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Solvent Effect on the Triplet Lifetime of Some Rhodamine Dyes

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ABSTRACT

The transient absorptions at 633 nm of some rhodamine dyes in various solvents have been measured by nanosecond laser flash photolysis. It can be considered that the transient absorptions result from the triplet or intramolecular charge transfer (Intra-CT) states of the dyes. It seems that the transient ΔOD lifetimes increase with increase in the viscosity in alcoholic solvents due to the decrease of oxygen diffusivity. The solvent effect on the formation of triplet or Intra-CT states in the rigid trichromorphoric rhodamine dyes is effectively influenced by the polarity of the solvent. In addition, the triplet and twisted intramolecular charge transfer (TICT) states are quenched by oxygen.

INTRODUCTION

Solvent effects are important in determining the photophysical properties of dye molecules in solution and an understanding of solvent effects is needed to improve the performance of dye lasers. Spectroscopic techniques have been widely used to study solute–solvent interactions of dye molecules in various solvent systems. Various dye molecules in solvents of different viscosities have been examined,[1-3] and several models have been proposed to explain the effect of solvent and molecular structure on internal conversion in xanthene dyes; viz. the intramolecular rotation model,[4,5] the twisted intramolecular charge transfer (TICT) model,[6] and the umbrella-like-motion (ULM) model.[7] In the intramolecular rotation

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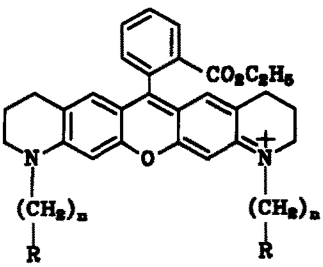
model, internal conversion is mainly governed by solvent viscosity, whereas in the TICT model, internal conversion is determined mainly by solvent polarity. In the ULM model, internal conversion is determined by specific solute–solvent interactions.

The influence of solvent polarity on the isomerization rate has been observed for many other molecules in addition to rhodamine dyes.[8] For instance, Fleming *et al.*[9] suggested that the activation energy from the planar to the twisted configuration decreases in polar solvents, based on studies of diphenyl butadiene. Hicks *et al.*[10] also found that the barrier height in the isomerization decreased with increasing solvent polarity for (dimethylamino)benzonitrile in solution. However, there have also been numerous studies on solvent effects that are manifested by a viscosity-dependent nonradiative rate constant (see Moog *et al.*,[2] and references therein). These effects are important in excited-state relaxation processes involving photoinduced torsional motion about chemical bonds.[4] However, the detailed role of the solvent in the photodynamics of rhodamine dyes is still controversial.[11–13]

In this paper, a study of the triplet or charge transfer state lifetime of some rhodamine dyes in various solvents by nanosecond time-resolved transient absorption measurements is described. The results indicate that, for the trichromophoric rhodamine dyes used in this study, there are intramolecular charge transfer (Intra-CT) states whose energy is polarity-dependent, and which may determine the quantum yield of triplet state formation. To further examine the possible viscosity effect, solutions of dyes in a high viscosity solvent (glycerol) were also examined.

EXPERIMENTAL

The structures of the dyes used in this study are shown in Fig. 1. Rhodamine 6G chloride (**Rh6G**) (Janssen) was used without further purification. The trichromorphic rhodamine dyes were synthesized in our



Dyes	n	R
Rh630	1	CH$_3$
PPO-rhod.1	1	2,5-diphenyloxazole
PPO-rhod.2	2	2,5-diphenyloxazole
DR271	1	o-nitrobenzene
DR260	1	benzene

Fig. 1. Structure of dyes.

laboratory and their structures confirmed.[14] Measurements were effected using air-equilibrated absolute ethanol (Merck), ethylene glycol (Fluka), ammonyx LD (Lambda Physik) and glycerol (Janssen). All solutions for the measurements had the same optical density at 308 nm, i.e. OD_{308} (1 mm) = 0·02 ± 0·002. Time-resolved absorption decay kinetics were measured by laser flash kinetic spectrophotometry; details of the apparatus are described elsewhere.[18] The solutions were excited at 308 nm (XeCl excimer laser, 10 ns with 100 mJ/pulse); transient optical density changes at 633 nm (He–Ne laser as monitoring light) were detected by a photodiode and displayed on an oscilloscope. In the measurements, 'deaerated' means that the solutions were deaerated by bubbling with nitrogen for 2 h (for low viscosity solvents) and >4 h (for high viscosity solvents, e.g. glycerol); 'O_2-saturated' implies that the solutions were 'in saturation' by bubbling with oxygen for 2 h.

RESULTS AND DISCUSSIONS

In deaerated condition

The transient absorption decay lifetimes at 633 nm for the rhodamine dyes in a series of alcoholic solvents at 20°C are tabulated in Table 1. It appears that the transient ΔOD lifetimes increase with increase in the viscosity of the alcoholic solvents in the absence of oxygen. In fact, the deaerated conditions used in our experiments were not sufficient for complete removal of oxygen. After purging with nitrogen, the solution also contained oxygen at 20–100 ppm. However, we only wished to demonstrate the observed transient ΔOD resulting from triplet or charge transfer states absorption; deaeration by the bubbling method obviously decreases the concentration of oxygen in the solutions. Under this condition, the decay lifetimes of the transient ΔOD are prolonged (Table 1). Comparison of the results between the 'deaerated' and aerated solutions used allowed the conclusion that the observed transient ΔOD can be assigned to the triplet or charge transfer state absorption; therefore, a freeze–pump–thaw process was not used. It could be concluded that the triplet lifetime of deaerated solutions, with a freeze–pump–thaw process, would be longer than that in deaerated solutions using the bubbling method.

In the same solvent, under the same deaerated conditions, the concentration of oxygen in the solutions is nearly the same. At this time, the diffusion and concentration of oxygen has a similar influence on the decay of the transient ΔOD for different dyes. For example, the decay lifetimes

TABLE 1

Kinetic Data of Transient ΔOD at 633 nm for the Dyes in Solutions (OD_{308} (1 mm) = 0·02 ± 0·002). Errors in τ values are ±10%.

Dyes		**Rh6G**	**Rh630**	**PPO-rhod.1**	**PPO-rhod.2**	**DR271**	**DR260**
Aerated τ (μs)	1	0·15	0·14	0·12	0·12	0·75	0·08
	2	3·8	4·0	2·5	2·6	6·2	1·45
	3	4·5	5·0	2·95	3·0		
Deaerated τ (μs)	1	2·2	2·45	3·7	4·0	10	3·5
	2	34	38	39·5	40	9·5	31
	3	38	40	41	43		
O_2-Saturated τ (μs)	1		0·07	0·11	0·11	0·06	0
	2	1·5	1·1	1·15	0·85	0·04	0·18
	3	1·5	1·1	1·85	1·65		

Solvents: 1, Ethanol; 2, Ethylene glycol; 3, Glycerol.

of **Rh6G** and **Rh630** in ethanol are approximately equal. However, antenna rhodamine dyes (e.g. **PPO-rhod.1** and **PPO-rhod.2**), which have a rigid xanthene–amino bond, have a longer transient ΔOD decay lifetime compared to **Rh6G**. This implies that intramolecular charge transfer or electron transfer (ET) processes occur in these trichromophoric rhodamine dyes. For different antenna, the efficiencies of the Intra-CT or ET processes are different, and therefore the energies of the Intra-CT or ET states are also different. The reactions between oxygen and these Intra-CT states are quite different for different antenna dyes. This may be the main reason why the trichromophoric rhodamine dyes have different transient ΔOD decay lifetimes compared with **Rh6G** or **Rh630** in the same solvent.

For a dye in different solvents, the decay lifetimes of transient ΔOD are different. For example, **Rh630** in ethanol has a decay lifetime of 2·45 μs, whereas in glycerol τ_T is 40 μs. This indicates that deaeration by bubbling with nitrogen in our experiments is not enough for complete removal of oxygen from the solutions. Oxygen solubility and diffusivity in different solvents are quite different, so that the influences on the transient ΔOD decay are also quite different. The fact that the observed transient ΔOD of the dyes decay with different lifetimes in different solvents indicates that the observed transient absorptions result from the absorption of triplet or Intra-CT states of the dyes. Even though deaeration by the bubbling method is not complete, the decay lifetimes of the dyes in deaerated glycerol solutions (Table 1) may be considered to approach, relatively, that of the dyes in the absence (absolute) of oxygen, since the solubility and diffusivity of oxygen in glycerol are very small.

Since twist of the xanthene–amino bond in **Rh630**, **PPO-rhod.1** and **PPO-rhod.2** is difficult, the formation of a twisted intramolecular charge transfer (TICT) state is inhibited in these dyes, giving a consequent prolongation in τ_T relative to **Rh6G**. Therefore, the solvent effect on the deactivation of excitation energy and the formation of the triplet state in the rigid rhodamine dyes is essentially governed by the polarity of the solvent.

In aerated and O_2-saturated conditions

In the presence of oxygen, the triplet or Intra-CT state will be effectively quenched by oxygen. For the excited singlet state, the oxygen quenching rate $k_{QM} \cong k_{XT}$ (where k_{XT} is total diffusion-controlled collisional rate).[17] The decay rate of $^3M^*$ in presence of O_2 is given by

$$k'_{TD} = k_{TD} + k_{QT}[O_2] \tag{1}$$

where k_{TD} is the decay rate of the triplet state in the absence of oxygen and k_{QT} is the oxygen quenching rate of triplet state.

From the expression of k_{QT} in reference [18], we have

$$k'_{TD} = k_{TD} + \frac{k_{XT}[O_2]}{9}\left[\frac{1}{1+\alpha} + \frac{3k_{G3X}}{k_{G3X} + k_{T3X}}\right] \tag{2}$$

where $\alpha = k_{T1X}/(k_{\Sigma 1X} + k_{\Delta 1X})$.[10,18]

For a dye in different alcoholic solvents (aerated and O_2-saturated), the decrease in k_{XT} with increase in the viscosity η ($k_{XT} \propto 1/\eta^m$) will reduce k'_{TD}, consequently prolonging the triplet lifetime τ_T. The experimental results agree with the prediction mentioned above (Tables 1 and 2). On the other hand, it is well known that oxygen is an effective quencher for the triplet state or charge transfer state. The quenching of the triplet state or of the CT state by oxygen depends on the oxygen solubility and diffusivity in the solvents. Table 3 lists[15] oxygen solubility δ values ($Ncm^3[O_2]/cm^3$[solvent]atm). An empirical correlation between the oxygen diffusivities D_L in pure liquids and the viscosity (η) is:[16] $D_L \propto \eta^{-2/3}$. The results observed in the present experiments are not satisfactorily explained by the changes of oxygen solubility and diffusivity in various solvents. For instance, δ in ethanol is about 10 times larger than that in water, whereas η for both solvents is approximately equal. However, the triplet lifetimes of **Rh6G** in the solvents are approximately equal; η of PVA + H_2O and ethylene glycol are the same, and the oxygen solubility δ in both solvents is not very different, but the triplet lifetimes for the rhodamine dyes in both solvents are very different. It may be considered that in low or medium viscosity solvents, the concentration and diffusivity of oxygen are sufficient for triplet or Intra-CT state quenching.

TABLE 2

Triplet Lifetimes (Aerated Solutions) of the Dyes in Various Solvents, Together with Viscosity (η) and Normalized Polarity Parameter E_T^N.[12]

Solvents	*Ethanol*	*Ethylene glycol*	*Glycerol*	*$(PVA+H_2O)^1$*	*$(PVA+H_2O)^2$*	*Ammonyx*	*H_2O*
η (cp)	1·2	19·9	1490	19·9	80	28	1·0
E_T^N	0·654	0·79	0·812				1·0
τ (μs) **Rh6G**	0·15	3·8	4·5	0·15		2	0·15
τ (μs) **Rh630**	0·14	4·0	5·0	0·14	1·8		

Solvent	*$PVA + H_2O$ (η = 19·9 cp)*					
Dyes	**Rh6G**	**Rh630**	**PPO-rhod.1**	**PPO-rhod.2**	**DR271**	**DR260**
ΔOD_{max}	0·1	0·08	0·05	0·06	0·03	0·1
τ (ns)	150	140	215	215	930	75

In a high viscosity solvent (glycerol), D_L of oxygen may influence the lifetime of the triplet, since in this case the concentration of oxygen is very small and the importance of viscosity emerges through D_L. This was confirmed by the results that τ_T are much longer in glycerol. However, the relationship between the triplet decay lifetime τ_T and the concentration of oxygen $[O_2]$ is complicated.

For different dyes in the same solvent (in the presence of O_2), the decrease in energy of ${}^3M^*(E_T)$ will decrease α (see eqn (2)), and as a consequence, increase k'_{QT}, since the decrease in $\Delta E_{T\Sigma} = E_T(\text{dye}) - E({}^1O_2, {}^1\Sigma_g^+)$ and $\Delta E_{T\Delta} = E_T(\text{dye}) - E({}^1O_2, {}^1\Delta_g)$ will increase $k_{\Sigma 1X}$ and $k_{\Delta 1X}$. This results in the triplet lifetimes of the dyes being shortened relative to that of **Rh6G**. In this time (the same solvent in aerated condition), in spite of the same concentration of oxygen in the solutions, the quenching efficiencies by O_2 are different due to the difference in E_T of the dyes. On the other hand, for the excited state of antenna rhodamine dyes, there is an intramolecular CT or ET process:

$$[\text{Rh–D}]^* \longrightarrow \text{Rh}^{\bullet -}\text{–D}^{\bullet +} \qquad (3)$$

where D is an electron donating antenna moiety. In the presence of oxygen, the $\text{Rh}^{\bullet -}\text{–D}^{\bullet +}$ species may easily react with oxygen to produce

TABLE 3

Oxygen Solubilities δ ($Ncm^3[O_2]/cm^3$[Solvent]atm) in Various Solvents at 20°C

Solvents	*Ethanol*	*Ethylene glycol*	*Glycerol*	*H_2O*	*$PVA+H_2O$*
δ	0·227	0·013	0·007	0·0299	~0·03

$^1(\mathrm{D}^{\bullet+}\text{–}\mathrm{Rh}^{\bullet-}\bullet\mathrm{O}_2)^*$, so that the rate parameter k_{T1X} decreases, with consequent increase in k_{QT}, i.e. the transient ΔOD observed in the antenna rhodamine dyes decay more rapidly than that for **Rh6G** (Tables 1 and 2). However, when the group on the amino atom is a strong electron-withdrawing group A (e.g. **DR271**), it can be expected that the Intra-CT or ET for the excited state should mainly be a backward transfer:

$$[\mathrm{Rh\text{–}A}]^* \rightarrow \mathrm{Rh}^{\bullet+}\text{–}\mathrm{A}^{\bullet-} \tag{4}$$

Under aerated conditions, the $\mathrm{Rh}^{\bullet+}\text{–}\mathrm{A}^{\bullet-}$ species is unlikely to recombine with oxygen, since the species is already a semi-oxidized form of the rhodamine moiety; therefore, the transient ΔOD of **DR271** decays relatively slowly. Data for **DR271** are significantly different from those of other rhodamines. This indicates that the transient ΔOD, in the case of **DR271**, does not result from a normal triplet.

In addition, in order to determine solvent viscosity dependence alone, we would first have to eliminate solvent polarity effects by carrying out the experiments in nonpolar solvents. This is difficult to do, because the dyes are ionic and will therefore be insoluble in nonpolar solvents. Hence, a detailed discussion about viscosity-dependence cannot be given at the present stage of this investigation.

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