

TICT and ULM models for the radiationless deactivation of rhodamines

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Abstract. The formation of a twisted intramolecular charge transfer state (TICT model) and changing of the amino group from a planar to a pyramidal structure (ULM model) are applied to explain the radiationless deactivation of rhodamines with different molecular structures in water and in ethanol. Both theories offer valid interpretations for the photophysics of rhodamines if intramolecular xanthene-carboxyphenyl and specific solute-solvent interactions are considered.

Keywords. Rhodamines; fluorescence; internal conversion; solvent effect; TICT model; ULM model.

1. Introduction

It has long been known that the fluorescence quantum yield and lifetime of the excited state of aromatic compounds, with an amino group directly attached to the aromatic ring, depend on the degree of amine alkylation. These influences are due to a progressive increase in the rate constant of the radiationless deactivation by alkylation of the amino group. The elucidation of the mechanism for the non-radiative deactivation of such molecular systems is, from a scientific and technological point of view, of great interest since most of the laser dyes (i.e. rhodamines, coumarins etc.) present this particular structure.

First theories in rhodamine dyes considered the rotation of the xanthene-amine bond as being responsible for the internal conversion of rhodamines (Drexhage 1977). However, in the eighties, some experimental results showed that the intramolecular rotation of the amino groups hindered by solvent viscosity is too simple a process for the radiationless deactivation of rhodamines (López and Rohatgi-Mukherjee 1986; Vogel *et al* 1988). New theories have been applied to the radiationless deactivation of rhodamines: (i) via a twisted intramolecular charge transfer like state (TICT model) in which the amino group transfers an electron to the xanthene ring (Vogel *et al* 1988; Casey and Quitevis 1989; Chang and Brost 1990; Chang and Cheung 1990). The TICT state acquires a twisted structure in order to minimize the overlap between the π -orbitals of the xanthene chromophore and the n -orbital of the nitrogen atom (Rettig 1986, 1988; Grabowski 1987); (ii) via a structural change of the iminium group from a planar xanthene = N⁺ structure to a pyramidal xanthene-N one, an open-close

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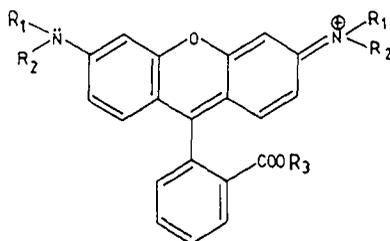


Figure 1. General molecular structure of rhodamine dyes: - with diethylamino groups ($R_1 = R_2 = \text{Et}$) RB^+ ($R_3 = -$), RBH^+ ($R_3 = \text{H}$) and R3B^+ ($R_3 = \text{Et}$) - with monoethylamino groups ($R_1 = \text{H}$ and $R_2 = \text{Et}$) R19^+ ($R_3 = -$), R19H^+ ($R_3 = \text{H}$) and R6G^+ ($R_3 = \text{Et}$) - with non-ethylated amino groups ($R_1 = R_2 = \text{H}$) R110^+ ($R_3 = -$), R110H^+ ($R_3 = \text{H}$) and R123^+ ($R_3 = \text{Me}$).

umbrella like motion (ULM model) (López and Rohatgi-Mukherjee 1986; López *et al* 1989a). This structural change disrupts the π -electron density at the xanthene-amine bond (López *et al* 1989a).

This paper discusses the photophysical properties of rhodamines with different molecular structures in water and ethanol solutions by means of the TICT and ULM model. Rhodamines with di- (RB and R3B), mono- (R19 and R6G) and non-ethylated amino groups (R110 and R123) are considered in this study, figure 1. The carboxylate group can be free (Ph-COO^- : RB^\pm , R19^\pm and R110^\pm), or protonated (Ph-COOH : RBH^+ , R19H^+ and R110H^+) or esterified (Ph-COOEt : R3B^+ , R6G^+ and R123^+). These molecular structures permit the discussion of the effects of amino ethylation and of protonation or esterification of the carboxyphenyl group on the photophysics of rhodamines. Water and ethanol are chosen as solvents due to their different tendencies to solvate the amino and carboxyphenyl groups of rhodamines. Water molecules solvate the Ph-COO^- group better than ethanol. Ethanol is a good solvent for the ethylamino groups whereas water molecules are avoided at this part of the molecule mainly for the diethylamino dyes due to hydrophobic reasons (López and Rohatgi-Mukherjee 1986).

2. Experimental

Rhodamines (Kodak, Laser Grade) were used without further purification. Water was double distilled and ethanol was supradried by distillation to avoid water traces. Dye solutions were very dilute ($\sim 10^{-6} \text{ mol dm}^{-3}$) in order to neglect dye aggregation (López *et al* 1989b) and to minimize the reabsorption and reemission effects on the emission light (López 1980). The molecular forms of RB, R19 and R110 were obtained by controlling the pH of the solutions. The emission beam was recorded in the front-face mode with respect to the excitation beam and the fluorescence quantum yield was calculated using RB^\pm in ethanol as reference. Sample preparations and instrumentals were described previously (López *et al* 1991a, 1992).

3. Results and discussion

The absorption and emission spectral maxima and the fluorescence quantum yield (ϕ) and lifetime (τ) of rhodamines have been previously published (López *et al*

Table 1. Influence of the amino ethylation on the photophysics of rhodamines with the Ph-COO⁻ group in water at 20°C.

Absorption (Δv_{ab}) and emission (Δv_{em}) spectral shift (in cm⁻¹), and the ratio of the radiative (k_f) and of the non-radiative rate constant (k_{nr}) of R19[±] (López *et al* 1991a) versus R110[±] (López *et al* 1992) (first ethylation) and of RB[±] (López *et al* 1991b) versus R19[±] (López *et al* 1991a) (second ethylation).

	R19 [±] vs. R110 [±]		RB [±] vs. R19 [±]	
	(1)	(2)	(1)	(2)
$\Delta v_{ab}(1-2)$	-1040		-1130	
$\Delta v_{em}(1-2)$	-950		-850	
$k_f(1)/k_f(2)$		0.77		1.00
$k_{nr}(1)/k_{nr}(2)$		4.3		5.4

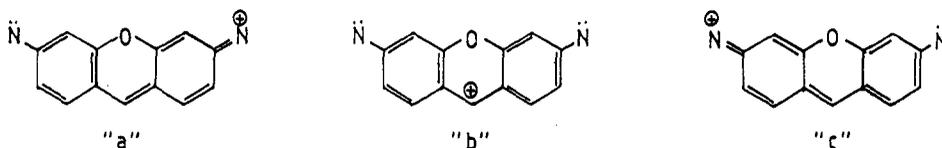
1991a, b, 1992). Radiative (k_f) and non-radiative deactivation (k_{nr}) rate constants were calculated from ϕ and τ by the relations $k_f = \phi/\tau$ and $k_{nr} = (1 - \phi)/\tau$. The influence of the refractive index of the solvent on the k_f value (Birks 1973) was taken into account. The influence of the amino ethylation is discussed by comparing the photophysics of the mono- with respect to the non-ethylamino rhodamines and the di- with respect to the mono-ethylamino rhodamines. The results are listed in table 1 for the particular case of rhodamines with the Ph-COO⁻ group in water (R19[±] over R110[±] and RB[±] over R19[±]), although similar qualitative results are obtained for rhodamines with the Ph-COOH or Ph-COOEt group in water and in ethanol (López *et al* 1991).

The ethylation of the amino groups not only increases the radiationless deactivation rate constant but also shifts the absorption and emission spectra to lower energies, as is shown in table 1. The increase in the k_{nr} value by amino ethylation is attributed, by the TICT model, to an augmentation in the electron donor capacity of the amino groups due to the inductive effect +I of the substituents (Casey and Quitevis 1988; Vogel *et al* 1988). Thus, the TICT state is lower in energy than the S₁ locally excited state for rhodamines with diethylamino groups and radiationless deactivation via this mechanism is possible in these rhodamines (Vogel *et al* 1988). The TICT state is thought to be not formed in rhodamines with mono- or with non-ethylated amino groups, since the energy of the TICT state for these rhodamines seems to be higher than that of the S₁ state (Vogel *et al* 1988). This interpretation is corroborated by the activation energy associated to the internal conversion of rhodamines, table 2. In fact, since the TICT state formation requires an activation energy, E_a , corresponding to a potential barrier (Rettig 1986, 1988; Grabowski 1987), an important E_a value is observed for rhodamines with diethylamino groups while rhodamines with mono-ethylamino groups present a small E_a value. It is interesting to note from table 2 that when the rate constant of the radiationless deactivation of rhodamines is higher, its associated activation energy is also higher. So, the process is more probable but is energetically more difficult.

The ULM model takes into account the resonant structures of the rhodamine chromophore, figure 2 (Drexhage 1977; Tredewil and Osborne 1980), to explain not

Table 2. Rate constant of the radiationless deactivation and activation energy of rhodamines at 20°C in water and ethanol (López *et al* 1991, 1992).

	Monoethylated			Diethylated		
	R19 [±]	R19H ⁺	R6G ⁺	RB [±]	RBH ⁺	R3B ⁺
H₂O						
$k_{nr}(10^8 \text{ s}^{-1})$	0.8	1.0	1.1	3.9	4.8	5.3
$E_a(\text{kJ mol}^{-1})$	0.3	1.3	1.7	25	23	23
EtOH						
$k_{nr}(10^8 \text{ s}^{-1})$	0.1	0.5	0.6	1.0	1.9	2.6
$E_a(\text{kJ mol}^{-1})$	0.3	0.8	0.6	20	22	20

**Figure 2.** Resonance structure of the rhodamine chromophore (Drexhage 1977).

only the variation in k_{nr} but also the absorption and emission spectral shifts observed by the amino ethylation (table 1). The statistical weight of the resonant structures "a" and "c" in figure 2 (in which the electron pair of the nitrogen atom forms part of the π -system) is increased by the amino ethylation because the inductive effect of the ethyl substituents stabilizes the rhodamine positive charge at the nitrogen atom (López and Rohatgi-Mukherjee 1986; López *et al* 1989a). This is corroborated by the spectral shift to lower energies observed by amino ethylation, table 1. Therefore, the probability for the structural change of the amino groups (and consequently, the rate constant of radiationless deactivation) is increased by amino ethylation. This interpretation is in agreement with the experimental results found for the activation energy (table 2): when the xanthenone–amine double bond character is increased then the structural change of the iminium group is more pronounced (k_{nr} value increases) but the process is energetically more difficult (E_a value also increases).

The protonation or esterification of the carboxyphenyl group also affects the photophysics of rhodamines. Table 3 compares the experimental results of rhodamines with the Ph–COOH or the PhCOOEt group with respect to that with the Ph–COO[−] group for the particular case of diethylamine rhodamines in water. Similar quantitative results are observed for mono- and non-ethylated amino rhodamines in water and ethanol (López *et al* 1991b, 1992). The augmentation observed in the k_{nr} value by protonation or esterification of the Ph–COO[−] group cannot be adequately explained by the described TICT model. In fact, the COOR group is not directly attached to one of the two moieties involved in the TICT state formation, and its influence on radiationless deactivation process should be very small. A second TICT state for rhodamines, in which the carboxyphenyl group is the electron donor and the xanthenone ring is the electron acceptor partner, has also been proposed (Vogel and Rettig 1985). However, this new TICT state cannot explain the experimental results (López *et al* 1991a) since the ionization potential of the benzoic acid (9.73 eV) is higher than that of its methyl ester (9.35 eV) (Weast 1976).

Table 3. Influence of the protonation or esterification of the carboxyphenyl group on the photophysics of rhodamines with diethylamino groups in water at 20°C. Absorption (Δv_{ab}) and emission (Δv_{em}) spectral shift (in cm^{-1}), and the ratio of the radiative (k_f) and of the non-radiative rate constant (k_{nr}) of R110H⁺ versus R110[±] (protonation) and R123⁺ versus R110[±] (esterification) (López *et al* 1991b).

	R110H ⁺ vs. R110 [±]		R123 ⁺ vs. R110 [±]	
	(1)	(2)	(1)	(2)
$\Delta v_{ab}(1-2)$	200		235	
$\Delta v_{em}(1-2)$	110		130	
$k_f(1)/k_f(2)$	0.84		0.81	
$k_{nr}(1)/k_{nr}(2)$	3.2		3.8	

An intramolecular electrostatic interaction between the π -system of the rhodamine chromophore and the electron lone-pairs of the COOR group has been proposed to explain the effect of the COOR group on the photophysics of rhodamines (López and Rohatgi-Mukherjee 1986; López *et al* 1989a). This interaction localizes the rhodamine positive charge at the central 9-carbon of the xanthene ring (resonant structure "b" in figure 2), reducing the π -electron density in the xanthene-amine bond. The intramolecular xanthene-COOR interaction decreases in the series Ph-COO⁻ >> Ph-COOH > Ph-COOEt (López *et al* 1991). The absorption and emission spectral shifts to higher energies of rhodamines with the Ph-COO⁻ group with respect to those with the Ph-COOH or the Ph-COOEt group, table 3, corroborate these assumptions.

If the xanthene-COOR interaction is considered, then the TICT and the ULM model can explain the diminution in the k_{nr} value of rhodamines with the Ph-COO⁻ group with respect to those with the Ph-COOH or the Ph-COOEt group, table 3. Indeed, the probability for the planar-pyramidal structural change of the amino groups (ULM model) would be reduced by this intramolecular interaction, since the π -electron density in the xanthene-amine bond is also reduced. Besides, the electron acceptor capacity of the xanthene ring would be decreased, reducing the probability for the formation of the TICT state.

Finally the effect of the nature of solvent on the photophysics of rhodamines is discussed. The TICT model suggests that the radiationless deactivation rate constant is affected by the solvent polarity and viscosity (Casey and Quitevis 1988; Vogel *et al* 1988; Chang and Brost 1990; Chang and Cheung 1990). In fact, the TICT formation involves an intramolecular rotation of the amino groups (favoured in low viscous solvents) and a charge-transfer state (favoured in polar media). The solvent polarity is also considered in the ULM model to explain the evolution of the k_{nr} value in a series of linear monoalcohols (López and Rohatgi-Mukherjee 1986). However, the k_{nr} value of rhodamines in aqueous solution presents a different behaviour to that which should be expected from its solvent polarity (López and Rohatgi-Mukherjee 1986). For this reason, specific rhodamine-solvent interactions have been claimed to affect the photophysics of rhodamines (López *et al* 1989a, 1991).

Table 4. Solvent effect on the photophysics of rhodamines at 20°C.

Absorption (Δv_{ab}) and emission (Δv_{em}) spectral shift (in cm^{-1}), and the ratio of the radiative (k_f) and of the non-radiative rate constant (k_{nr}) of rhodamines in water (1) with respect to that in ethanol (2) (López *et al* 1991, 1992).

	Nonethylated			Monoethylated			Diethylated		
	R110 [±]	R110H ⁺	R123 ⁺	R19 [±]	R19H ⁺	R6G ⁺	RB [±]	RBH ⁺	R3B ⁺
$\Delta k_{ab}(1-2)$	185	385	430	-150	80	115	-370	-135	-95
$\Delta v_{em}(1-2)$	80	165	215	-150	-25	15	-300	-140	-115
$k_f(1)/k_f(2)$	0.92	0.92	0.96	0.72	0.79	0.78	0.75	0.72	0.71
$k_{nr}(1)/k_{nr}(2)$	(5.6)	1.4	1.4	(5.8)	1.9	1.7	3.9	2.5	2.0

Table 4 compares the photophysics of rhodamines obtained in water with respect to that in ethanol. These results corroborate the existence of specific rhodamine-solvent interactions: (i) The spectral shifts observed by changing from ethanol to water as solvent cannot be attributed to a universal solvent effect since these spectral shifts depend on the molecular structure of rhodamines (i.e., the absorption and emission bands shift to lower and higher energies for RB[±] and R123[±], respectively, table 4). (ii) The value of k_f , corrected for the refractive index of the solvent (Birks 1973), is solvent dependent (table 4). (iii) A progressive addition of water to ethanol (different water/ethanol mixtures) does not cause a progressive variation in the photophysics of rhodamines, but different behaviours are observed depending on the content of water in the water/ethanol mixtures (López *et al* 1991).

On the basis of the experimental results, it is clear that the amino and the carboxyphenyl groups of rhodamines have to take part in the specific solute-solvent interactions. Two types of rhodamine-solvent interactions can be considered (López and Rohatgi-Mukherjee 1986): (i) those involving the rhodamine amino groups, and (ii) the solvation of the COOR group.

This last interaction (important in rhodamines with the Ph-COO⁻ group in water) disrupts the intramolecular xanthene-COOR interaction. Therefore, this specific rhodamine-solvent interaction will increase the radiationless deactivation probability and will shift the absorption and emission spectral bands to lower energies, as has been discussed above. This explains the higher increase in the k_{nr} value and the higher spectral shift to lower energies observed in rhodamines with the Ph-COO⁻ group relative to rhodamines with the Ph-COOH or the Ph-COOEt group when ethanol is replaced by water as solvent (table 4).

For hydrophobic reasons, specific rhodamine-solvent interactions at the amino fragment of the dye will be more important for rhodamine with diethylamino groups in ethanol (López and Rohatgi-Mukherjee 1986; López *et al* 1991a) whereas water molecules will be avoided at this part of the dye. The significantly different tendency for self-aggregation of rhodamine dyes in water with respect to that in ethanol (López *et al* 1989b) confirms this interpretation. This could explain the opposite spectral shifts observed between rhodamines with di-ethylamino groups and rhodamines with non-ethylated amino groups when ethanol is substituted by water as solvent (table 4). The rhodamine amine-solvent interactions would decrease the electron flow in the xanthene-amine bond, reducing the probability of the TICT state formation (TICT model) or of the planar-pyramidal structural change of the iminium group (ULM model).

4. Conclusions

Both the TICT and the ULM models can explain the radiationless deactivation of rhodamines if an intramolecular interaction between the xantheno ring and the carboxyphenyl group is taken into account. The inductive effect $+I$ of the amino substituents increases the probability of this process. Specific solute-solvent interactions are claimed to explain the effects of the solvent on the photophysics of rhodamines.

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