

## THE STUDY OF THE PHOTOPHYSICS AND PRIMARY PHOTO-CHEMISTRY OF RHODAMINE 6G AGGREGATES

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### Summary

The decay processes of the excited singlet and triplet states of rhodamine 6G aggregates were investigated. It was shown that aggregation results in a substantial increase of the quantum yield of intersystem crossing. The triplet-triplet (T-T) absorption spectra of rhodamine 6G aggregates were measured. The decay kinetics of the triplet state of dye aggregates were studied. It was shown that the main pathways of triplet state deactivation are unimolecular decay and T-T interaction. A correlation between the values of the rate constants of unimolecular triplet state decay and of some properties of the solvents is discussed. The mechanism of electron transfer in photoreactions of rhodamine 6G aggregates was considered. It was shown that electron transfer occurs via the triplet state of aggregates by T-T interactions and reactions with electron donors and acceptors. The ability of the triplet state of rhodamine 6G aggregates to sensitize redox reactions was established. Spectra of ion radical species and the values of rate constants for some elementary steps were determined.

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### 1. Introduction

Until recently the study of the photonics, *i.e.* the photophysics and primary photochemistry, of organic molecules was mainly concerned with the behaviour of monomers. However, the study of photonics of aggregates is of great significance because the migration and transfer of electronic excitation energy and its conversion into chemical energy in such important processes as photosynthesis and spectral sensitization in photography involves associated molecules of pigments and dyes.

It has been established that pigments in aggregate form not only luminesce at room and low temperatures but are also involved in various photochemical reactions [1, 2]. In particular, absorption of light by aggregates of pigments causes them to split up [3]. It is known that associated molecules of pigments sensitize the reduction of some dyes and cytochromes by ascor-

bic acid [2]. Photoconductivity of chlorophyll films has also been demonstrated; it has been shown that aggregates absorbing at long wavelength have a greater quantum efficiency of photoconductivity than those absorbing at short wavelength [4]. A study of photoeffects at the boundary of a pigment film and a pigment solution showed that the aggregated forms are able to sensitize redox reactions [5].

Most of the studies of photochemical reactions of dye aggregates have been carried out in connection with investigations of the mechanism and efficiency of spectral sensitization in photography. It has been established that various aggregated forms of cyanine dyes feature different types of photochemical activity [6 - 8], *e.g.* the quantum efficiency of spectral sensitization increases from H-aggregates to J-aggregates and in a number of cases exceeds that of the monomeric forms of the dyes. In these investigations the main emphasis was placed on the determination of the efficiency of the photochemical reactions. The pathways of degradation of electronic excitation energy in associates, the nature of the excited state involved in the photoreactions and the elementary steps of the photoprocesses are also of importance. Data on these topics have been limited to the detection of triplet states of aggregates of methylene blue [9], acridine orange [10], chlorophyll a [11], J-aggregates of cyanines [12] and reaction centres of bacterial photosynthesis [13].

In the present paper the important role of the triplet state in the degradation of electronic excitation energy in aggregated molecules of rhodamine 6G was established. The mechanisms of electron transfer in photoreactions of dye aggregates were examined.

## 2. Experimental

The transient spectra, quantum efficiency and decay kinetics of intermediates of rhodamine 6G aggregates were measured by means of flash photolysis [14]. The absorption spectra were recorded on a Unicam-SP-700 spectrophotometer. The luminescence spectra were recorded on an SDL-1 spectrofluorimeter.

Aggregates of rhodamine were obtained by two methods. Aggregates of the first type (type I) were formed in an almost non-polar solution, *i.e.* in mixtures of 0.1 - 0.2% polar solvent (alcohols, acetonitril, pyridine or dimethylsulphoxide) and 99.8 - 99.9% non-polar solvent (carbon tetrachloride, cyclohexane, toluene or benzene). Aggregates of the second type (type II) were prepared when known quantities of polymethacrylic acid (PMA) were added to an aqueous solution of the dye. In both cases the content of the monomeric form did not exceed 1% at a dye concentration of  $4 \times 10^{-6}$  -  $1 \times 10^{-5}$  M. Methylviologen, *p*-benzoquinone and *m*-dinitrobenzene were used as electron acceptors; ascorbic acid, diphenylamine, hydroquinone and *p*-phenylenediamine were used as electron donors. All the substances added were of reagent grade purity. Rhodamine 6G was purified chromatographically.

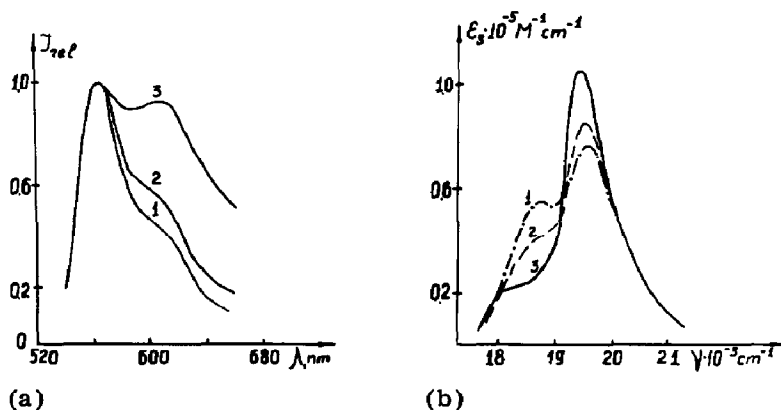


Fig. 1. Emission (a) and absorption (b) spectra of type I aggregates in a mixture of butanol with  $\text{CCl}_4$ : curve 1, 90%  $\text{CCl}_4$ ; curve 2, 98%  $\text{CCl}_4$ ; curve 3, 99.8%  $\text{CCl}_4$ .

### 3. Results and discussion

#### 3.1. Absorption and luminescence of aggregates and processes of degradation of electronic excitation energy

Until recently it was believed that aggregates of rhodamine dyes did not luminesce at room temperature. However, it has been shown [15, 16] that luminescence of rhodamine 6G aggregates can be observed in mixtures of polar and non-polar solvents of various concentrations ranging almost to non-polar mixtures (type I). Luminescence of type II rhodamine 6G aggregates was also observed. In Fig. 1 luminescence spectra of type I aggregates are shown. It is seen that starting from mixtures containing 90%  $\text{CCl}_4$  a broadening of the luminescent band occurs. Further increase in the non-polar solvent content leads to the appearance of a new luminescence band with a maximum at 610 nm. The formation of this band is due to fluorescence of the dye aggregates. The quantum yield  $\phi_{fl}$  of the fluorescence was found to be 0.02 by the method of comparison with a standard (a dilute solution of rhodamine 6G in ethyl alcohol). Analogous changes in the luminescence spectrum were observed for type II aggregates;  $\phi_{fl}$  is also approximately 0.02.

The absorption spectra of rhodamine aggregates are shown in Fig. 1(b). It is seen from Fig. 1 that the intensity of the short wavelength band is much greater than that of the long wavelength band. The ratio of intensities does not depend either on the method of aggregate production or on the solvent components for aggregates of type I. From the spectra the angles between the dye molecules in the aggregate were determined to be  $20^\circ$ . Thus the dye molecules in aggregates of both types were determined to exist in the form of a pile with practically parallel planes.

Flash excitation of solutions of type I aggregates of rhodamine 6G leads to reversible changes in absorption in the 400 - 500 nm and 600 - 800 nm regions as a result of triplet-triplet (T-T) transitions. The T-T absorption

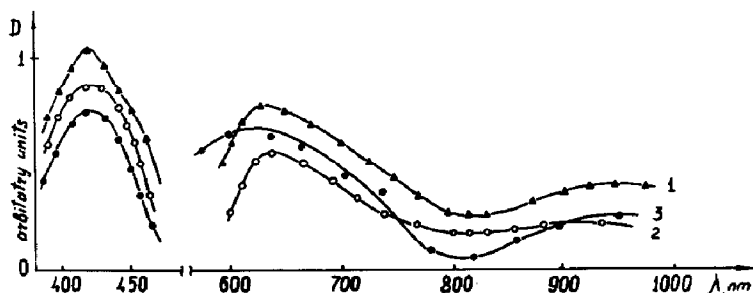


Fig. 2. Spectra of T-T absorption: curve 1, type I aggregates; curve 2, type II aggregates; curve 3, monomers in water (pH 6).

of rhodamine 6G monomers was not measured in these experimental conditions as it had been established earlier [17]. The T-T absorption spectrum of type I aggregates is shown in Fig. 2. Population of the triplet level of type I aggregates was proved by T-T energy transfer experiments. Addition of anthracene (up to  $10^{-4}$  M) to a solution of type I aggregates of rhodamine 6G results in both quenching of the triplet states of the aggregates and production of T-T absorption of anthracene.

Similar short lived changes in absorption were observed on flash excitation of deoxygenated rhodamine solutions in the presence of PMA (type II aggregates). The T-T absorption spectrum of type II aggregates measured  $10^{-4}$  s after the flash is shown in Fig. 2. The assumption that short lived changes in absorption are due to T-T transitions is also based on experiments on T-T energy transfer as well as on a comparison of the T-T absorption spectrum of type I aggregates and short lived changes in absorption observed for type II aggregates. The addition of anthracene sulphonic acid as the acceptor of triplet energy to type II aggregates leads to both the disappearance of transient absorption of rhodamine aggregates and the appearance of T-T absorption of the acceptor. For excitation of the mixture in the absorption band of aggregates in the visible T-T absorption of the acceptor may only arise as a result of T-T energy transfer from the triplet level of rhodamine type II aggregates.

The T-T absorption spectrum of rhodamine 6G monomer is also shown in Fig. 2. It is seen from Fig. 2 that the T-T absorption spectra of aggregates of both types coincide well with that of the monomer.

The values of the extinction coefficient  $\epsilon_{TT}$  for both types of aggregates were determined by means of T-T energy transfer. If the  $\epsilon_{TT}$  value is known, the number of dye molecules constituting the aggregate may be estimated assuming that all aggregates convert to the triplet state at high flash energy. In this case the optical density change is proportional to the concentration of aggregates which is equal to the ratio between the initial dye concentration and the number  $n$  of molecules in one aggregate;  $n$  was determined in this manner and was equal to 15 - 20 molecules for type I aggregates and 10 for type II aggregates [18].

TABLE 1

Values of rate constants of excited singlet and triplet state decay of rhodamine monomer and aggregates

Process	Rate constant			
	$K$	Monomer	Type I aggregates	Type II aggregates
$S^* \rightarrow T$	$K_T (s^{-1})$	$7 \times 10^5$	$\approx 10^7$	$\approx 10^7$
$T \rightarrow S_0$	$K_{eff} (s^{-1})$	$4 \times 10^2$	$3 \times 10^3$	$2 \times 10^2$
$T + S_0 \xrightarrow{R^+ + R^-}$	$K_1 (M^{-1} s^{-1})$	$4 \times 10^7$	} $< 10^7$	$< 10^6$
$T + S_0 \xrightarrow{S_0 + S_0}$	$K_2 (M^{-1} s^{-1})$	$1 \times 10^7$		$\approx 10^6$
$T + S_0 \xrightarrow{R^+ + R^-}$	$K_3 (M^{-1} s^{-1})$	$1.3 \times 10^9$	$< 1 \times 10^9$	$1 \times 10^7$
$T + T \xrightarrow{S^* + S_0}$	$K_4 (M^{-1} s^{-1})$	$1.5 \times 10^9$	$2 \times 10^9$	$8 \times 10^7$

The quantum yield  $\phi_{ST}$  of intersystem crossing (ISC) for aggregates of both types was determined by comparison with a standard (erythrosine).  $\phi_{ST}$  is 0.2 for type I aggregates and 0.5 for type II aggregates.

The data presented indicate that significant changes in the efficiency of deactivation pathways of singlet excited states occur upon aggregation of rhodamine 6G molecules. The quantum yield of luminescence decreases from 0.88 (for monomers) to 0.02 (for aggregates) but the quantum yield of ISC increases from 0.003 (water, pH 5) [19] to 0.2 (type I) and 0.5 (type II). Aggregation of the dye molecules also leads to an increase in the quantum yield of internal conversion.

There are a number of reasons for the increase of the ISC quantum yield for both types of aggregates. First, it is possible that increase of the rate constant  $K_T$  of ISC arises from the enhancement of spin-orbit coupling upon aggregation which was theoretically predicted by McRae and Kasha [20]. This agrees with data on the increase of the rate constant  $K_{eff}$  of ISC to the ground state in type I aggregates (Table 1). Second, the lifetime of the singlet excited state in dye aggregates, which have a more intense short wavelength absorption band, is approximately ten times greater than that for monomers of rhodamine 6G [21]. Third, the decrease of the singlet-triplet splitting results from the deformation of the absorption spectrum of aggregates [16].

The mere fact of the enhancement of the  $\phi_{ST}$  value on aggregation may play a decisive role in the formation of products of photochemical reactions of dye aggregates with substantial quantum efficiency.

### 3.2. Deactivation of the triplet state of aggregates

The spectral characteristics of aggregates of both types given in Section 3.1 lead to the conclusion that they have an ordered structure in which dye

molecules are present at short separations (about 10 Å) [22] that result in a strong exchange interaction between them. Therefore in rhodamine 6G aggregates triplet excitation may migrate inside the aggregate as do triplet excitons in molecular crystals. This peculiarity of triplet excitation in aggregates in comparison with monomers is displayed in the degradation mechanisms and the kinetics of electron transfer reactions.

We have made measurements of the decay kinetics of the triplet state of rhodamine 6G aggregates of both types. Measurements were made at different concentrations of the dye and at different flash energies as well as in the presence of electron donors and acceptors. The results of kinetic measurements of the decrease of T-T absorption of aggregates carried out with dilute solutions of the dye and at low flash intensities revealed the first order decay. It may be believed that under these conditions deactivation of the triplet state of aggregates occurs as a result of ISC to the ground state ( $T \rightarrow S_0$ ) with the rate constant  $K_{\text{eff}}$  which takes into account quenching of the triplet state by impurities (for example oxygen traces). In Table 1  $K_{\text{eff}}$  values for aggregates of both types and for monomers of the dye in water (pH 6) are given. Examination of  $K_{\text{eff}}$  values shows that in passing from monomers of rhodamine 6G to its aggregates in solution (type I)  $K_{\text{eff}}$  increases in agreement with the increase of spin-orbit coupling on aggregation as has already been noted.  $K_{\text{eff}}$  for type II aggregates is an order of magnitude smaller than that of type I. The observed increase of the lifetime  $\tau_T$  of the triplet state of type II aggregates is possibly connected with their stabilization on the polymer. An analogous stabilizing action of PMA was also established for monomers of rhodamine 6G. In the presence of high ( $1 \times 10^{-2}$  g ml $^{-1}$ ) concentrations of PMA the  $\tau_T$  value of the dye monomers increases by a factor of five in comparison with that for aqueous solutions.

These experiments have shown the dependence of  $K_{\text{eff}}$  for aggregates on different kinds of intermolecular interactions arising upon aggregation of dyes. It has been established that  $K_{\text{eff}}$  for type I aggregates depends on the nature of the polar component of the solution. For example one may cite the linear dependence of  $K_{\text{eff}}$  on the reciprocal viscosity of the polar component of the mixture (Fig. 3). The results obtained may be explained both by a decrease in the efficiency of quenching of the aggregate triplet state by traces of oxygen and by the impeded movement of dye molecules in the aggregate with increasing viscosity of the polar component. The  $K_{\text{eff}}$  value proved also to be dependent on the ability to form H bonds. A correlation between  $K_{\text{eff}}$  values and the value of the O-H vibration frequency shift of alcohols due to H-bond formation was obtained.

$K_{\text{eff}}$  depends most strongly on the H bond formed directly between the dye molecules. If  $K_{\text{eff}}$  for rhodamine 6G type I aggregates does not exceed  $10^4$  s $^{-1}$  then for the same aggregates of rhodamine 3B the  $K_{\text{eff}}$  value is much greater than  $10^4$  s $^{-1}$ . It is known that molecules of rhodamine 3B, in contrast to rhodamine 6G, do not form an H bond between themselves [23]. Lability of the structure of aggregates of rhodamine 3B is the cause of the efficient ISC process to the ground state. Stabilization of the aggregates of

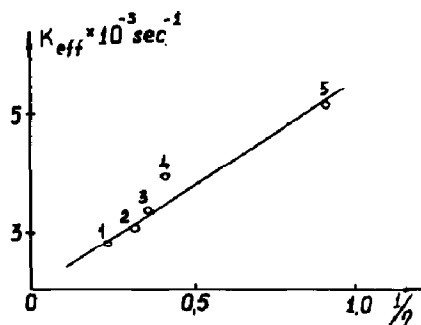


Fig. 3. The dependence of  $K_{\text{eff}}$  values of type I aggregates on the reciprocal value of the viscosity of the polar component of the mixture: point 1, amyl; point 2, butyl; point 3, isopropyl; point 4, propyl; point 5, ethyl alcohols.

this dye by the polymer (PMA) leads to an increase in  $\tau_T$  ( $K_{\text{eff}}$  falls to  $10^3 \text{ s}^{-1}$ ).

Measurements of the decay kinetics of the triplet state of aggregates at low flash intensities have shown that the lifetime of the triplet state does not depend on the dye concentration. However, in the case of aggregated molecules this does not mean that the process of the self-quenching of the triplet states which has been established for monomeric molecules of rhodamine 6G ( $K_1$  and  $K_2$ , Table 1) does not take place. Indeed, in each aggregate one molecule being in a triplet state accounts for 9 - 19 molecules in the ground state. Addition of the same number of molecules in the ground state occurring on collision of two aggregates must not bear on the rate of the  $T \rightarrow S_0$  process. This process may occur in each separate aggregate and its presence possibly contributes to the increase in  $K_{\text{eff}}$  for all aggregates of type I in comparison with monomers.

Measurements of the decay kinetics of the triplet state of aggregates of both types at high concentrations of rhodamine 6G and at high flash intensities have shown the presence of the second order decay and the appearance of a new short lived species absorbing differently compared with T-T absorption. The second order decay and the new absorption can result from T-T interactions. With increasing flash energy an increase in intensity of the new absorption was observed. It will be shown later that the short lived absorption is due to radicals produced by electron transfer reactions with the participation of aggregates in the triplet state. If we consider the triplet excitation in the aggregate as a triplet exciton, then the formation of radicals may occur as a result of interaction between two excitons during the collision of aggregates. In this case the rate of the reaction will be limited by diffusion of aggregates to one another and the value of the rate constant will be the same as that for the monomer. The values of  $K_3$  and  $K_4$  for type I aggregates are equal for monomers and decrease significantly in the case of solutions with PMA which significantly impedes diffusion (Table 1). However, there is a peculiarity in the T-T interaction in aggregates of both types, *i.e.* that T-T annihilation ( $K_4$ ) is more important than electron transfer ( $K_3$ ).

The results of this study show that the triplet states of rhodamine 6G aggregates have a number of properties which are typical for monomeric molecules of this dye, *i.e.* the long lifetime of the triplet state and the occurrence of bimolecular processes of deactivation and of electron transfer reactions. This suggests that the triplet state of rhodamine 6G aggregates, like that of the monomeric molecule, is highly reactive.

### *3.3. The electron transfer reactions of the triplet state of rhodamine 6G aggregates*

The study of the electron transfer reactions of the triplet state of the rhodamine 6G aggregates was based on measurements of transient absorption spectra and of the production and decay kinetics of short lived species which were carried out by flash excitation of solutions of dye aggregates in both the absence and the presence of electron donors and acceptors.

#### *3.3.1. Assignments of bands*

Flash excitation of rhodamine 6G aggregates of both types gives rise to both T-T absorption and another transient absorption at 400 - 460 nm. The transient spectrum observed for aggregates in the mixture of butanol and  $\text{CCl}_4$  is shown in curve 1 of Fig. 4. From kinetic measurements it follows that this absorption is complicated and consists of overlapping bands belonging to different species. The lifetime of the transient which absorbs at 450 nm is similar to that of the triplet state with an absorption maximum around 670 nm, while the lifetime of the transient absorbing at 410 nm is slightly longer.

The small difference in the lifetime of these species does not allow absorption spectra to be separated. However, at low concentrations of triplet molecules, so that the formation of any reaction products involving triplet aggregates is excluded, the absorption measured may be composed of T-T absorption alone. The T-T absorption spectrum of rhodamine aggregates measured in butanol and  $\text{CCl}_4$  mixtures at low flash intensities is given in Fig. 4 (curve 2). The differences in the spectra shown in curves 1 and 2 of Fig. 4 indicate that flash excitation of dye aggregates leads to the formation of short lived products of a redox reaction as well as the appearance of T-T absorption.

When  $\text{CCl}_4$  is replaced by toluene the lifetime of the reaction product greatly exceeds the lifetime of the triplet state; this makes it possible to separate the absorption spectrum of the triplet aggregates from that of the products of the redox reaction. Curve 3 in Fig. 4 represents the change of optical density of the solutions of the type I aggregates measured  $10^{-3}$  s after the flash. Since the lifetime of the triplet state is about  $0.2 \times 10^{-3}$  s, the observed absorption cannot be attributed to T-T absorption.

Addition of electron donors to solutions of aggregates of both types leads to the production of a transient with absorption only around 410 nm (Fig. 5, curves 1, 2). When diphenylamine was used as the electron donor there was an increase in optical density at 410 nm and the appearance of a



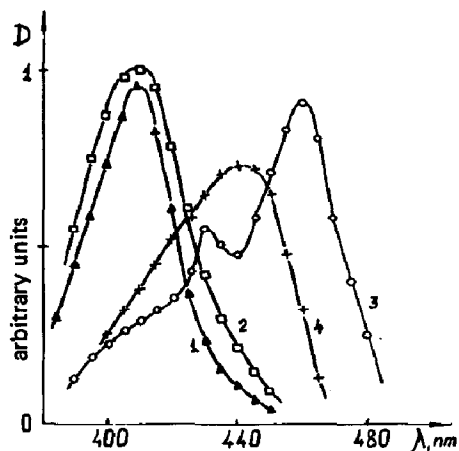
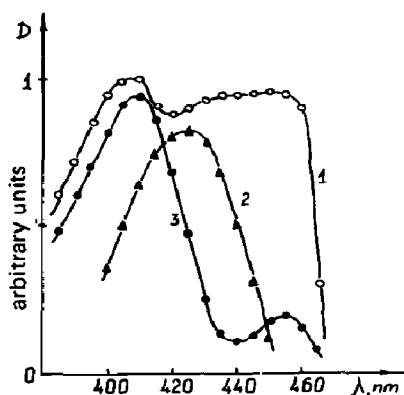


Fig. 4. The differential absorption spectrum (curve 1) and T-T absorption (curve 2) of type I aggregates in a mixture of butanol with  $\text{CCl}_4$ , and differential absorption spectrum of type I aggregates in a mixture of butanol with toluene (curve 3).

Fig. 5. The differential absorption spectra of intermediates of rhodamine 6G aggregates: curve 1, anion radical in a mixture of butanol with  $\text{CCl}_4$  (donor, diphenylamine); curve 2, anion radical of type II aggregates (donor, ascorbic acid); curve 3, cation radical of type II aggregates and semiquinone; curve 4, exciplex in a mixture of butanol with  $\text{CCl}_4$ .

new absorption at 680 nm owing to the diphenylamine cation radical. Addition of *p*-benzoquinone to a solution of type II aggregates resulted in an increase in absorption at 460 nm and a decrease in absorption at 410 nm (Fig. 5)<sup>†</sup>.

The experimental data presented allow the transient absorption to be assigned to absorption of semi-reduced ( $\lambda = 410$  nm) and semi-oxidized ( $\lambda = 460$  nm) radicals of rhodamine aggregates. A comparison of the spectra shown in Figs. 4 and 5 suggests that ion radicals of aggregates were formed not only during the interaction of aggregate triplets with electron donors and acceptors but also in their absence.

The following experimental data indicate that electron transfer occurs via the triplet state of rhodamine aggregates.

(a) The addition of electron donors and acceptors results in quenching of the triplet state. The values of the rate constants of triplet state quenching are given in Table 2.

(b) The addition of triplet energy acceptors (naphthacene and anthracene sulphonic acid) results in the decrease of the relative yield of ion radicals without noticeable shortening of their lifetimes. Addition of air to the cell with an outgassed solution of aggregates also decreased the yield of ion radicals as a result of competitive quenching of the triplet state by oxygen.

(c) Absorption of ion radicals of aggregates was also observed in experiments on sensitized excitation (T-T energy transfer). 1,2,5,6-Dibenzanthra-

<sup>†</sup>The absorption band at 430 nm belongs to the semiquinone radical.

TABLE 2  
 Values of rate constants of reactions of rhodamine 6G aggregates with electron donors  $D_e$  and acceptors  $A_e$

Process	Electron donor	Medium	$K_5 + K_6$ ( $M^{-1} s^{-1}$ )	$K_5$ ( $M^{-1} s^{-1}$ )	$K_9$ ( $M^{-1} s^{-1}$ )
$\begin{array}{l} K_5 \swarrow \\ \text{---} \rightarrow \dot{R}^- + \dot{D}_e^+ \\ K_6 \searrow \\ \text{---} \rightarrow S_0 + D_e \end{array}$	Ascorbic acid	$H_2O + PMA$	$1.2 \times 10^7$	$0.7 \times 10^7$	
	<i>p</i> -Phenylenediamine	$H_2O + PMA$	$4.2 \times 10^6$	$3.0 \times 10^6$	
$\begin{array}{l} K_5 \swarrow \\ \text{---} \rightarrow \dot{R}^- + \dot{D}_e^+ \\ K_6 \searrow \\ \text{---} \rightarrow S_0 + D_e \end{array}$	Hydroquinone	$H_2O + PMA$	$2.5 \times 10^6$	—	
	EDTA	$H_2O + PMA$	$2 \times 10^5$	—	
	Phenol	$H_2O + PMA$	$2 \times 10^4$	—	
	Diphenylamine	$CCl_4 + C_4H_9OH$	$1.3 \times 10^8$	—	
$K_9 \xrightarrow{\quad} S_0 + \dot{D}_e^+$	Diphenylamine	$H_2O + PMA$			$1.5 \times 10^7$
	Electron acceptor	Medium	$K_7 + K_8$ ( $M^{-1} s^{-1}$ )	$K_7$ ( $M^{-1} s^{-1}$ )	$K_{10}$ ( $M^{-1} s^{-1}$ )
$\begin{array}{l} K_7 \swarrow \\ \text{---} \rightarrow \dot{R}^+ + \dot{A}_e^- \\ K_8 \searrow \\ \text{---} \rightarrow S_0 + A_e \end{array}$	<i>p</i> -Benzoquinone	$CCl_4 + C_4H_9OH$	$7.2 \times 10^8$	—	
	<i>p</i> -Benzoquinone	$H_2O + PMA$	$7.0 \times 10^7$	$1.4 \times 10^7$	
$\begin{array}{l} K_7 \swarrow \\ \text{---} \rightarrow \dot{R}^+ + \dot{A}_e^- \\ K_8 \searrow \\ \text{---} \rightarrow S_0 + A_e \end{array}$	FeCy	$H_2O + PMA$	$5.2 \times 10^8$	$5.2 \times 10^6$	
	Methylviologen	$H_2O + PMA$	$6 \times 10^5$	—	
	<i>m</i> -Dinitrobenzene	$H_2O + PMA$	$6 \times 10^5$	—	
$K_{10} \xrightarrow{\quad} S_0 + \dot{A}_e^-$	<i>m</i> -Dinitrobenzene	$H_2O + PMA$			$5.2 \times 10^7$
	<i>p</i> -Benzoquinone	$CCl_4 + C_4H_9OH$			$4.0 \times 10^7$

cene (for type I aggregates) and naphthalene (for type II aggregates) were used as triplet energy donors.

(d) From a comparison of the duration of the flash, the lifetime of the triplet states of the aggregates and the time to reach a maximum cation radical concentration it can be seen that the production of cation radicals occurs during the decay of the triplet state and after the flash terminates (Fig. 6). The data presented above are in good agreement with results obtained for monomers of rhodamine 6G [24].

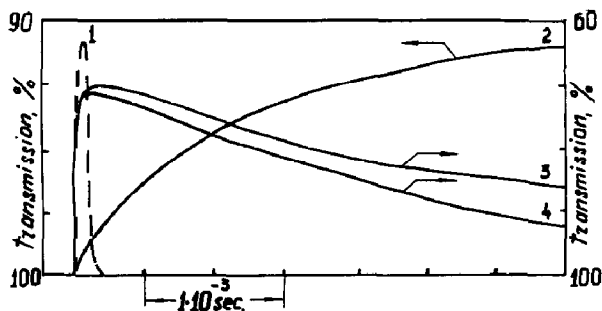


Fig. 6. Time course of the flash emission (curve 1, arbitrary units) and of the changes in transmission due to the production of cation radicals (curve 2) ( $\lambda = 470$  nm) and the decay of the triplet state of type II aggregates measured in the absence (curve 3) and in the presence (curve 4) of *p*-benzoquinone ( $\lambda = 600$  nm).

### 3.3.2. Mechanisms of electron transfer processes

For monomeric forms of various dyes it is known that the production of semi-reduced and semi-oxidized dyes in the absence of foreign electron donors and acceptors may occur as a result of self-quenching of the triplet state as well as through T-T interaction [25, 26]. It was noted above that self-quenching of triplet aggregates is possible in each separate aggregate but that T-T interaction is also observed when the concentration of aggregates is increased. However, the absorption of ion radicals was not recorded at low flash intensities and in the absence of electron donors and acceptors. This implies that the production of ion radicals results in the T-T interaction. The quantum efficiency of this reaction is about 0.3 for type I aggregates and about 0.1 for type II aggregates.

It has already been noted above that electron donors and acceptors are able to quench the triplet state of dye aggregates leading to the production of ion radicals. It is known [25, 26] that interaction of triplet monomers of various dyes with electron donors and acceptors includes both the process of electron transfer and the process of induced ISC to the ground state (see Table 2). The kinetic measurements carried out on rhodamine aggregates have shown that values of rate constants for electron transfer are less than those for quenching of the triplet state (see Table 2).

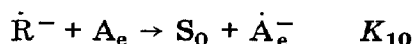
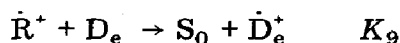
The quantum efficiencies of the photoreduction of type II aggregates by ascorbic acid and *p*-phenylenediamine are 0.6 and 0.7 respectively. It should be noted that addition of EDTA or phenol (concentrations up to

$10^{-3}$  M) does not lead to a noticeable quenching of the triplet state of type II aggregates.

The formation of transients on photo-oxidation of rhodamine aggregates was recorded only for *p*-benzoquinone as the electron acceptor in aqueous solutions of PMA. The quenching of the triplet states of aggregates by potassium ferricyanide does not result in spectral changes in the visible. Hence the quenching is completely due to induced ISC to the ground state. Methylviologen and *m*-dinitrobenzene do not quench the triplet states of rhodamine aggregates.

In contrast to the aqueous solution, transient absorption with  $\lambda_{\max} = 440$  nm (Fig. 5, curve 4) was observed on photo-oxidation of type I aggregates in a mixture of butanol and  $\text{CCl}_4$ . The decay kinetics of the transient were first order with a rate constant of  $7.5 \times 10^3 \text{ s}^{-1}$ . The observed transient was shown not to be a semiquinone radical. The latter absorbs with a maximum at 405 nm. It is difficult to assign the absorption at 440 nm to cation radicals of aggregates. This follows from the fact that diphenylamine does not diminish the intensity of absorption at 440 nm. It can be assumed that the transient with  $\lambda_{\max} = 440$  nm is the exciplex formed between the aggregates and *p*-benzoquinone. It is known that certain media can stabilize these exciplexes; the triplet exciplex was observed for porphyrins [27] and chlorophyll [28] on photo-oxidation by *p*-benzoquinone and other electron acceptors.

We have also established that rhodamine aggregates in the triplet state are able to sensitize redox reactions. It is known that the process of sensitization can be represented by a scheme comprising reduction or oxidation of the sensitizer in the triplet state as the first stage and an electron transfer process as the second stage, according to reactions



It has already been noted that ion radicals were not observed on photo-oxidation of dye aggregates by *m*-dinitrobenzene (about  $10^{-4}$  M). However, addition of this acceptor to a solution of type II aggregates containing ascorbic acid results first in the production of  $\dot{\text{R}}^-$  radicals as a result of photoreduction of aggregates and additionally in the shortening of the  $\dot{\text{R}}^-$  lifetime because of the second reaction above. The values of the rate constants of reaction (with  $K_{10}$ ) for aggregates of both types are given in Table 2. Therefore the reduction mechanism of sensitization was shown to occur for aggregates of types I and II. The oxidation mechanism of sensitization was observed only for aqueous solutions of PMA. The value of the rate constant  $K_9$  is given in Table 2 (*p*-benzoquinone, type II aggregates, diphenylamine).

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