ELSEVIER

Journal of Photochemistry and Photobiology A: Chemistry 91 (1995) 125–130

Journal of PHOTOCHEMISTRY AND PHOTOBIOLOGY A: CHEMISTRY

The influence on the triplet state in antenna rhodamine dyes of intramolecular energy transfer and charge transfer

He Tian

Institute of Fine Chemicals, East China University of Science and Technology [1], *Shanghai 200237, China*

Received 15 April 1994; accepted 6 December 1994

Abstract

The triplet lifetimes of 2,5-diphenyloxazole–rhodamine dyes and trichromophoric antenna rhodamines have been measured by nanosecond laser flash photolysis and phosphorescence decay measurements. The intramolecular energy transfer and intramolecular charge transfer in these dye systems have been discussed. These may affect the lasing efficiency as well as the emission wavelength of the antenna dyes. The oxygen influence on the energy transfer has also been discussed.

Keywords: Rhodamine dyes; Triplet state; Antenna rhodamines

1. Introduction

Triplet–triplet energy transfer (TTET) in fluid solution is of great importance in both mechanistic and synthetic organic photochemistry. Several workers have studied the intramolecular transfer of triplet excitation energy between two relatively isolated chromophores on the same molecule [1–5]. The goal of these studies was to gain some insight into the mechanism of triplet excitation energy transfer. The results of these works were interpreted to indicate that the exchange (collisional) mechanism [6] operates in TTET and triplet energy can be transferred between chromophores which are separated by 7–15 Å. For molecules containing donor and acceptor groups separated by one, two or three methylene groups, the same transfer efficiency was attained in each case [1], which indicated that the methylene bridge plays no part in the transfer. The lengthening of the "bridge" from one to three methylene groups does not significantly alter the distance between the chromophores because of the flexibility of the methylene chain.

In this paper we describe a preliminary study of intramolecular ET in 2,5-diphenyloxazole (PPO)–rhodamine dyes and trichromophoric antenna rhodamines (Fig. 1) by comparing the triplet lifetimes of the dyes, which were measured by nanosecond laser flash photolysis and phosphorescence decay measurements. PPO has a high absorption coefficient at the wavelengths of UV radiation (e.g. 308 nm, which is the most likely pump radiation for rhodamine laser dyes), PPO–rhodamines have absorption spectra that agree with the spectra of one rhodamine and two PPO molecules, and therefore the absorption of them at 308 nm is quite strong. The fluorescence quantum yield η_{fl} of PPO–rhodamine 1 (PPO molecules are connected by a single CH_2– group to the rhodamine) has the value 0.94 [7]. At the same time the blue fluorescence of the PPO groups is quenched, which indicated effective intramolecular singlet–singlet energy transfer (SSET) from PPO antennas to rhodamine. Intramolecular SSET from PPO to rhodamine was also found in PPO–rhodamine 2, in which the chromophores are separated by two CH_2– groups [8].

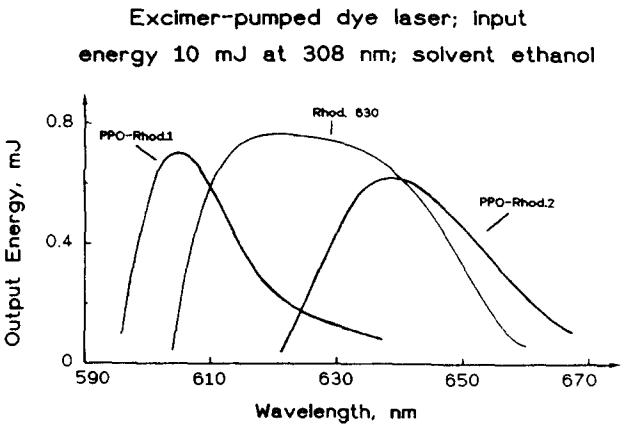
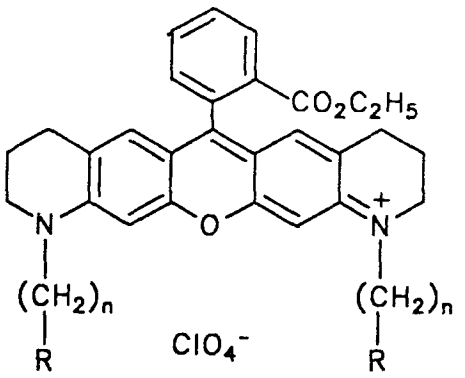


Fig. 1. The lasing properties of the antenna rhodamine dyes.

[1] Renamed, formerly the East China University of Chemical Technology.

SSDI 1010-6030(95)04014-1



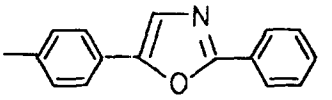
Dyes	n	R
Rh630	1	CH_3
PPO-rhod.1	1	
PPO-rhod.2	2	
DR260	1	benzene
DR261	2	

Fig. 2. The structures of the dyes.

In addition, the lasing properties of some laser dyes in excimer-pumped dye lasers have been investigated [8,9]. Because the emission of the dyes overlaps the low energy tail of the absorption band, the dye laser radiation is partly reabsorbed by the dye in its ground state. This loss is especially high if a high dye concentration is required in order to absorb the pump light, a frequent situation in pumping by an excimer laser at 308 nm. When PPO, which absorbs strongly at the pump wavelength, is connected with rhodamines, the energy absorbed by the PPO moiety would be transferred efficiently to the rhodamine laser chromophore. The lasing properties of the antenna dyes pumped by excimer laser were shown in Fig. 1 [8]. PPO–rhodamine 1 exhibits, compared with rhodamine 630 at the same optical density at the UV pumping wavelength, increased efficiency in the 590–610 nm region. The increased efficiency of PPO–rhodamine 2 in the 640–660 nm region is due to the shifted fluorescence spectrum. However, in the range 610–640 nm the efficiency of these antenna dyes is much lower than that of rhodamine 630 (Fig. 1). This may be evidence for some excited state interaction which causes an absorption and therefore additional resonator loss during the lasing process. We try to explain this by the description of intramolecular interaction in this paper.

2. Experimental details

2.1. Materials and transient absorption measurement

The structures of the dyes in this study are shown in Fig. 2. Rhodamine 6G chloride (Rh6G) (Janssen) was used without further purification. The antenna rhodamine dyes were synthesized [7]. The measurements were done using absolute ethanol (Merck) and ethylene glycol (Fluka). All solutions for measurements have the same optical density at 308 nm: $OD_{308}(1\ mm) = 0.02 \pm 0.002$. Time-resolved absorption decay kinetics was measured by laser flash kinetic spectrophotometry. The solutions (in 2 cm × 2 cm quartz cells) were excited at 308 nm (XeCl excimer laser, LPX 100, 10 ns with 100 mJ pulse^{-1}), and transient ΔOD at 633 nm (He–Ne laser (Spectra Physics 205) as monitoring light) can be detected by a photodiode and displayed on the oscilloscope (TDS 520, Tektronix). The 100 mJ pulse input is the optimum condition for the detection. In the measurements, "deaerated" means that the solutions were deaerated by bubbling with nitrogen gas for more than 4 h and "O_2 aerated" means that the solutions were saturated by bubbling with oxygen gas for 1 h. All samples in the same solvent were degassed or saturated with the same experimental conditions.

2.2. Phosphorescence lifetime τ_p measurement

The ethanolic solutions (10^{-3} M) of the dyes were put into a Dewar vessel filled with liquid nitrogen (77 K) and excited by an XeCl excimer laser flash (LPX 100, Lambda Physik; 308 nm, 30 mJ pulse^{-1}). The emission signal of the samples was very weak, so that 30 mJ pulse^{-1} was used for easy detection. The phosphorescence intensity of the samples was detected by a photodiode (detection path at 90° from the excitation path) and then recorded on an oscilloscope (20 MHz Storage Scope, HM 205-3, Hameg), and plotted on a plotter (SE 120, ABB Goerz) by means of a plotter interface (HO 75-2, Hameg). In the front of the detecting photodiode there is a cut-off filter (thickness, 3 mm; Schott), which allowed transmission of wavelengths longer than that of the fluorescence maximum of the monomer (e.g. OG 590 or RG 630).

3. Results and discussion

For antenna dyes PPO–rhodamine 1 and PPO–rhodamine 2, a transient absorption at 633 nm has been obtained by our experiments (Table 1). It is known that the T–T_n absorption spectral region of PPO and Rh630 is 500–600 nm [9,10]. The aerated ethanol solution of PPO gives no transient absorption at 633 nm (at least within the sensitivity of our measurement system). However, for the deaerated ethanol

Table 1
The kinetic data of transient ΔOD for the dyes in the solutions (OD_{308}(1 mm) = 0.02 ± 0.002)

Solvent	Ethanol						
Dyes	Rh6G	PPO	Rh630	PPO–rhodamine 1	PPO–rhodamine 2	DR260	DR261
ΔOD_{max}	0.1	0	0.3	0.06	0.04	0.04	0.1
aerated	0.15		0.14	0.12	0.12	0.08	0.09
τ (μs)							
ΔOD_{max}	0.05	0.1	0.03	0.03	0.026	0.03	0.03
deaerated	2.2	7.2	2.45	3.7	4.0	3.5	3.65
τ (μs)							
ΔOD_{max}	0	0	0.08	0.2	0.1		
O_2 aerated			0.07	0.11	0.12		
τ (μs)							
Solvent	Ethylene glycol						
Dyes	Rh6G	PPO	Rh630	PPO–rhodamine 1	PPO–rhodamine 2		
ΔOD_{max}	0.04	0.06	0.22	0.15	0.05		
aerated	3.8	2.85	4.0	2.5	2.6		
τ (±0.1 μs)							
ΔOD_{max}	0.08	0.1	0.04	0.05	0.06		
deaerated	32	120	38	40	40		
τ (±1.0 μs)							
ΔOD_{max}	0.03		0.1	0.1	0.13		
O_2 aerated	1.5		1.1	1.1	0.9		
τ (±0.1 μs)							

solution of PPO, the transient absorption at 633 nm is observed, its lifetime τ_T(PPO) = 7.2 μs. The transient absorptions at 633 nm at lower excimer laser intensity (25 mJ pulse^{-1}; 15 mJ pulse^{-1}) decay with lifetimes of about 7.0 μs. This means that the transient absorption at 633 nm results from the triplet absorption of PPO, since oxygen is a particularly effective quencher of triplet states and charge transfer (CT) states (the O_2 quenching rate of PPO is 2.5×10^9 M^{-1} s^{-1} [10]).

On flashlamp pumping, Rh630 exhibits lower threshold and higher slope laser efficiency than Rh6G and Rh101 [7]. In a continuous dye laser, pumped by a Kr ion laser, Rh630 is again more efficient than Rh6G. The markedly higher slope efficiency can only be attributed to the superior dye properties of Rh630 compared with Rh6G [7]. The fact that Rh630 exhibits higher efficiency in continuous dye lasers indicates a reduced triplet loss (intersystem crossing from the singlet and loss in gain via absorption by the triplet of the laser light) in this dye. When PPO is connected by one or two CH_2– groups to the six-membered ring rigid rhodamine (like Rh630), i.e. PPO–rhodamine 1 or PPO–rhodamine 2, triplet lifetimes of the dyes in deaerated solution are larger than that of Rh630 in spite of good singlet energy transfer from PPO to rhodamine. In general, for a donor–acceptor bichromophoric dye the triplet–triplet absorption of the donor can be eliminated by fast intramolecular SSET from donor to acceptor. Therefore, for PPO–rhodamine dyes the triplet absorption of the donor (PPO) could be eliminated and the transient absorption of antenna dyes measured here is characteristic of the triplet acceptor (rhodamine).

At a pumping wavelength of 308 nm (excimer laser) the absorption coefficient of rhodamines is rather low. Therefore, concentrations of about 10^{-3} mol l^{-1} are needed in order to absorb 90% of the pump light along a pathlength of 1 mm. Such a high concentration results in a high absorbance in the long-wavelength tail of the main absorption band. Since this is the stimulated emission wavelength, the laser efficiency is impaired. On the contrary, the absorption of the antenna rhodamine dyes at 308 nm is quite strong; at the same time, the blue fluorescence of the PPO groups is quenched. Energy transfer from antenna to rhodamine is very efficient as expected. Also, now the concentration of PPO–rhodamine 1 for equally efficient absorbance at the pumping UV light wavelength is lower than that of Rh630 because the absorption in the UV region for these antenna dyes is quite strong. This results in the reduction in the reabsorption of dye molecules in laser-stimulated emission region and consequently leads to increased lasing efficiency in the short-wavelength region of the stimulated emission spectrum. This explanation is consistent with the experimental results as shown in Fig. 1. On the contrary, the PPO moiety may act as an electron donor relative to the rhodamine moiety. This may affect the lasing efficiency of the antenna dyes in the 620–640 nm region in spite of effective intramolecular SSET in the dyes.

On excitation of one of the chromophores (D) of a non-conjugated bichromophoric system (D–A) several non-radiative processes may occur [11]:

$$A\text{–}{}^1D^* \xrightarrow{k_{ET}^{SS}} {}^1A^*\text{–}D \xrightarrow{k_{isc}^{A}} {}^3A^*\text{–}D \quad (1)$$

$${}^1A^*\text{–}D \xrightarrow{k_e} (A^{\cdot -}\text{–}D^{\cdot +}) \xrightarrow{k_r} A\text{–}D \quad (2)$$

Table 2
The fluorescence lifetime τ_{fl} of the dyes in ethanol solution [13] at room temperature

Dye (EtOH)	Rh630	PPO–rhodamine 1	PPO–rhodamine 2	AN–rhodamine [a]
τ_{fl} (ns)	4.20	4.03	2.94	0.57

[a] Molecular structure shown in Fig. 4 of [7], in which the antenna group is anthracene.

$$(A^{\cdot -}\text{–}D^{\cdot +}) \xrightarrow{k_1} {}^3A^*\text{–}D \quad (3)$$

$${}^3A^*\text{–}D \xrightarrow{k_2} A\text{–}D \quad (4)$$

where Eq. (1) is the intramolecular SSET process and intersystem crossing in the acceptor (A) moiety and Eq. (2) is the intramolecular CT process and recombination of charge. Eq. (3) is the process proposed by us which produces the triplet state of the molecule so that a transient absorption with longer lifetime than that of an isolated acceptor could be observed. If a transient absorption of antenna rhodamine dyes could be observed only from process (1), its lifetime should be almost the same as that of the isolated rhodamine. However, this expection is not consistent with the experiments. In fact, the triplet lifetime of antenna dyes is longer than that of Rh630. In general, other processes (e.g. formation of dimer or trimer) could affect non-radiative decay. However, under the experimental condition in our work, the concentration of the solutions measured is between 10^{-6} and 10^{-5} mol l^{-1}. In these dilute solutions there is a linear relationship between optical density and concentration, so intermolecular dimers or trimers can be neglected. In these dilute solutions and low viscosity solvents the intramolecular multipole–multipole interaction could be also neglected. The intramolecular electron transfer and intramolecular CT interaction between the chromophores could be attributed to the intramolecular interaction in this paper. From kinetic equations [12] (see Appendix A), we have the total non-radiative decay rate $k_D{}^A$ of $^1A^*$–D:

$$k_D{}^A = \frac{k_1 k_e}{k_r} + k_{isc}{}^A + k_e \quad (5)$$

If there is only complete intramolecular SSET without intramolecular CT processes for $^1A^*$–D, i.e. processes (2) and (3) are inhibited, the non-radiative decay rate of $^1A^*$–D is given by

$$k_{D0}{}^A = k_{isc} \quad (6)$$

It is obvious that $k_D{}^A > k_{D0}{}^A$. Since the fluorescence lifetime of the singlet state is given by

$$\tau_{fl} = (1 - \eta_{fl})/k_D$$

where k_D is non-radiative decay rate, the increase in k_D will reduce the fluorescence lifetime τ_{fl}. For antenna rhodamine dyes, the fluorescence of the antenna was almost completely quenched owing to the fast intramolecular SSET from the antenna to rhodamine moiety. Therefore, the data listed in Table 2 should be the fluorescence lifetimes of rhodamine moiety in the antenna dyes. On the basis of the data for η_{fl} [7] for Rh630 ($\eta_{fl} = 0.95$; $\tau_{fl} = 4.2$ ns), PPO–rhodamine 1 ($\eta_{fl} = 0.94$; $\tau_{fl} = 4.03$ ns), PPO–rhodamine 2 ($\eta_{fl} = 0.75$; $\tau_{fl} = 2.94$ ns) and AN–rhodamine 1 ($\eta_{fl} = 0.22$; $\tau_{fl} = 0.57$ ns) [13] (measured by means of a single-photon counting technique with 0.1 ns time resolution), it may be concluded that in PPO–rhodamine dyes or AN–rhodamine 1 there is intramolecular CT, which obviously quenches the fluorescence lifetime of the dyes by the increasing in non-radiative decay rate ($k_D{}^A > k_{D0}{}^A$). The natural radiative lifetimes $\tau = \tau_{fl}/\eta_{fl}$ of these dyes vary: 4.4 ns, 4.3 ns, 3.9 ns and 2.6 ns for Rh630, PPO–rhodamine 1, PPO–rhodamine 2 and AN–rhodamine 1 respectively. This shows that the natural lifetimes of the molecules vary and therefore the nature of the excited state also varies, since the structures are very different and new perturbations could be influencing k_{isc} even though the prepared singlet state is not affected. However, no matter how k_{isc} changes, $k_D{}^A > k_{D0}{}^A$ is always established, i.e. intramolecular CT charge transfer quenches the fluorescence lifetime of the dyes by increasing the non-radiative decay rate. $k_D{}^A$(Rh630) $= 1.19 \times 10^7$ s^{-1}; $k_D{}^A$(PPO–rhodamine 1) $= 1.49 \times 10^7$ s^{-1}; $k_D{}^A$(PPO–rhodamine 2) $= 8.5 \times 10^7$ s^{-1}; $k_D{}^A$(AN–rhodamine 1) $= 1.37 \times 10^9$ s^{-1}.

From the fact that η_{fl} of PPO–rhodamine 2 is markedly lower than that of Rh630 and PPO–rhodamine 1 (η_{fl}(PPO–rhodamine 2) $= 0.75$ at 20 °C) [7], we attributed these phenomena to a change in conformation: PPO substituents interact more strongly with the rhodamine system because of the higher flexibility of a CH_2–CH_2 link, i.e. PPO–rhodamine 2 exists in a folded conformation [8].

The presence of oxygen quenches the triplet state or CT state [12] (see Appendix B):

$$k_{QT} = k_{XT}/9(1 + \alpha) \quad (7)$$

where k_{XT} is the total diffusion-controlled collisional rate parameter, k_{QT} is the triplet oxygen quenching rate, $\alpha = k_{T1X}/(k_{\Sigma 1X} + k_{\Delta 1X})$, k_{T1X} depends on the triplet energy E_T of dyes, $k_{\Sigma 1X}$ and $k_{\Delta 1X}$ depend on the energy gap between E_T and the energies of the $^1\Sigma_g{}^+$ and $^1\Delta_g$ states respectively of $^1O_2{}^*$ [12]. On the contrary, there is an intramolecular electron transfer or intramolecular CT process to produce ($A^{\cdot -}$–$D^{\cdot +}$) species in the antenna dyes. For antenna rhodamine dyes, their intramolecular CT state can react with oxygen like a triplet as mentioned in processes (1)–(4). That is, in the presence of oxygen ($A^{\cdot -}$–$D^{\cdot +}$) may easily react with oxygen to produce ($D^{\cdot +}$–$A^{\cdot -} \cdot O_2$)* so that k_{T1X} decreases and k_{QT} increases. Consequently the transient ΔOD observed decays more rapidly than that for Rh6G. Our experimental results (Table 1) support this explanation.

Even though the phosphorescence decay of the antenna rhodamine dyes does not have to be exponential, it could in principle oscillate between the two PPOs and at the same time decay; however, in our experiments the phosphorescence intensity decays according to a first-order process. The phosphorescence decay of PPO–rhodamine 1 or PPO–rhodamine 2 is appreciably faster than that of PPO alone. The decay of a coherent mixture of the two PPOs could be twice as fast as that of a single PPO if the coherent mixture of the two PPO wavefunctions was in phase. If the coherent mixture was out of phase, then the coherent mixture would not, in principle, decay via intrinsic pathways. Thus if the triplet state of the dyes is an in-phase coherent mixture of the triplet states locally excited on the two PPOs, then the intrinsic decay time of the dyes with two PPOs should be $2/\tau_p(\text{PPO})$. Thus, the triplet energy transfer rate in these dyes is given by $k_{ET} = 1/\tau_p(\text{dye}) - 2/\tau_p(\text{PPO})$ and the energy transfer efficiency by $\phi_{ET} = k_{ET}\tau_p(\text{dye})$. Therefore, about 20% of the triplet energy is transferred away from PPO to the rhodamine moiety for PPO–rhodamine 1 or PPO–rhodamine 2.

Acknowledgements

H.T. is grateful for an Alexander von Humboldt research fellowship and the support by Professor Dr. K.H. Drexhage and Dr. E. Thiel in the University of Siegen and also for the referee's critical discussion of the manuscript.

Appendix A

From processes (1)–(4), we assume that the $^1A^*$–D state decays to form A–D and $^3A^*$–D, i.e. the decay rate of $^1A^*$–D is equal to the sum of formation rates of A–D and $^3A^*$–D:

$$-\frac{d[^1A^*\text{–}D]}{dt} = \frac{d[A\text{–}D]}{dt} + \frac{d[^3A^*\text{–}D]}{dt} \quad (A1)$$

Then from the steady state condition for $(A^{-\bullet}\text{–}D^{+\bullet})$ and assumption of $[A\text{–}^1D^*] = M_0 \exp(-k_s t)$, we can obtain

$$[^1A^*\text{–}D] = \frac{k_{ET}{}^{SS}[A\text{–}^1D^*]}{k_e + k_{isc}{}^A - k_s} \quad (A2)$$

$$\frac{d[A\text{–}D]}{dt} + \frac{d[^3A^*\text{–}D]}{dt} = \left(k_e + k_{isc}{}^A + \frac{k_1 k_e}{k_r}\right)\frac{k_{ET}{}^{SS}[A\text{–}^1D^*]}{k_e + k_{isc}{}^A - k_s}$$

$$= \left(k_e + k_{isc}{}^A + \frac{k_1 k_e}{k_r}\right)[^1A^*\text{–}D] \quad (A3)$$

From Eqs. (A1) and (A3), we have the total non-radiative decay rate constant $k_D{}^A$ of $^1A^*$–D:

$$k_D{}^A = \frac{k_1 k_e}{k_r} + k_{isc}{}^A + k_e \quad (5)$$

Appendix B

The oxygen quenching of the excited triplet state $^3M^*$ of an aromatic molecule involves the following spin-allowed processes [12]:

$$^3M^* + {}^3O_2 \underset{k_{T1X}}{\overset{k_{1XT}}{\rightleftharpoons}} {}^1(M\cdot O_2)^* \quad (B1)$$

$$^1(M\cdot O_2)^* \xrightarrow{k_{\Sigma 1X}} {}^1M + {}^1O_2{}^*(^1\Sigma_g{}^+) \quad (B2)$$

$$^1(M\cdot O_2)^* \xrightarrow{k_{\Delta 1X}} {}^1M + {}^1O_2{}^*(^1\Delta_g) \quad (B3)$$

$$^3M^* + {}^3O_2 \underset{k_{T3X}}{\overset{k_{3XT}}{\rightleftharpoons}} {}^3(M\cdot O_2)^* \quad (B4)$$

$$^3(M\cdot O_2)^* \xrightarrow{k_{G3X}} {}^1M + {}^3O_2(^3\Sigma_g{}^-) \quad (B5)$$

$$^3M^* + {}^3O_2 \underset{k_{T5X}}{\overset{k_{5XT}}{\rightleftharpoons}} {}^5(M\cdot O_2)^* \quad (B6)$$

If there is no mixing of the $^{1,3,5}(M\cdot O_2)^*$ states, then

$$k_{1XT} = k_{XT}/9;\ k_{3XT} = k_{XT}/3;\ k_{5XT} = 5k_{XT}/9 \quad (B7)$$

where k_{XT} is the total diffusion-controlled collisional rate parameter. The total $^3M^*$ oxygen quenching rate parameter is given by

$$k_{QT} = k_{XT}\left[\frac{k_{\Sigma 1X} + k_{\Delta 1X}}{9(k_{\Sigma 1X} + k_{\Delta 1X} + k_{T1X})} + \frac{k_{G3X}}{3(k_{G3X} + k_{T3X})}\right] \quad (B8)$$

In low viscosity solutions $k_{T3X} \gg k_{G3X}$ and this was confirmed by the $^1M^*$ oxygen quenching results [14]. The process (B1) is the slowest step for diffusion-controlled processes. Under these conditions Eq. (B8) reduces to

$$k_{QT} = k_{XT}/9(1+\alpha);\ \alpha = k_{T1X}/(k_{\Sigma 1X} + k_{\Delta 1X}) \quad (B9)$$

k_{QT} decreases with the increase in the $^3M^*$ energy E_T. Patterson et al. [15] attributed the observed decrease in k_{QT} with increase in E_T to a decrease in the Franck–Condon factors for processes (B2) and (B3) and a consequent decrease in $k_{\Sigma 1X}$ and $k_{\Delta 1X}$. The wavenumbers of $^1\Sigma_g{}^+$ and $^1\Delta_g$ states of $^1O_2{}^*$ are 13 121 cm^{-1} and 7882 cm^{-1} [12]. For Rh6G, the energy gaps $\Delta E_{T\Sigma}$ and $\Delta E_{T\Delta}$ are given by [16]

$$\Delta E_{T\Sigma} = E_T(\text{Rh6G}) - E(^1\Sigma_g{}^+) = 2179\ cm^{-1}$$

$$\Delta E_{T\Delta} = E_T(\text{Rh6G}) - E(^1\Delta_g) = 7418\ cm^{-1}$$

Patterson et al. [15] assumed that k_{T1X} and k_{T3X} are determined by the $^{1,3}(M\cdot O_2)^*$ binding energy, which is proportional to $(E_{CT} - E_T)^{-2}$, where E_{CT} is energy of the CT state:

$$E_{CT} = E^{ox}(M) - E^{red}(O_2{}^-/O_2) \pm \Delta \quad (B10)$$

where Δ is the Coulomb term and $E^{ox}(M)$ is the oxidized potential of the molecule [16]. At this time for a dye in

different oxygen vapour pressures, the changes in quenching rate k_{QT} can be reflected by the changes in E_{CT}, as shown above (from Eqs. (B9) and (B10)). These imply that the triplets of the rhodamine dyes in this study are quenched by oxygen according to processes (B2) and (B3), which are diffusion-controlled collisional processes. In addition, oxygen quenching depends on the energy of the CT state, and hence the relationship between τ_T and the concentration $[O_2]$ of oxygen is complicated rather than being a simple inverse relationship.

References

[1] A.A. Lamola, P.A. Leermakers, G.W. Byers and G.S. Hammond, *J. Am. Chem. Soc., 85* (1963) 2670; *87* (1965) 2322.

[2] D.E. Brean and R.A. Keller, *J. Am. Chem. Soc., 90* (1968) 1935; R.A. Keller, *J. Am. Chem. Soc., 90* (1968) 1940; R.A. Keller and L.J. Dolby, *J. Am. Chem. Soc., 91* (1969) 1293.

[3] T. Okada, T. Fujita, M. Kubota, S. Masaki, N. Mataga, R. Ide, Y. Sakata and S. Misumi, *Chem. Phys. Lett., 14* (1972) 563.

[4] F.C. DeSchryver, N. Boens and J. Put, *Adv. Photochem., 10* (1977) 359.

[5] H.E. Zimmerman and R.D. McKelvey, *J. Am. Chem. Soc., 93* (1971) 3638.

[6] D.L. Dexter, *J. Chem. Phys., 21* (1953) 836.

[7] J. Arden, G. Deltau, V. Huth, U. Kringel, D. Peros and K.H. Drexhage, *J. Lumin., 48–49* (1991) 352.

[8] G. Deltau, U. Kringel, D. Peros, B. Runde and K.H. Drexhage, in B. Jordanov, N. Kirov and P. Simova (eds.), *Recent Developments in Molecular Spectroscopy*, World Scientific, Singapore, 1989, p. 539.

[9] D. Peros, *Dissertation, Universität-GH-Siegen, 1991.*

[10] I. Carmichael and G. Hug, *J. Phys. Chem. Ref. Data, 15(1)* (1986) 1.

[11] N.J. Turro, in *Modern Molecular Photochemistry*, Bejamin–Cummings, Menlo Park, CA, 1978, Chap. 9.

[12] J.B. Birks, in J.B. Birks (ed.), *Organic Molecular Photophysics*, Vol. 2, Wiley, New York, 1975, Chap. 9.

[13] K.H. Drexhage, unpublished results.

[14] R. Potashnik, G.R. Goldschmidt and M. Ottolenghi, *Chem. Phys. Lett., 9* (1971) 424.

[15] L.K. Patterson, G. Porter and M. Topp, *Chem. Phys. Lett., 7* (1970) 612.

[16] T.A. Shakhverdov, V.N. Kalinin and V.L. Ermolaev, *Izv. Akad. Nauk SSSR, Ser. Fiz., 54* (1990) 460.