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Excited states quenching of phenosafranine dye by electron donors

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Abstract

The quenching of the excited singlet and triplet states of phenosafranine by aromatic amines, methoxybenzenes and triethanolamine was investigated in acetonitrile and methanol. The rate constants for the aromatic quenchers present a typical dependence of an electron transfer process with the one-electron redox potential of the donor. A Rehm–Weller correlation is obtained with the driving force. The fitting parameters are very similar in both solvents. The electron transfer nature of the quenching reaction is further confirmed by the detection of the radical cations of the quenchers and the semireduced form of the dye in laser flash photolysis experiments. The absorption coefficients of the transient species were estimated, and the quantum yield of the charge separation process was determined.

Keywords: Quenching process; Laser flash photolysis; Semireduced dye; Electron transfer; Dyes; Phenosafranine

1. Introduction

Phenosafranine, 3,7-diamino-5-phenylphenazinium chloride, (PSH^+Cl^-) (Scheme 1), is a synthetic dye that absorbs strongly in the region 500–550 nm. It has been extensively employed as a sensitizer in energy and electron transfer reactions in homogeneous media [1–3], in semiconductors [4] and in polymeric media [5]. The dye was also employed as a probe in reverse micellar systems [6] and its photostability in polymer-coated semiconductors was investigated [7]. We have previously measured the quenching of the related dye safranine by aromatics donors in methanol [8] and by aliphatic amines in organic solvents [9] and in water [10]. An electron transfer mechanism was established. These dyes have numerous applications as probes in organized systems and as sensitizer in visible light photopolymerization [11]. For the latter application the kinetics of the electron transfer quenching of the excited states of the dye and the yield of radicals is of particular concern. Therefore, a systematic investigation of these processes is of interest.

Here we report on the electron transfer quenching of PSH^+ excited singlet and triplet states by aromatic amines, *N*-heterocyclics and methoxybenzenes and an aliphatic donor, triethanolamine. Bimolecular quenching rate constants were determined by time-resolved fluorescence emission in the case of the singlet state, and by laser flash photolysis for triplet quenching. Transient absorption spectra confirm the electron transfer nature of the quenching process. The studies were carried out in a polar aprotic solvent, acetonitrile, and in a protic medium, methanol. These two solvents are of similar macroscopic polarity and it was of interest to investigate if the differences previously found for the electron transfer kinetics in these solvents [12] were also present in this case.

2. Experimental

Phenosafranine was purchased from Aldrich and was used without further purification. It was checked that its photophysical properties coincided with those reported in the literature. The quenchers were all commercially available and were purified by standard procedures when necessary. Methanol and acetonitrile, both HPLC grade, were from Merck or Sintorgan.

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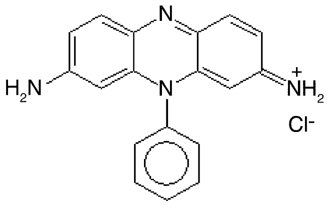


Scheme 1.

Absorption spectra were recorded using a HP8453 diode array spectrophotometer. Steady-state fluorescence experiments were carried out with a Spex Fluorolog spectrofluorometer. Fluorescence lifetime measurements were done with the time-correlated single photon counting technique using Edinburgh Instruments OB-900 equipment. Transient absorption spectra and triplet quenching were determined by laser flash photolysis. A Spectron SL400 Nd:YAG laser generating 532 nm laser pulses (20 mJ per pulse, ca. 18 ns FWHM) was the excitation source. The laser beam was defocused in order to cover all the path lengths (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 digitising scope (Hewlett-Packard 54504) where it was averaged and then transferred to a computer. All the kinetic determinations were performed at 20 ± 1 °C.

For the laser photolysis experiments the solutions were deoxygenated by bubbling for 30 min with solvent-saturated high-purity argon. The fluorescence quenching experiments were carried out with air-equilibrated solutions. At the quencher concentrations employed, the fluorescence was quenched without changes of the spectral shape. In addition, there were no changes in the absorption spectra of the dye. Thus, ground-state complex formation can be disregarded.

The quantum yield of semireduced dye was determined by laser flash photolysis, employing the triplet yield in the absence of quencher as relative actinometer, through Eq. (1)

$$\Phi_R = \Phi_T^0 \frac{A_R \varepsilon_T}{A_T \varepsilon_R} \qquad (1)$$

where Φ_T^0 is the triplet quantum yield in the absence of quencher, A_T the initial absorbance of the triplet in the absence of quencher and A_R the top absorbance of the semireduced form, measured at the wavelength of maximum absorption. ε_T and ε_R are the absorption coefficients of the triplet and semireduced form, respectively.

3. Results

Bimolecular quenching rate constants were determined from fluorescence lifetime determinations according to Eq. (2)

$$\tau^{-1} = \tau_0^{-1} + k_q[Q] \qquad (2)$$

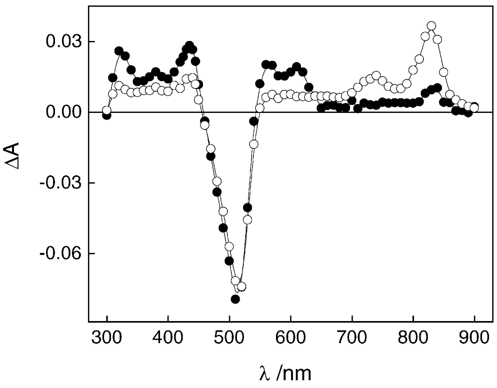


Fig. 1. Transient absorption spectrum taken at 2 μs after the laser pulse at 532 nm of PSH^+ in the absence (○) and the presence (●) of TMPD 1 × 10^{-4} M in MeCN.

where τ^0 and τ stand for the fluorescence lifetime in the absence and the presence of the quencher Q, respectively. The lifetimes of PSH^+ in air-equilibrated solution were 2.1 ns in MeOH and 3.5 ns in MeCN.

Triplet quenching was determined by laser flash photolysis. Bimolecular quenching rate constants, ^3k_q, were obtained from a plot of the pseudo-first-order decay rate constants of the triplet state k_{obs} as a function of the quencher concentrations [Q] (Eq. (3)).

$$k_{obs} = k^0 + {}^3k_q[Q] \qquad (3)$$

Singlet and triplet quenching rate constants are given in Table 1.

The electron transfer nature of the quenching process was confirmed by the transient absorption spectra in the presence of the quencher. These spectra reveal the characteristic absorption bands of the radical cation of the quencher and the semireduced form of the dye. Typical spectra are shown in Figs. 1 and 2. In Fig. 1, the transient absorption spectrum of PSH^+ in the presence of tetramethyl *p*-phenylendiamine (TMPD) 1 × 10^{-4} M is shown. The triplet state of PSH^+ presents two main absorption bands: 830 and 740 nm.

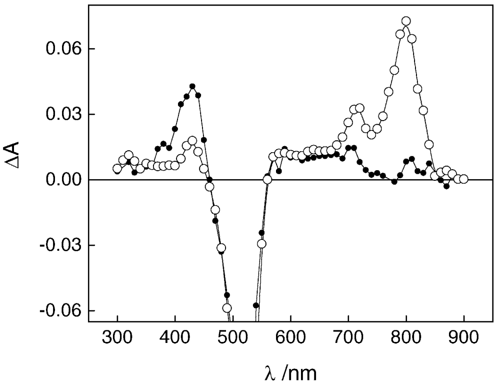


Fig. 2. Transient absorption spectrum taken at 2 μs after the laser pulse at 532 nm of PSH^+ in the absence (○) and the presence (●) of TEOA 0.01 M in MeOH.

Table 1
Rate constants (in units of 10^9 M^{-1} s^{-1}) for the quenching of excited singlet and triplet states of phenosafranine by electron donors

Quencher	$E_{1/2}$ (V)[a]	Singlet		Triplet	
		MeOH	MeCN	MeOH	MeCN
N,N,N′,N′-Tetramethyl *p*-phenylenediamine (TMPD)	0.13	10.7	18.7	9.36	15.8
N,N,N′,N′-Tetramethyl benzidine	0.43	–	18.0	8.32	10.6
p-Anisidine	0.66	8.36	13.9	4.71	8.23
N,N′-Dimethylaniline	0.77	10.9	15.4	6.25	8.14
p-Toluidine	0.78	7.87	13.4	4.38	6.77
N-Methylaniline	0.82	9.84	14.2	4.50	7.35
Aniline	0.93	6.90	12	2.81	2.96
2-Methylindole	1.07	8.50	11.6	0.21	0.44
1,2,4-Trimethoxybenzene	1.12	5.53	8.99	0.04	0.50
Indole	1.2	7.42	9.89	0.0015	0.0038
1,4-Dimethoxybenzene	1.3	6.30	8.01	0.00026	0.0007
Triethanolamine	0.90	2.08	6.15	0.021	0.40

[a] One-electron oxidation potential in MeCN vs. SCE. References quoted in [13].

In the presence of the aromatic amine these two bands are suppressed and two new bands at 565 and 610 nm appear. The new bands correspond to the radical cation of $TMPD^{\bullet+}$ [14]. In this region, 650–550 nm, the semireduced form of the dyes also absorbs. The absorption in the region 370–450 nm can be ascribed to the difference absorption spectrum of the semireduced dye, $PSH^{\bullet}$, by similarity with the known absorption spectrum of semireduced form of the dye safranine [9]. Therefore, the quenching process may be described by the electron transfer reaction.

$$^3PSH^+ + TMPD \rightarrow PSH^{\bullet} + TMPD^{\bullet+}$$

Using the known absorption coefficient of TMPD radical cation, $TMPD^{\bullet+}$, at 610 nm (ε = 13,000 M^{-1} cm^{-1}) [14] a value of ε = 19,000 M^{-1} cm^{-1} can be estimated for the combined absorption of the semireduced form of the dye, $PSH^{\bullet}$, and the radical cation $TMPD^{\bullet+}$ at 430 nm. From the known spectrum [15] of $TMPD^{\bullet+}$ and the ε at the maximum, its absorption coefficient at 430 nm may be estimated as 1000 M^{-1} cm^{-1}, affording a value of 18,000 M^{-1} cm^{-1} for the absorption coefficient of the semireduced form of the dye. According to the rate constants in Table 1 and the singlet lifetime of PSH^+, for TMPD 1×10^{-4} M the quenching of the singlet state is negligible, while more than 95% of the triplets are quenched. The intersystem crossing quantum yield of phenosafranine was reported as 0.1 and 0.06 in acetonitrile and water, respectively [1]. Also, a value of 0.10 was given for the dye in methanol [16]. However, these values seem rather low by comparison with the closely similar dye safranine, for which triplet quantum yields of 0.5 and 0.34 [17,18] were reported in ethanol. Therefore, we redetermined the triplet yield by the method of relative actinometry [19]. The triplet of ZnTPP (zinc tetraphenyl porphyrin) in benzene was employed as actinometer. The triplet yield of ZnTPP was measured at 470 nm immediately after the laser pulse. Values of 7.3×10^4 $M^{-1}cm^{-1}$ and 0.83 were used for ε_T and ϕ_T of ZnTPP, respectively [20]. In this way a value of 9700 $M^{-1}cm^{-1}$ was obtained at 825 nm for the product $\phi_T\varepsilon_T$ of phenosafranine in acetonitrile. Using ε_T = 22,000 $M^{-1}cm^{-1}$ for the dye in acetonitrile [1] 0.44 results for the triplet yield. This figure is more in line with the values of safranine quoted above.

With this value for the triplet yield, and the absorption coefficients of the triplet and semireduced dye, a quantum yield of radical formation results in Φ_R = 0.41 from Eq. (1). This means an efficiency of more than 90% for the charge separation process in the triplet state quenching of the dye by TMPD in acetonitrile.

In Fig. 2, the effect of triethanolamine (TEOA) on the transient absorption of PSH^+ in MeOH is depicted. The maxima of the T–T spectrum are at 800 and 720 nm in this solvent. The peak at 430 nm in assigned to the semireduced form of the dye. In Table 2, the spectral characteristics of the transient species are collected.

On the assumption that the only absorbing species at 430 nm is the semireduced form of the dye, the yield of semireduced dye for the quenching by TEOA 0.01 M in MeOH may be estimated as Φ_R = 0.32, assuming the photophysical parameters of the dye are the same as those in MeCN. This corresponds to an efficiency of charge separation of 0.91. In Fig. 3, the growth and decay of the absorption at 430 nm and the triplet decay measured at 830 nm in the presence of TEOA 1×10^{-3} M in MeCN are presented. In this solvent the triplet quenching is more effective than in MeOH by a factor of 10. It must be noticed that at this concentration the singlet is not intercepted. It can be seen that at 430 nm the signal presents a fast initial growth, due to the formation of the triplet of PSH^+, and afterwards a slower growth that matches the decay at 830 nm.

Table 2
Absorption bands (λ_{max} in nm) of the triplet state and the semireduced form of phenosafranine

	MeOH	MeCN
Triplet	800, 710, 430, 320	830, 740, 440, 320
Neutral radical	430	435

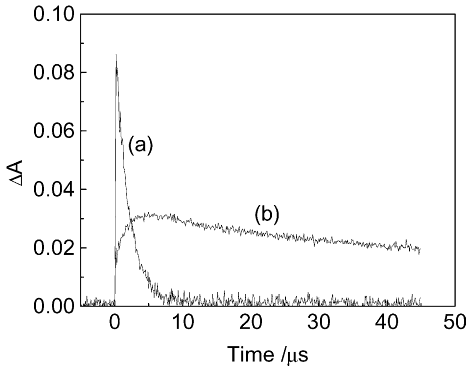


Fig. 3. Transient absorption profiles of PSH^+ in the presence of TEOA 1 × 10^{-3} M in MeCN. (a) 830 nm; (b) 430 nm.

Thus, the laser flash photolysis experiments substantiate an electron transfer quenching process. Therefore, a correlation of the rate constants with the Gibbs energy change for the overall electron transfer process, ΔG°, is expected. The latter was calculated from the redox potentials of the donor $E(D/D^+)$ and acceptor $E(A/A^-)$, and the energy E^* of the excited state involved, with the Rhem–Weller equation [21]

$$\Delta G^\circ = E_{(D/D^+)} - E_{(A/A^-)} - E^* + C \tag{4}$$

where C is the coulombic energy term. In the present case, since in the quenching process the neutral radical of the dye is formed, this term is negligible. The photophysical and electrochemical parameters for phenosafranine are [22]: E_S = 2.34 eV; E_T = 1.77 eV; $E(A/A^-) = -0.67$ V. In this way, ΔG° was estimated in MeCN and assumed to be the same in MeOH on the basis of the similar polarity of the two solvents. Corrections in the redox potentials for solvent change on going from acetonitrile to methanol are in the order of 0.01 V [23]. In Figs. 4 and 5, the rate constants for the quenching by aromatic donors are plotted versus ΔG° in MeOH and MeCN, respectively.

In both solvents the data are well fitted (solid line) by the Rehm–Weller mechanism (Scheme 2), where D^* and Q stands for the excited dye and the quencher respectively.

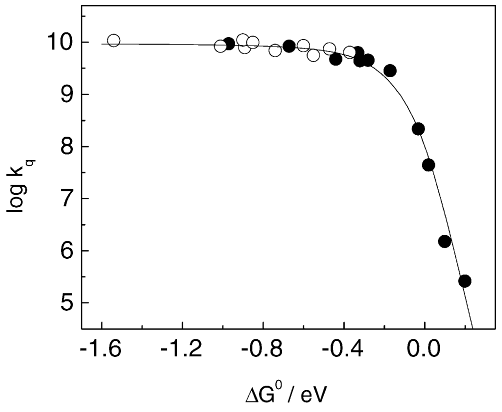


Fig. 4. Singlet (○) and triplet (●) quenching rate constants in MeOH as a function of the free energy change.

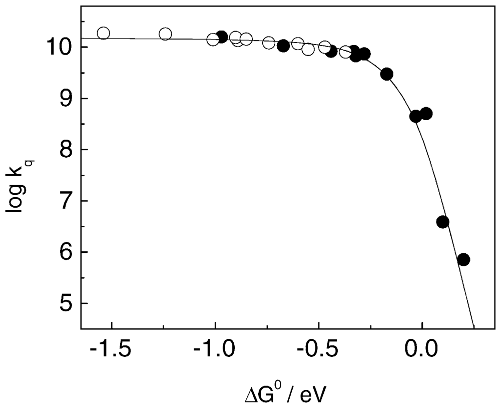
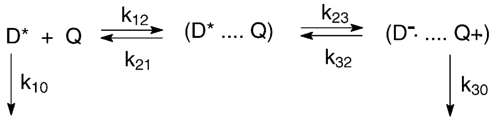


Fig. 5. Singlet (○) and triplet (●) quenching rate constants in MeCN as a function of the free energy change.



Scheme 2.

The steady-state quenching rate constant is

$$k_q = \frac{k_{12}}{1 + \frac{k_{21}}{k_{23}}\left(\frac{k_{32}}{k_{30}} + 1\right)} \tag{5}$$

introducing the Gibbs energy change for the electron transfer process,

$$\frac{k_{23}}{k_{32}} = \exp\left(\frac{-\Delta G^\circ}{RT}\right) \tag{6}$$

and

$$k_{23} = k_{23}^0 \exp\left(\frac{-\Delta G^*}{RT}\right) \tag{7}$$

Eq. (5) becomes:

$$k_\mathrm{q} = \frac{k_{12}}{1 + \frac{k_{21}}{k_{23}^0}\exp(\Delta G^*/RT) + \frac{k_{21}}{k_{30}}\exp(\Delta G^\circ/RT)} \tag{9}$$

In order to fit the experimental results for bimolecular charge separation reactions, an expression of ΔG_{23}^* that tends asymptotically toward zero for highly negative values of ΔG_{23}° is necessary; the Rehm–Weller relationship (Eq. (10)) meets this requirement.

$$\Delta G^\circ = \frac{\Delta G^\circ}{2} + \left[\left(\frac{\Delta G^\circ}{2}\right)^2 + \Delta G^*(0)^2\right]^{1/2} \tag{10}$$

where $\Delta G^*(0)$ is the free energy change for driving force = 0 and it is an adjustable parameter. The solid lines in Figs. 4 and 5 are drawn using Eqs. (9) and (10) with the fitting parameters given in Table 3.

Table 3
Fitting parameter for the quenching of excited states of PSH^+ by aromatic electron donors

	MeOH	MeCN
k_{12} ($M^{-1}s^{-1}$)	1.0×10^{10}	1.6×10^{10}
k_{21} (s^{-1})	3.0×10^{10}	3.0×10^{10}
k_{23}^0 (s^{-1})	1×10^{12}	1×10^{12}
k_{30} (s^{-1})	1×10^{9}	1×10^{9}
ΔG^* (0)	0.2	0.2

It can be seen that in both solvents the data could be fitted with the same parameters with the exception of k_{12} corresponding to the diffusional limit. A remarkable feature of the fitting parameters is the low value of k_{30}, $1 \times 10^9\ s^{-1}$. This value is two orders of magnitude lower than that proposed in the original work of Rehm and Weller. However, in this case it is impossible to adjust the experimental results with a higher value. The fall off of the curve, in the region corresponding to triplet quenching, is especially sensitive to the value of k_{30}. This rate constant actually is the sum of at least two processes, the back electron transfer to ground state and the cage escape of the radicals. The first one, in the case of triplet quenching, involves a spin inversion process, and this may introduce a low transmission factor. On the other hand, the cage escape is expected to have a higher value, since one of the species is a neutral radical. Nevertheless, the results of the efficiency of the charge separation process for the triplet quenching are not incompatible with such a low value for the escape rate constant, if it is assumed that the recombination is much slower.

From the data in Table 1, it can be observed that the quenching rate constant by TEOA is smaller than those for aromatic quenchers like aniline or *N*-methylaniline with similar redox potential. This is not an unexpected result, since it is well known that aliphatic donors in polar solvents are poor quenchers as compared with aromatics of similar donating capability.

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