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Dark and Photoinduced Interactions Between Xanthene Dyes and Quinones

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ABSTRACT

The interaction of quinones with ground and electronically excited states of xanthene dyes was investigated. Ground state xanthene derivatives form aggregates with quinones. Apparent association constants range from 20 to 1500 M^{-1}*, depending on the particular xanthene derivative–quinone interaction partners, involved in the association, which possess negative temperature coefficients. The association constants, determined by fluorescence and electronic absorption standard methods were not affected by solvent polarity. The driving interactions for the complexation were due to dispersive forces, accompanied by a component of charge–transfer. Triplet excited xanthene derivatives interact with quinonic compounds. Rate constants for the process (*k_{qT}*) in acetonitrile, were determined by laser flash photolysis, for the systems rose bengal–benzoquinone (*$k_{qT} = 8 \times 10^9\ M^{-1}s^{-1}$*) and rose bengal–duroquinone (*$k_{qT} = 2.2 \times 10^9\ M^{-1}s^{-1}$*). The mechanism was identified as an electron transfer process, playing the xanthene derivatives the role of electron donors. The implication of these results on the sensitizing effect of xanthene dyes for Type II photooxidations is discussed. © 1998 Elsevier Science Ltd. All rights reserved*

Keywords: quinones, xanthene dyes.

1 INTRODUCTION

Xanthene derivatives (xanD), occupy an important position among different families of dyes, owing to a number of reasons related to their photochemical

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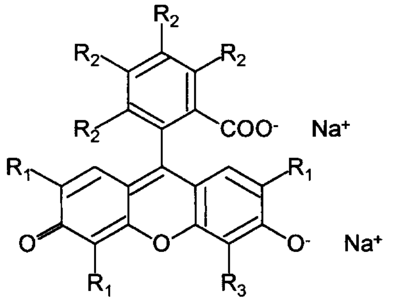
and photophysical properties [1]. Besides, xanthene dyes, and especially rose bengal (RB) and eosin (Eos) are the most frequently employed dye-sensitizers when a quantitative interpretation of the photodynamic effect is required [2].



Xanthene derivative	R_1	R_2	R_3
Rose Bengal	I	Cl	I
Eosin	Br	H	Br
Erythrosin	I	H	I
Mercurochrome	Br	H	HgOH
Fluorescein	H	H	H

In a recent paper [3] we reported a study on the sensitized oxygenation (mainly a singlet molecular oxygen-mediated, Type II photooxidation) of a series of quinones and hydroxy-quinones. We intended the employment of RB as a dye-sensitizer for such a study, but strong preliminary evidences on the existence of dark- and photo-promoted interactions in the dye–quinone system precluded this possibility. The same vas true for the series of xanD constituted by Eos, erythrosine (Ery), and mercurochrome (Mc).

On the other hand, quinones and hydroxyquinones belong to an important class of biologically active and commercially valuable compounds. They are involved in a huge number of electron–transfer processes representing individual steps in a variety of enzymatic systems. The participation of quinone derivatives in light-induced processes constitutes, therefore, a topic of special interest. Finally, quinones are one of the most frequent primary products in the Type II photooxidations of a series of environmentally relevant aromatic hydrocarbons and derivatives [4]. As a consequence, they are present in practically all natural systems. In this way, the knowledge of the behavior of a given sensitizer, such as xanD in the present case, in the presence of quinonic compounds can contribute to the interpretation of experiments or events in which photosensitization through xanD takes place. In this context, the aim of the present study is to obtain an integral and quantitative idea of the thermal and photo-induced interactions xanD-quinonic derivatives, especially as referred to both the conditions in which a given reaction mechanism operates, and to the mutual influence of the molecular structure of the reaction partners, if any, on the kinetics of the involved processes.

2 EXPERIMENTAL

2.1 Materials

The xanD RB, Eos (yellowish), Ery, Mc and Fl were from Sigma Chem. Co. (St Louis, USA). The quinones (generically named Q in the following) benzoquinone (BQ), tetramethyl benzoquinone (DQ), anthraquinone (AQ), anthraquinone-2-sulfonic acid (2-SAQ), were purchased from Aldrich (Milwakee, USA). The compound 2,6-dihydroxy anthraquinone (2,6-DOHAQ) was from Pfaltz and Bauer (Waterbury, USA). Water was triply distilled. Ethanol (EtOH), acetonitrile (MeCN) and toluene (Tol) were from Sintorgan (Buenos Aires, Argentina), HPLC quality.

2.2 Methods

Ground state absorption measurements were carried out using a Hewlett–Packard 8452A diode-array spectrophotometer. A Spex Fluoromax apparatus was employed for the fluorescence measurements.

The laser flash photolysis apparatus employed was as follows: a Nd:Yag laser (Spectron) served as the excitation source. The frequency-doubled output at 532 nm was employed to excite RB. A 150 W xenon lamp was used as the analysing light. The detection system comprised a PTI monochromator and a red-extended photomultiplier (Hamamatsu R666). The signal was acquired by digitizing osciloscope (Hewlett–Packard 54504A) where it was averaged. It was then transferred to a PC via an HPIB parallel interface where it was analysed and stored.

The MeCN solutions were deoxygenated by bubbling with ultrapure solvent-saturated argon for 30 min. Transient absorbance decays were fitted to a monoexponential decay plus a constant term.

3 RESULTS

3.1 Dark complexation

The absorption spectrum of xanD in water suffers a number of qualitatively common perturbations in the presence of the different Q. The magnitude of these perturbations is dependent on both Q and xanD concentrations. The respective absorption spectra of the mixture xanD–quinones decreases at the blue edge of the visible band of the xanD and increases at the red edge. The xanD concentrations were maintained lower than 10 μM in order to avoid massive aggregation [2]. For the quinonic derivatives typical concentrations were in the order of 0.1 to 5 mM. The spectral changes could be better visualized by taking the respective difference spectra XanD–quinones against xanD. The cases, for the system Ery–DQ (Fig. 1) and RB–BQ [Fig. 1 (inset)] are shown as typical examples.

The presence of only two absorbing species in equilibrium is denoted by the well-defined isosbestic points in the difference spectrum. This was also true for the all the systems xanD–quinones to be mentioned in this work. Since no absorption from the quinonic compounds is expected over 500 nm, the species absorbing in this region should be free xanD and the complex xanD–quinones [xanD–Q], as described in eqn (1).

$$\text{xanD} + \text{Q} \overset{K_{ass}}{\Longleftrightarrow} [\text{xanD}-\text{Q}] \tag{1}$$

In the present study we employed two different standard procedures (as described below) to obtain the apparent association constants (K_{ass}). For the

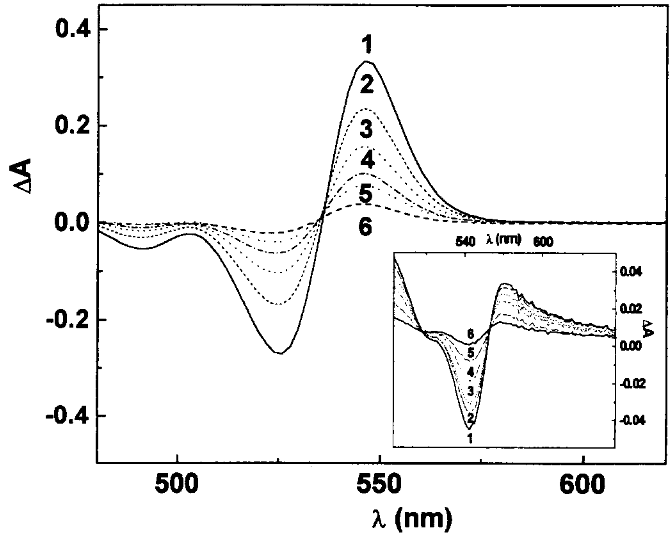


Fig. 1. Difference spectra of Ery + DQ vs Ery in EtOH. Dye concentration: 7.80×10^{-3} mM. Quinone concentration: 1: 1.30 mM; 2: 0.91 mM; 3: 0.65 mM; 4: 0.52 mM; 5: 0.39 mM; 6: 0.18 mM. Inset: the same for the system RB + BQ in water. Dye concentration 9.20×10^{-3} mM. Quinone concentration: 1: 6.71 mM; 2: 6.00 mM; 3: 5.43 mM; 4: 4.22 mM; 5: 2.70 mM; 6: 1.52 mM.

cases of Fl–Q complexes, the superimposition between the absorption bands of the dye, the quinones and the complex, precluded the neat evaluation of the spectral data. As a consequence, even when the complexation Fl–Q exists, this system was disregarded for quantitative evaluations.

3.1.1 Fluorescence quenching method

The xanD are characterized by a measurable fluorescence emission in solution (fluorescence quantum yields [1] > 0.01, depending on the particular compound and the solvent). This fluorescence was quenched to a different extent by the presence of the individual quinonic compounds. Assuming that the quenching does not proceed via interaction with the singlet excited state of xanD, the $K_{ass(F)}$ values for complexing in the ground state of the dye can be calculated from the Stern–Volmer plots (Fig. 2), according to eqn (2)

$$I_o/I = 1 + K_{ass(F)}[Q] \tag{2}$$

where I_o and I are the values of xanD fluorescence intensity in the absence and in the presence of the quencher (Q), respectively.

The assumptions involved in the derivation of this equation are: (a) excitation in the isosbestic point and (b) non-fluorescent complex. Both conditions were fulfilled in the present case. Excitation wavelength was in all cases in the blue region of the main absorption band of xanD where all xan–Q

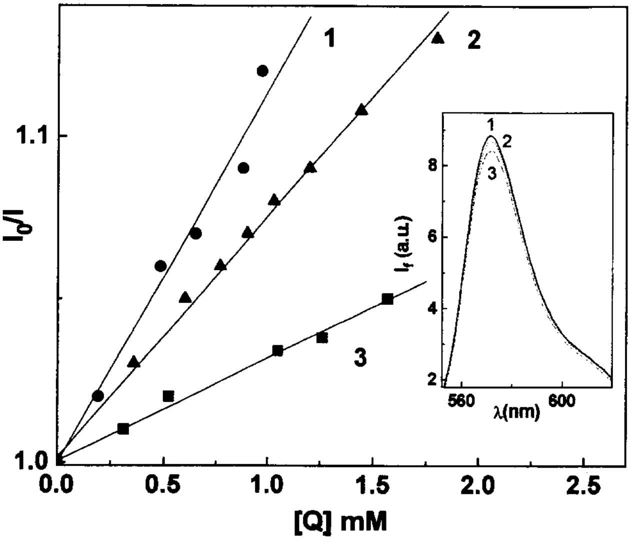


Fig. 2. Stern–Volmer plots for the fluorescence quenching of the systems: 1: RB–DQ in EtOH; 2: Ery–DQ in EtOH and 3: RB–BQ in water. Inset: uncorrected fluorescence spectra of RB: 1: in the absence and in the presence of BQ 2: 0.31 mM and 3: 1.57 mM in water.

mixtures show an isosbestic point. On the other hand, the similarity in spectral shape between the fluorescence spectra of xanD and the mixtures xanD–Q [Fig. 2 (inset)] and the excellent linearity of the Stern–Volmer plots, even up to I_{fo}/I_f, values higher than 2, minimizes the possibility of emission from the complex.

The $K_{\text{ass(F)}}$ values for the association of Q with xanD are collected in Table 1.

The assumption of absence of a hypothetical interaction of the quinonic compounds with the excited singlet state of xanD is supported by the fact that this state in solution has a lifetime of a few nanoseconds to subnanoseconds [1] and cannot be efficiently intercepted by the quinones in concentrations in the order of millimolar as those employed in the fluorescence experiments.

The K_{ass} values for the system RB–Q in EtOH, as a representative example, were fluorometrically determined at 8, 20 and 40°C. The respective $K_{\text{ass(F)}}$ values were 56, 49 and 36 M^{-1}. This evidence eliminates the possibility of a chemical reaction between the association partners.

3.1.2 Benesi–Hildebrand method

By this method, which is based on spectrophotometric measurements on the XanD–Q systems, and the validity of which has been sufficiently discussed in the literature [5], it is possible to obtain the values for the association constants and molar absorption coefficients for the complex. In the following, they will be named $K_{\text{ass-(BH)}}$ and $\varepsilon_{\text{(BH)}}$ for the absorption coefficients. Although both values, $K_{\text{ass(F)}}$ (from the fluorescence method, see above) and $K_{\text{ass(BH)}}$ are referred to the same association constant [eqn (1)], the subscripts indicate the method by which they were obtained.

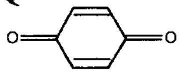
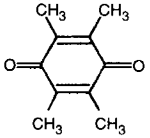
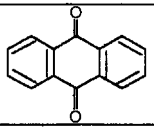
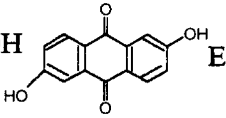
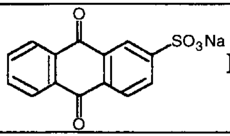
In Fig. 3, inset, is shown a plot of the absorbance of the positive band vs Q concentration for the system Eos–2,6–DOHAQ, which results in a saturation curve. The full line in the figure shows the best fit obtained by means of this procedure, by monitoring at 538 nm. Similar plots were obtained for the systems whose association constants and molar extinction coefficients are included in Table 1. From the Benesi–Hildebrand method, straight lines were obtained [see Fig. 3 (main)] by plotting xanD concentration/absorbance of the positive band vs 1/Q concentration in water. From slope and ordinate $K_{\text{ass(BH)}}$ and $\varepsilon_{c(BH)}$ were evaluated.

As can be seen in Table 1, the values for association constants determined by fluorescence and absorption methods exhibit a fair coincidence. The experimental error was estimated within ±10% and ±15% for the fluorescence and absorption methods, respectively.

In order to obtain information to elucidate the nature of the association, both xanD and quinones were varied. Also, solvents of different polarity

TABLE 1

Apparent Association Constants (K_{ass}) and Molar Absorption Coefficients (ε, M^{-1} cm^{-1}) for the Complexes xanD–Q in Different Solvents, as Determined by Fluorescence Quenching ($K_{ass(F)}$, M^{-1}) and Electronic Absorption ($K_{ass(BH)}$, M^{-1}) Experiments.

Quinone	Solvent	RB			EOS			ERY			MC		
		$K_{ass(BH)}$	ε	$K_{ass(F)}$	$K_{ass(BH)}$	ε	$K_{ass(F)}$	$K_{ass(BH)}$	ε	$K_{ass(F)}$	$K_{ass(BH)}$	ε	$K_{ass(F)}$
BQ 	EtOH	33	21100		162	5400		275	7770		240	19500	
	EtOH-Tol(1:4)	36	3400	35									
	MeCN				218	95700							
	H_2O	28	24100	28									
DQ 	EtOH	96	23100	112	106	200000	104	75	358000	72	242	23300	
	MeCN	395	64400		168	51600							
AQ 	EtOH				309	26700		2700	9020		647	2900	
2,6-DOH AQ 	EtOH	259	49000		1500	15000		211	76000	276	350	42600	
2-SAQ 	H_2O	104	36300		581	26500		820	25600		378	11900	

[water, MeCN, EtOH and EtOH:tol 1:4 (v/v)] were employed. Results are shown in Table 1.

3.2 Interaction of quinones with RB excited triplet state

For the study of the interactions of the xanD in the triplet state with ground state Q [eqn (3)] we chose the systems RB–BQ and RB–DQ.

The triplet state of RB was generated and detected as described in the experimental section. The solvent was MeCN, for which the RB-triplet state is well characterized [6]. In the region of the ground state absorption, a strong bleaching occurs in the spectrum of the transient species [see Fig. 4 (inset)]. Positive absorbance can be observed at both sides of this ground state maximum (approximately 550 nm). Our transient absorption spectrum determined at delay of 10 μs after the laser pulse was similar to that reported by Witgens *et al.* [6]. These authors established that the absorptions below 500 nm are due not only to the triplet state but also to the semioxidized and semireduced forms of the dye.

The presence of Q in concentrations up to 2×10^{-4} M appreciably decreases the lifetime of RB excited triplet state. Our triplet lifetime measurements were done at 650 nm. In this region the interference from other species is negligible. The values of the bimolecular rate constants for the quenching of

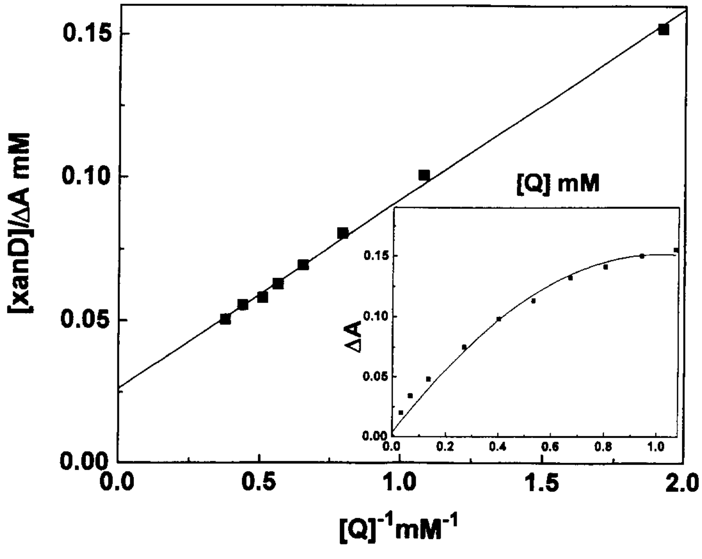


Fig. 3. Benesi–Hildebrand plot (see text) for the association Mc–2,6–DOHAQ in EtOH. Inset: Saturation curve for the system Eos–2,6–DOHAQ in EtOH. Monitoring wavelength 538 nm.

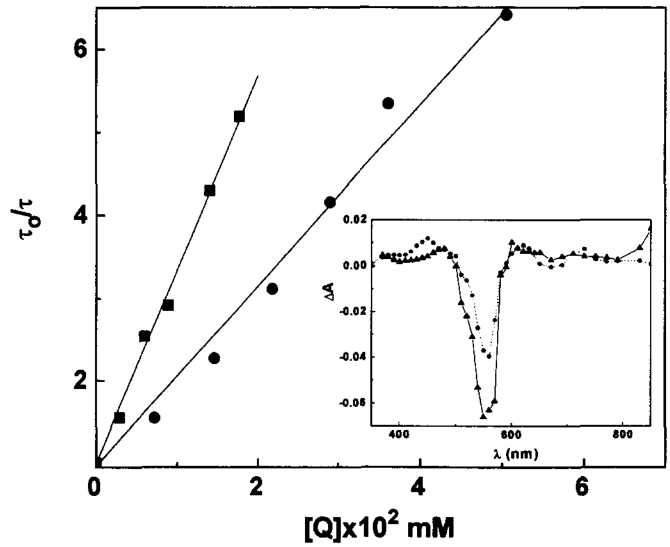


Fig. 4. Stern–Volmer plots for the quenching of $^3RB^*$ by DQ (●) and BQ (■) in MeCN at RT. Inset: Difference absorption spectra (10 ms after the laser pulse, 532 nm) of RB, $Abs_{532} = 0.1$, in degassed MeCN solution, in the absence (▲) and in the presence (●) of DQ 3×10^{-2} mM.

triplet RB by the Q (k_qT) in MeCN were 8×10^9 and $2.2 \times 10^9\,M^{-1}s^{-1}$ for BQ and DQ, respectively, at RT. They were obtained through Stern–Volmer treatment, [eqn (3), Fig. 4 (main)] by determining the triplet lifetime of RB in the absence (τ°) and in the presence (τ) of different concentrations of the Q-derivatives ([Q]), in argon-saturated solutions.

$$\tau^\circ/\tau^\circ = 1 + k_qT\tau^\circ[Q] \qquad (3)$$

4 DISCUSSION

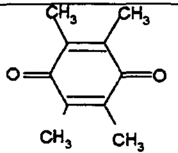
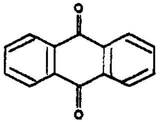
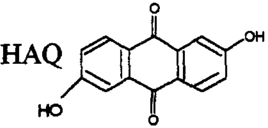
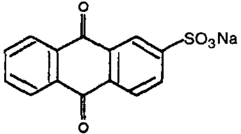
4.1 Dark association xanD–Q

As stated in the preceeding section, the temperature dependence of the interaction RB–BQ indicates the formation of a complex, rather than a chemical reaction between the dyes and the quinones. The K_{ass} values were obtained by two different standard methods in order to quantitatively ensure the respective stability of the association complexes. This was done in view of the lack of correlation of K_{ass} values with certain parameters of currently accepted criteria (see further) for the assignment of a given association mechanism.

Articles regarding dark association of xanthene dyes with organic electron-donors have been published by other authors [7–10] and by ourselves [11]. The work by Labos [7] and the two contributions by Molnar *et al.* [9, 10], attribute the interaction of xanD–chloropromazine to the formation of charge-transfer complexes, through indirect experimental evidence. Chrysochoos [8] describes the association of aromatic amines and pyridine with eosin. Martinez *et al.* [11] studied the ground state interaction between Mc and some amino acids such as tryptophan and histidine. In the mentioned papers the description of spectral changes caused by the association are very similar in shape to those described in the present work for the system xanD–Q. Chrysochoos [8] postulated that the molecular association is due to a composition of charge–dipole and charge–transfer (CT) processes. In all cases described in the literature, the xanD constituted the electron-acceptor entity. It is known that when a CT complex is formed, the energy of the new absorption bands (Table 2), which are not affiliated to either the donor or the acceptor, linearly depends on the electron affinity (E_A) of the acceptor and on the ionization potential (I_p) of the donor [5]. Unfortunately E_A and I_p values for our set of compounds in Table 1 are not reported in the literature; nevertheless, in a first coarse approximation, some dependence should be expected employing and the redox potentials of the interaction partners, whose values are known [12, 13]. Following this line, a bathochromic shift should be observed as follows: $\bar{\nu}$ RB complexes $<\bar{\nu}$ Eos complexes $<\bar{\nu}$ Ery complexes, as a function of the reduction potentials of the xanD (RB, $E_{1/2} = -0.533$ volts, Eos, $E_{1/2} = -0.463$ volts and Ery, $E_{1/2} = -0.290$ volts, from Ref. 12. No information on the redox potential of MC could be found). This trend is not verified by the series xanD–Q (the energies for the respective complex absorption bands, are given in Table 2). Furthermore, the data in Table 2 correlates nearly as the opposite to the expectations for XanD playing the role of the acceptor entity. In other words, experimental data indicate that if a charge charge transfer process between XanD and quinones is operating, the dyes should play the role of electron donors. This is not a surprising result if the picture is observed from the corner of the quinone derivatives. These compounds have been profusely described in the literature as strong electron acceptors in charge transfer-like complexes with a variety of organic molecules and inorganic couples, including some dyes such as rivoflavin [14, 15] and phenothiazine [16]. In the present case, assuming a charge-transfer mechanism from the xanD, a bathochromic shift of the complex absorption band, for a given xanD, should be observed, in the order: energy AQ ($E_{1/2} = 0.94$ volts) $\cong$ 2-SAQ ($E_{1/2} = 0.941$ volts) $>$ DQ ($E_{1/2} = 0.84$ volts) $>$ BQ ($E_{1/2} = 0.50$ volts). The electrochemical data were obtained from Ref. 13. As can be seen in Table 1, this correlation is also not reflected by the respective energy values for the band of the complex. As a

TABLE 2

Energy of the Transition for the Complexes xanD–Q in Different Solvents as Determined by Electronic Absorption Experiments

Quinone		*Solvent*	*RB*	*EOS*	*ERY*	*MC*
			$\bar{\nu}x10^{-4}(cm^{-1})$	$\bar{\nu}x10^{-4}(cm^{-1})$	$\bar{\nu}x10^{-4}(cm^{-1})$	$\bar{\nu}x10^{-4}(cm^{-1})$
BQ		EtOH	1.79	1.87	1.83	1.87
		EtOH-Tol(1:4)	1.79			
		MeCN		1.85		
		H_2O	1.76			
DQ		EtOH	1.74	1.86	1.83	1.87
		MeCN	1.74	1.85		
AQ		EtOH		1.87	1.83	1.85
2,6-DOHAQ		EtOH	1.75	1.86	1.84	1.84
2-SAQ		H_2O	1.77	1.87	1.83	1.91

consequence, we think that, even when a certain component of charge transfer from the xanD could partially operate, the main driving force for the association xanD–Q should be attributed to some other phenomena. An additional strong evidence against a pure charge transfer mechanism is given by the lack of dependence of $\bar{\nu}$ values on the solvent polarity. In the case of the complex RB–BQ for example, even when $\bar{\nu}$, in water, reaches the lower value, the equality between the respective ν for (Tol–EtOH (4 : 1, v/v)) and $\bar{\nu}$ (EtOH) is not in agreement with the expected behaviour for a charge–transfer process.

Under the conditions of this study, the different xanD exist either as monoanionic, dianionic or neutral species [2]. In all cases, the dyes constitute relatively highly polar species. On this basis, intermolecular interactions in the XanD–Q systems are probably due to a governing mechanism constituted by dispersive forces. In this way, ion-induced dipole and dipole-induced dipole interactions (depending on the solvent and on the xanthene molecule) could constitute the main driving force for the association, which is possibly accompanied by a minor charge transfer-like component, in which the xanD operates as the donor molecule. In Fig. 5 we graphically represent the energy value for electronic absorption of the complexes XanD–DQ as a function of the respective energy values for the complexes of the

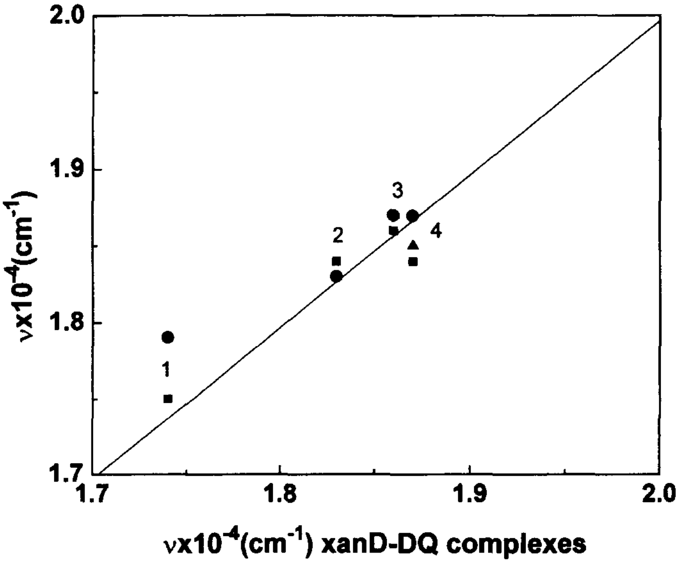


Fig. 5. Energy values for the electronic absorption of the complexes xanD–DQ as a function of the respective energy values for the complexes xanD–Q. ●: BQ; ▲: AQ and ■: 2,6-DOHAQ. Group 1: RB-complexes; group 2: Ery-complexes; group 3: Eos-complexes; and group 4: MC-complexes.

XanD with BQ, AQ and 2,6-DOHAQ. Even when the energy values do not correlate with the redox potential of the association partners, as already said, a certain trend of the experimental points is observed. This trend could indicate similar behaviour in the respective specific interactions driving XanD–Q associations, which do not obey a pure charge–transfer mechanism.

4.2 The interaction of quinones with ^{3}xanD*

The photochemical literature, especially in the 1970s, describes photo-oxidative and photo-reductive reactions of xanD, especially through interactions of triplet excited states of the dyes with a variety of electron acceptors and donors [17]. While a large number of reports have been published on the photoreduction of xanD with different reductants, not many studies have been made about the photooxidation with oxidants other than oxygen.

Some evidence for the interaction of quinonic derivatives with excited triplet states of xanD have been reported in the literature [7]: the closest to our case was investigated by Ohno *et al.* [18]. The authors state that when BQ is added to a concentration 1 mM to Eos, the transient absorption due to half-oxidized Eos is exactly proportional to the absorbance at 430 nm, due to the appearance of benzosemiquinone. No quantitative kinetic determinations were reported. The picture can be described by reaction (4) as follows:

$$^3\mathrm{Eos}^* + \mathrm{BQ} \rightarrow \mathrm{Eos}^{\cdot+}\mathrm{BQ}^{\cdot-} \qquad (4)$$

Apparently, the systems triplet-RB–BQ and triplet-RB–DQ behave in a similar fashion: the transient absorption due to semioxidized RB greatly increases in the presence of DQ [Fig. 4 (inset)]. The same was true for the experiments in the presence of BQ. The rate constant for triplet sate quenching by BQ is closer to the diffusional value [19] in MeCN. For the less oxidant DQ (see above for reduction potentials) the rate constant was clearly decreased.

5 CONCLUSION

The existence of ground state and triplet excited xanD interactions in natural media, in which a variety of quinonic derivatives could exist, formed as primary photoproducts of environmental contaminants photooxidation, may have a serious implication in the context of Type II photooxidations, sensitized by xanD; it is the inhibitory effect on O_2 ($^1\Delta_g$) generation in the presence of relatively low concentrations of Q. At 0.1 mM quinone concentrations, reaction (5) (quenching of triplet RB by the quinones) favourably competes with reaction (6) (singlet molecular oxygen generation), i.e. $k_{ET}\left[O_2\left({}^3\Sigma_g^-\right)\right] < k_{qT}[Q]$, being $\left[O_2\left({}^3\Sigma_g^-\right)\right]$ the ground state oxygen concentration, and assuming that k_{ET} is 1/9 of the diffusional value [18] and air-saturated solutions were employed (concentration of dissolved oxygen in water 0.26 mM [20]).

$$ {}^3RB^* + Q \xrightarrow{k_{qT}} RB^{\cdot+} + Q^{\cdot-} \tag{5} $$

$$ {}^3RB^* + O_2\left({}^3\Sigma_g^-\right)\Big] \xrightarrow{k_{ET}} RB + O_2({}^1\Delta_g)] \tag{6} $$

Besides, the formation of aggregates xanD–Q, possessing high association constants (Table 1) in most of the cases, diminishes the availability of exitable (free) xanD to negligible concentrations.

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