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PRIMARY PROCESSES IN THE PHOTOCHEMISTRY OF RHODAMINE DYES

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Summary

Quantum yields for intersystem crossing in rhodamine 6G, N,N'-diethylrhodamine and rhodamine B as well as their triplet–triplet (T–T) absorption spectra were measured in aqueous solutions. The main pathways of rhodamine singlet excited state decay are fluorescence and internal conversion. The main pathways of rhodamine triplet state decay are radiationless deactivation, quenching by impurities and by ion radicals, T–T interaction and self-quenching. The process of the electron transfer is considered to be the result of T–T interaction and self-quenching of rhodamine triplets in plain aqueous solutions. Triplet states of rhodamine dyes play a major role in redox reactions that occur in the presence of exogenic electron donors and acceptors. The kinetic decay of half-reduced and half-oxidized rhodamine species was studied. The peculiar properties of rhodamine 6G photoreactions occurring in alcohol solutions are considered. The rate constants of the rhodamine triplet and ion radical decay processes are determined.

1. Introduction

The study of organic dyes has become very important in recent years because of their extensive use in quantum electronics. Rhodamine 6G (Rd 6G) and other rhodamine dyes show effective laser action [1, 2]. In many papers the effect upon the efficiency of laser action of triplet–triplet (T–T) absorption [3 - 5] and of the products of photoreactions [6, 7] is noted.

However, many of the data on the photochemistry of rhodamine dyes are contradictory and incomplete. The mechanisms of the photoreactions and the nature of the transients being formed are either not valid or not given. For example, widely differing values of the extinction coefficient of T–T absorption of Rd 6G have been found by many authors [8, 9]. The lifetime of the triplet state measured in an air-saturated solution [3, 10] and the quantum yield of intersystem crossing (ISC) [8, 11] differ by more than one order of magnitude.

Few data on the T–T absorption of rhodamine dyes in the blue and IR regions of the spectrum and on the decay kinetics of the triplet state exist in the literature. In a number of papers [8, 12, 13] attempts have been made to establish the true mechanism of the photoreactions of rhodamine dyes and the nature of the intermediates formed in these reactions. However, the conclusions obtained in these papers are not sufficiently valid.

The study of the photophysics and the primary steps in the photochemistry of rhodamine dye molecules is of great interest. The main objects of this work were to measure the T–T absorption spectra and the ISC quantum yields for Rd 6G, N,N'-diethylrhodamine (DeRd) and rhodamine B (Rd B), to study the deactivation pathways of the triplet state of these rhodamine dyes, to determine the rate constants of the triplet state quenching and to study the production and decay of rhodamine ion radicals.

2. Experimental

Measurements of both the absorption spectra and the production and decay kinetics of short lived intermediates of rhodamine dyes were carried out by flash photolysis using an apparatus described previously [14]. Flashlamp pumping was accomplished using glass filters in the spectral region $\lambda >$ 420 nm; the electric energy of pumping was 400 J and the flash duration was 15 μs.

The rhodamine dyes and the electron donors and acceptors used were purified by the usual procedures. The measurements were carried out in aqueous (doubly distilled or buffer) and alcohol (propanol) solutions. The DeRd concentration was 3×10^{-6} M; the Rd 6G and Rd B concentrations were each 5×10^{-6} M.

3. Results and discussion

3.1. *Triplet state*

3.1.1. *Assignment of transient absorption*

Flashing of deoxygenated solutions of rhodamine dyes leads to the appearance of reversible absorption in the 390 - 1000 nm region. In Fig. 1(a) such absorption spectra for the aqueous Rd 6G solution 250 μs (curve 1) and 2 ms (curves 2 and 3) after the flash excitation are shown. The difference in the positions of the absorption bands measured at different time intervals after the flash is caused by the occurrence of different species.

It follows from the results on T–T energy transfer between Rd 6G (donor) and anthracene sulphonic acid and between naphthalene (donor) and Rd 6G and from the effect of oxygen on the lifetime of transient absorption that the absorption bands located at 630 and 950 nm are caused by T–T transitions in the Rd 6G molecule.

In view of the similarity of the T–T absorption spectra of Rd 6G monomers and dimers [15] the transient absorption of the Rd 6G aqueous

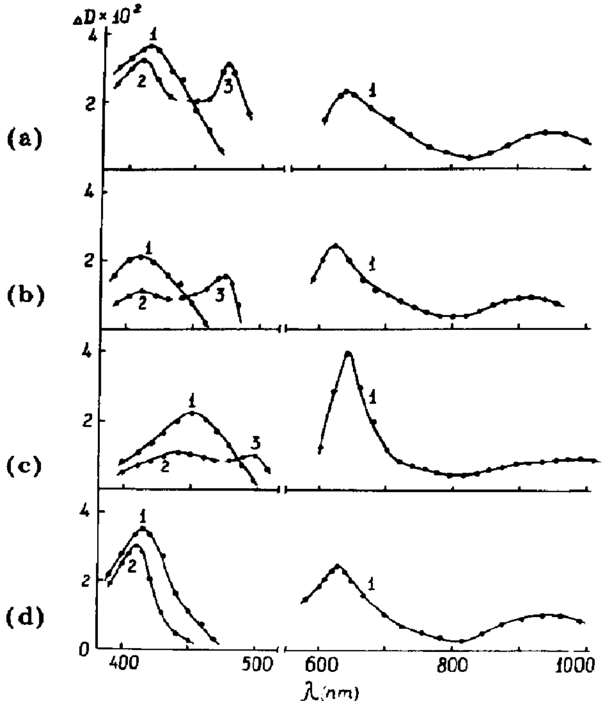


Fig. 1. Differential absorption spectra of Rd 6G (a), DeRd (b) and Rd B (c) in aqueous solution and Rd 6G (d) in propanol measured at 250 μs (curve 1), 2 ms (curves 2 and 3, (a) and (d)) and 3 ms (curves 2 and 3, (b) and (c)) after the flash.

solution in the red and near IR regions could be expected to occur by T–T absorption of rhodamine aggregates. The marked tendency of Rd 6G molecules to form aggregates in aqueous solution and the significant value of the probability of ISC for rhodamine aggregates [15] is further evidence in favour of this.

It is known that detergents affect the degree of dimerization of the dye [16]. Therefore measurements of the dependence of the relative intensities of both the T–T absorption and the luminescence of Rd 6G upon detergent concentration (sodium dodecyl sulphate) were carried out. The data obtained are presented in Fig. 2. It follows from the parallel shape of the curves

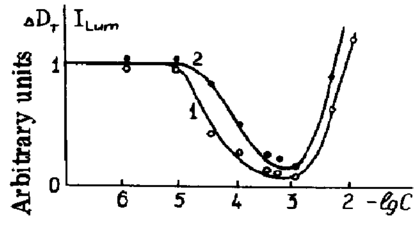


Fig. 2. Dependence of relative fluorescence intensity (curve 1) and of T–T absorption intensity (curve 2) of rhodamine 6G on detergent concentration.

that the observed T–T absorption is caused by the monomeric form of the dye.

The transient absorption observed in the blue region of the spectrum is more complicated (Fig. 1(a)). A band with a maximum at 415 nm is observed 250 μs after triggering the flash. Two bands with maxima at 410 and 475 nm (curves 2 and 3 of Fig. 1(a)) are observed 2 ms after the flash, *i.e.* at the moment that T–T absorption disappears

In order to assign these bands the effect of electron donors and acceptors and of oxygen on the intensities of transient absorption was studied.

A gradual addition of an electron donor (ascorbic acid) to the Rd 6G solution leads to a decrease of the T–T absorption intensity and of the band intensity with a maximum at 475 nm and to an increase in the band intensity with a maximum at 410 nm. Addition of an electron acceptor (dinitrobenzene) to the Rd 6G solution also leads to a decrease of both T–T absorption intensity and band intensity at 410 nm. The band intensity with a maximum at 475 nm increased. Gradual addition of oxygen to a cell containing an outgassed solution of the dye shortens the lifetime of the species absorbing at 410 nm. These experiments prove that the band with a maximum at 475 nm should be assigned to the half-oxidized form of Rd 6G ($\dot{R}^+$) and the band with a maximum at 410 nm should be assigned to the half-reduced form of the dye $\dot{R}^-$.

The absorption band with a maximum at 415 nm is also observed with Rd 6G in a film of polyvinyl alcohol where the formation of ion radicals is excluded. The lifetime of this absorption agrees well with that for T–T absorption in the red region of the spectrum; therefore the band with a maximum at 415 nm is also a T–T transition.

The transient absorption spectrum of DeRd is shown in Fig. 1(b). Three bands with maxima at 410, 615 and 920 nm were observed 250 μs after triggering the flash in an outgassed aqueous solution of the dye (curve 1). Two bands with maxima at 410 and 475 nm (curves 2 and 3) were observed 3 ms after the flash when the transient absorption in the red and IR regions of the spectrum had completely decayed. The experiments on the influence of electron donors and acceptors on the absorption intensity and transient lifetimes and the results on T–T energy transfer proved that the absorption measured 250 μs after the flash is caused by the T–T transition in the dye molecule. The transient absorption observed 3 ms after the flash is caused by the half-reduced (λ_{max} = 410 nm) and half-oxidized (λ_{max} = 475 nm) forms of the dye.

The T–T absorption spectrum of Rd B consists of three bands with maxima at 450, 640 and 1000 nm (curve 1, Fig. 1(c)) but ion radicals of the dye absorb at 440 and 495 nm (curves 2 and 3).

Transient absorption measured after flash excitation of a Rd 6G solution in propanol is shown in Fig. 1(d). 250 μs after the beginning of photoexcitation the transient absorption (curve 1) consists of three bands with maxima around 415, 630 and 950 nm which agrees well with the T–T absorption observed for the aqueous solution of the dye. The assignment of these bands to T−T transitions in the dye molecule was made in the same manner as for the aqueous solution of the dye.

The transient absorption of Rd 6G solution in propanol measured 2 ms after the flash consists of one band with a maximum at 410 nm (curve 2, Fig. 1(d)). Addition of ascorbic acid to the Rd 6G solution in propanol leads to a decrease of T−T absorption and an increase of the band intensity with a maximum at 410 nm. The presence of oxygen and of dinitrobenzene results in a decrease of both intensity and lifetime of the absorption band at 410 nm. The results presented above prove that the absorption around 410 nm is due to the half-reduced form of the dye.

The T−T absorption spectra of DeRd and Rd B in propanol agree with those observed for aqueous solutions of these dyes. However, the transient absorption measured 3 ms after the flash consists of only one band with maxima at 410 nm for DeRd and at 425 nm for Rd B owing to the production of the half-reduced forms of these dyes.

It is noteworthy that the T−T absorption of rhodamine dyes in the red region of the spectrum overlaps with the spectrum of laser action of rhodamines and affects its efficiency.

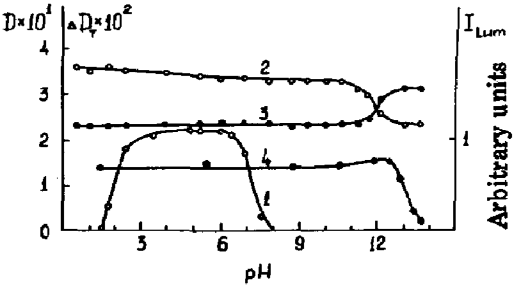
3.1.2. Determination of the quantum yield of intersystem crossing and its dependence on pH

The quantum yield φ_T of ISC is an important characteristic of lasing dyes. A knowledge of the extinction coefficient ϵ_T for T−T absorption is necessary to calculate φ_T. ϵ_T was determined by comparing the optical density changes measured at the wavelengths at which the main absorption was extinguished and the T−T absorption appeared. As noted in Section 3.1.1 the transient absorption 250 μs after the flash was caused by the rhodamine triplets only. The differential spectrum of T−T absorption in the region where $\lambda > 510$ nm is symmetrical with the spectrum of ground state absorption of Rd 6G (10^{-6} M). Consequently, ϵ_T is negligibly small in comparison with the extinction coefficient for ground state absorption. Using this fact it was found that ϵ_T is equal to 1.3×10^4, 1.2×10^4 and 1.3×10^4 M^{-1} cm^{-1} at maximum T−T absorption for Rd 6G, DeRd and RdB respectively in propanol solutions.

In this study we have determined φ_T by comparison with a standard [17]. An aqueous solution of erythrozine (pH 9, $\varphi_T = 1$ [18]) was used as the standard. φ_T for Rd 6G was found to be 0.002 ± 0.0005 [16]; φ_T for DeRd and RdB are 0.005 and 0.006 respectively.

We have established the dependence of φ_T for Rd 6G on pH value [19] (curve 1, Fig. 3). From this dependence it follows that the intensity of T−T absorption is markedly decreased in alkaline and strongly acidic media.

To clarify the shape of curve 1 of Fig. 3 the transient absorption was measured by sensitized excitation as a result of T−T energy transfer between naphthalene (donor) and Rd 6G (acceptor). In Fig. 4 curves 1 and 2 display T−T absorption spectra of Rd 6G at pH 1.4 and 5.2 respectively. Only the IR band (curve 3, Fig. 4) was observed in the alkaline medium.



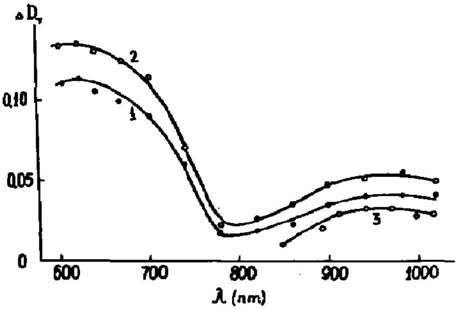


Fig. 3. Influence of pH values on spectral and luminescence properties of Rd 6G: D, optical density of ground state absorption at 545 nm (curve 2) and 475 nm (curve 3); ΔD, changes in optical density due to T–T absorption (curve 1); I_{lum}, relative fluorescence intensity (curve 4); dye concentration, 1×10^{-5} M.

Fig. 4. T–T absorption spectra of Rd 6G on sensitized excitation at different pH values: curve 1, pH 1.4 (5×10^{-6} M, flash energy 200 J); curve 2, pH 5.2 (5×10^{-6} M, flash energy 200 J); curve 3, pH 8.8 (2×10^{-5} M, flash energy 400 J).

The difference between T–T absorption spectra measured in alkaline and in acidic media is due to protonation of Rd 6G molecules in the triplet state. It has been established in a number of papers [20 - 22] that Rd 6G molecules can be found in different forms (coloured and colourless, luminescent and non-luminescent). The constant pK_0 of acid–base equilibrium for Rd 6G molecules in the ground state was determined by following the shift in the ground state absorption, but that for dye molecules in the singlet excited state (pK^*) was determined by following the change in luminescence intensity as a function of the pH value. The pK_0 value is 12.5 which follows from the data shown in Fig. 3 (curves 2 and 3). In Fig. 3 curve 4 shows the dependence of the relative luminescence intensity of Rd 6G molecules on the pH value. It follows from the shape of this curve that in strong alkaline solutions the dye molecules exist in non-luminescent form with $pK^* = 13.0$.

The data obtained prove that Rd 6G molecules in the triplet state undergo changes in alkaline solution that result in the disappearance of the T–T absorption band with a maximum at 630 nm. The acid–base equilibrium constant for Rd 6G molecules in the triplet state was found to be 7.3 (Fig. 3).

It follows from curves 1 and 2 of Fig. 4 that the dye molecules in the triplet state are not changed in acid solutions (pH < 1.4). The decrease of intensity of T–T absorption in acid solutions is due to a decrease in φ_T. It has been established [23] that the luminescence maximum of Rd 6G in strong acid solutions was shifted to lower frequency by 75 cm^{-1} compared with that in a neutral medium, but the lifetime of the fluorescent molecules decreased from 4.3 ns in a neutral medium to 1.9 ns in an acidic medium. The φ_T value estimated from the sensitivity of the present flash photolysis apparatus did not exceed 2×10^{-4} for a pH of less than 1.4 and was 2×10^{-3} at pH 5.2.

Thus the intensity of the T–T absorption of Rd 6G molecules at the wavelength of laser action substantially decreases in acidic media (pH < 1.4) owing to a decrease in φ_T but in alkaline media (pH > 7.3) the observed decrease is due to changes in ϵ_T.

3.1.3. Deactivation pathways of the rhodamine 6G triplet state in aqueous solution

The following primary steps were obtained by kinetic analysis of triplet state decay of Rd 6G molecules [24]:

$S^* \rightarrow T$	$(4 \pm 1) \times 10^5\ s^{-1}$	(a)
$T \rightarrow S$	$(4 \pm 1) \times 10^1\ s^{-1}$	(0)
$T + q \rightarrow S + q$	$(5 \pm 1) \times 10^2\ s^{-1}$	(1)
$T + S \nearrow \dot{R} + \dot{R}^+$	$(1 \pm 0.5) \times 10^7\ M^{-1}\ s^{-1}$	(2)
$T + S \searrow S + S$	$(2 \pm 0.5) \times 10^7\ M^{-1}\ s^{-1}$	(3)
$T + T \nearrow \dot{R}^- + \dot{R}^+$	$(5 \pm 3) \times 10^8\ M^{-1}\ s^{-1}$	(4)
$T + T \searrow S^* + S$	$(5 \pm 3) \times 10^8\ M^{-1}\ s^{-1}$	(5)
$T + \dot{R}^+ \rightarrow \dot{R}^+ + S$	$(3 \pm 1) \times 10^9\ M^{-1}\ s^{-1}$	(6)
$T + \dot{R}^- \rightarrow \dot{R}^- + S$		(7)

The value of the rate constant K_a of ISC was calculated using φ_T and the lifetime τ_S of the singlet excited state ($\tau_S = 5.0 \times 10^{-9}$ s [25]). The decay kinetics of the triplet state of Rd 6G can be described by the following equation:

$$-\frac{d[T]}{dt} = K_1[T] + K_{23}[S][T] + 2K_{45}[T]^2 + K_6[\dot{R}^+][T] + K_7[\dot{R}^-][T] \tag{I}$$

where $K_1 = K_0 + K_q[q]$, $K_{23} = K_2 + K_3$ and $K_{45} = K_4 + K_5$. The decay kinetics were monitored at 670 nm. The process of ISC to the ground state (K_0) was studied in the rigid matrix. The K_0 value given above was found for Rd 6G in polyvinyl film. In fluid solutions quenching of the dye triplet state by impurities (*e.g.* oxygen traces) can occur (K_1). When the concentration of the triplet molecules is less than 10^{-7} M the decay kinetics of the triplet state are obtained using the first order equation (with an effective rate constant K_T)

$$-\frac{d[T]}{dt} = K_T[T] \tag{II}$$

Increase of the dye concentration results in a rise of the K_T value that indicates the process of self-quenching of the triplet state (K_{23}). From a comparison of (II) and (I) it follows that

$$K_T = K_1 + K_{23}[S] + 2K_{45}[T] + K_6[\dot{R}^+] + K_7[\dot{R}^-] \qquad \text{(III)}$$

K_{23} was determined from the dependence of K_T on the initial dye concentration provided that the concentrations of triplets and ion radicals were low enough. This made it possible to neglect the last three terms of eqn. (III). The K_{23} and K_1 values were found from the linear dependence of K_T on [S] which is shown in Fig. 5.

We have also established that the K_T value increases with increasing ion radical concentration in the dye proving the validity of the steps with K_6 and K_7. The rate constants for triplet state quenching by ion radicals were determined from the dependence of K_T on $[\dot{R}^{\pm}]$. Assuming that the concentrations of $\dot{R}^+$ and $\dot{R}^-$ are equal during the triplet state decay only the $K_{67} = K_6 + K_7$ value was found to be equal to 3×10^9 M^{-1} s^{-1}. The determination of the rate constant K_{45} of the T–T interaction needed a high concentration of dye triplets. This was achieved in experiments on T–T energy transfer between naphthalene (sensitizer) and Rd 6G. The decay kinetics of the triplet state were found to obey first and second order equations. In this case K_{45} was determined after conversion of eqn. (I):

$$-\left(\frac{d[T]}{dt} + K_{67}[\dot{R}^+]\right) = K_1 + K_{23}[S] + 2K_{45}[T] \qquad \text{(Ia)}$$

In Fig. 6 the experimental dependence of the left-hand side of eqn. (Ia), denoted by Φ_1, on [T] is given. From the slope of this line $2K_{45}$ was found to be 2×10^9 M^{-1} s^{-1}.

The rate constants K_2 and K_4 can be determined from measurements of both triplet state decay and the formation of dye ion radicals, *e.g.* $\dot{R}^+$. In this context it should be noted that the disappearance of the R^+ species follows a first order equation with rate constant K_2. The production of the half-oxidized dye $\dot{R}^+$ can be described by

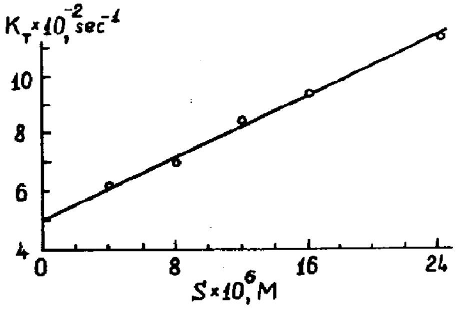


Fig. 5. Dependence of the effective rate constant K_T of Rd 6G triplet state decay on the initial dye concentration S.

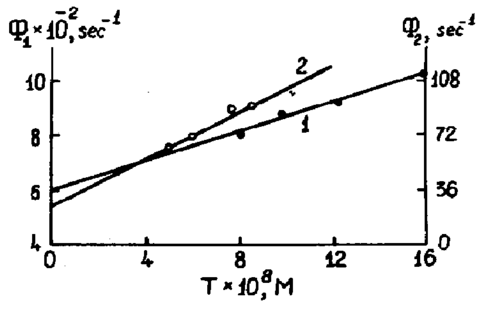


Fig. 6. Dependence on Φ_1 and Φ_2 (lines 1 and 2 respectively) on the concentration of Rd 6G triplets (see text for further explanation).

$$\frac{\mathrm{d}[\dot{\mathrm{R}}^+]}{\mathrm{d}t} = K_2[\mathrm{S}]\,[\mathrm{T}] + K_4[\mathrm{T}]^2 - K_\mathrm{R}[\dot{\mathrm{R}}^+] \tag{IV}$$

From eqns. (II) and (IV) it follows that

$$-K_\mathrm{T}\,\frac{\mathrm{d}[\dot{\mathrm{R}}^+]}{\mathrm{d}[\mathrm{T}]} + K_\mathrm{R}\,\frac{[\dot{\mathrm{R}}^+]}{[\mathrm{T}]} = K_2[\mathrm{S}] + K_4[\mathrm{T}] \tag{V}$$

The left-hand side of eqn. (V) can be determined directly. Figure 6 shows the dependence of the left-hand side of eqn. (V), denoted by Φ_2, on the concentration [T] of triplet molecules (curve 2). The values of K_4 and K_2 were found from the slope of the straight line and the intercept on the vertical axis respectively.

Thus the kinetic decay of the Rd 6G triplet state showed that degradation of the triplet state energy occurs as a result of ISC to the ground state, quenching by impurities, self-quenching processes, T–T interactions and interactions between triplets and dye ion radicals.

3.1.4. Quenching of rhodamine 6G triplet state

We have studied the quenching of dye triplet states by certain organic compounds (electron donors and acceptors), by non-complexed and complexed inorganic ions and by oxygen. The data obtained are summarized in Table 1. In the first column the quenchers are listed and in the second column the values of rate constant quenching are summarized. In the next two columns the changes in optical density measured in the absorption maxima of half-reduced (ΔD_{405}) and half-oxidized (ΔD_{475}) dye are presented.

The ΔD values were measured when the concentration of quenchers was high enough to quench completely the triplet state. An exception is the first line in which data for the Rd 6G solution in the absence of any quenchers are given. The organic compounds used quench the Rd 6G triplet state with approximately equal rate constants approaching the diffusion limit. As can be seen from Table 1 the quenching is followed by the formation of half-oxidized (in the presence of electron acceptor) and half-reduced (in the presence of electron donor) dye.

The complexed ions quench the T state as effectively as the organic compounds examined do but the efficiency of electron transfer in the former is much lower as is shown from the ΔD values. Thus the complexed ions can be used as inhibitors of photochemical reactions involving Rd 6G. The values of the rate constants for quenching by non-complexed (aqueous) ions are lower by two orders of magnitude than those for quenching by complexed ions.

The rate constant for quenching the Rd 6G triplet state by oxygen was measured in experiments carried out with degassed solutions and with solutions containing calibrated volumes of air. If it is assumed that the concentrations of dissolved oxygen in alcohol and aqueous solutions are 1.2×10^{-3} M and 3.1×10^{-4} M respectively [26] the quenching rate constants of the T state in propanol and in aqueous solutions were found to be 6×10^8 M^{-1} s^{-1} and 9×10^8 M^{-1} s^{-1}.

TABLE 1

Quenching of the triplet state of Rd 6G by various quenchers

Quenchers	K_{quench} ($M^{-1} s^{-1}$)	ΔD_{405}	ΔD_{475}
Rd 6G	3×10^7	0.030	0.024
m-Dinitrobenzene	3.8×10^9	—	0.160
p-Benzoquinone	2.5×10^9	—	0.150
Ascorbic acid	8.0×10^8	0.164	—
α-Naphthylamine	ND[a]	0.172	—
Hydroquinone	2.0×10^9	0.163	—
p-Phenylenediamine	1.0×10^9	0.142	—
$[Co(NO_2)_6]^{3-}$	$\approx 10^9$	—	0.042
$[Fe(CN)_6]^{3-}$	5.0×10^9	—	0.004
$[Fe(CN)_6]^{4-}$	8.0×10^9	0.014	—
Ni^{2+}	2.9×10^7	ND	ND
Co^{2+}	0.7×10^7	ND	ND
Co^{3+}	2.6×10^7	ND	ND
Fe^{3+}	2.2×10^7	ND	ND
$S_2O_4^{2-}$	4.3×10^7	ND	ND
O_2	6×10^8	ND	ND
O_2 (in propanol)	9×10^8	ND	ND

[a] ND, value not determined.

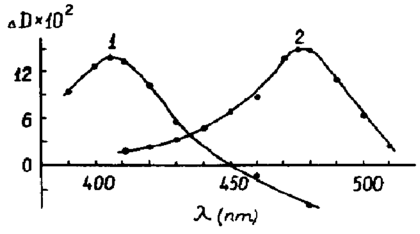
3.2. Ion radicals

3.2.1. Absorption spectra of half-reduced and half-oxidized rhodamines

As was noted in Section 3.1.1 transient absorption of $\dot{R}^-$ and $\dot{R}^+$ species was observed in the degassed aqueous solution of Rd 6G 2 ms after the flash. Addition of ascorbic acid to the dye solution results in a decrease of the intensities of both T–T absorption and half-oxidized dye absorption. When the concentration of electron donors reached 2×10^{-5} M the absorption of these species disappeared and an absorption band with a maximum at 405 nm appeared (curve 1, Fig. 7) which was assigned to a half-reduced rhodamine dye.

In the plain aqueous solution the absorption maximum of $\dot{R}^-$ is shifted to 410 nm owing to overlap with $\dot{R}^+$ absorption. To measure the absorption spectra of $\dot{R}^+$ species dinitrobenzene was added to the solution. When the concentration of dinitrobenzene was 2×10^{-5} M triplet absorption and the half-reduced form of the dye were no longer observed but a new band appeared with a maximum at 475 nm (curve 2, Fig. 7) which was assigned to $\dot{R}^+$ absorption.

The absorption spectra of the half-oxidized forms of DeRd and Rd B measured in aqueous solution containing dinitrobenzene consist of one band with maxima at 475 and 495 nm respectively. The absorption maxima of the half-reduced forms of DeRd and Rd B measured in aqueous solutions of dyes containing ascorbic acid are located at 400 and 430 nm respectively.



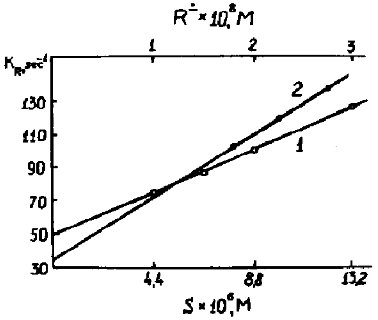


Fig. 7. Differential absorption spectra of half-reduced (curve 1) and half-oxidized (curve 2) species of Rd 6G in aqueous solution.

Fig. 8. Dependence of the effective rate constant K_R of R^+ decay on the initial dye concentration S (line 1) and on the R^- concentration (line 2).

3.2.2. Primary steps in the formation and decay of rhodamine ion radicals

It is necessary to determine the nature of the excited states involved in the photochemistry of rhodamine dyes in order to understand the primary steps in electron transfer reactions. We have obtained the following data which prove that the electron transfer processes occur via the triplet states of the dyes: (a) the time to reach the absorption maximum at 475 nm corresponds to the lifetime of the triplet state of the dye molecules; (b) a tenfold increase of the concentration of triplet molecules by the T–T energy transfer from naphthalene produces a tenfold increase in the ion radical yield and a reduction in the luminescence intensity of Rd 6G by a factor of 16; (c) quenching of the triplet state of the dye molecules by oxygen results in a decrease of the ion radical yield and no change in the luminescence intensity.

When an aqueous solution of Rd 6G was flashed at an energy of 350 J triplet molecules and ion radicals were formed in concentrations of 1.3×10^{-7} and 3×10^{-8} M respectively. Hence the efficiency of ion radical production was found to be 0.23 but the value of the quantum yield was 5×10^{-4}.

The kinetic decay of $\dot{R}^+$ species was measured 3 ms after the flash at 450 nm. The results of the kinetic study revealed that the half-reduced and half-oxidized dye molecules decay via different pathways. The decay of the half-reduced dye molecules follows a second order equation whereas the decay of the half-oxidized molecules follows a first order equation.

It has already been noted that the effective rate constant of $\dot{R}^+$ decay depends on the concentrations of both ground state molecules and the half-reduced form of the dye. It followed from the data obtained that ion radical decay occurred via recombination (eqn. (8)), disproportionation (eqn (9)) and interaction with ground state molecules (eqn. (10)):

$$\dot{R}^+ + \dot{R}^- \rightarrow S + S \qquad (3.5 \pm 1) \times 10^9\ M^{-1}\ s^{-1} \qquad (8)$$

$$\dot{R}^- + \dot{R}^- \rightarrow R^{2-} + S \qquad (1 \pm 0.5) \times 10^9\ M^{-1}\ s^{-1} \qquad (9)$$

$$\dot{R}^+ + S \rightarrow \text{product (P)} \qquad (5 \pm 2) \times 10^6\ M^{-1}\ s^{-1} \qquad (10)$$

The kinetic decay of ion radicals can be described by the following equations:

$$-\frac{d[\dot{R}^+]}{dt} = (K_8[\dot{R}^-] + K_{10}[S])[\dot{R}^+] \qquad (VI)$$

$$-\frac{d[\dot{R}^-]}{dt} = (K_8 + 2K_9)[\dot{R}^-]^2 \qquad (VII)$$

To determine the rate constants K_8 and K_{10} the dependence of the effective rate constant $K_R = K_8\ [\dot{R}^-] + K_{10}[S]$ of $\dot{R}^+$ decay on concentrations of [S] and $[\dot{R}^-]$ was studied. Figure 8 shows the dependence of the K_R on the initial concentration of the dye (line 1). The flash energy was changed such that the initial concentration of the half-reduced dye species was constant in all runs. From the slope of the straight line K_{10} was found to be equal to $6 \times 10^6\ M^{-1}\ s^{-1}$ and from the intercept on the vertical axis $K_8 = 3.5 \times 10^9\ M^{-1}\ s^{-1}$. Line 2 in Fig. 8 shows the dependence of K_R on the $\dot{R}^-$ concentration when the concentration of S was kept constant at 9×10^{-6} M. From this line the values of K_8 and K_{10} were found to be 3.5×10^9 and $4 \times 10^6\ M^{-1}\ s^{-1}$ respectively.

The second order rate constant of R^-decay $(K_8 + 2K_9)$, which was measured directly from the rate of disappearance of the absorption band at 405 nm, was found to be equal to $6 \times 10^9\ M^{-1}\ s^{-1}$. Finally we found that $K_9 = 1.2 \times 10^9\ M^{-1}\ s^{-1}$. From analysis of the elementary steps of ion radical decay it follows that the recovery of the dye is not complete after photoexcitation. Some of the dye molecules are converted into stable photoproducts which are probably present as the reduced form R^{2-} of the dye and the product P.

3.2.3. Peculiarities of rhodamine 6G photoreactions in alcohol solutions

As was noted in Section 3.1.1, 2 ms after the flash excitation of the propanol solution of Rd 6G only one absorption band was observed which was due to the half-reduced form of the dye. Similar facts were observed in other alcohols (ethanol, butanol and amyl alcohol).

The absence of the absorption band with a maximum at 475 nm in alcohol solution can be explained either by the absence of steps (2) and (4) or by the processes leading to fast decay of the $\dot{R}^+$ species in an alcoholic medium.

The transient absorption band at 475 nm was observed in an alcohol solution of Rd 6G containing dinitrobenzene. In this case the $\dot{R}^+$ decay follows the first order equation. This fact shows that the decay of the $\dot{R}^+$ species occurs as a result of the interaction between $\dot{R}^+$ and the solvent molecules. The reaction between $\dot{R}^+$ and the dye molecules in the ground state was excluded because the rate constant of $\dot{R}^+$ decay was independent of [S] concentration.

The $\dot{R}^+$ decay can be explained by reduction according to the following step:

$$CH_3CH_2CH_2OH + \dot{R}^+ \rightarrow CH_3CH_2\dot{C}HOH + S + H^+ \qquad (11)$$

The reduction in the lifetime of $\dot{R}^+$ species after the addition of specific amounts of propanol to the aqueous solution of the dye proves that there is an interaction between half-oxidized dye molecules and alcohols. The value of the rate constant of reaction (11) was found to be equal to 25 M^{-1} s^{-1}.

The quantum efficiency for the formation of half-reduced Rd 6G in alcohol solution is 0.1 which is higher than the value of the quantum efficiency for the formation of the half-oxidized form of the dye (<0.02). This can apparently be explained by the reduction of dye triplets by alcohol molecules according to

$$CH_3CH_2CH_2OH + T \rightarrow CH_3CH_2\dot{C}HOH + \dot{R}^- + H^+ \qquad (12)$$

Similar reactions were observed for triplets of fluorescein [27], eosin [28] and erythrozine [29] with ethanol.

Additional evidence in favour of reaction (12) is based on experiments where the lifetime of the triplets is the same as the time required to reach maximum concentration of $\dot{R}^-$ species. These data were obtained on Rd B solutions because the T−T absorption spectrum and the $\dot{R}^-$ absorption of dye do not overlap markedly so that the production of the $\dot{R}^-$ species can be followed.

The disappearance of dye radicals in alcohol solution follows the second order equation because of the reactions of disproportionation and/or recombination with alcohol radicals. The effective photobleaching of degassed dye solution favours the former reaction, leading to the formation of the stable photoreduced form of the dye.

Thus the present study established firstly that the dye triplets are important species in electron transfer reactions and secondly that the mechanisms of energy degradation and of redox photoreactions of rhodamines are similar in many respects to those for xanthene [30, 31], thiazine [31], cyanine dyes [32] and chlorophyll pigments [14, 33].

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