THERMAL DEACTIVATION OF THE TRIPLET STATE OF ACRIDINE ORANGE IN POLY(VINYL ALCOHOL) FILMS

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Summary

Measurements of the mean phosphorescence lifetime τ_P, the delayed fluorescence lifetime τ_{DF}, the fluorescence quantum yield ϕ_F and the ratios of the phosphorescence quantum yield ϕ_P and the delayed fluorescence quantum yield ϕ_{DF} to the fluorescence quantum yield were carried out for acridine orange in poly(vinyl alcohol) films as a function of temperature. On the basis of the results obtained, rate constants were determined for radiative and radiationless transitions from the triplet state, and the quantum yields ϕ_T of the triplet state population were found in the temperature range 77 - 300 K.

1. Introduction

Acridine orange (3,6-bis-dimethylaminoacridine) and its cationic form have in recent years been the objects of numerous photophysical and photochemical investigations, owing to the luminescent properties and the ability to intercalate with biological macromolecules. In particular, acid–base equilibria in the ground [1] and singlet and triplet excited states [2] were studied, and the photochemical reactions and the quantum yield efficiencies ϕ_T of the triplet state population as a function of pH [3] were investigated. The interaction of acridine orange, as well as other dyes, with deoxyribonucleic acid has been reported [4 - 7]. Recently, the probability of the $S_1 \rightarrow T_1$ transition was investigated for a series of dyes using the method of sensitized delayed fluorescence (Parker's method), and ϕ_T for acridine orange in ethanol was found to be 0.30 ± 0.05 [8].

The effect of temperature on the shift [9] and broadening [10] of the fluorescence and delayed fluorescence spectra of the cationic form of acridine orange in poly(vinyl alcohol) films was studied. In some cases the investigations of the temperature effect on the quantum yields and mean lifetimes enabled the rate constants of the radiationless deactivation of the
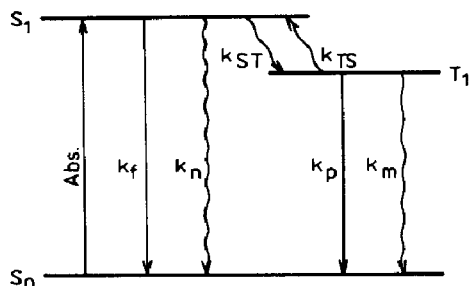
Fig. 1. Jabłoński diagram.

excited states to be determined. According to the notation in the Jabłoński diagram (Fig. 1), the following relation is obtained:

$$\phi_{\mathrm{T}} = \phi_{\mathrm{P}} \, \frac{1}{k_{\mathrm{P}}} \, \frac{1}{\tau_{\mathrm{P}}} = \frac{\phi_{\mathrm{DF}}}{\phi_{\mathrm{F}} k_{\mathrm{TS}} \tau_{\mathrm{DF}}} \tag{1}$$

where

$$\tau_{\mathrm{DF}} \approx \tau_{\mathrm{P}} = (k_{\mathrm{P}} + k_{\mathrm{m}} + k_{\mathrm{TS}})^{-1}$$

In the rest of this paper we shall assume that the rate constants k_f and k_{p} of the radiative transitions are weakly affected by temperature compared with the rate constant k_x of the radiationless transition for which the dependence on temperature is in general expressed by

$$k_{\mathrm{x}} = k_{\mathrm{x}}{}^0 + A_{\mathrm{x}} \exp\left(-\frac{E_{\mathrm{A}}{}^{\mathrm{x}}}{kT}\right) \tag{2}$$

where x denotes n, m, ST, TS. The aim of the present paper is to determine the rate constant k_{p} of the radiative transition, and the effect of temperature on radiationless transitions for the triplet state of the cationic form of acridine orange in poly(vinyl alcohol) films.

2. Experimental details

Acridine orange (Fluka AG.) was purified by the method given in ref. 11. The technique for preparing poly(vinyl alcohol) films was similar to that employed by Tanizaki et al. [12]. The phosphorescence decay measurements were performed with a spectrofluorometer using two coupled shutters. The ratio of the phosphorescence quantum yield to the fluorescence quantum yield, $\phi_{\mathrm{P}}/\phi_{\mathrm{F}}$, and the ratio of the delayed fluorescence quantum yield to the fluorescence quantum yield, $\phi_{\mathrm{DF}}/\phi_{\mathrm{F}}$, were measured by means of two synchronous choppers supplied with power by a generator at a frequency of 40 Hz. The real values of $\phi_{\mathrm{P}}/\phi_{\mathrm{F}}$ and $\phi_{\mathrm{DF}}/\phi_{\mathrm{F}}$ were computed by the application of a Fourier analysis of the measured signals. The fluorescence quantum yields were measured with an instrument described previously [13]. A special cryostat for optical spectroscopy was employed in a temperature

range 80 - 300 K. The measuring cell was thermostatted with an accuracy to ±1 K.

3. Results and discussion

The results of the measurements of the mean phosphorescence and delayed fluorescence lifetimes, τ_P and τ_{DF}, and the ratios ϕ_P/ϕ_F, ϕ_{DF}/ϕ_F and ϕ_{DF}/ϕ_P are shown in Figs. 2 and 3. At temperatures lower than 140 K, the values of ϕ_F, ϕ_P/ϕ_F and τ_P are constant. At low temperatures the fluorescence quantum yield $\phi_F{}^0$ attains a value of 0.975, which implies that because
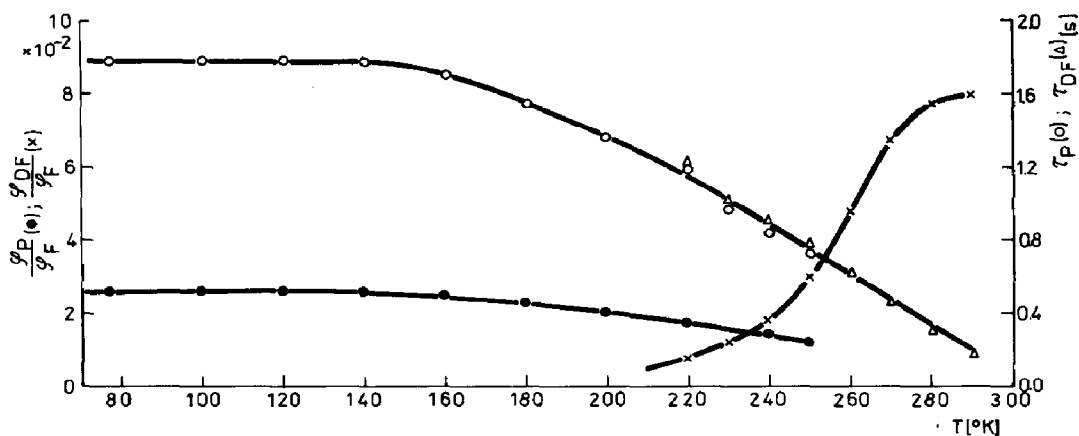

Fig. 2. Effect of temperature on the quantum yield ratios, ϕ_{DF}/ϕ_F (×) and ϕ_P/ϕ_F (●), and the mean lifetimes, τ_P (○) and τ_{DF} (△), for acridine orange in poly(vinyl alcohol) films.
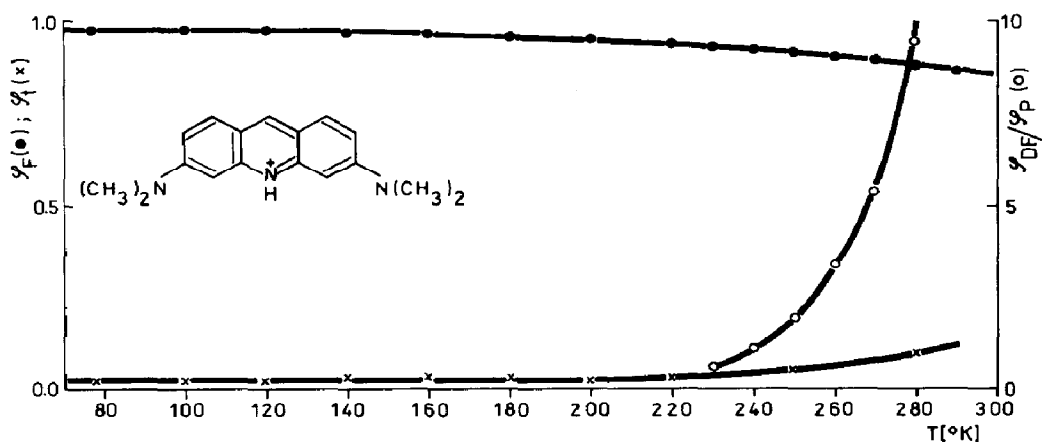

Fig. 3. The fluorescence quantum yield ϕ_F (●) (measured with respect to the fluorescence quantum yield for acridine orange in ethanol, $\phi_F{}^S = 0.46$ [3]), the triplet state population quantum yield ϕ_T (×) and the ratio ϕ_{DF}/ϕ_P (○) as functions of temperature for acridine orange in poly(vinyl alcohol) films.

the $\phi_P{}^0/\phi_F{}^0$ ratio of 0.026 is constant within this temperature range the following holds true:

$$\phi_P{}^0 \equiv \phi_T{}^0 = 1 - \phi_F{}^0 \tag{3}$$

This relation is already valid at 140 K and shows that for all radiationless transitions (except for the intersystem crossing) the term $k_x{}^0$ in eqn. (2) equals zero, and the values of the activation energies $E_A{}^x$ are relatively high. The mean phosphorescence lifetime $\tau_P{}^0$ found at low temperatures ($T <$ 140 K) is equal to the radiative phosphorescence lifetime $\tau_P{}^0 = 1/k_P = 1.78$ s. This enables the relation between ϕ_T and temperature to be determined from eqn. (1) (Fig. 3). Even at temperatures close to the room temperature, ϕ_T does not exceed a value of 0.2, whereas in liquid solutions it attains a value of 0.3 [8]. At temperatures higher than 200 K, delayed fluorescence of the cationic form of acridine orange in poly(vinyl alcohol) films is observed. The rate constant k_{TS} of the radiationless transition was determined as a function of temperature from eqns. (1) and (3). Simultaneously, according to eqn. (2),

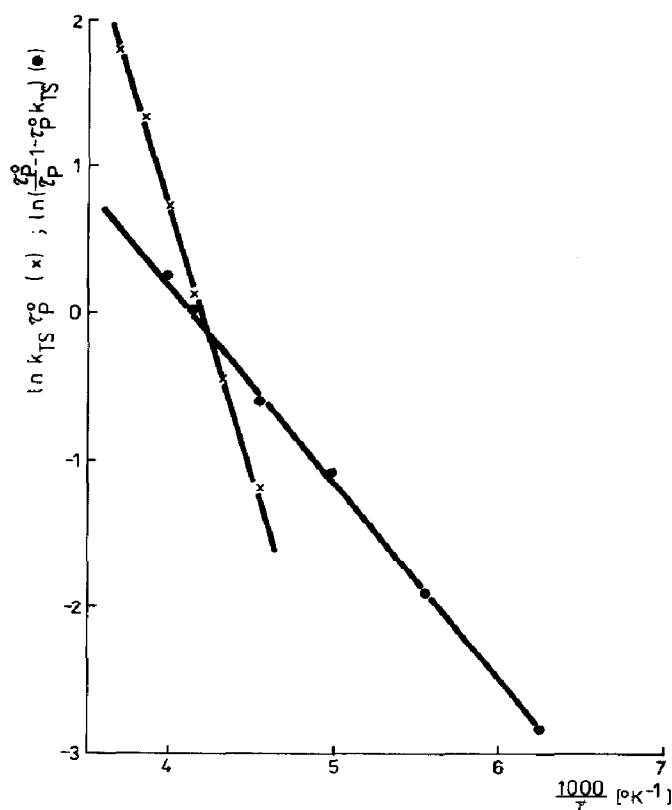$$k_{TS} = A_{TS} \exp\left(-\frac{E_A{}^{TS}}{kT}\right) \tag{4}$$

Fig. 4. Logarithmic plots of $k_{TS}\tau_P{}^0$ (×) and $\tau_P{}^0/\tau_P - k_{TS}\tau_P{}^0 - 1$ (●) vs. $1/T$ (according to eqns. (4) and (5) respectively) for acridine orange in poly(vinyl alcohol) films.

Analogically,

$$k_{\mathrm{m}} = \frac{1}{\tau_{\mathrm{P}}} - k_{\mathrm{P}} - k_{\mathrm{TS}} = A_{\mathrm{m}} \exp\left(-\frac{E_{\mathrm{A}}{}^{\mathrm{m}}}{kT}\right) \quad (5)$$

Logarithmic plots of eqns. (4) and (5) (Fig. 4) enable the values of $E_{\mathrm{A}}{}^{\mathrm{TS}}$, $E_{\mathrm{A}}{}^{\mathrm{m}}$, A_{TS} and A_{m} to be determined (Table 1). The $E_{\mathrm{A}}{}^{\mathrm{TS}}$ value of 2550 cm^{-1} thus obtained is slightly lower than that determined from the absorption and fluorescence spectra, $E_{\mathrm{S}_1} - E_{\mathrm{T}_1} \approx 3000$ cm^{-1}, which implies that the relation

$$k_{\mathrm{TS}} = k_{\mathrm{ST}} \exp\left(-\frac{E_{\mathrm{S}_1} - E_{\mathrm{T}_1}}{kT}\right)$$

usually assumed is only approximate. The value of $E_{\mathrm{A}}{}^{\mathrm{m}}$ is almost twice that of the corresponding energy of radiationless deactivation of the triplet state of a series of aromatic compounds [14]. Such a high energy barrier for the radiationless transition $\mathrm{T}_1 \to \mathrm{S}_0$ is one of the reasons for the occurrence of delayed fluorescence.

TABLE 1

Acridine orange in poly(vinyl alcohol) films

$\phi_{\mathrm{F}}{}^0$	$\phi_{\mathrm{P}}{}^0$	k_{p} (s^{-1})	$E_{\mathrm{A}}{}^{\mathrm{TS}}$ (cm^{-1})	A_{TS} (s^{-1})	$E_{\mathrm{A}}{}^{\mathrm{m}}$ (cm^{-1})	A_{m} (s^{-1})
0.975	0.025	0.56	2550	8.76	937	3.12

Acknowledgments

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