Unimolecular Decay of the Excited States of Rhodamine Dyes

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Summary Internal conversion and fluorescence are unimolecular decay processes for the singlet excited states of Rhodamine dyes in ordinary solvents (not containing heavy atoms).

The study of unimolecular decay of the excited states of Rhodamine dyes is important both for the study of photophysics and photochemistry of polyatomic molecules and for laser dyes with flash pumping. We report data on the degradation of energy of singlet-excited and triplet-ground states of certain Rhodamine dyes in solution.

Dilute solutions of Rhodamine dyes are known to be strongly fluorescent,[1] but there is little information about their triplet states.[2] We have used flash photolysis to determine the quantum yields of intersystem crossing (ϕ_{ST}) to the triplet state of Rhodamines.[3]

The triplet–triplet (T–T) absorption of Rhodamine derivatives (10^{-6} M) was found to be absent on flash excitation of solutions in degassed alcohols (EtOH, BuOH), which indicates that the ϕ_{ST} values are extremely low. T–T absorption was observed on flashing solutions in BuOH–$CHBr_3$ (3:1). In this case decrease in fluorescent intensity also occurred owing to perturbation of spin-orbit coupling (external heavy-atom effect).

TABLE. *Quantum yields and rate constants of singlet excited and triplet ground states decay for Rhodamine dyes*

Dye	Solvent[a]	ϕ_{fl}	ϕ_{ic}	ϕ_{ST}	$k_1 \times 10^{-8}/s^{-1}$	$k_2 \times 10^{-6}/s^{-1}$	$k_3 \times 10^{-6}/s^{-1}$	$k_4 \times 10^{-3}/s^{-1}$
Unsubstituted rhodamine ..	A	0·88	0·12	$<0·01$	2·0	27	$<2·3$	
NN'-Diethylrhodamine ..	A	0·94	0·06	$<0·01$	21	13	$<2·2$	
	B	0·83	0·03	0·14	1·9	6·7	31	2·4
Rhodamine 6G	A	0·83	0·17	$<0·01$	1·5	31	$<1·8$	
	B	0·80	0·08	0·12	1·4	14	22	1·5
Rhodamine 3B	A	0·68	0·32	$<0·01$	2·1	94	$<2·9$	
	B	0·65	0·26	0·09	1·9	76	26	2·2
Rhodamine B	A	0·61	0·39	$<0·01$	1·8	110	$<3·0$	
	B	0·58	0·36	0·06	1·7	101·9	18	1·6
NN'-Diphenylrhodamine ..	A	0·01	0·99	$<0·01$				

[a] A, EtOH; B, $CHBr_3$–BuOH (1:3).

The measured ϕ_{ST} values[3] are summarized in the Table. T–T absorption was also observed for Rhodamines in thin films of PVA (polyvinyl alcohol) and PMMA (polymethyl methacrylate).

The triplet states of Rhodamines were efficiently populated by triplet–triplet energy transfer and energy transfer was used when T–T absorption of Rhodamines was found to be absent on direct flashing of the solutions ($\phi_{ST} < 0·01$). In experiments with sensitized excitation, naphthalene and anthracene were used as triplet energy donors [for sensitization by naphthalene in water, λ_{max} (Rhodamine B), 605 nm (ϵ_T $4·5 \times 10^3$ M^{-1} cm^{-1}); *NN*-diethylrhodamine, 620 ($3·7 \times 10^3$); Rhodamine 6G, 630 nm ($9·0 \times 10^3$); for sensitization by anthracene in BuOH, λ_{max} (Rhodamine 3B), 620 nm ($9·6 \times 10^3$)].

The measurements of fluorescene quantum yields (ϕ_{fl}) are also presented in the Table. It follows from the Table that the sum: $\phi_{fl} + \phi_{ic} = 1$ is valid for Rhodamines dissolved in pure alcohols. Thus, internal conversion (i.c.) is the only path for radiationless decay of singlet excited states of Rhodamines.

In the presence of heavy atoms the increase in ϕ_{ST} is accompanied by a decrease in both ϕ_{fl} and ϕ_{ic}. Thus the sum: $\phi_{fl} + \phi_{ic} + \phi_{ST} = 1$ is valid for Rhodamines in

$CHBr_3$–BuOH (1 : 3). The following scheme illustrates the processes on excitation of Rhodamines:

$$S^* \rightarrow S_0 + \text{fluorescence} \qquad (K_1)$$

$$S^* \rightarrow S_0 + \text{heat} \qquad (K_2)$$

$$S^* \rightarrow T \qquad (K_3)$$

$$T \rightarrow S_0 + \text{heat} \qquad (K_4)$$

Rate constants K_1, K_2, and K_3 calculated from quantum yield data and τ_{S^*} of S^* states are also summarized in the Table. The τ_{S^*} values were measured directly using a fluorimeter with picosecond laser excitation.

The decay of the Rhodamine triplets (low concentration) followed first order kinetics, owing to a radiationless process (K_4).

The K_4 values in the Table also show the effect of possible impurity quenching, as well as the quenching by heavy atoms. The true values of K_4 are somewhat lower (80 s^{-1} for Rhodamine 6G in PVA films).

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