the overall $O_2(^1\Delta_g)$ -quenching rate

Table 1

Rate constants for the overall (k_t) and chemical (k_r) quenching of $O_2(^1\Delta_g)$ by monosubstituted naphthalenes, calculated quantum efficiencies of their $O_2(^1\Delta_g)$ -mediated photooxidations ($[MSN]=1\text{ mM}$) and quantum yields of their $O_2(^1\Delta_g)$ generation (Φ_Δ) under direct irradiation. For comparison, described values of fractions of triplet states that yield $O_2(^1\Delta_g)$ ($F_{\Delta(T)}$, see text) are also included

Comp.	Solvent	$k_t/10^7\text{ M}^{-1}\text{ s}^{-1}$	$k_r/10^7\text{ M}^{-1}\text{ s}^{-1}$	φ_r	$\Phi_\Delta (F_{\Delta(T)})$
1-OHN	MeCN	0.43			0.30
	MeCN-MeOH 3:1	0.40	0.18	0.04	
	MeCN-MeOH 3:1 (+KOH)	23.0	22.1	0.67	
	H ₂ O		2.1	0.05	ND ^a
	D ₂ O	8.5			
	D ₂ O, pD=3	3.7	<0.001		
	H ₂ O, pH=11		39.0	0.49	
	D ₂ O, pD=11	39.2			
	Benzene	<0.05 ^b			
<i>n</i> -BuOH	0.76 ^b				
2-OHN	MeCN	0.013			0.32
	MeCN	0.009 ^c			
	MeCN-MeOH 3:1	0.25	0.18		
	MeCN-MeOH 3:1 (+KOH)	6.4	4.1	0.33	ND ^a
	H ₂ O		0.85		
	D ₂ O	1.5		0.03	
	D ₂ O, pD=3	<0.001	<0.001		
	H ₂ O, pH=11		25.0		
	D ₂ O, pD=11	23.5		0.41	
Benzene	<0.01 ^b				
<i>n</i> -BuOH	3.2 ^b				
1-MeON	MeCN	0.021 ^f			0.33 (0.34) ^d
	MeCN-MeOH 3:1(+KOH)	0.01	<0.001		
2-MeON	MeCN	<0.001			0.44 (0.50) ^d
	MeCN-MeOH 3:1(+KOH)	0.03	<0.001		
1-AN	MeCN-MeOH 3:1	1.65	1.6	0.25	0.11
	Benzene				
	H ₂ O		2.3		
	D ₂ O	4.1		0.06	
2-AN	MeCN-MeOH 3:1	1.61	1.6	0.25	0.18
	Benzene				
	H ₂ O		1.0		
	D ₂ O	2.3		0.03	
1-MeN	MeCN-MeOH 3:1	<0.001	<0.001		(0.56) ^d
	MeCN	<0.001 ^e			
1-FN	MeCN-MeOH 3:1	<0.001	<0.001		(0.68) ^d
1-CNN	MeCN-MeOH 3:1	<0.001	<0.001		(0.75) ^d
NAP	MeCN-MeOH 3:1	<0.001	<0.001		(0.62) ^d
	MeCN-MeOH 3:1(+KOH)	<0.001	<0.001		

^aNon-detected.

^bData from [22].

^cData from [23].

^dData from [9].

^eData from [24].

^fData from [10].

constant (k_t). According to the Rehm–Weller treatment [28], ΔG can be calculated by Eq. (8):

$$\Delta G = F[E_{\text{ox}} - E_{\text{red}}(O_2)] - E(O_2(^1\Delta_g)) \quad (8)$$

where F is the Faraday constant, E_{ox} is the half-wave oxidation potential for each MSN [29], $E_{\text{red}}(O_2)$ is -0.78 V versus SCE [30], and $E(O_2(^1\Delta_g))$ is the energy differ-

ence between $O_2(^1\Delta_g)$ and $O_2(^3\Delta_g)$ (23 kcal mol^{-1}) [4]. The plot of the k_t values of the respective MSN versus the deduced ΔG values (Fig. 4) clearly shows that k_t decreases as ΔG increases. Definitely, this dependence constitutes a strong argument in favour of the existence of a charge-transfer process in the $O_2(^1\Delta_g)$ -mediated photooxidations of MSN.

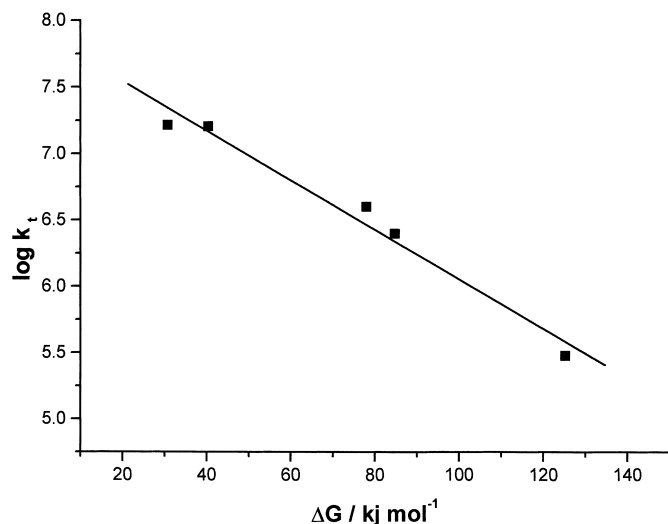
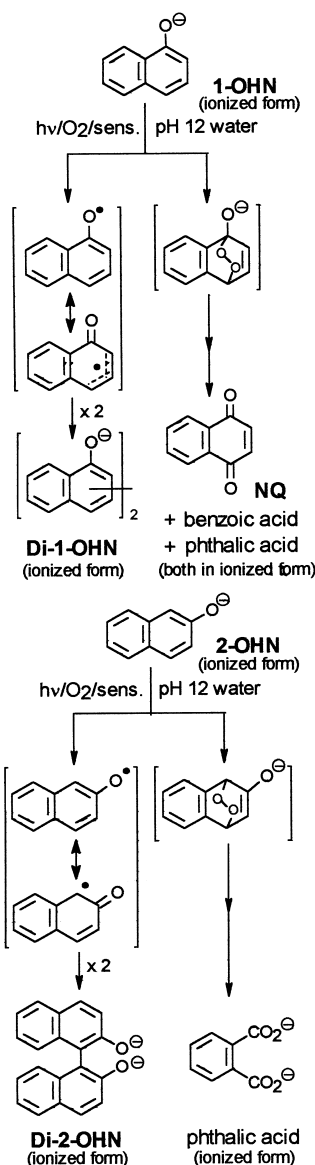


Fig. 4. Dependence of the overall $O_2(^1\Delta_g)$ -quenching rate constant of monosubstituted naphthalenes, upon the free energy change (ΔG) for the electron transfer reaction from their ground state to $O_2(^1\Delta_g)$. Solvent: MeCN-MeOH 3 : 1 v/v.

The values of k_t , k_r and ϕ_r for 1-OHN are much higher than the corresponding values for 2-OHN in the same medium (Table 1). On the other hand, the amino derivatives 1-AN and 2-AN seem to be less sensitive to the position of the substituent. Theoretical calculations [31] indicate higher electron densities in Positions 2 and 4, and lower in 1 and 3, in 1-OHN with regard to 2-OHN, and the same is true when the corresponding ionised forms are compared. These facts could explain both the kinetic behaviour and the different product distribution (see Scheme 2) in both isomers.

3.3. Monosubstituted naphthalenes as singlet molecular oxygen generators

All MSN herein studied are fair to good photosensitisers for the generation of $O_2(^1\Delta_g)$ by direct irradiation in air-equilibrated solutions, with values in MeCN or benzene in the range 0.11 (1-AN in benzene) to 0.74 (1-CNN in MeCN-MeOH 3 : 1) (Table 1). A typical experimental result that allows the determination of the Φ_Δ value of 2-OHN is shown in Fig. 5. The quenching mechanism of the excited states of a compound in general, and of naphthalene derivatives in particular, by molecular oxygen is a complex process, with a kinetics highly dependent on the nature of the excited states of the compound, their oxidation potentials, the type of solvent, and the presence of heavy atoms, as already stated by different authors [9,10,32,33,34]. In principle, both the lowest singlet and triplet excited states could generate $O_2(^1\Delta_g)$, and the overall Φ_Δ value should be the sum shown in Eq. (9), where $\Phi_{\Delta(S)}$ and $\Phi_{\Delta(T)}$ are the respective quantum yields of $O_2(^1\Delta_g)$ generation from these excited states. $\Phi_{\Delta(S)}$ and $\Phi_{\Delta(T)}$ can be expressed as shown in Eq. (10), where $\Phi_{(S)}$ and $\Phi_{(T)}$ are the quantum yields of singlet and triplet excited states generation,



Scheme 2. Proposed photochemical pathways in the photooxidations of 1-hydroxynaphthalene (1-OHN) and 2-hydroxynaphthalene (2-OHN).

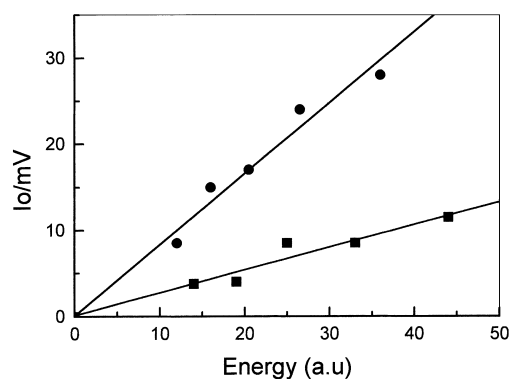


Fig. 5. Laser fluence dependence of the amplitude of $O_2(^1\Delta_g)$ phosphorescence emission at zero-time (I_0) in MeCN. Upper curve, perynaphthenone (PN, the reference); lower curve, 2-hydroxynaphthalene (2-OHN).

respectively, and $F_{\Delta(S)}$ and $F_{\Delta(T)}$ are the fractions of these states that yield $O_2(^1\Delta_g)$.

$$\Phi_{\Delta} = \Phi_{\Delta(S)} + \Phi_{\Delta(T)} \quad (9)$$

$$\Phi_{\Delta(S)} = F_{\Delta(S)}\Phi_{(S)}; \quad \Phi_{\Delta(T)} = F_{\Delta(T)}\Phi_{(T)} \quad (10)$$

When the lifetime of the singlet excited state of the compound is relatively short (some nanoseconds or lower), it can be assumed that $O_2(^1\Delta_g)$ is only generated from the triplet state of the sensitizer ($\Phi_{\Delta(S)} = 0$, and hence $\Phi_{\Delta} = \Phi_{\Delta(T)}$). In the case of MSN, with singlet lifetimes in the range 10–100 ns, [35] and taking into account that the concentration of oxygen in air-saturated solutions in MeCN or benzene is ca. 10 mM [36], it can be deduced that the singlet state contribution to the $O_2(^1\Delta_g)$ generation from MSN even when cannot be neglected, is lower than 1%.

$O_2(^1\Delta_g)$ can also be generated by aromatic excimers when sufficiently high concentrations of the studied compounds are employed. In particular, excimer from naphthalene derivatives are better $O_2(^1\Delta_g)$ generators than the respective monomer [37], and the excimer of the parent compound naphthalene has been observed at ground-state concentrations higher than 0.01 M [37]. As the highest concentration used in the present work was 6×10^{-3} M (for 1-MeON), we can conclude that the Φ_{Δ} values here reported should be ascribed mainly to triplet excited MSN monomers.

3.4. Products of the sensitised photooxidation of 1-hydroxynaphthalene

The MB sensitised photooxidation of several substituted 1-hydroxynaphthalenes, including the parent compound 1-OHN, in CH_2Cl_2 -MeOH 9:1, yields the corresponding 1,4-naphthoquinones as the only identified products [38]. For 1-OHN, the proposed mechanism involves a primary endoperoxide formed through singlet oxygen addition to the 1,4 positions. The involvement of singlet oxygen in this reaction, and not of radical intermediates, were respectively supported by photooxidations in the presence of diazabicyclo[2,2,2]octane -no reaction at all was observed- and 2,6-diterbutylphenol -the oxidation was unaffected. This mechanism must be somewhat different for 1-MeON, as its photooxidation under the same conditions yields 4-methoxy-1,2-naphthoquinone, very likely through a dioxetane formed at the 3 and 4 positions by rearrangement of the former 1,4-endoperoxide.

In our case, during the RB sensitised photooxidation in alkaline water of 1-OHN the UV-Vis spectrum of the reaction mixture changed, showing absorbance decreases at ca. 300–350 nm and increases at ca. 350–450 nm. The direct GC/MS analysis of the isolated mixture of products, with ca. 20% maximum UV change, showed, besides the initial 1-OHN (t_R 8.7 min, 80% of the mixture), three main compounds. Two of them (t_R 2.9 min, 4 %, and t_R 6.1 min, 9%) were identified as benzoic acid and 1,4-naphthoquinone, respectively. The third one (t_R 27.5 min, 6%), with the same

retention time as the dimer Di-2-OHN (from 2-OHN, see latter), showed a mass spectrum with also the same m/z signals, although their intensities were different, mainly at m/z 286 (9%), 285 (100%) and 119 (28%). These data indicate a very similar, but not identical structure, and that the photooxidation gives rise to a dimeric compound (Di-1-OHN) different to the one obtained from 2-OHN. The structure of this dimer has not been elucidated. Another much minor compound (t_R 4.2 min, ca. 1%) was identified as phthalic acid, detected as phthalic anhydride formed by dehydration in the GC inlet block.

The mechanism of the formation of these products from 1-OHN has not been clarified. However, the presence of the dimeric compound Di-1-OHN in the reaction mixture clearly suggests the photoformation of a radical in 1-OHN, in anionic form in the medium. This radical may be generated by electron transfer from 1-OHN to the excited sensitizer (Type I photooxidation) or to $O_2(^1\Delta_g)$ (Type II) [39] (Scheme 2). Subsequent radical dimerization, very likely through the 2- or 4-position, and rearomatization would produce the observed dimer. The radical may also give rise to 1,4-naphthoquinone (NQ), via a 4-peroxy radical (not shown) formed by addition of triplet oxygen at the *para* position. However, in accordance with the formerly proposed mechanism for the cited photooxidation of 1-OHN in organic solvents [38], a more plausible alternative pathway can be envisaged for the photoformation of NQ, based on a intermediate 1,4-endoperoxide generated by [4+2] cycloaddition of singlet oxygen to 1-OHN (Scheme 2). The other two identified compounds, benzoic acid and phthalic acid, may be produced by oxidative cleavage of the substituted aromatic ring, likely through the same 1,4-endoperoxide. All the detected products, and with similar percentages, have been also observed in reaction mixtures with ca. 10% conversion, supporting their generation through competitive reactions.

3.5. Products of the sensitised photooxidation of 2-hydroxynaphthalene

To our knowledge, the products of the sensitised photooxidation of 2-OHN have not been analysed before. In the case of its thermal oxidation, phthalic acid, the dimer 2,2'-dihydroxy-1,1'-binaphthyl (Di-2-OHN) and some hydroxyketones and *o*-quinones have been found, the products depending on the experimental conditions [13,40,41,42,43].

In our case, the RB sensitised photooxidation in alkaline water of 2-OHN produced a general absorbance decrease at ca. 270–370 nm. The GC/MS analysis of the reaction mixture after 15% maximum UV change showed the presence of traces (ca. 1%) of two compounds: the dimer Di-2-OHN and phthalic acid, the appearance of which may follow mechanisms similar to that proposed in the case of 1-OHN, i.e., radical dimerization and ring cleavage, respectively (Scheme 2). As already observed in the photooxidation of 2,3-dihydroxynaphthalene [7], the possible formation of a

polymeric product cannot be disregarded, as TLC analysis of the isolated irradiated mixture showed the presence of a strongly retained product of unresolved structure.

4. Conclusions

The monosubstituted naphthalenes 1-hydroxynaphthalene, 2-hydroxynaphthalene, 1-methoxynaphthalene, 2-methoxynaphthalene, 1-aminonaphthalene and 2-aminonaphthalene behave as physical and chemical quenchers of singlet molecular oxygen, with relatively high rate constants and photooxidative quantum efficiencies, whereas 1-methylnaphthalene, 1-fluoronaphthalene, 1-cyanonaphthalene and naphthalene do not show any interaction with said species. The necessary condition for the existence of interaction is the presence of an electron releasing substituent. In the cases of 1-hydroxynaphthalene and 2-hydroxynaphthalene, the OH ionisation greatly enhances the efficiency of the processes. Experimental evidence also indicates that the interaction occurs through an encounter complex between singlet molecular oxygen and the monosubstituted naphthalene, with partial charge-transfer character, as corroborated by the observed dependence of the overall quenching rate constants with the global free energy changes. The presence in the irradiated mixtures of products derived from the cleavage of the substituted ring in 1-hydroxynaphthalene and 2-hydroxynaphthalene suggests the existence of typical singlet molecular oxygen reactions. All the former naphthalenes are good $O_2(^1\Delta_g)$ generators upon direct irradiation in organic solvents, with quantum yields of $O_2(^1\Delta_g)$ production of 0.11 or higher.

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