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The excited states quenching of phenothiazine dyes by p-benzoquinones in polar solvents

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Abstract

The quenching of the excited singlet and triplet states of Methylene Blue and the Azures A, B and C by p-benzoquinones was investigated in methanol and acetonitrile. Fluorescence lifetimes were determined for the dyes, and from fluorescence quenching experiments rate constants were obtained for the singlet state process. Singlet quenching rate constants are nearly diffusion controlled in both solvents. Triplet state processes and transient absorption spectra were investigated by laser flash photolysis. Triplet quenching rate constants were obtained from the decay of the triplet at 830 nm as a function of the quinone concentration. The rate constants for the triplet state reaction are lower than those of the excited singlet, but the triplet process is efficient at lower quinone concentrations. From the transient absorption determinations it was concluded that the quenching proceeds by an electron transfer reaction from the dye excited states to the quinones. It is concluded that these dyes may function as very efficient photochemical reductants. © 1999 Published by Elsevier Science Ltd. All rights reserved.

Keywords: Methylene Blue; Azures; Fluorescence quenching; Triplet quenching; T–T absorption spectra; Electron transfer

1. Introduction

The one electron photoreduction of dyes by various types of electron donors has been the subject of numerous studies. The interest in these processes arises mainly from its potential application as sensitizers in photogalvanic cells [1,2] and as photoinitiating systems in vinyl polymerization [3,4]. On the other hand, the one electron photo-oxidation of dyes has received much less attention. Only a few studies seem to exist on the one electron oxidation of the excited states of dyes by neutral organic electron acceptors [3]. In particular the quenching of excited states of dyes by quinones is of interest due to the important role of the quinone moiety as an electron acceptor in photobiological processes [5]. Recently we have reported on the photo-oxidation of the excited states of the dye Safranine T by p-benzoquinones in polar solvents [6]. Both the excited singlet and triplet states react by an electron transfer quenching mechanism.

Methylene Blue is a well-known photochemical oxidant. The photoreduction reaction of this dye by various types of electron donors has been studied quite often, and in most cases an electron transfer mechanism was proposed for explaining the observed results [7,8]. However the photo-oxidation of Methylene Blue has been the subject of minor concern compared with the photoreduction reactions. The triplet quenching of Methylene Blue by p-benzoquinone was investigated in ethanolic solutions by Misran et al. [9]. An electron transfer mechanism was proposed for the quenching

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reaction. Since we have observed that the photooxidation of Safranine T, a dye of the phenazine class, by quinones proceeds very efficiently in polar solvents, we decided to undertake a similar study with dyes of the phenothiazine group. According to the excited state properties and oxidation potential of Methylene Blue, it is expected that the electron transfer reaction from both the excited singlet and triplet state to quinones would proceed and will favorable compete with the decay of the dye's excited states.

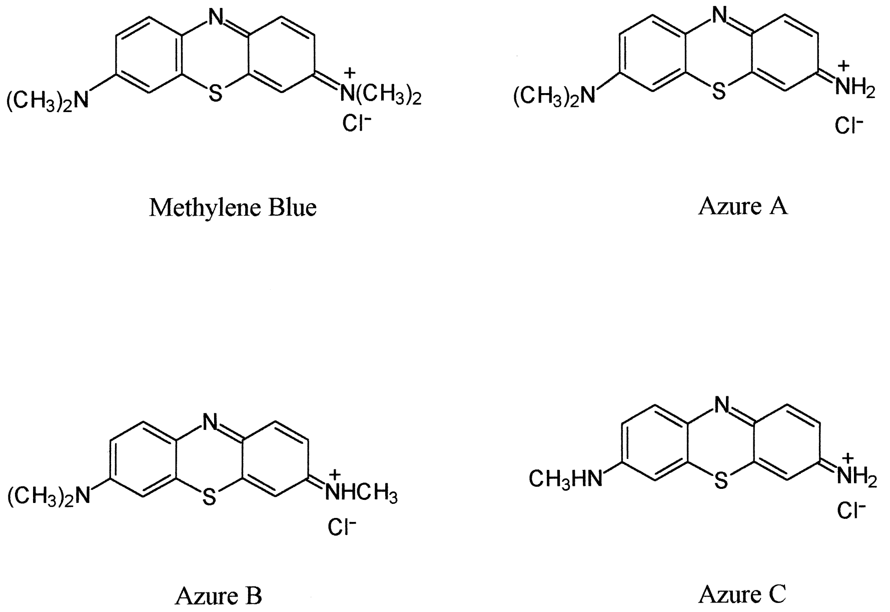
In this work we present results of fluorescence quenching and laser flash photolysis of Methylene Blue and the azures A, B and C (Scheme 1) in the presence of several p-benzoquinones in methanol and acetonitrile. It is known that bimolecular deactivation of the excited states of dyes in organic solvents may occur by proton transfer, or hydrogen bonding in the excited state, as a parallel route to electron transfer quenching [10]. Here we present a study on the excited states quenching of a series dyes with a common structural pattern, differing only on the extent of methyl substitution. The possibility of hydrogen bonding will change on going from Methylene Blue, a tetramethylated dye, to Azure C with only one methyl on the amino groups. In this way a further mechanistic evidence may be obtained.

For the four dyes it is found that singlet quenching rate constants are nearly diffusion controlled in both solvents. The rate constants for the triplet state reaction are lower, but the triplet process is effective at lower quinone concentrations. It is concluded that these dyes may function as very efficient photochemical reductants.

2. Materials and methods

Methylene Blue (MB) (Merck) was used as received. Azures A, B, and C were purified by column chromatography. The quinones, chloranil (tetrachloro p-benzoquinone) (Chl), p-benzoquinone (BQ), methyl-p-benzoquinone (MQ) 2,5-dimethyl-p-benzoquinone (DMQ) and duroquinone (tetramethyl p-benzoquinone) (DQ) were obtained from various commercial sources. They were purified by recrystallization and/or sublimation when necessary. The solvents methanol (MeOH) and acetonitrile (MeCN) were HPLC grade.

Stationary fluorescence quenching experiments were carried out at room temperature in air



Scheme 1.

equilibrated solutions (25 ± 1°C) with a Spex Fluoromax spectrofluorometer. Fluorescence lifetime measurements were carried out with the time-correlated single photon counting technique on an Edinburgh OB-900 instrument.

Transient absorption spectra and triplet quenching were determined with a laser flash photolysis. A Spectron SL400 Nd-YAG laser generating 532 nm laser pulses (~18 ns pulse width) was the excitation source. The laser beam was defocused in order to cover all the path length (10 mm) of the analyzing beam from a 150 W Xe lamp. The experiments were performed with rectangular quartz cells with right angle geometry. The detection system comprises a PTI monochromator coupled to a Hamamatsu R666 PM tube. The signal was acquired by a digitizing scope (Hewlett–Packard 54504) where it was averaged and then transferred to a computer. The solutions were deoxygenated by bubbling with high purity argon. The dyes' concentrations were ca 5×10^{-5} M in order to minimize self quenching effect on the triplet decay. At these concentrations and in the solvents here employed, dimerization processes are unimportant.

3. Results and discussion

3.1. Singlet quenching

In polar solvents and at low concentration, the dyes are present as monomer species. Fluorescence lifetimes for the four dyes in the two solvents were determined by the single photon counting technique and are collected in Table 1. Ground state interactions with the quencher can be disregarded because no changes were observed in the absorption spectrum of the dye on addition of the quenchers in the concentration range studied. The fluorescent emission of the dye is quenched by the quinones in both solvents. Bimolecular quenching rate constants for the excited singlet quenching were determined from the slopes of Stern–Volmer plots with the aid of the lifetimes in Table 1.

Singlet quenching by chloranil in MeOH was not measured due to its very low solubility in this solvent. The quenching rate constants are collected in Tables 2 and 3 in acetonitrile and methanol, respectively. Fluorescence quenching studies of Azure C in acetonitrile were precluded by a dark chemical reaction with the quinones.

In can be seen that the rate constants reach limiting values of 1.5×10^{10} and $2.9\times10^{10}\mathrm{M}^{-1}\,\mathrm{s}^{-1}$ were obtained in MeOH and MeCN, respectively, for chloranil. These values coincide with the diffusional limit in these solvents [11]. In Table 2 the reduction potentials of the quinones are presented. It can be seen that in both solvents the rate constants decrease when the reduction potential of the quinones increases. The dependence on the reduction potential is more pronounced in the case of MeCN. In this solvent the rate constants are reduced by a factor between

Table 1
Excited singlet lifetimes (ns) in air equilibrated solutions at 25°C

	MePH	MeCN
Methyl blue	0.7	1.2
Azure A	0.9	1.3
Azure B	0.8	1.1
Azure C	1.1	–

Table 2
Methylene Blue and Azures singlet quenching rates constants in acetonitrile (in units of 10^{10} M^{-1} s^{-1})

Quencher ($E_{1/2}/V$)	Azure A	Azure B	Methylene Blue
Chl (−0.01)	2.2	2.9	2.4
BQ (0.50)	1.6	1.8	1.1
MQ (0.58)	1.3	1.5	1.1
DMQ (0.67)	0.9	1.9	0.4
DQ (0.84)	0.2	0.3	0.3

Table 3
Methylene Blue and Azures singlet quenching rates constant in methanol (in units of 10^{10} M^{-1} s^{-1})

Quencher ($E_{1/2}/V$)	Azure A	Azure B	Azure C	Methylene Blue
BQ (0.50)	1.3	1.5	1.0	1.5
MQ (0.58)	1.7	1.3	1.15	1.3
DMQ (0.67)	1.0	0.8	0.8	0.8
DQ (0.84)	0.9	0.8	0.7	0.6

2 and 3 on going from chloranil (diffusion limit) to duroquinone, while in MeOH the decrease is less notable.

From the dependence of the rate constants on the acceptor capability of the quinones, an electron transfer mechanism may be advanced for the quenching reaction:

$$ {}^{1}D^{+*} + Q \rightarrow D^{+2\cdot} + Q^{-\cdot} $$

where ${}^{1}D^{+*}$ stands for the excited singlet of the dye and $D^{+2\cdot}$ and $Q^{-\cdot}$ are the semireduced form of the dye and the radical anion of the quinone, respectively.

3.2. Triplet quenching and laser flash photolysis experiments

When MB or azures solutions are laser flash irradiated, the only transient species after the laser pulse is the excited triplet of the dye. The T–T absorption spectra of the four dyes are very similar, with peaks near 420 and 850 nm in both solvents. A typical spectrum is shown in Fig. 1 for the case of azure A in MeCN. Immediately after the laser pulse, the two bands of the T–T absorption spectrum at 830 and 420 can be seen. At longer times, the absorption at 830 nm is greatly reduced, while a slight red shifted absorption remains in the region 400–450 nm and a new band is present ca 500 nm and beyond. The latter cannot be defined in the region beyond 500 nm due to the strong absorption of the ground state of the dye. The long lived bands can be ascribed to the semireduced and semioxidized forms of the dye [7,8], that arise in the self-quenching process:

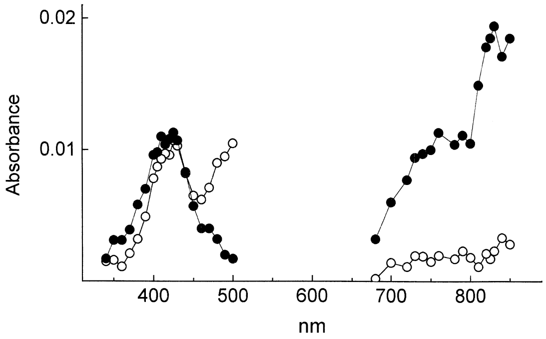


Fig. 1. Transient absorption spectra of Azure A in MeCN, taken (●) immediately and (○) at 10 µs after the laser pulse at 532 nm.

$$ {}^{3}D^{+*} + D \rightarrow D^{\cdot} + D^{+2\cdot} $$

where ${}^{3}D^{+*}$ stands for the dye triplet state and $D^{\cdot}$ and $D^{+2\cdot}$ are the semireduced and semioxidized forms, respectively. The corresponding spectra for MB in MeOH are shown in Fig. 2.

In the presence of the quinones at concentrations such that the excited singlet of the dye is not quenched, a shortening of the lifetime of the long wavelength band is observed, while an increase in the intensity and a different time profile is observed in the region of 400–450 nm. These changes are shown in Fig. 3 for the case of Azure A quenched by Chl in acetonitrile. It can be seen that the decay in the red absorbing region is shortened while the absorption increases at 405 nm. These changes are also presented in the form of transient absorption spectra for the case of MB/BQ in MeOH in Fig. 4. Here again, an enhancement in the absorption in the region of 420 nm is evident in the presence of the quinone. In all cases the absorption ca 400 nm increases with a time constant that parallels the triplet decay in the presence of the quinone (Fig. 3b). It is well known that benzoquinone radical anions and their protonated forms absorb in the wavelength range of 400–450 nm [12] and the semioxidized dye may also be absorbing at these wavelengths. Thus, the

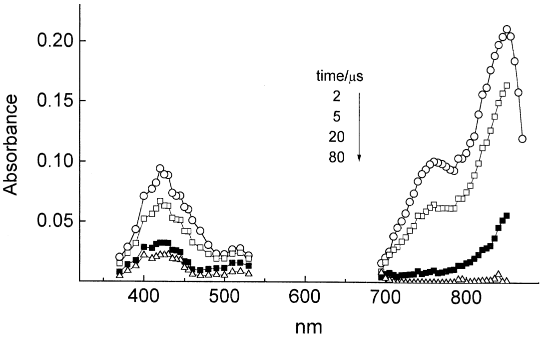


Fig. 2. Transient absorption spectra of MB in MeOH.

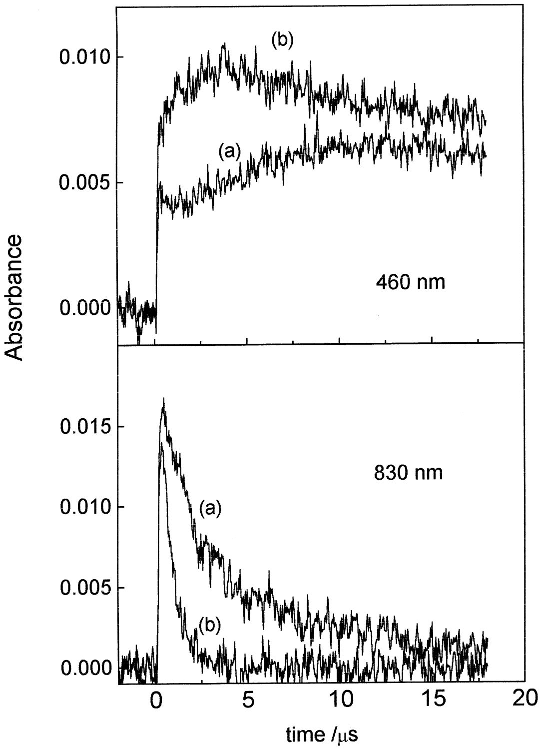


Fig. 3. Transient absorption profiles of Azure A in MeCN in (a) the absence and (b) the presence of chloranil 1.6×10^{-4} M.

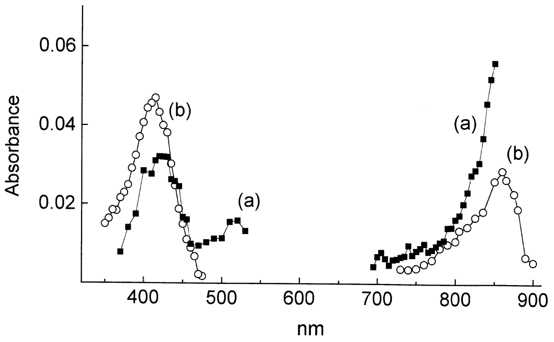


Fig. 4. Transient absorption spectrum of MB in MeOH in (a) the absence and (b) the presence of BQ 0.0016 M taken at 20 μs after the laser pulse.

triplet quenching of MB and the Azures by p-benzoquinones can be described by the electron transfer process:

$$^3D^{+*} + Q \rightarrow D^{+2\cdot} + Q^{-\cdot}$$

Bimolecular quenching rate constants were obtained from the triplet decay monitored at 830 nm. First order decay rate constants were plotted as a function of the quinone concentration, and from the slope, the second order rate constant resulted. Examples of those plots are presented in Fig. 5 for the quenching of MB in acetonitrile and in Fig. 6 for the quenching in methanol. The rate constants for the for dyes are collected in Tables 4 and 5 in acetonitrile and methanol, respectively.

In their classic work on electron transfer fluorescence quenching, Rehm and Weller demonstrated that the rate constants depend on the free energy change involved in the electron transfer process. The latter is normally calculated [13,14] from the redox potential of the donor $E_{(D/D^+)}$ and acceptor $E_{(A/A^-)}$, and the energy of the excited state involved

$$\Delta G^o = E_{(D/D^+)} - E_{(A/A^-)} - E^* + \frac{z_1 z_2}{D r_{12}} \tag{1}$$

where E^* is the energy of the excited state, and the last term represents the coulombic energy necessary to form an ion pair with charges z_1 and z_2 in a medium of dielectric constant D for a distance r_{12}.

The free energy changes were estimated with Eq. (1) using an oxidation potential of 1.17 V for the MB cation [15]. The reduction potentials of the quinones in MeCN vs SCE were from Refs. [16,17]. The excited singlet energy of MB was taken as 1.84 eV [18] in both solvents. Similarly for the triplet energy we used 1.44 eV [19]. The coulombic term was calculated as -0.12 eV, assuming $+2$ and -1 charges in the final state and a charge separation of 0.7 nm.

In Fig. 7, a plot of the rate constants vs the free energy change is shown for the quenching of the excited singlet and triplet states of MB. The solid line was calculated with the theoretical expression derived by Rehm and Weller [13] for the electron transfer quenching, with a value of $3 \times 10^{10} M^{-1} s^{-1}$ for the diffusion limit rate constant. The broken line was obtained by application of Marcus

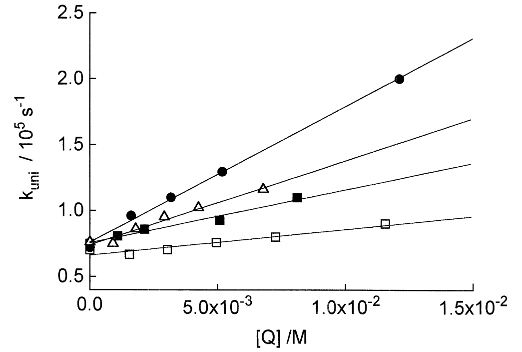


Fig. 5. Triplet first order decay rate constants for MB in MeCN as a function of quinones' concentration: (■) DMQ; (□) BQ; (●) MQ; (△) DQ.

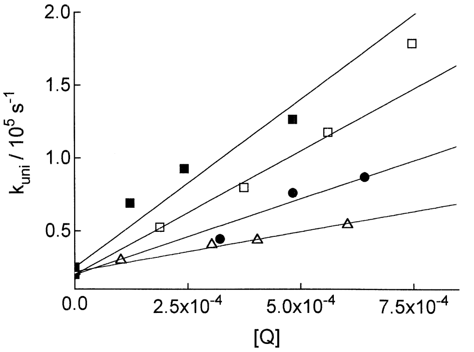


Fig. 6. Triplet first order decay rate constants for MB in MeOH as a function of quinones' concentration: (■) DMQ; (□) BQ; (●) MQ; (△) DQ.

theory for excited state electron transfer reaction as previously described [6]. The fitting parameters are the same as those employed for the quenching of Safranine T by quinones in MeCN, except for the pre-exponential factor that is $1\times10^{12}M^{-1}$ s^{-1} for the quenching of MB excited states to be compared with 3.5×10^{11} M^{-1} s^{-1} for the quenching of Safranine T. Although the difference between the two theoretical models is small, the one based on Marcus theory offers a better agreement with the experimental data.

Table 4
Methylene Blue and Azures triplet quenching rates constant in acetonitrile (in units of M^{-1} s^{-1})

Quencher ($E_{1/2}/V$)	Azure A	Azure B	Azure C	Methylene Blue
Chl (−0.01)	0.6×10^9	4.8×10^9	4.6×10^9	2.6×10^9
BQ (0.50)	2.8×10^7	8.4×10^6	8.6×10^6	2.0×10^6
MQ (0.58)	1.5×10^7	1.7×10^6	2.4×10^7	1.0×10^7
DMQ (0.67)	8.2×10^6	9.3×10^6	1.7×10^7	4.0×10^6
DW (0.84)	6.0×10^6	1.8×10^7	1.4×10^6	6.4×10^6

Table 5
Methylene Blue and Azures triplet quenching rates constant in methanol (in units of M^{-1} s^{-1})

Quencher ($E_{1/2}/V$)	Azure A	Azure B	Azure C	Methylene Blue
BQ (0.50)	3.6×10^8	1.9×10^8	3.6×10^8	1.7×10^8
MQ (0.58)	5.6×10^8	2.5×10^8	1.3×10^8	1.0×10^8
DMQ (0.67)	3.9×10^8	2.2×10^8	1.1×10^8	2.3×10^8
DQ (0.84)	8.4×10^7	1.2×10^8	1.3×10^8	5.5×10^7

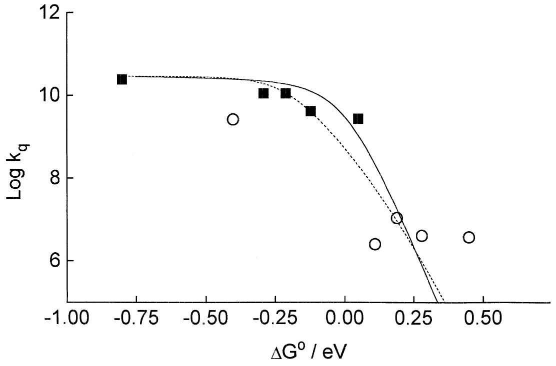


Fig. 7. Plot of log k_q vs the free energy change for the electron transfer process: (■) singlet quenching; (○) triplet quenching.

The experimental data in MeOH is not plotted in Fig. 7 since the rate constants are consistently higher in this solvent. This difference was formerly observed for the quenching of Safranine T by quinones [6]. This solvent effect may be due to several causes. Since it is found that in MeCN the data follow a correlation with the driving force, the solvent effect may be analyzed in terms of the accepted models for electron transfer reactions. According to Marcus classical theory, the solvent may influence the electron transfer rate constant by altering several of the parameters involved. However, in the classical version of the theory, the kinetics depends only on the driving force and the reorganization energy, and these quantities are only a function of the macroscopic dielectric properties of the solvent. For MeOH and MeCN these quantities, the dielectric constant and the refractive index, are very similar. Therefore, large differences in the kinetics are not expected between MeCN and MeOH. The experimental trend must be due to some specific solvent effect. Higher rates in MeOH were previously observed for several electron transfer processes involving excited states [19]. However, in the case of the quenching of excited states of dyes by quinones, the effect is very much remarkable. This strong dependence on the solvent type probably reflects the hydrogen bonding interaction of the quencher with the hydroxylic solvent. This interaction may alter the kinetics by changes in the reduction potential or the reorganization energy. At this point it is important to note that there were not large differences in the kinetics of quenching among the four dyes. Therefore, a common mechanism is probably operating in all cases.

It may be seen in Fig. 7 that the data for the triplet, when considered independently of the rest, presents a very weak dependence on the driving force. As similar conclusion can be extracted from inspection of Tables 4 and 5 for the triplet quenching of the azures in both solvents. This could be caused by some contribution of a parallel quenching pathway other than single electron transfer. The intermediacy of an exciplex may explain the high values at positives ΔG^0 and the small dependence with the driving force. A similar model was proposed by Kiyota et al. [20] for the quenching of triplet benzophenone by naphthylamines, and by Kuzmin [21] for the excited singlet quenching in polar solvents, when departure from Rehm–Weller behavior is observed.

In summary, the excited states of Methylene Blue and the related dyes, Azures A, B and C, are quenched by p-benzoquinones by a charge transfer mechanism. In the quenching reaction, long lived species are formed absorbing in the region of 400–450 nm that are tentatively assigned to the radicals formed in a single electron transfer process.

Acknowledgements

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