

PHOTOREDUCTION OF SAFRANINE BY SUBSTITUTED ANILINOMETHANESULPHONATES

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Summary

The reactions between the triplet state of safranine and various anilines and substituted anilinomethanesulphonates (RAMS) have been studied by monitoring the formation of the semireduced form of the dye using flash photolysis. The reaction with RAMS at low concentrations and anilines corresponds to the formation of an encounter complex which allows electron transfer or deactivation. The Hammett reaction constant for poor electron-donating substituents is -2.7 . At high RAMS concentrations, the semi-reduced dye yield decreases for increasing quencher concentrations. This effect is ascribed to the formation of a ground state ion-pair complex ($K \approx 140$) with an unfavourable configuration for electron transfer. When excited, this complex is rapidly deactivated by static quenching.

1. Introduction

The photoreduction of dyes occurs generally through an electron transfer mechanism from an appropriate reductant to the excited state of the dye [1, 2]. This transfer proceeds inside the solvent-stabilized encounter complex formed by the excited dye species and the reductant. When the electron back transfer is fast, deactivation of the excited species to its ground state is observed in addition to the formation of the reduction products. Rehm and Weller [3, 4] developed a theory based on this model and included a number of the postulates for the electron-exchange activation energy from the theory of Marcus [5]. This theory has been successfully used to explain fluorescence quenching of several excited species by electron donors [3, 4], as well as the photoreduction of dyes by substituted dimethylanilines and methoxybenzenes [6]. The theory was later extended by Kramer and co-workers [7] to explain the photoreactions of dye triplets. Several systems studied in the last few years showed abnormal quenching behaviour which could not be readily explained by simple electron or hydrogen transfer quenching mechanisms.

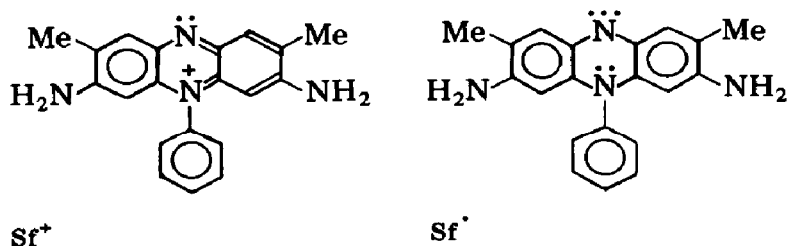
Ground state association between the species to be excited and the quencher has been postulated to explain these effects, as for the photoreactions of porphyrins with dimethylaniline [8], the quenching of methylviologen by several anions [9] and the photoreduction of methylene blue by charged amine compounds [10].

In this paper we show results for the photoreduction of safranin by anilinomethanesulphonates (RAMS). This system does not show simple quenching behaviour, and the results can be explained by assuming the formation of a ground state ion pair between the reactants. These results can be extended to similar systems.

2. Experimental details

The RAMS ($\text{RC}_6\text{H}_4\text{NHCH}_2\text{SO}_3^-$) were prepared from the corresponding anilines and hydroxymethanesulphonate, as described by Neumann and De Groot [11]. Anilines and hydroxymethanesulphonate were obtained from Carlo Erba (RPE grade) and Aldrich respectively. The anilines were distilled or recrystallized before use and kept under nitrogen. Safranin T chloride (3,7-diamino-2,8-dimethyl-5-phenylphenazinium chloride; C.I. 50240 (colour index)) (Sf^+) was obtained from Merck and was recrystallized from alcohol before use. The spectra of the products before and after purification were identical. The methanol was Merck Lichrosorb.

All experiments were performed in methanolic solution at 25 °C. The safranin concentration was always 2×10^{-6} M and the reductants were in the concentration range $(1 \times 10^{-2}) - (2 \times 10^{-4})$ M. Solutions were prepared at methanolic proton concentrations at which the dye triplet and the semi-reduced form (Sf^\cdot) are in the same protonation state ($\text{p}K_{\text{a,triplet}} = 7.5$; $\text{p}K_{\text{a,semired}} = 9.5$) [12]. Additionally, the reductant had to be in its basic form. This was achieved by adding enough sodium hydroxide or perchloric acid to reach the desired pH^* (methanol).



The flash photolysis experiments were performed using an Applied Photophysics conventional system (KNO 20), which produced 30 μs flashes of 10 kV. An R446 Hamamatsu photomultiplier was used for detection at 700 nm. At this wavelength, neither the triplet form nor the dye in its ground state absorb [12]. The amount of semireduced safranin was measured 50 μs after the initiation of the flash. Experiments without reductant

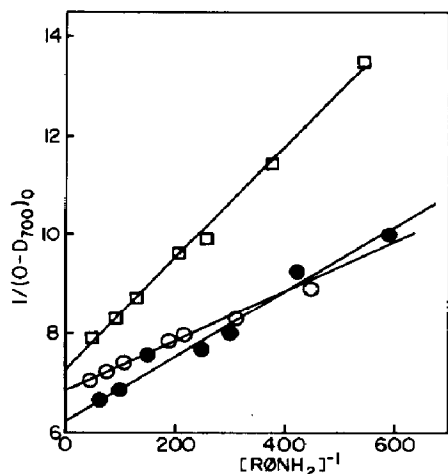


Fig. 1. Reciprocal plot of the yield of semireduced safranin 50 μ s after the excitation of safranin-aniline mixtures: \square , aniline; \circ , *m*-toluidine; \bullet , *p*-anisidine.

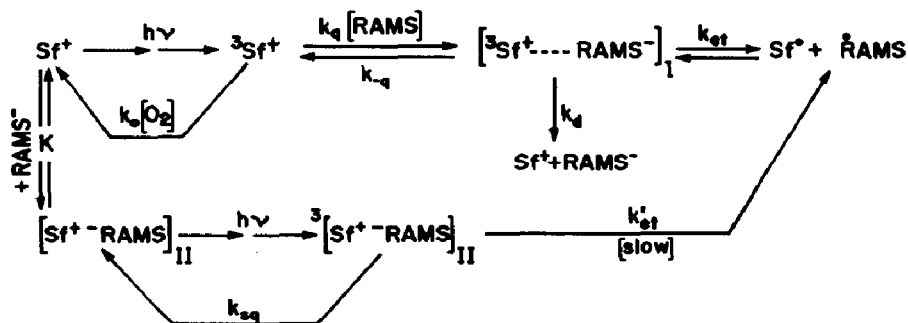
TABLE 1

Relative rate constants and equilibrium constants for the quenching of triplet safranin by substituted anilines and anilinomethanesulphonates

Substituent	Anilines	Anilinomethanesulphonates		
	$k_q/k_0[\text{O}_2]$ (M^{-1})	$[\text{RAMS}]_{\text{min}}^{-1}$ (M^{-1})	K	$k_q/k_0[\text{O}_2]$ (M^{-1})
<i>p</i> -Methoxy-	1060	250	50	1250
<i>p</i> -Methyl-	1540	700	280	1900
<i>m</i> -Methyl-	1600	530	200	1450
H-	660	200	35	1060
<i>p</i> -Fluoro-	—	30	120	620
<i>p</i> -Chloro-	250	—	—	230
<i>p</i> -Bromo-	200	—	—	150

When using substituted RAMS as reductants, the plots of $1/(\text{OD}_{700})_0$ versus $1/[\text{RAMS}]$ show curvatures at relatively low RAMS concentrations (about 10^{-3} M), as can be seen in Fig. 2. This curvature can be ascribed to the formation of ground state ion pairs, as previously suggested [10] to explain the results of the photoreduction of methylene blue by RAMS. To account for this equilibrium, Scheme 1 has to be modified as shown in Scheme 2. $[\text{Sf}^{+-}\text{RAMS}]_{\text{II}}$ and $^3[\text{Sf}^{+-}\text{RAMS}]_{\text{II}}$ represent ion-pair associations in the ground state and triplet state respectively. When using the method described for Scheme 1, the relationship between $1/[\text{Sf}^+]_0$ and $1/[\text{RAMS}]$ is

$$\frac{1}{[\text{Sf}^+]_0} = \frac{k_d + k_{et}}{k_{et}} \left(1 + \frac{Kk_0[\text{O}_2]}{k_q} + \frac{k_0[\text{O}_2]}{k_q} \frac{1}{[\text{RAMS}] + K[\text{RAMS}]} \right) \frac{1}{[{}^3\text{Sf}^+]_0} \quad (5)$$



Scheme 2.

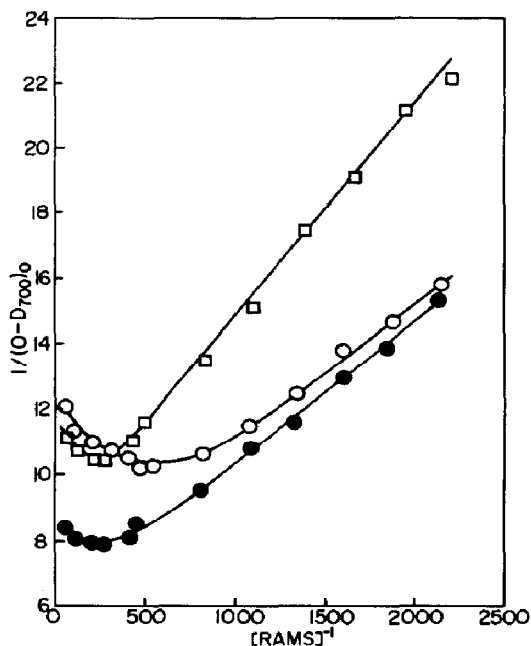


Fig. 2. Reciprocal plot of the yield of semireduced safranin $50 \mu\text{s}$ after the excitation of safranin-RAMS mixtures: \square , HAMS; \circ , *m*-MeAMS; \bullet , *p*-MeOAMS.

which reproduces the form of the curve in Fig. 2, *i.e.* branching upward at high and low RAMS concentrations.

From the experimental data at low RAMS concentrations, where the plot is similar to that in Fig. 1, the new slopes and zero intercepts are

$$\alpha' = C \frac{k_d + k_{et}}{k_{et}} \frac{k_0[\text{O}_2]}{k_q} \frac{1}{[{}^3\text{Sf}^+]_0} \quad (6)$$

$$I' = C \frac{k_d + k_{et}}{k_{et}} \left(1 + \frac{Kk_0[\text{O}_2]}{k_q} \right) \frac{1}{[{}^3\text{Sf}^+]_0} \quad (7)$$

and

$$\frac{I'}{\alpha'} = \frac{1 + Kk_0[\text{O}_2]/k_q}{k_0[\text{O}_2]/k_q} \quad (8)$$

To evaluate the ratio of k_q to k_0 from this equation, it is necessary to know the value of the equilibrium constant K , or the form of some other relationship between K and $k_q/k_0[\text{O}_2]$. The RAMS concentration $[\text{RAMS}]_{\text{min}}$ at which $(\text{OD}_{700})_0^{-1}$ is at its minimum provides this additional equation. Mathematically, eqn. (5) has to be differentiated and equated to zero:

$$\frac{d([\text{Sf}']_0^{-1})}{d([\text{RAMS}]^{-1})} = C' \left(\frac{k_0[\text{O}_2]}{k_q} - \frac{K}{[\text{RAMS}]^2} \right) = 0 \quad (9)$$

and

$$K = \frac{k_0[\text{O}_2]}{k_q} [\text{RAMS}]_{\text{min}}^2 \quad (10)$$

The values for K obtained using eqns. (8) and (10) are given in Table 1.

As can be seen in Table 1, the values for the equilibrium constant are quite scattered, varying from 35 to 400, probably owing to the uncertainty in determining the minima from the experimental plots. However, there is no apparent reason to believe that ion-pair formation should be influenced by substitution on the phenyl ring, which is well separated from the negative charge in the RAMS. Therefore, a unique value for this constant, equal to the mean value of the experimental determinations, has been used. Thus, K has been taken as 140. This value corresponds to an ion-association free energy of about -3 kcal mol^{-1} , which, in turn, corresponds to a separation of 3.3 \AA between the positive and negative charges. This distance may be compared with that between the electron donor and acceptor sites in the exciplexes leading to photoreduction or deactivation ($6-7 \text{ \AA}$) [7]. Using this value of K , the ratios $k_q/k_0[\text{O}_2]$ were recalculated and the results are shown in the last column in Table 1. These values, together with those for substituted anilines, are shown in a Hammett plot in Fig. 3. This figure has two distinct regions: for good electron-donating substituents, a plateau

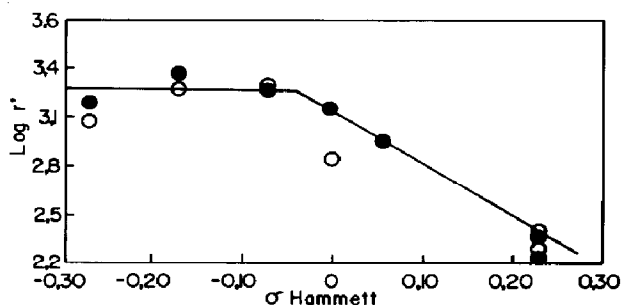


Fig. 3. Hammett plot of the relative quenching rate of triplet safranine by substituted anilines (\circ) and RAMS (\bullet).

is reached at 1340 M^{-1} , and a straight line with a slope of -2.7 is found for electron-accepting substituents.

The value at the plateau is believed to correspond to k_q being in the diffusion-limited region. Using the extrapolated value together with $k_q = k_{\text{diff}} = 6.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$ (in methanol) and assuming the oxygen concentration in methanol to be $2 \times 10^{-3} \text{ M}$ [14], the rate constant for the quenching of triplet safranin by oxygen can be estimated as $2.5 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$. This value is in very good agreement with the similar reaction with the methylene-blue triplet [13] (rate constant, $2.2 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$).

The ρ value of -2.7 obtained from the straight line in Fig. 3 corresponds to the creation of a negative charge at the reaction site, *i.e.* an electron-transfer mechanism, as has been found for most dye triplet quenching reactions [1, 2].

The formation of ground state associations, ion pairs or electron donor-acceptor complexes, has already been postulated by various authors. Mercer-Smith *et al.* [8] and Iwa *et al.* [15] suggested ground state electron donor-acceptor complexes to explain the results obtained at high quencher concentrations for the quenching of palladium(II) porphyrin phosphorescence by dimethylaniline and the quenching of oxonine fluorescence by several electron donors. In the first case the spectroscopic properties of the ground state association and the separated absorbing species were similar, whereas for the oxonine systems some changes were observed. Ion pairs are assumed to be responsible for the modification of the quenching efficiencies of methyl viologen by several anions [9] (including ethylenediaminetetraacetic acid) and the quenching of $(\text{UO}_2^{2+})^*$ luminescence by nitrate ions [16]. Once again, differences could be noticed only in the spectra of the MV^{2+} systems. In all cases the abnormal quenching behaviour has been ascribed to static quenching or favourable electron transfer within the excited association.

We believe that in the system studied in this work, as well as in the methylene blue-RAMS [10] and methylene blue-phenylglycine [17] systems, the ground state association and the encounter complex which leads to electron transfer have different spatial configurations. The latter presents a sandwich-type structure, as proposed by Steiner [18], with the abstractable electrons in a position near to the π system of the dye. The ground state

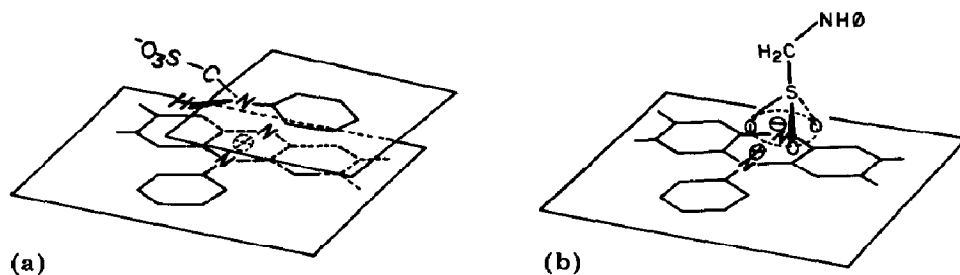


Fig. 4. Structure of the encounter complex leading to (a) electron transfer and (b) the ground state ion-pair complex.

ion-pair complex should have a structure in which the sulphonic group is near to the dye and the rest of the molecule points away from the dye rings, as shown in Fig. 4. The excited ion pair will maintain its geometry in accordance with the Franck-Condon principle, so that an electron transfer from the nitrogen to the dye is quite unfavourable. A large rearrangement energy would be necessary for the nitrogen to approach the dye ring, making this reaction very slow compared with the other processes and allowing the deactivation of the excited triplet ion association II to proceed preferentially by static quenching.

Acknowledgments

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