

## Short Communication

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### Fluorescence quenching of 1-naphthylamine by paraquat

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#### 1. Introduction

The redox properties of paraquat (1,1'-dimethyl-4,4'-bipyridinium chloride ( $PQ^{2+}$ )) are widely known [1]. Its colourless oxidized form is readily reduced by a variety of compounds to a blue radical cation which is stable in the absence of oxygen [2]. This one-electron reduction of  $PQ^{2+}$  is believed to be a process of importance in determining its herbicidal and biological properties. In the case in which the electron donor is an electronically excited molecule the redox process is of potential applicability to the photochemical storage of solar energy [3].

As an intermediate state in the electron transfer reaction  $PQ^{2+}$  forms a series of charge transfer complexes with a number of molecules of biological relevance [4]. These complexes can be formed either in the ground state or in excited electronic states, and it is of great importance to determine the thermodynamic and kinetic parameters of these interactions.

In order to obtain further information on the interaction of  $PQ^{2+}$  with electronically excited molecules a systematic investigation of the reactions of  $PQ^{2+}$  with excited aromatic amines is in progress in our laboratory. Aromatic amines are well-known electron donors in the ground state, and in alcoholic solution  $PQ^{2+}$  forms a 1:1 charge transfer complex with 1-naphthylamine (1-NA) [4].

In this communication we report the results of static and dynamic investigations of the quenching of 1-NA fluorescence by  $PQ^{2+}$  in aqueous solutions. These results allow us to determine the equilibrium constant and  $\Delta H$  for the association between 1-NA and  $PQ^{2+}$ , and the rate constant for the deactivation of the excited singlet of 1-NA by  $PQ^{2+}$ .

#### 2. Experimental details

1-NA (Fluka, pure) was recrystallized at least three times from an ethanol-water solution followed by vacuum sublimation. Paraquat was obtained from a commercial solution and was recrystallized at least three times from an ethanol-water solution.

$10^{-3}$  M solutions of 1-NA in doubly distilled 96% ethanol were prepared and were then diluted to  $10^{-5}$  M with triply distilled water. The  $PQ^{2+}$  solutions were prepared by adding 0.02 - 0.15 M  $PQ^{2+}$  to the 1-NA solution. The quenching studies were performed by adding small quantities of the  $PQ^{2+}$  solution to 1.5 ml of the 1-NA solution contained in a fluorescence cell.

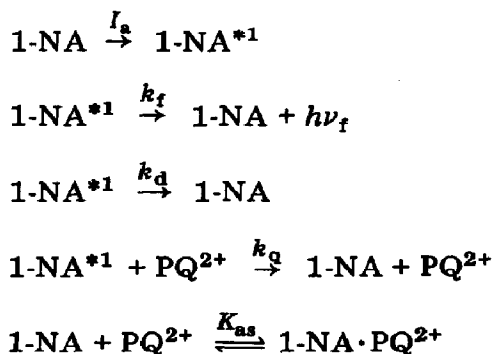
Absorption spectra were obtained using a Cary 17 spectrophotometer. Fluorescence quenching experiments were carried out under photostationary conditions and by measuring the emission lifetime. In the former case an Aminco SPF 125 spectrofluorometer was employed. The photocurrent was measured using an external picoammeter (Keithley 417). The solutions were degassed by bubbling nitrogen or argon through them. The cell compartment was thermostatted to  $\pm 0.5$  °C by water circulation. The excitation wavelength was 320 nm and the emission was monitored at 440 nm.

Lifetime measurements were performed at room temperature. A nitrogen laser (CIOP) gated at 50 Hz (full width at half-maximum 4 ns at 337 nm) was used as the excitation source, and an oscilloscope with a sampling unit was used to monitor the signal from a TRW 31A fluorometer.

### 3. Results and discussion

The Stern-Volmer plots obtained from the photostationary experiments showed a positive deviation from linearity at all temperatures. A typical plot at room temperature is shown in Fig. 1. We checked that the chloride ions did not quench 1-NA fluorescence in our concentration range and we carried out the measurements near neutrality where there was no proton quenching [5].

At the excitation wavelength used (320 nm) light absorption by paraquat, which produces a decrease in the fraction of light absorbed by 1-NA, cannot be neglected. When the values of  $I_0/I$  where  $I_0$  and  $I$  are the fluorescence intensities in the absence and the presence of  $PQ^{2+}$  respectively are corrected for this effect [6] the Stern-Volmer plots still show positive curvature. This deviation from the Stern-Volmer law can be attributed to the existence of two different quenching mechanisms, one dynamic and one static [7, 8]. Accordingly the results can be analysed in terms of the following simple kinetic scheme:



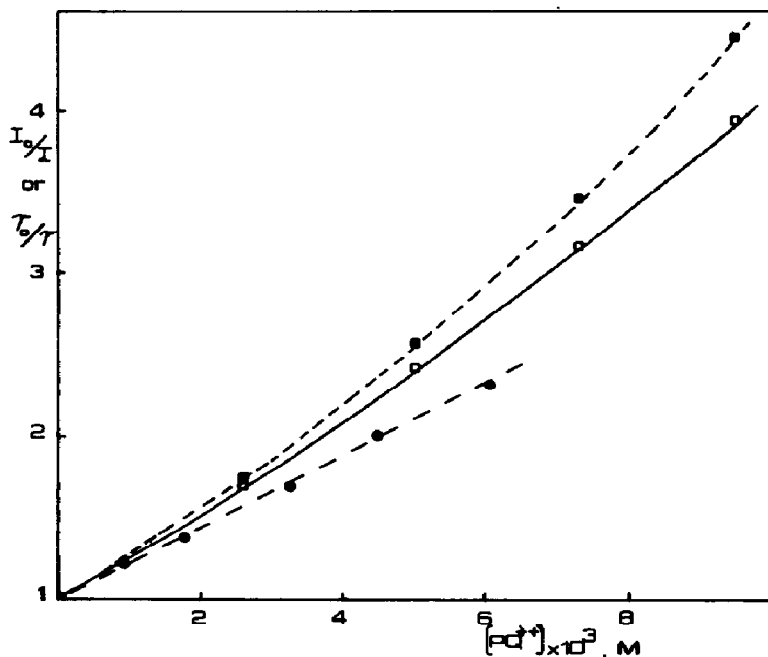


Fig. 1. Stern-Volmer plots for the quenching of the fluorescence of 1-NA by  $PQ^{2+}$  in water at 298 K:  $\blacksquare$ , uncorrected measurements;  $\square$ , measurements corrected for light absorption by  $PQ^{2+}$ ; —, calculated using eqn. (1) and the parameters given in the text;  $\bullet$ , lifetime measurements.

where  $1-NA^{*1}$  represents the first excited singlet of 1-NA and  $K_{as}$  is the equilibrium constant for the association between 1-NA in its ground state and  $PQ^{2+}$ .

The following equation results [7] from this mechanism:

$$(I_0/I)_{corr} = 1 + (K_{as} + k_q \tau_0)[PQ^{2+}] + K_{as} k_q \tau_0 [PQ^{2+}]^2 \quad (1)$$

where  $\tau_0 = (k_f + k_d)^{-1}$  and  $(I_0/I)_{corr}$  represents the experimental data corrected for the absorption of paraquat. A  $\tau_0$  value of 22 ns was obtained from the lifetime measurements. Tsutsumi and Shizuka [5] reported a value of 27 ns for  $\tau_0$ .

A plot of  $\tau_0/\tau$  is shown in Fig. 1.  $k_q$  can be evaluated from the slope of the graph by employing the equation

$$\tau_0/\tau = 1 + k_q \tau_0 [PQ^{2+}] \quad (2)$$

This gives a value of  $9.9 \times 10^9 \text{ M}^{-1} \text{ s}^{-1}$  for  $k_q$  which indicates that  $PQ^{2+}$  interacts with excited singlets of 1-NA by a diffusion-controlled process. This result was used to fit eqn. (1) to the experimental data with  $K_{as}$  as an adjustable parameter. The full line in Fig. 1 was calculated by assuming a value of  $29 \text{ M}^{-1}$  for  $K_{as}$  at 298 K.

In order to study the temperature effect eqn. (1) was rearranged in the form

$$\frac{(I_0/I)_{\text{corr}} - 1}{[\text{PQ}^{2+}]} = k_q \tau_0 + K_{\text{as}} + k_q \tau_0 K_{\text{as}} [\text{PQ}^{2+}] \quad (3)$$

Plots of the left-hand side of eqn. (3) versus  $[\text{PQ}^{2+}]$  at different temperatures are shown in Fig. 2. The values of  $K_{\text{as}}$  and  $k_q \tau_0$  were obtained from the slopes and intercepts by using the value of  $K_{\text{as}}$  at 298 K determined previously as a reference point. The results are given in Table 1.

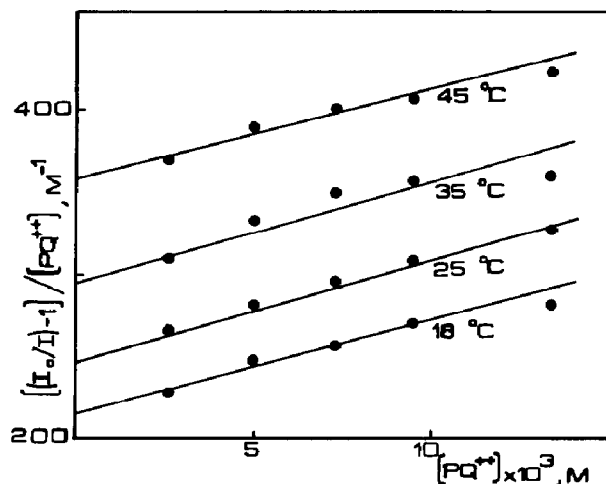


Fig. 2. Plots of the photostationary experiments at various temperatures obtained using eqn. (3).

TABLE 1

Temperature (°C)	18	25	35	45
$k_q \tau_0$ ( $\text{M}^{-1}$ )	180	217	272	342
$K_{\text{as}}$ ( $\text{M}^{-1}$ )	34	29	23	17

We obtained a value of  $-4.5 \text{ kcal mol}^{-1}$  for the  $\Delta H$  of association between 1-NA and  $\text{PQ}^{2+}$  from a plot of  $\ln K_{\text{as}}$  versus  $1/T$ . Correspondingly, since the product  $K_{\text{as}} k_q \tau_0$  does not change with temperature within the estimated experimental error (10%), the apparent activation energy for the product  $k_q \tau_0$  must be  $4.5 \text{ kcal mol}^{-1}$ .

The values of  $K_{\text{as}}$  and  $\Delta H$  for the association are in agreement with those expected for a charge transfer complex. Moreover for the same equilibrium in methanolic solutions White [4] gives  $8.7 \text{ M}^{-1}$  for  $K_{\text{as}}$  and  $-5.5 \text{ kcal mol}^{-1}$  for  $\Delta H$  in the system  $\text{PQ}^{2+}$ -hydroquinone.

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