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The excited states quenching of safranine T by *p*-benzoquinones in polar solvents

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Abstract

Safranine T 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 many cases mechanism accounting for the observed results were proposed and explained in terms of electron transfer theories. Only a few studies seem to exist on reactions of this dye with electrons acceptor. In this work we present results of fluorescence quenching and laser flash photolysis which demonstrate that safranine T may function also as a photochemical reductant with *p*-benzoquinones as electron acceptors in methanol and acetonitrile. Singlet quenching rate constants are nearly diffusion controlled in both solvents. Triplet quenching rates constants were obtained from the decay of the triplet at 830 nm as a function of quinone concentration. They follow a Rehm and Weller type correlation for electron transfer in acetonitrile, while in methanol the rate constants for triplet quenching are substantially larger. © 1997 Elsevier Science S.A. All rights reserved.

Keywords: Dyes; Safranine; Photooxidation; Electron transfer

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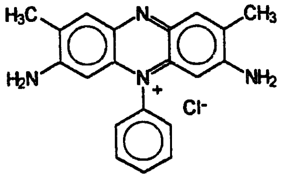
1. Introduction

The photoreduction of dyes by various types of electron donors has been studied quite often. The interest in these processes arises mainly from its potential application as sensitizers in photogalvanic cells [1] and in photoinitiating systems in vinyl polymerization [2]. In most cases the photoreduction mechanism involves an electron transfer step [3] and the observed results were explained in terms of the current theories for these reactions [4]. In particular safranine T (Scheme 1), a dye of the phenazine class, has received considerable attention as a sensitizer for photoinitiating system [5,6] and for several other applications including solar energy conversion (see [7] and references therein). We have previously studied the photoreduction of safranine excited states by substituted anilines and phenols in methanol [8] and by aliphatic amines in polar solvents [9]. The photoreduction of the dye by aliphatic amines was also employed successfully as a photoinitiating system for vinyl polymerization [5]. Since the dye is water soluble, its interaction with aliphatic amines in aqueous solution has attracted our interest from the mechanistic point of view [10] and also as a polymerizing system for water soluble monomers [11].



Scheme 1. Safranine T chloride.

However, the photooxidation of dyes in general and that of safranine in particular has been a subject of minor concern compared with the photoreduction reactions. Only a few studies seem to exist on the one electron oxidation of the excited states of dyes by neutral organic electron acceptors [2]. Using pulse radiolysis Guha et al. [12] studied the oxidation of safranine using specific one electron oxidizing radicals such as Cl_2^-, Tl^{+2}, $Tl(OH)^+$ and $N_3^{\cdot}$. They were able to characterized the semioxidized safranine by its absorption spectrum (λ_{max} 470 nm). To our knowledge the photochemical one electron oxidation of safranine has not been reported in the literature. It is well known that quinones are efficient one electron oxidants in photochemical reactions. According to their reduction potentials and the properties of singlet and triplet excited states of safranine [6,12] benzoquinones may act as efficient photooxidant of the dye. In this paper we present results on the quenching of the excited states of the dye by *p*-benzoquinones. Both the singlet and the triplet states

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are quenched by the quinones, and the kinetics and spectral data confirm that the quenching process is a one electron oxidation of the dye. Bimolecular quenching rate constants were measured in methanol and acetonitrile. A pronounced specific solvent effect was observed when the rate constants are below the diffusion limit.

2. Experimental details

Safranine T chloride (SfCl) from Aldrich, was recrystallized from ethanol before used. Its purity was checked by comparison of its spectral and photophysical properties with the known data. The quinones, chloranil, *p*-benzoquinone, methyl-*p*-benzoquinone, 2,5-dimethyl-*p*-benzoquinone, and duroquinone were obtained from various commercial sources. They were purified by recrystallization and/or sublimation when necessary, otherwise they were used as received. The solvents methanol and acetonitrile (MeCN) were HPLC grade.

Stationary fluorescence quenching experiments were carried out at room temperature (25 ± 1 °C) using a Spex Fluoromax spectrofluorometer. Excitation and emission wavelengths in MeOH were 529 and 567 nm respectively. In MeCN the corresponding wavelengths were 518 and 560 nm.

Triplet quenching and transient absorption spectra were measured with a Spectron SL400 Nd–YAG system generating 532 nm laser pulses (≈ 8 ns pulse width). The laser beam was defocused in order to cover all the path length (10 mm) of the analysing 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.

All Sf solutions were of concentration 1×10^{-5} M in order to minimize self quenching effect on the triplet decay. For the fluorescence quenching experiments the solutions were air equilibrated. For triplet measurements they were deoxygenated by bubbling with high purity argon.

3. Results and discussion

3.1. Singlet quenching

In polar organic solvents and at the low dye concentration the dye is totally in the form of the monocation, Sf^+. Changes were not observed in the absorption spectrum of the dye on addition of the quenchers in the concentration range studied. Therefore ground state interactions can be disregarded. Bimolecular quenching rate constants for the excited singlet quenching were determined from the slopes of Stern–Volmer plots. The rate constants were evaluated with singlet lifetimes of 2.3 ns in MeOH and 3.6 ns in MeCN [13] and they are collected in Table 1. Singlet quenching by chloranil in MeOH was not measured due to its very low solubility in this solvent. In Table 1 it may be observed that the rate constants increase when the reduction potential of the quinone decreases. Limiting values of 1.5×10^{10} dm^3 mol^{-1} s^{-1} and 2.2×10^{10} dm^3 mol^{-1} s^{-1} were obtained in MeOH and MeCN respectively. This values coincide with the diffusional limit in these solvents [14]. The dependence on the reduction potential of the quencher is more pronounced in the case of MeCN. In this solvent the rate constants are reduced by a factor of 2.5 on going from chloranil (diffusion limit) to duroquinone, while in MeOH the decreasing factor is only 1.6.

3.2. Triplet quenching

Laser flash photolysis experiments, show as the only transient species after the laser pulse, the excited triplet of the monoprotonated form of Sf with peaks at 820 nm and 435 nm in MeOH and 840 nm in MeCN. Typical time profiles at two wavelengths are shown in Fig. 1 in MeOH. In the absence of quenchers the triplet decays by a first order kinetics due to the self quenching process [9]. In these conditions the species contributing to the absorption at 450 nm are the triplet and the semioxidized and semireduced form of the dye, the latter being formed in the self quenching reaction:

$${}^3Sf^{+*} + Sf^+ \rightarrow Sf^{2+\bullet} + Sf^\bullet$$

When Sf^+ is laser flash irradiated in the presence of quinones, Q, a shortening of the lifetime of the long wavelength band is observed, while an increase in intensity and a different

Table 1
Safranine singlet and triplet quenching rate constants by quinones

Quencher	$E_{1/2}$ (V)	k_q (dm^3 mol^{-1} s^{-1})			
		Singlet (MeOH)	Triplet (MeOH)	Singlet (MeCN)	Triplet (MeCN)
Chloranil	−0.01		5.4×10^9	2.2×10^{10}	1.1×10^{10}
p-Benzoquinone	0.50	1.5×10^{10}	3.1×10^9	1.7×10^{10}	3.6×10^8
Methyl-*p*-benzoquinone	0.58	1.5×10^{10}	3.1×10^9	1.5×10^{10}	1.2×10^8
2,5-dimethyl-*p*-benzoquinone	0.67	1.2×10^{10}	1.3×10^9	1.5×10^{10}	3.6×10^7
Duroquinone	0.84	9.6×10^9	3.6×10^7	8.8×10^9	4.1×10^6

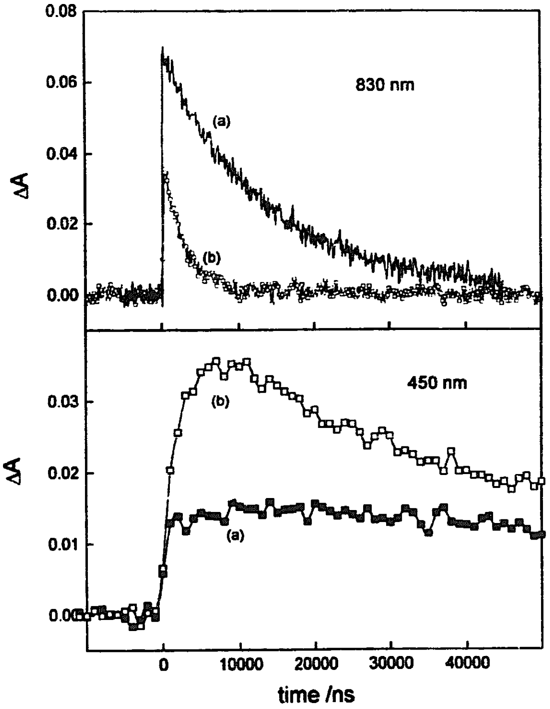

Fig. 1. Transient absorption of Sf after laser flash irradiation at 532 nm in the absence (a) and in the presence of *p*-benzoquinone 1×10^{-4} M in MeOH (b).

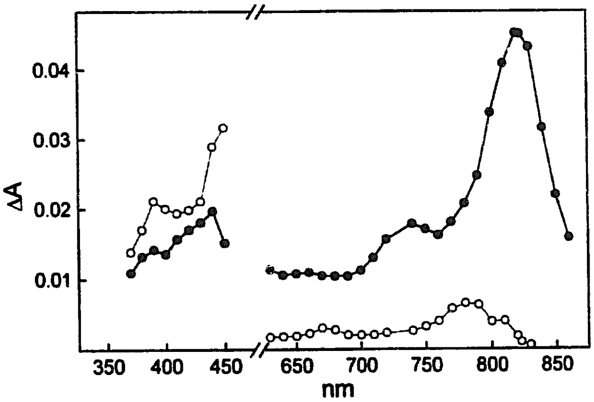

Fig. 2. Transient absorption spectrum of Sf 1×10^{-5} M in MeOH at 10 μs after the laser pulse, in the absence (●) and in the presence of *p*-benzoquinone 1×10^{-4} M (○).

time profile is observed at 450 nm in MeOH, Fig. 1. This may be explained by an electron transfer reaction:

$$^3Sf^{+*}+Q^{+}\rightarrow Sf^{2+\bullet}+Q^{-\bullet}$$

Typical transient absorption spectra in MeOH and MeCN are shown in Figs. 2 and 3 respectively. In both cases it can be observed that in the presence of the quinone the triplet is suppressed while an enhancement in the absorption in the region of 450 nm is evident. The latter absorption may be ascribed to the semioxidized form of Sf according to Guha et al. [12] although the reduced form of the quinones may be absorbing in the same region [15]. The bands can not be defined precisely, since at these wavelengths starts the strong absorption of Sf ground state. Nevertheless the augmenting of absorption in the presence of quinones may be taken as an evidence for the one electron photooxidation reaction.

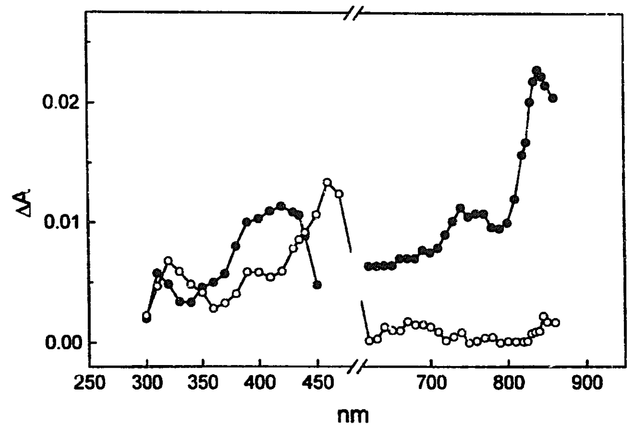

Fig. 3. Transient absorption spectrum of Sf 1×10^{-5} M in MeCN at 10 μs after the laser pulse, in the absence (●) and in the presence of *p*-benzoquinone 1×10^{-3} M (○).

From the decay of the T–T absorption as a function of quinone concentration triplet quenching rate constants were determined. They are also collected in Table 1. It can be noticed that they decreased markedly with the reduction potential of the quinone. Here again the values in MeOH are noticeable higher than those in MeCN. For each solvent individually singlet and triplet quenching rate constants may be correlated with a single mechanism involving an electron transfer process from the Sf excited states to the quinones.

Following the Rehm–Weller reaction scheme, [16] the electron transfer steps in both singlet and triplet states can be written as:

$$A^{*}+D\underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}}(A^{*}\cdots D)\underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}}(A^{+\bullet}\cdots D^{-\bullet})\xrightarrow{k_{30}}\text{products}$$

By using steady state conditions, the experimental quenching rate constant can be expressed as:

$$k_q=\frac{k_{12}}{1+k_{21}/k_{23}(1+k_{32}/k_{30})} \qquad (1)$$

If k_{30} is assumed to be much larger than k_{32} (k_{30} includes all processes competing with the electron back-transfer to the precursor complex: cage escape, electron back-transfer to the ground state, etc.) then,

$$k_q=\frac{k_{12}k_{23}}{k_{21}+k_{23}} \qquad (2)$$

or

$$\frac{1}{k_q}=\frac{1}{k_{12}}+\frac{1}{K_Dk_{23}} \qquad (3)$$

where K_D is the equilibrium constant for the formation of precursor complex (k_{12}/k_{21}) which, for uncharged reactants, depends only on r_{12}, the distance between the charges in the complex. Usually K_D is assumed to be between 0.2 and 1.0

According to the Marcus classical theory [4] for electron transfer, k_{23} is a function of the overall free energy change ΔG°

$$k_{23}=\kappa\nu_{23}\exp\left\{-\frac{\lambda}{4RT}\left[1+\frac{\Delta G^\circ}{\lambda}\right]^2\right\} \quad (4)$$

whereas κ is the transmission coefficient (unity for an adiabatic reaction), ν_{23} is a nuclear frequency factor (usually between 10^{11} and $10^{12}\ \mathrm{s}^{-1}$) and λ is the reorganization energy.

For an outer sphere mechanism, λ is given mainly by the reorganization of the solvent molecules [4]. For methanol ($D=32.5$) and acetonitrile ($D=37.5$) and molecular radii of about 5–8 Å for the dye and the organic donor, this energy can be calculated between 20 and 22 kcal mol^{-1} [17].

In their classic work on electron transfer fluorescence quenching, Rehm and Weller demonstrated that the rate constant depends on the free energy change involved in the electron transfer process. The latter is normally calculated [16] from the redox potentials of the donor $E_{(\mathrm{D/D^+})}$ and acceptor $E_{(\mathrm{A/A^-})}$, and the energy of the excited state involved

$$\Delta G^\circ=E_{(\mathrm{D/D^+})}-E_{(\mathrm{A/A^-})}-E^*+\frac{Z_1Z_2}{Dr_{12}} \quad (5)$$

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. (5) using an oxidation potential of 1.13 ± 0.02 V for the safranine cation [12] vs. NHE in water at neutral pH. The reduction potentials of the quinones in MeCN vs. SCE were from Refs. [18]. It was assumed that the redox potentials do not change appreciably with the solvent. The data was referred to a common reference electrode with a value of 0.27 V for the SCE. The excited singlet energy of safranine cation from Ref. [6] 2.36 eV was increase to 2.41 eV in MeCN taking into account the blue shift of the absorption and fluorescence spectra in the latter solvent with respect to MeOH. Similarly for the triplet energy we used 1.78 eV in MeOH [6] and 1.83 eV in MeCN. 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.

The Rehm–Weller type free energy correlation of the rate constants is shown in Fig. 4. The full line is the best fitting in MeCN according to Eqs. (4) and (5) with the following parameters $k_{12}=2\times10^{10}\ \mathrm{dm^3\,mol^{-1}\,s^{-1}}$, $\lambda=0.78$ eV; $K_D\nu_{23}=3.5\times10^{11}\ \mathrm{dm^3\,mol^{-1}\,s^{-1}}$. This parameters are the same than those that provide the best fit for the electron transfer quenching of triplet states of anthracene and a,h-dibenzanthracene by nitrobenzenes as electron acceptors in MeCN [19]. This is a further confirmation of the quenching mechanism.

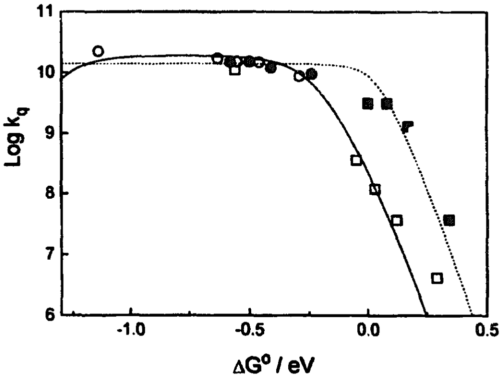

Fig. 4. Plot of log k_q vs. free energy change. ■, triplet quenching in MeOH; □, triplet quenching in MeCN; ●, singlet quenching in MeOH; ○, singlet quenching in MeCN.

According to Marcus classical theory the solvent may influence the electron transfer rate constant by altering several of the parameters involved. First, the driving force ΔG° may be altered by different stabilization of the product ion pair. Second the solvent contribution to the reorganization energy λ is modified through changes in the static and optical dielectric constants. Finally, the nuclear frequency ν_{23} may be expected to be solvent dependent if it is predominantly a solvent mode. For MeOH and MeCN λ is practically the same. If the redox potentials of the reactants are assumed to depend only upon the macroscopic dielectric properties of the solvent the driving force is not expected to differ significantly from one solvent to the other. Therefore similar values for the rate constants may be expected in MeOH and MeCN. In Fig. 4 it is clear that in the endergonic region the rate constants in MeOH are higher than those in MeCN by more than one order of magnitude. Also for the singlet quenching, where ΔG° is negative, the rate constants are closer to the diffusion limit in MeOH than in MeCN. This specific solvent effect of MeOH was previously observed for several electron transfer processes involving excited states [20]. However in this case the effect is very much remarkable. Moreover, the results in MeOH could not be fitted by a judicious choice the fitting parameters. Thus the dotted line in Fig. 4 is obtained with the experimental value for the diffusion constant, $k_d=1.5\times10^{10}\ \mathrm{dm^3\,mol^{-1}\,s^{-1}}$, 0.78 eV for the reorganization energy (the same as in MeCN) but now it requires an abnormally high value of $5\times10^{13}\ \mathrm{dm^3\,mol^{-1}\,s^{-1}}$ for the product $K_D\nu_n$.

In the reductive quenching of the dye by aliphatic amines the solvent effect was the opposite, but the differences were small. The large effect of the protic solvent observed here seems to be a distinctiveness of the oxidative quenching by quinones. A similar departure from the normal behaviour was observed for the electron transfer quenching of anthracene by benzoquinones in MeOH [21]. This effect 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.

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