

Singlet molecular oxygen-mediated photooxidation of nitrophenolic compounds in water-in-oil microemulsions. A kinetic study

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The aerobic singlet molecular oxygen-mediated photooxidation of 2-nitrophenol (2NP) and 4-methyl-2-nitrophenol (4M2NP) has been studied in water-in-oil (W/O) microemulsion media. The microemulsions used were sodium bis(2-ethylhexyl)sulfosuccinate (AOT)–heptane–water or benzylhexadecyldimethylammonium chloride (BHDC)–benzene–water. The kinetic profile of the reaction was investigated as a function of variables such as (a) surfactant structure and concentration and (b) amount of water dispersed in the microemulsion. Rate constants for overall quenching (k_q) and chemical reaction (k_r) for the interaction of 2NP and 4M2NP with singlet molecular oxygen in the microemulsion media were determined. The quantum efficiencies for the nitro-derivatives' photooxidation (ϕ_r) in both anionic and cationic W/O microemulsions are one to two orders of magnitude larger than in aqueous solutions. A mechanism based on polarity effects and probe location in the microemulsions is proposed in order to rationalize the results.

Introduction

Phenol derivatives such as nitrophenolic compounds are known environmental pollutants.¹ They are basic components in the commercial synthesis of pesticides, being incorporated into waste waters in different steps of industrial processing. Several research groups have studied with considerable attention the dye-sensitized photodecomposition of phenolic pollutants in aqueous media in order to investigate alternative methods for the treatment of natural and industrial effluents.^{2–5} However, photooxidation processes in aqueous solutions have the disadvantage of the low solubility of molecular oxygen, $O_2(\Sigma_g^-)$, and the short lifetime of the singlet molecular oxygen, $O_2(^1\Delta_g)$, producing low quantum yields of photooxidation.⁵

Product analysis in the photooxidation of phenolic derivatives by $O_2(^1\Delta_g)$ has been carried out for a number of compounds. It is important to point out that in all cases the main product detected possesses a quinonic structure, independently of both substitution pattern and nature of the solvent employed.⁶

Water-in-oil (W/O) microemulsions or reversed micelles are characterized by a microdroplet of water surrounded by a monolayer of surfactant molecules, with their hydrocarbon tails directed into the organic solvent. This structure allows the solubilization of water-soluble probes in the water pools and/or into the micellar interface, and non-polar probes in the dispersing organic phase.⁷ Furthermore, the properties of the water pool and the micellar interface can be modified by changing the water/surfactant molar ratio ($R = [H_2O]/[Surf]$).⁸

Recently, we have studied the nucleophilic aromatic substitution (S_NAr) of fluoride by hydroxide ion in 1-fluoro-2,4-dinitrobenzene in W/O microemulsions of sodium bis(2-ethylhexyl)sulfosuccinate (AOT)–heptane–water or benzylhexadecyldimethylammonium chloride (BHDC)–benzene–water.⁹ The second-order rate constant of the reaction was largely dependent on the nature of the surfactant, but in both systems the product observed was 2,4-dinitrophenol in its anionic form, due to the alkaline pH of the water pools. This means that W/O microemulsions with alkaline microdroplets are suitable media

for the solubilization of phenolic compounds. Furthermore, these media supply an appropriate environment for the solubilization of both ionic¹⁰ and neutral¹¹ sensitizers.

Since it is well known that both $O_2(\Sigma_g^-)$ solubility and lifetime of $O_2(^1\Delta_g)$ are several times larger in organic solvents than in water,¹² an enhancement in the overall speed of the reactions in the microheterogeneous medium is expected. However, in spite of this, there are few systematic studies on the effect of W/O microemulsions upon singlet oxygen reactions.^{13,14}

We report in this paper a study of W/O microemulsions as media for $O_2(^1\Delta_g)$ -mediated photooxidation reaction of 2-nitrophenol (2NP) and 4-methyl-2-nitrophenol (4M2NP) in AOT–heptane–water and BHDC–benzene–water microemulsions. Both compounds were chosen as representative examples of phenolic pollutants and their quantum efficiencies of photooxidation (ϕ_r) at several compositions of the W/O microemulsions were calculated. We also present a detailed mechanism of the reaction in these media.

Experimental

Materials

2-Nitrophenol (2NP), 4-methyl-2-nitrophenol (4M2NP), and 9,10-dimethylantracene (DMA) (Aldrich, 99%); rose bengal (RB) as sodium salt (Sigma) and sodium hydroxide (Merck, PA) were employed as received.

Sodium bis(2-ethylhexyl)sulfosuccinate (AOT) from Sigma was dried under vacuum and used without further purification. Benzylhexadecyldimethylammonium chloride (BHDC, Sigma) was recrystallized several times from ethyl acetate and dried under vacuum.

Benzene and heptane (Sintorgan, HPLC) were used as received. Water was triply distilled.

Instrumentation

Stationary photolyses were performed with a 150 W filament lamp coupled with an orange cut-off filter ($\lambda > 530$ nm). UV–VIS spectra were recorded on a Hewlett-Packard HP 8452A diode-array spectrophotometer.

The photooxidations of 2NP and 4M2NP were evaluated using 9,10-dimethylantracene (DMA) as actinometer,¹⁵ under the same experimental conditions. The quenching process of

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$O_2(^1\Delta_g)$ by this compound goes exclusively through a chemical reaction. The bimolecular rate constants (k_{DMA}) for the photooxidation reaction of DMA in AOT and BHDC microemulsions were obtained by monitoring $O_2(^1\Delta_g)$ decays at 1270 nm using time-resolved phosphorescence detection (TRPD) as previously described.¹⁶ The k_{DMA} values obtained were 0.8 and $3.0 \times 10^7 \text{ l mol}^{-1} \text{ s}^{-1}$ in AOT and BHDC microemulsions, respectively, in good agreement with values previously reported in similar media.^{14,17} They were independent of both surfactant concentration and R values, indicating that DMA remains in the external phase and that the $O_2(^1\Delta_g)$ concentration in this phase is nearly constant, independent of the number and size of the microdroplets present in the microemulsion.¹⁴

For all time-resolved experiments a Nd:YAG laser (Spectron) operating in a Q-switched mode was used as the excitation source. The frequency-doubled output at 532 nm was employed to excite the sensitizer rose bengal (RB).

Preparation of solutions

A solution of the surfactant was prepared in the appropriate organic solvent. Subsequently, 5 μl of a stock solution of RB and 10 μl of stocks of 2NP or 4M2NP in a sodium hydroxide (0.063 M) ($M = \text{mol l}^{-1}$) aqueous solutions were injected. The amount of water present in the system was expressed as the molar ratio between water and the surfactant (R). The R values were adjusted with a 0.063 M NaOH aqueous solution. These mixtures were sonicated to obtain perfectly clear microemulsions. The substrate to surfactant ratio was kept below 1×10^{-3} .

All experiments were performed at $25 \pm 1^\circ\text{C}$.

Results and discussion

Site of localization of the probes and sensitizer

In W/O microemulsions with alkaline water pools and in NaOH (0.063 M) aqueous solutions the UV-VIS spectra of 2NP and 4M2NP display absorption only by the anionic form of nitrophenols. In Table 1 are presented the absorption maxima of the nitrophenols. The bands are red shifted in W/O microemulsions relative to alkaline aqueous solutions. The same behaviour was observed for the absorption maximum of the sensitizer RB, (Table 1). Furthermore, the bathochromic displacements are larger in the cationic BHDC than in the anionic AOT microemulsions, independent of the R values.

These results can be explained by the association of the probes and of the sensitizer with the interface of both anionic and cationic microemulsions. The sensitizer RB is a xanthene anionic dye derivative insoluble in organic solvents, whereas the nitrophenol compounds are in their anionic form, and therefore the association with the micellar interface is stronger in cationic microemulsions due to the higher electrostatic interactions. Similar results were found previously for RB in SDS and CTAB micellar aqueous solutions.¹⁸

On the other hand, as control experiments (not shown), the UV-VIS spectra of 2NP and 4M2NP, in W/O microemulsions with neutral water pools showed absorption bands of both anionic and phenolic forms of the nitrophenols. Thus, under our experimental conditions the probes 2NP and 4M2NP are completely dissociated in their anionic forms and included in the dispersed phase of the W/O microemulsions.

Photooxidation of 2NP and 4M2NP

The aerobic irradiation of AOT or BHDC W/O microemulsions with alkaline water pools containing RB and nitrophenols produced spectral absorption changes similar to those shown in Fig. 1. No reaction was detected in N_2 -saturated solutions. The spectral changes for the substrates examined were qualitatively similar, independent of the nature of the surfactant, and the composition of the microemulsions. Furthermore, as shown by

Table 1 UV-VIS maximum absorption (λ/nm) of RB, 2NP, and 4M2NP in W/O microemulsions and in NaOH (0.063 M) aqueous solutions

Solvent	RB	2NP	4M2NP
Water	548	416	434
AOT 0.1 M			
$R = 10$	558	420	436
$R = 20$	558	420	436
BHDC 0.1 M			
$R = 10$	566	424	442
$R = 20$	566	424	442

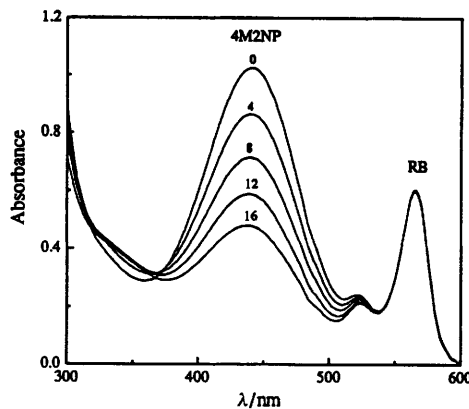


Fig. 1 Spectral evolution of photooxidation of 4M2NP in BHDC (0.1 M)-benzene-water ($R = 20$) microemulsion, sensitized by RB ($A_{566} = 0.66$). Numbers on the spectra represent irradiation time in minutes.

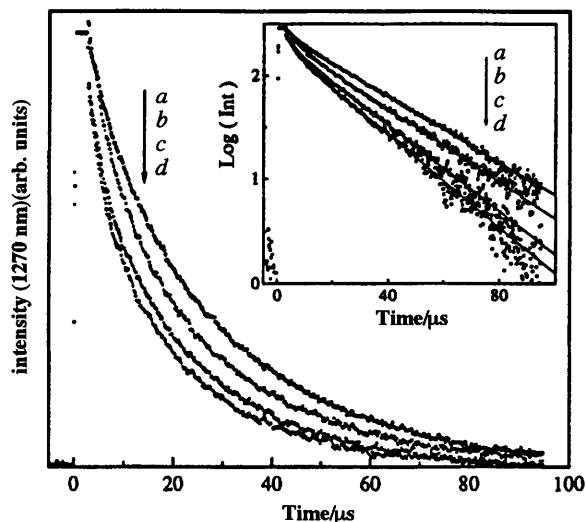


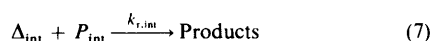
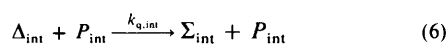
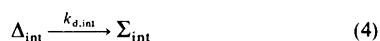
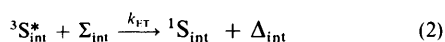
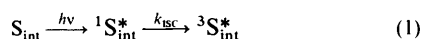
Fig. 2 Decay traces of $O_2(^1\Delta_g)$ emission in AOT (0.1 M)-heptane-water ($R = 20$) microemulsion at various 4M2NP concentrations (M): (a) 0, (b) 0.5×10^{-4} , (c) 1.0×10^{-4} , (d) 1.4×10^{-4} . Insert: monoexponential fit for the decay traces.

the stability of the absorption band of RB in Fig. 1, no consumption of sensitizer was observed.

The nature of an $O_2(^1\Delta_g)$ -mediated interaction with nitrophenols was confirmed by performing TRPD of the $O_2(^1\Delta_g)$ emission as a function of nitrophenol concentration. Fig. 2 shows the decay times of $O_2(^1\Delta_g)$ in AOT-heptane-water microemulsion in the absence and in the presence of various 4M2NP concentrations. The decay times were monoexponential during almost 1.5 decades of the decay (see insert Fig. 2), in accord with the $O_2(^1\Delta_g)$ decay model in reversed micelles solutions proposed by Lee and Rodgers.¹³

The experimental results are interpreted in terms of the

kinetic Scheme 1, in the presence of nitrophenols (P) exclusively solubilized in the disperse pseudophase.^{13,14} S_{int} , $^1S_{\text{int}}^*$ and



Scheme 1

$^3S_{\text{int}}^*$ represent the ground, excited singlet and triplet states of RB in the interior phase (water + surfactant). Δ_{int} , Δ_{ext} and Σ_{int} , Σ_{ext} represent $O_2(^1\Delta_g)$ and $O_2(\Sigma_g^-)$ in the interior and in the exterior phase (organic solvent), respectively. k_+ and k_- are the unimolecular entrance and exit rate constants; $k_{\text{d,int}}$ and $k_{\text{d,ext}}$ are the decay rate constants in the interior and in the exterior phases whereas $k_{\text{q,int}}$ and $k_{\text{r,int}}$ are the physical and the reactive quenching rate constants, respectively. P_{int} is the quencher concentration in the interior phase. The sum of the rate constants ($k_{\text{r,int}} + k_{\text{q,int}} = k_{\text{t,int}}$) is the overall rate constant accounting for $O_2(^1\Delta_g)$ interaction with the nitrophenol compounds.

The single exponential behaviour observed for the $O_2(^1\Delta_g)$ decay in W/O microemulsions is rationalized in terms of a very rapid equilibration of $O_2(^1\Delta_g)$ between the internal and the external phases in comparison with the $O_2(^1\Delta_g)$ decay in both phases, *i.e.* $k_+, k_- \gg k_{\text{d,int}}, k_{\text{d,ext}}$. These conditions are completely reached here, since the rates by which $O_2(\Sigma_g^-)$ [and presumably $O_2(^1\Delta_g)$] enters into and exits from micellar aggregates have been reported¹⁹ as not less than $1 \times 10^7 \text{ s}^{-1}$, several times larger than the decay of $O_2(^1\Delta_g)$ in typical hydrocarbon media or in aqueous solutions.¹² Therefore, under these conditions, both Δ_{int} and Δ_{ext} species decay with a common lifetime and an apparent rate constant k_Q for $O_2(^1\Delta_g)$ quenching by nitrophenol compounds is obtained using eqn. (8),¹³

$$k_d = k_d^0 + k_Q[P_T] \quad (8)$$

with

$$k_Q = \frac{k_{\text{t,int}}K_{\text{eq}}}{fK_{\text{eq}} + (1-f)} \quad (9)$$

where k_d and k_d^0 are the unimolecular rate constants for the $O_2(^1\Delta_g)$ deactivation in the presence and in the absence of nitrophenol compounds, respectively; $K_{\text{eq}} (= [\Delta_{\text{int}}]/[\Delta_{\text{ext}}])$ is the partition constant of the $O_2(^1\Delta_g)$ between the internal and external phases, $[P_T]$ is the total molar concentration of nitrophenol and f is the volume fraction of the dispersed pseudophase, calculated by eqn. (10),²⁰ where V_w , V_{surf} and

$$f = \frac{V_w + V_{\text{surf}}}{V_T} = \frac{[\text{Surf}](18 \times R + v_m)}{1000} \quad (10)$$

V_T are the water, surfactant and total volume, respectively. $[\text{Surf}]$ is the molar concentration of surfactant; R is the molar ratio water/surfactant and v_m is the volume per mole of

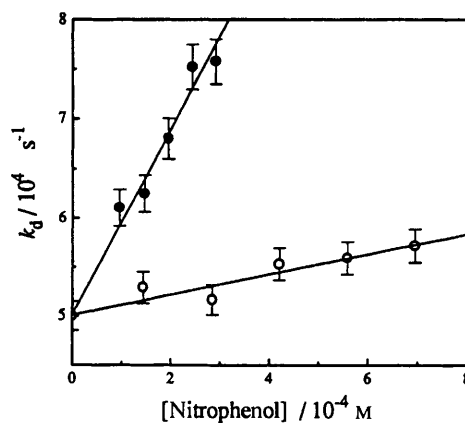


Fig. 3 Plots of eqn. (8) for the quenching of $O_2(^1\Delta_g)$ emission by nitrophenol compounds in BHDC (0.1 M)-benzene-water ($R = 10$) microemulsions: (●) 4M2NP; (○) 2NP

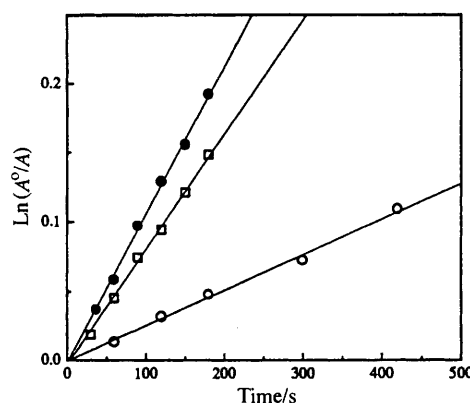


Fig. 4 First-order plots for the photooxidation of nitrophenol and actinometer compounds in AOT (0.1 M)-heptane-water ($R = 15$) microemulsion: (●) 4M2NP; (○) 2NP; (□) DMA

surfactant (389 and $443 \text{ cm}^3 \text{ mol}^{-1}$ for AOT and BHDC, respectively).^{20,21} Typical plots of eqn. (8) are shown in Fig. 3.

Under steady-state irradiation, taking into account f , K_{eq} and $[P_T]$ ($= f[P_{\text{int}}]$) the nitrophenol consumption is given by eqn. (11),

$$-\frac{d[P_T]}{dt} = fk_{\text{r,int}}[\Delta_{\text{int}}][P_{\text{int}}] = k_{\text{obs}}[P_T] \quad (11)$$

where

$$k_{\text{obs}} = k_{\text{exp}}[\Delta_{\text{ext}}] = k_{\text{r,int}}K_{\text{eq}}[\Delta_{\text{ext}}] \quad (12)$$

According to this rate law, the photooxidation process of 2NP and 4M2NP should follow a first-order kinetics decay, as confirmed by the plots for the consumption of 2NP and 4M2NP in W/O microemulsions shown in Fig. 4. From the ratio of the first-order slopes between the actinometer and nitrophenol, the values $k_{\text{DMA}}/k_{\text{exp}}$ for 2NP and 4M2NP consumption were obtained (see Experimental section).

The $k_{\text{t,int}}$ and $k_{\text{r,int}}$ values for the nitrophenol compounds calculated from eqns. (9) and (12), respectively, are collected in Table 2. For these calculations, $K_{\text{eq}} = 0.11$ was used, as reported by Lee and Rodgers for AOT-heptane-water microemulsions, with the assumption that K_{eq} is independent of the amount of water present in the microemulsion and of the surfactant concentration.¹³ Since the partition constant of $O_2(^1\Delta_g)$ in BHDC microemulsions has not been reported in the literature, we assumed the same K_{eq} value in BHDC-benzene-water for AOT-heptane-water microemulsions, due to the similarity in oxygen solubilities in both organic solvents.²²

Table 2 Rate constant for overall quenching ($k_{t,int}$) and chemical reaction ($k_{r,int}$) with $O_2(^1\Delta_g)$ and quantum efficiency (ϕ_r) values for nitrophenolic compounds in AOT and in BHDC W/O microemulsions, and in alkaline aqueous solutions^a

Compound	Solvent	R	$k_{r,int}$	$k_{t,int}$	ϕ_r	
2NP	AOT 0.1 M	10	2.6	11	230	
		15	2.0	13	150	
		20	1.5	17	84	
	AOT 0.05 M	20	1.6	23	70	
		BHDC 0.1 M	10	1.0	15	70
			15	0.9	14	65
	20		1.0	13	70	
	BHDC 0.05 M	20	1.0	15	65	
		Water	—	1.6	150	7
4M2NP	AOT 0.1 M	10	14	33	420	
		15	11	61	170	
		20	9.2	98	95	
	AOT 0.05 M	20	9.4	92	100	
		BHDC 0.1 M	10	5.8	89	65
	15		5.8	88	65	
	20		5.8	88	65	
	BHDC 0.05 M	20	5.6	94	60	
		Water	—	2.8	430	5

^a $k_{r,int}$, $k_{t,int}$ ($\times 10^{-7}$ l mol⁻¹ s⁻¹), and ϕ_r ($\times 10^3$). Error $\pm 5\%$.

Table 2 also gives values of k_r and k_t in alkaline homogeneous aqueous solutions.⁵

From Table 2 it can be seen that for both W/O microemulsions media, at $R = 20$, the rate constant values do not change with the surfactant concentration, within experimental error. This result is explained considering that in W/O microemulsions an increment of the surfactant concentration in solutions with the same R value produces an increase in the number of microdroplets, but their size is kept almost constant.^{7,20,21} Under our experimental conditions, the nitrophenol compounds are completely associated to the micellar aggregates, therefore their localization and the $k_{r,int}$ and $k_{t,int}$ values are independent of the number of microdroplets present in the medium. Regardless, the rate constants should be dependent on the size of the micellar aggregates. This effect is clearly observed in AOT microemulsions. For both 2NP and 4M2NP, the $k_{r,int}$ values decrease whereas the values of $k_{t,int}$ increase with the increment of the amount of water dissolved.

The observed dependence of $k_{r,int}$ and $k_{t,int}$ with R can be due to changes in the characteristics of the interface where the probe is located and/or to a displacement of the probe from the interface towards the water pool when R increases. In the case of AOT microemulsions the anionic interface could eject the anionic probes more efficiently towards the water pool as R increases. This can be explained considering that the water pools of W/O microemulsions consist of a layer of 'bound' water associated with the polar head group of the surfactant, surrounding a core of 'free' water at the centre of the water pool. As the size of the water pool increases, the proportion of the 'free' component also increases until the water environment closely resembles that of bulk water.²³ When this occurs the nitrophenol compound is located in a more polar environment. This effect explains the similarity between the values of $k_{r,int}$ for 2NP obtained in AOT microemulsions at $R = 20$ and in aqueous solutions. However, for 4M2NP the values of $k_{r,int}$ in AOT are larger than in water solutions, even at $R = 20$. This result could reveal the effect of alkyl substitution on the solubility of the phenolic compound in the microemulsion. Probably, in AOT microemulsions at the same R value, 4M2NP remains in a less polar region of the interface than 2NP.

Nevertheless, in BHDC microemulsions both $k_{r,int}$ and $k_{t,int}$ are practically independent of R . In this case, the displacement effect is not observed because both anionic probes are bound

to the micellar interface by electrostatic forces, thus the environment sensed for the nitrophenol compounds is practically the same, independent of R values.

In order to compare the efficiency of photodegradation process in W/O microemulsions relative to homogeneous aqueous solutions, the quantum efficiency for photooxidation, ϕ_r , was calculated with eqn. (13). Values of 3.8 and

$$\phi_r = \frac{k_{r,int}[P_T]}{fk_d^0 + k_{t,int}[P_T]} \quad (13)$$

5.0×10^4 s⁻¹ for k_d^0 were measured in AOT and BHDC, respectively; and 2.3×10^5 s⁻¹ in aqueous solutions. In Table 2 are presented the ϕ_r values calculated with eqn. (13), using 1×10^{-3} M as the concentration of the nitrophenol compounds.

It can be observed that for both compounds the ϕ_r values are one or two orders of magnitude larger in W/O microemulsions than in alkaline water. This increment of ϕ_r is consistent with the longer lifetime of $O_2(^1\Delta_g)$ and the lower values of $k_{t,int}$ in W/O microemulsions than in aqueous solutions. In this way, the probe location in the micellar interface, where the environment is less polar than in the water pool, favours the reactive pathway ($k_{r,int}$) as compared with the physical interaction ($k_{q,int}$). This result is in agreement with those observed for solvent effects of nitrophenolic derivatives in homogeneous solutions.⁵

In BHDC microemulsions the ϕ_r values do not depend on the R values, on the surfactant concentration, nor on the phenolic derivative. These results are explained by the association of the anionic nitrophenols in the cationic micellar interface and that for both 2NP and 4M2NP, the ratio between $k_{t,int}$ and $k_{r,int}$ is almost constant, providing further evidence that the nitrophenols are anchored in the micellar interface and sense the same environment, independent of the R value and of the phenolic derivative.

On the other hand, in AOT microemulsions the ϕ_r values decrease as R increases and the photooxidation process is less efficient for 2NP than for 4M2NP. These results reflect the probe displacement from the micellar interface towards the water pool when the R values increase. In this case, the inverse effect of a larger polarity on $k_{t,int}$ and $k_{r,int}$ contributes to the decrease of ϕ_r values observed. The probe displacement is larger for 2NP than for 4M2NP, favouring the non-reactive pathway for the $O_2(^1\Delta_g)$ deactivation, and thus yielding lower ϕ_r values for the unsubstituted nitrophenol.

Conclusions

The above results show that W/O microemulsions are suitable media for $O_2(^1\Delta_g)$ -mediated photooxidation process of nitrophenol compounds. Basically, the larger reactivity in W/O microemulsions than in water solutions is due to both a longer lifetime of the reactive species $O_2(^1\Delta_g)$ and a decrease of the physical quenching component in these organized media. However, a catalytic effect could be dependent on the characteristics of the system under study, e.g. probe location, and reactivity of the compound in non-polar solvents relative to water media.

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