

TRIPLET STATES OF CYANINE DYES AND REACTIONS OF ELECTRON TRANSFER WITH THEIR PARTICIPATION

A. K. CHIBISOV

V. I. Vernadsky Institute of Geochemistry and Analytical Chemistry of Academy of Sciences, Moscow (U.S.S.R.)

(Received June 10, 1976)

Summary

The radiationless decay processes of the excited singlet states of thiocarboyanines are considered. It was revealed that the quantum yield (Φ_{ST}) of intersystem crossing is low ($\Phi_{ST} \ll 0.1$) for certain unsubstituted (in the meso position) thiocarboyanines. The triplet level for unsubstituted thiocarboyanines can be populated efficiently owing to triplet-triplet energy transfer. The values of Φ_{ST} are increased markedly for 9-CH₃O- and 9-NH₂-thiocarboyanines where T-T absorption is observed on direct flash excitation. Using triplet-triplet energy transfer it was established that *cis-trans* isomerization for certain unsubstituted thiocarboyanines occurs *via* a singlet excited state.

For unsubstituted thiocarboyanines the main pathways of the singlet excited states decay are *cis-trans* isomerization and internal conversion.

The main processes of the triplet state decay are radiationless deactivation, quenching by impurities (*e.g.* traces of oxygen), triplet-triplet annihilation and self-quenching. The values of rate constants were determined for certain thiocarboyanines. Mixed triplet-triplet annihilation was established on sensitized excitation of thiocarboyanines in the presence of anthracene (sensitizer).

Triplet states of thiocarboyanines play a major role in redox reactions. Experimental evidence favours the extreme participation of triplet states in electron transfer processes. Efficiency of triplet state quenching by certain electron donors (ascorbic acid, β -naphthylamine) and acceptors (*p*-benzoquinone, methylviologen) was considered. In some cases quenching is accompanied by the production of ion-radicals. The oxidative and reductive mechanisms of sensitization are considered and the values of rate constants for some elementary steps with thiocarboyanines triplet states involved are determined.

Introduction

Cyanine dyes form one of the most important classes of organic dyes because of their practical applications. First, there is the wide use of cyanine dyes in photography as spectral sensitizers [1, 2]. Many cyanine dyes have also found wide application in laser techniques [3, 4]. This underlines the significance of investigating the mechanism of the interaction of light (in particular of intensive light flashes) with molecules of cyanine dyes.

In contrast with molecules of other classes of dyes (xanthene, thiazine) for which the nature of the intermediates of photochemical reactions is well known [5], the photophysics and photochemistry of cyanine dye molecules have been studied in less detail. Only the ability of the molecules of many cyanines for *cis-trans* photoisomerization is well known [6 - 9]. However, some questions remain unsolved, such as the nature of the excited state of cyanines being responsible for photoisomerization, the factors hindering photoisomerization etc.

Information about triplet states of cyanine dyes are on the whole limited to data on their phosphorescence [10, 11] and to results of triplet-triplet absorption spectra of dyes measured in films of poly(vinyl alcohol) [12, 13]. However, just this region (the region of the photonics of cyanine dyes triplet states) must be of great interest for the understanding of the mechanism of light energy conversion into energy of chemical processes. It is known [14 - 16] that triplet states of many aromatic compounds play an important role in various photochemical reactions. Great importance is attached to triplet states in processes of electron transfer in photoreactions of many dyes and chlorophyll pigments [5, 17, 18]. Triplet states also play substantial role in oxidation-reduction photosensitized reactions in solutions.

In this connection the study of the photonics of cyanine dyes triplet states are of paramount interest. This problem is also closely connected to the problem of the spectral sensitization mechanism.

This paper summarizes results obtained in the study of triplet states of certain cyanine dyes and as well as reactions of electron transfer.

Experimental

Measurements of both absorption spectra and production and decay kinetics of short-lived intermediates of cyanine dyes were carried out by flash photolyses which were set up as described elsewhere [19]. The solutions of dyes were flashed with energy up to 1000 J at a duration of $\tau_{1/2} = 12 \mu\text{s}$ in a cell with a 20 cm path length. The kinetics of delayed fluorescence was measured with the same apparatus while the monitoring light beam had been switched off.

As objects of investigation symmetric thia- and oxo-carbocyanines with different length of the polymethine chain and different substituents in the meso position of the polymethine chain were used. The purity of dyes was

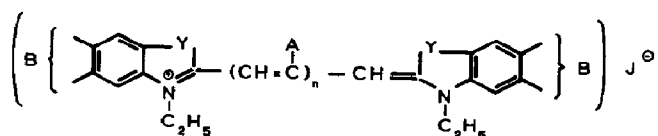
controlled chromatographically and spectrophotometrically. Naphthalene, anthracene and 1,2,5,6-dibenzanthracene were used as triplet energy donors. Ascorbic acid, β -naphthylamine, diphenylamine and hydroquinone were used as electron donors; methylviologen, *p*-benzoquinone, *m*-dinitrobenzene served as electron acceptors. All substances added were of reagent grade purity.

Measurements were carried out with solutions of dyes in propanol, butanol, *t*-butanol, chloroform and glycerol at room temperature.

Introduction of cyanine dyes into films of poly(vinyl alcohol) was accomplished by methods described earlier [20]. The absorption spectra of dyes were recorded on a Unicam SP-700 spectrophotometer.

Results and Discussion

The cyanine dyes under study may be conditionally divided into groups depending on the nature of heterocyclic residues, the substituents in the latter and in the meso position as well as on the length of the polymethine chain, and may be represented by the common formula



where

N	Y	B	A	<i>n</i>
I	S	H	H	0
II	S	H	H	1
III	S	H	OCH ₃	1
IV	S	H	NH ₂	1
V	S	6-N(CH ₃) ₂	H	1
VI	O	H	H	1
VII	S	H	H	2
VIII	S	H	H	3

Intersystem crossing: triplet-triplet absorption

Many cyanine dyes belong to the class of phototropic compounds reversibly changing their colour during flash photolysis. One of the causes of phototropism may be *cis-trans* isomerization. We [8] and other authors [6, 7] have earlier revealed short lived changes in absorption spectrum of 3,3'-diethylthiacarbocyanine iodide (DTCI, dye II) on flash excitation of its

solutions. Based on the observed hypsochromic shift of the absorption band a conclusion about the photoinduced conversion of DTCl-*trans* (initial form) into DTCl-*cis* (photo) isomer has been drawn. In a subsequent work [21] *cis-trans* photoisomerization was established for a number of other carbocyanines (dyes V, VI and VII). From the obtained data it followed first not only a bathochromic but also a hypsochromic shift of the photoisomer bands in relation to the initial absorption and secondly low values of the quantum yield of photoisomerization for dyes III and IV. Unlike DTCl the meso substituted thiocarbocyanines (DTCl-OCH₃, dye III and DTCl-NH₂, dye IV) in air-saturated solutions do not display reversible short-lived changes in absorption. The obtained results could be accounted for by steric hinderances of *cis-trans* photoisomerization caused by the presence of methoxy and amino groups in the meso position of the polymethine chain. In this connection it seemed important to elucidate the ability of the molecules of cyanine dyes for intersystem crossing as well as to establish the interrelation between processes of photoisomerization and intersystem crossing.

Non-substituted carbocyanines

As it already has been noted that flash excitation (100 J) of both deoxygenated and of air-saturated solutions of dyes II, V, VI and VII in alcohols (10^{-6} - 10^{-7} M) leads to reversible changes in absorption as a result of *cis-trans* photoisomerization. The observed changes in absorption did not depend on the presence of dissolved oxygen. This fact indicates first of all that the photoinduced changes in absorption of dye solutions are not connected with triplet-triplet (T-T) absorption. On the basis of the results obtained two alternative explanations of the lack of T-T absorption can be given. In accordance with the first the molecules of dyes II, V, VI and VII have extremely low values of the quantum yield of intersystem crossing ($\Phi_{ST} \ll 0.1$) and the process of *cis-trans* isomerization occurs via singlet excited state. In accordance with the second one the *cis-trans* isomerization proceeds via the triplet state and the value $\Phi_{ST} \gg 0.1$. In order to establish the nature of the excited state being responsible for photoisomerization of the dyes under study as well as to elucidate the ability of molecules for intersystem crossing, experiments on triplet-triplet energy transfer were carried out. Population of the triplet level of molecules having a low quantum Φ_{ST} yield may be effective on the triplet-triplet energy transfer [22]. In this case the value of the rate constant of triplet-triplet energy transfer is close to a maximum if the distance between the triplet levels of the donor and the acceptor is ≥ 1000 cm⁻¹ [23]. From this position naphthalene ($E_T = 21,250$ cm⁻¹) was in most cases used as donor of triplet energy. For cyanine dyes with low positioned triplet level 1,2,5,6-dibenzanthracene ($E_T = 18,250$ cm⁻¹) and anthracene ($E_T = 14,900$ cm⁻¹) were used as donor. Flashing of a mixture of the donor and the dye in the absorption band of the donor gives rise to short-lived changes in absorption owing to the well known T-T absorption of the donor and to a new absorption which has to be attributed to the T-T transitions of the dye. The intensity of the cyanine dye T-T absorption increased

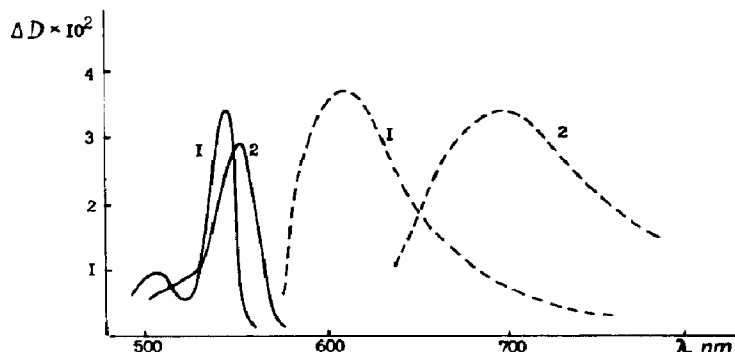


Fig. 1. Transient spectra of cyanine dye II (1) and dye V (2) in butanol: —, photoisomer absorption; - - -, triplet-triplet absorption.

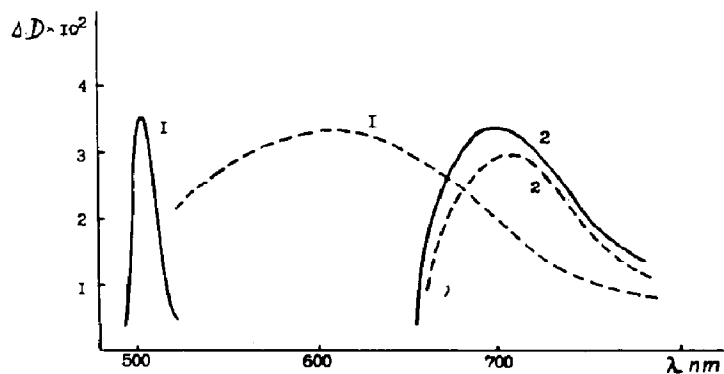


Fig. 2. Transient spectra of cyanine dye VI (1) in butanol and dye VII (2) in isopropanol: —, photoisomer absorption; - - -, triplet-triplet absorption.

with the increase of dye concentration while the lifetime of donor triplet molecules decreased. In Figs. 1 and 2 the T-T absorption spectra of non-substituted cyanine dyes are shown. From the comparison of T-T absorption spectra with absorption spectra of photoisomers (Figs. 1 and 2) of the same dyes it follows that there is a substantial difference in the position of absorption maxima. This circumstance allowed us to come to the unambiguous conclusion about the nature of the excited state of cyanine dye molecules involved in photoisomerization. In both cases when photoisomerization occurs on a singlet excited or triplet level the sensitized excitation of the dye molecule leads to a population of its triplet level. If the process of isomerization occurs, a triplet level in the absorption spectrum of the dye under conditions of sensitized excitation band of the photoisomer must be observed. If the process of isomerization occurs via the singlet excited state under the same conditions of excitation bands of T-T absorption must appear in the spectrum of the dye. From results of measurements on triplet-triplet energy transfer it follows that in the spectrum of cyanine dyes only bands of T-T absorption but not of photoisomers are observed. Consequently the process of *cis-trans* photoisomerization of cyanine dyes occurs on the singlet excited level [24, 25]. Recently Buettner has come to the same conclusion when he

TABLE 1

Values of fluorescence quantum yields (Φ_{fl}), intersystem crossing (Φ_{ST}), *cis-trans* isomerization ($\Phi_{isom.}$) and internal conversion (Φ_{ic}) for cyanine dyes

Dyes	Φ_{fl}	Φ_{ST}	$\Phi_{isom.}$	Φ_{ic}
I	0.0006 [29]	<0.03	<0.001	0.96 - 0.99
II(<i>trans</i>)	0.048 [29]	<0.001	0.72 - 0.95	0.00 - 0.23
III(<i>cis</i>)	0.015 [32]	0.16 - 0.20	<0.001	0.78 - 0.83
VI(<i>cis</i>)	0.04	<0.001	0.66 - 0.96	0.00 - 0.30
VII(<i>cis</i>)	0.33 [29]	<0.001	0.42 - 0.57	0.10 - 0.25

investigated the triplet state of DTCI in methanol as was indicated in the paper of Cooper and Rome [26].

It seemed of interest to determine the values of quantum yields of processes of radiationless deactivation of singlet excited states of cyanine dyes. The Φ_{ST} values were estimated according to data of the sensitivity of the flash photolysis method, of values of extinction coefficients of T-T absorption of dyes which have been determined by the method of triplet-triplet energy transfer [27] and of actinometric data. An aqueous solution of erythrosine was used as actinometer. The number of absorbed quanta was determined according to erythrosine T-T absorption intensity using the Φ_{ST} value equal to unity [28]. The Φ_{ST} values found are listed in Table 1. The values of the quantum yield of the photoisomerization ($\Phi_{isom.}$) of cyanine dyes were found by the method of comparison with the standard being identical with the above described. In Table 1 values of $\Phi_{isom.}$ as well as the values of fluorescence quantum yields (Φ_{fl}) [29] and of internal conversion (Φ_{ic}) are listed. The values of Φ_{ic} were found according to data of $\Phi_{isom.}$, Φ_{ST} and Φ_{fl} in accordance with the relationship:

$$\Phi_{fl} + \Phi_{ST} + \Phi_{ic} + \Phi_{isom.} = 1 \quad (1)$$

Thus, the analysis of quantum yields shows that the main process of radiationless deactivation of singlet excited states of non-substituted cyanine dyes is the *cis-trans* isomerization which competes effectively with the process of intersystem crossing. A direct populating of triplet level of cyanine dyes occurs under conditions preventing or limiting the process of *cis-trans* photoisomerization. We have established the existence of both the process of intersystem crossing and of the *trans* \rightarrow *cis* conversion for DTCI in glycerol. It has been shown that with a temperature decrease to +10 °C a redistribution of absorption bands intensity of *cis*-isomer and T-state occurs (Fig. 3). The viscosity increase of the medium with temperature decrease impedes the *trans* \rightarrow *cis* photoinduced conversion as a consequence of which the intensity of *cis*-isomer absorption decreases. Simultaneously an intensification of T-T absorption is observed. The prevention of *cis-trans* photoisomerization of cyanine dyes occurs in rigid matrices. Measurements of transient absorption

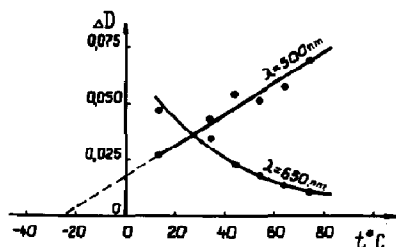


Fig. 3. Temperature dependence of optical density changes for photoisomer ($\lambda = 500$ nm) and triplet ($\lambda = 650$ nm) of dye II in glycerol.

spectra of cyanine dyes embedded into the poly(vinyl alcohol) (PVA) film show that on flash excitation of dyes in PVA only T-T absorption is observed [13, 20, 25].

Thus, the relation between the probabilities of the intersystem crossing and the *cis-trans* photoisomerization is determined by the factors hindering photoisomerization.

Substituted carbocyanines

The presence of methoxy and amino groups in the meso position of the polymethine chain substantially impedes the process of *cis-trans* photoisomerization of dyes III and IV. As already noted above the flashing of air-saturated solutions of dyes III and IV in alcohols as well as in chloroform does not lead to noticeable changes in absorption. It could be expected that for these dyes the intersystem crossing will be one of the pathways of energy degradation of singlet excited states. Indeed photoexcitation of deoxygenated solutions of dyes III and IV as well as dye I in alcohols in the absence of donors of triplet energy gives rise to T-T absorption (Fig. 4). Evidence of the correctness of the made assignments are based on facts of quenching of the triplet state by oxygen and naphthalene (triplet energy acceptor). It has been shown that gradual air removal from solutions of dyes results in appearance of T-T absorption and an increase of triplet molecule lifetime. Addition of naphthalene to the deoxygenated solution of dye III in isopropanol leads to the disappearance of T-T absorption of dye and to the appearance of T-T absorption of naphthalene in the region of 400 - 480 nm. According to the experimental conditions the production of triplet naphthalene molecules could only occur as a result of triplet-triplet energy transfer from DTCl-OCH₃ to naphthalene.

It is known [30, 31] that the DTCl-OCH₃ and DTCl-NH₂ molecules are present in alcoholic solutions prevailing in the *cis*-form, while in chloroform the *cis-trans* equilibrium is displaced towards the *trans* isomer. It is of importance to note that in our experiments on flash photolysis of DTCl-OCH₃ solutions an effective intersystem crossing was occurring when the *cis*-form of the dye was selectively excited.

As with non-substituted carbocyanines we have determined the values of quantum yields of deactivation processes of dyes I and III singlet excited states. The obtained values are listed in Table 1.

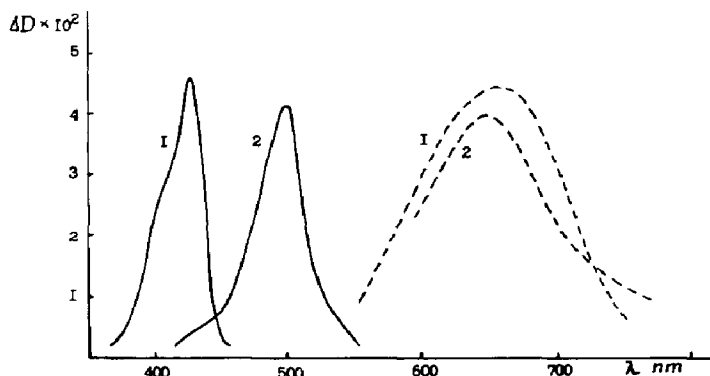
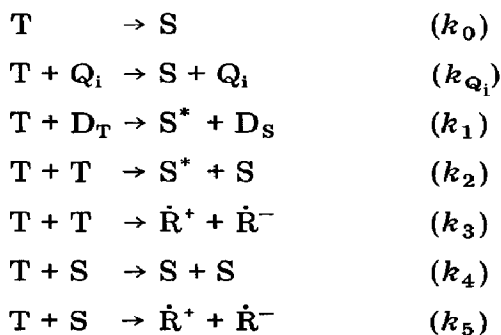


Fig. 4. Ground state absorption (—) and triplet-triplet absorption (- - -) of dye I (1) in isopropanol and dye III (2) in butanol.

Thus for liquid (not viscous) solutions of cyanine dyes the process of intersystem crossing is on the whole little affected. A conclusion about the existence of two different mechanisms of radiationless deactivation of cyanine dyes singlet excited states may be made. The transition from the singlet excited state into the ground state is for non-substituted carbocyanines a double-stage process proceeding through the formation of the photoisomer, while the energy degradation of singlet excited molecules of substituted carbocyanines in the meso position of the polymethine chain prevalingly occurs as a result of internal conversion and is a single-stage process.

Deactivation of the triplet state: delayed fluorescence

Kinetic measurements of the deactivation of cyanine dye triplet states were based on data of T-T absorption intensity decrease. Measurements were carried out with diluted (10^{-7} - 10^{-8} M) and concentrated (10^{-5} - 10^{-4} M) solutions of dyes as well as in PVA films at different energies of the flash excitation (100 - 1000 J) and with or without donors of the triplet energy (D_T). On the ground of the kinetic analysis carried out in the present study it may be considered that the existence of the following steps composing the process of energy degradation of cyanine dye triplet molecules (T) has been established:



where Q_i is the quenching impurities (*e.g.*, O_2 traces). One must bear in mind

that so far as the cyanine dyes are cationic ones, it may be considered that for diluted alcoholic solutions molecules in the triplet (T) and ground (S) state are a cation (T^+ , S^+), while the cation-radical (\dot{R}^+) is the dication-radical \dot{R}^{+2} and the anion-radical (\dot{R}^-) is the neutral radical \dot{R} . However, later on for simplification we shall use the symbols T, \dot{R}^+ , and \dot{R}^- .

The determination of the rate constant values (k_0) - (k_5) was based on the following measurements:

(1) Measurements in PVA films. Under these conditions diffusion processes of the triplet state quenching are lacking and the decrease of the triplet molecules concentration is described by the exponent with k_0 index, the found values of which are listed in Table 2.

(2) Measurements in solutions at low S, T and D_T concentrations. In this case the processes with k_1 to k_5 may be disregarded and the decrease of triplet molecules concentration is also described by the exponent with an index equal to ($k_0 + \sum k_{Q_i} [Q_i]$). The found values ($k_0 + \sum k_{Q_i} [Q_i]$) are listed in Table 2. From the examination of the data of Table 2 it follows that the lifetime of triplet molecules (τ_T) of cyanines in the solution is always less than the τ_T values measured for dyes in PVA films. This is connected on the one hand with the presence in the de-aerated solution of O_2 traces and on the other hand with the possible stabilization of the dye structure by the PVA matrices, which results in a retardation of the radiationless $T \rightarrow S$ process (for dye I). At the same time a decrease in the τ_T value in passing from propanol to chloroform (dye III) is probably conditioned by the "external heavy atom effect".

(3) Measurements in solutions at low S and T concentrations and high D_T concentrations (sensitized excitation). In this case only the processes with k_0 , k_Q and k_1 must be taken into account. The equation for the deactivation rate of cyanine triplets can be written in the following form:

$$-\frac{d}{dt} \ln[T] = k_0 + \sum_i k_{Q_i} [Q_i] + k_1 [D_T] \quad (1)$$

The k_1 value was found from the ($k_0 + \sum k_{Q_i} [Q_i] + k_1 [D_T]$) dependence on $[D_T]$ concentration (Table 2). The D_T concentration was determined according to T-T absorption. The ($k_0 + \sum k_{Q_i} [Q_i]$) value for dyes II and III was found from the linear ($k_0 + \sum k_{Q_i} [Q_i] + k_1 [D_T]$) dependence on $[D_T]$ by extrapolation to the zero concentration of D_T (Table 2).

The dependence of τ_T lifetime of cyanines on the concentration of the donor triplets D_T which was revealed in this work is conditioned by the process of mixed triplet-triplet annihilation [33]. We have found the appearance of a delayed fluorescence of dyes II and III on flash excitation (250 - 290 nm) of their solutions in the presence of anthracene or naphthalene. The spectra of delayed fluorescence (550 - 740 nm) of cyanines coincided with the spectra of normal fluorescence but the time of the delayed fluorescence $\tau_{d.fl.}$ in all experiments exceeded the time duration of the flash and was close to the lifetime of the donor triplets.

Evidence that the observed delayed fluorescence has been correctly attributed to the mixed type is based on the comparison of calculated and

TABLE 2
 Values of rate constants of triplet state decay and electron transfer reactions of cyanine dyes

Dye	Medium	k_0 (s^{-1})	$k_0 + \sum_i k_{Q_i}$ (s^{-1})	k_1 ($M^{-1} s^{-1}$)	$k_2 + k_3$ ($M^{-1} s^{-1}$)	k_3 ($M^{-1} s^{-1}$)	$k_4 + k_5$ ($M^{-1} s^{-1}$)	k_5 ($M^{-1} s^{-1}$)
I	PVA	4	—	—	—	—	—	—
	butanol	—	1.4×10^4	—	—	—	—	—
	propanol	—	2.5×10^4	—	—	—	—	—
II	propanol	—	2.3×10^2	1.8×10^9	1.3×10^9	1.2×10^9	4×10^7	2.6×10^7
	PVA	4.3×10^1	—	—	—	—	—	—
III	propanol	—	4.0×10^2	—	1.0×10^9	0.6×10^9	1.9×10^7	—
	chloroform	—	3.3×10^3	—	—	—	—	—
IV	propanol	—	8.0×10^3	—	—	—	—	—
VII	propanol	—	3.0×10^2	—	1.2×10^9	1.0×10^9	1.3×10^7	0.4×10^7

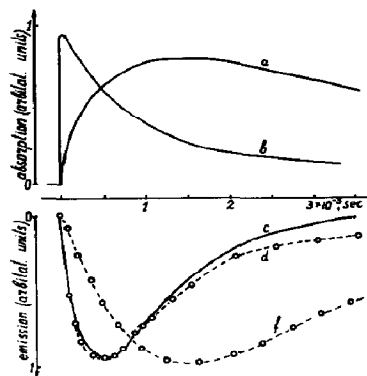


Fig. 5. Changes in absorption due to production and decay of the triplet state of anthracene (b) and of dye II (a) and changes in intensity of delayed fluorescence of dye II (c). Curves (d) and (f) are calculated curves of the intensity changes of delayed fluorescence of the mixed and molecular types respectively due to triplet-triplet annihilation of dye II.

experimental kinetic curves of the after-glow intensity. The intensity of delayed fluorescence of the mixed type is proportional to the $[T]$ and $[D_T]$ concentrations.

$$\tau_{d.fl.} = \beta [T] [D_T] \quad (2)$$

where β is the multiplier taking into account the probability of T and D_T encounters as well as the efficiency of triplet-triplet annihilation and the quantum yield of fluorescence [34]. In Fig. 5 oscillograms of absorption changes as a result of production and decay of triplets of the donor (anthracene) and the dye II as well as of the distribution of delayed fluorescence intensity are given. Also in Fig. 5 points are marked which correspond to the fluorescence intensities obtained by multiplying the values of T and D_T concentrations in accordance with eqn. (2). The T and D_T values were found from kinetics decay curves for each of the time moments after the flash. Under the same conditions we did not observe delayed fluorescence of the donor D_T . Thus, one of the mechanisms of the triplet state decay of cyanines includes mixed triplet-triplet annihilation.

(4) In order to elucidate the contribution of reactions with the rate constants k_2 and k_3 in the process of triplet state decay of cyanines, measurements were carried out at relatively high $[T]$ concentrations [35].

It has been revealed that both on sensitized excitation of dyes II, VII and VIII and on direct excitation of the dyes III and IV (10^{-6} - 10^{-4} M) relatively fast absorption changes in the short wavelength region of the spectrum are observed (Fig. 6) which become intensified (20 times) when ascorbic acid (10^{-4} M) is added to the alcohol solutions. This allows us to draw the conclusion that the new short-lived absorption of dyes is conditioned by the production of the intermediate for example by anion-radical \dot{R}^- , in the result of electron transfer process. The absorption spectra of \dot{R}^+ are most likely masked by the intense absorption of cyanines (ground state absorption).

Addition of quenchers (naphthalene, oxygen) of the triplet state to the solutions of dyes results in a decrease of both the triplet state lifetime and the intensity of the short wavelength absorption band without a noticeable

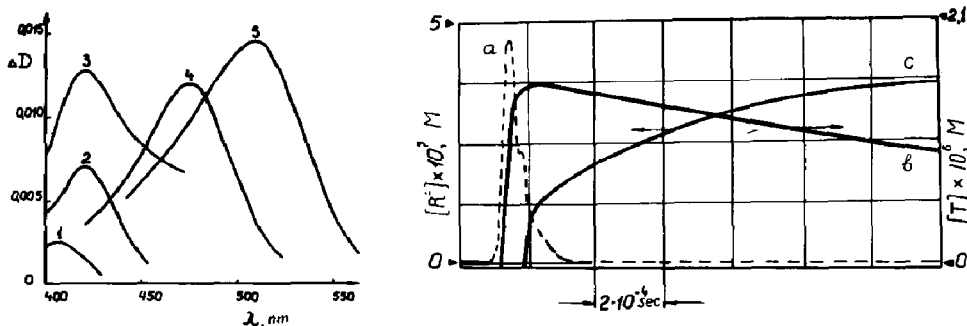


Fig. 6. Absorption spectra of the anion-radicals of cyanine dyes in propanol: 1, dye IV; 2, dye III; 3, dye II; 4, dye VII; 5, dye VIII.

Fig. 7. Time course of the flash emission (a, arbitrary units) and of the changes in concentration due to decay of the triplet state (b) and to production of anion-radicals (c) of dye III.

change of the lifetime of the \dot{R}^- intermediate. These data indicate that electron transfer occurs with the participation of the triplet state of dye. Additional proof of the participation of cyanine triplets in electron transfer reactions is based on comparative measurements of both the time decay of T-state and time production of ion-radicals (\dot{R}^-). In Fig. 7 oscillograms of intensity distribution of the flash, changes of the TCC-OCH₃ light transmission both of the population and decay of T-state and the production of \dot{R}^- are shown. It follows from Fig. 7 that the production of the \dot{R}^- intermediate occurs in the course of T-state decay. These data, as well as comparative experiments carried out in *t*-butanol, have revealed that the electron transfer and consequently the formation of ion-radicals (in the absence of foreign electron donors) occurs between molecules of dyes with the triplet state involved and also that the reaction of hydrogen abstraction of α -atom from the molecules of propyl alcohol seems to be little probable.

The equation for the rate of triplet state decay when the contribution of reactions with k_4 and k_5 may be neglected and for the rate of ion-radicals production can be given in the following form:

$$-\frac{d}{dt} \ln[T] = (k_0 + \sum_i k_{Q_i}[Q_i]) + 2(k_2 + k_3)[T] \quad (3)$$

$$\frac{d}{dt} [\dot{R}^\pm] = k_3 [T]^2 \quad (4)$$

The $(k_2 + k_3)$ values were found from the linear dependence plot of $(d/dt) \times \ln \Delta D_0 / \Delta D$ against ΔD , where ΔD_0 is the optical density change in the result of T-T absorption measured immediately after the flash. In Table 2 the sum $(k_2 + k_3)$ and k_3 values are given.

(5) The values of rate constants k_4 and k_5 were found according to data of the concentration dependence of the triplet decay kinetics and of the production of ion-radicals:

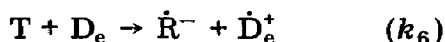
$$-\frac{d}{dt} \ln[T] = (k_0 + \sum_i k_{Q_i}[Q_i]) + (k_4 + k_5)[S] \quad (5)$$

$$\frac{d}{dt} [\dot{R}^+] = k_5 [T] [S] \quad (6)$$

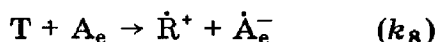
In this case measurements were carried out with relatively concentrated solutions of dyes (10^{-5} - 10^{-4} M) at low flash intensities. The $(k_4 + k_5)$ values were found from the linear dependence of $d/dt \ln \Delta D_0/\Delta D$ on the concentration of ground state molecules S. The k_5 values were obtained both from the kinetics of \dot{R}^- production and from the joint solution of eqns. (5) and (6). The sum of $(k_4 + k_5)$ and k_5 values found in this way are listed in Table 2. Thus, in the absence of foreign electron donors or acceptors, molecules of the cyanines in the triplet state are able to electron transfer processes with production of ion-radicals as a result of disproportionation reaction of two triplets (T-T mechanism, k_3) and of interaction between triplet molecule and non-excited one (T-S mechanism, k_5).

Electron transfer in oxidation-reduction photoreactions

Flash excitation of deoxygenated alcohol solutions of dyes III and IV (direct excitation) as well as dyes II, VII and VIII (sensitized excitation) in the presence of electron donors D_e (ascorbic acid, diphenylamine, 10^{-3} M) results in the disappearance of the T-T absorption of dyes and in the formation of new absorption bands which have to be attributed to products of electron transfer in reaction:



The absorption spectra of anion-radicals of cyanines coincide well with the spectra of ion-radicals being observed without electron donors added (Fig. 6). As with donors the electron acceptors A_e (methylviologen, *m*-dinitrobenzene, *p*-benzoquinone) also effectively quench the triplet state of cyanines. However, the formation of intermediates on photo-oxidation:



occurred only in the presence of methylviologen. In Fig. 8 the absorption spectrum of the dye III cation-radical is presented. For comparison the absorption spectra of anion-radical and triplet state of TCC-OCH₃ are shown in the same Figure.

Participation of triplet state of cyanines in reactions with k_6 and k_8 is based on the following results:

(1) Competing quenching by oxygen. Gradual removal of the oxygen from the solution containing D_e or A_e results in increase of the ion-radical yield per flash. The dependence of the ion-radical yield on the concentration of the dissolved O₂ is conditioned by the quenching of the triplet state of cyanine dyes by oxygen.

(2) Comparative measurements of the time duration of flash, the lifetime of triplet molecules and the time of attainment of ion-radical maximum

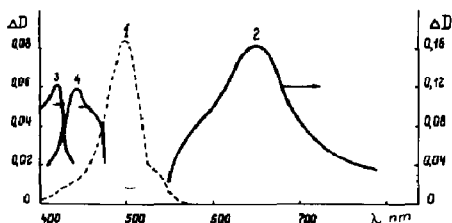


Fig. 8. Absorption spectra of dye III in propanol: 1, ground state absorption (arbitrary units); 2, triplet-triplet absorption; 3, anion-radical; 4, cation-radical.

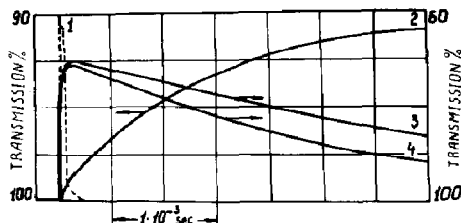
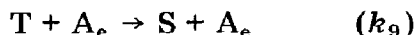
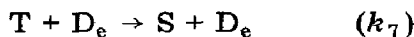


Fig. 9. Time course of the flash emission (1, arbitrary units) and of the changes in transmission due to production of anion-radicals (2) ($\lambda = 420$ nm) and to decay of the triplet state of dye III measured in the absence (3) and in the presence (4) of β -naphthylamine ($\lambda = 650$ nm).

concentration. It follows from Fig. 9 that \dot{R}^- production occurs in the course of triplet state decay when the flash had ceased.

(3) Sensitized population of triplet levels of cyanines. For dyes II, VII and VIII the production of ion-radicals only occurs on sensitized excitation. For dyes III and IV being capable of intersystem crossing, an increase of the yield of ion-radicals per flash is observed under conditions of simultaneous direct and sensitized excitation in comparison with only direct excitation.

Quenching of triplet state of cyanines is not only possible as a result of reactions with k_6 and k_8 but also as a result of induced internal conversion process:



Indeed, as it has already been noted above the quenching of the triplet state by A_e acceptors (*m*-dinitrobenzene and *p*-benzoquinone) does not result in the formation of ion-radicals. In Table 3 the values of rate constants ($k_6 + k_7$) and ($k_8 + k_9$) are listed which were found from kinetic decay of triplet state measured in the presence and absence of quenchers (D_e and A_e). In Table 3 are also listed the values of k_6 and k_8 determined from the kinetics of ion-radical production as well as found from solutions of kinetic equations which describe the processes of triplet state decay and of ion-radical production.

From the examination of the data of Table 3 it follows that the process of induced internal conversion becomes substantially dominating during interaction of triplet molecules with *m*-dinitrobenzene and *p*-benzoquinone. The efficiency of electron transfer in reactions (6) and (8) determined as $\gamma_1 = k_6/(k_6 + k_7)$ and $\gamma_2 = k_8/(k_8 + k_9)$ can be calculated from the data of Table 3. For dye III the value $\gamma_1 = 0.6$ (ascorbic acid) and $\gamma_1 = 0.8$ (β -naphthylamine) and $\gamma_2 < 10^{-2}$ (*p*-benzoquinone, *m*-dinitrobenzene). The γ_2 value for dye III using methylviologen has been estimated as 0.1 - 0.2. Photo-oxidation and photoreduction processes can proceed more effectively in the presence of a sensitizer. The sensitization process can be represented by a

TABLE 3

Values of rate constants of reactions of 3,3'-diethyl-9-methoxythiacarbocyanine triplet molecules with electron donors (D_e) and acceptors (A_e)

Electron donors and acceptors	$k_6 + k_7$ ($M^{-1} s^{-1}$)	k_6 ($M^{-1} s^{-1}$)	$k_8 + k_9$ ($M^{-1} s^{-1}$)	k_8 ($M^{-1} s^{-1}$)	k_{10} ($M^{-1} s^{-1}$)
D_e ascorbic acid	2.5×10^8	1.6×10^8	—	—	—
β -naphthyl-amine	2.0×10^6	1.6×10^6	—	—	—
A_e <i>p</i> -benzoquinone	—	—	6.7×10^8	$<6.7 \times 10^6$	3.7×10^8
<i>m</i> -dinitrobenzene	—	—	2.2×10^9	$<2.2 \times 10^7$	3.6×10^9
methylviologen	—	—	1.4×10^8	1.4×10^7	0.9×10^8

scheme including at the first stage reduction (6) or oxidation (8) of the sensitizer. At the second stage are the processes (10) and (11) respectively:



In this connection measurements of intermediates of electron transfer were carried out in ternary systems: donor-photosensitizer (carbocyanine dye)-electron acceptor. As has been shown above on photo-oxidation of cyanines by *p*-benzoquinone and *m*-dinitrobenzene ($2 \times 10^{-4} M$) no appreciable absorption of ion-radicals has been observed, although ion-radicals may be expected in accordance with the reaction (8). However, addition of the indicated acceptors to the solution of the dye containing the donor of electrons leads to the shortening of \dot{R}^- lifetime and to the appearance of the \dot{A}_e^- absorption band in accordance with reaction (10). In Table 3 the values of the rate constant k_{10} for dye III are listed. It follows from the obtained results that the electron transfer in the system: ascorbic acid or β -diphenylamine (donor D_e)-TCC-OCH₃ (sensitizer)-*p*-benzoquinone or *m*-dinitrobenzene (acceptor A_e) proceeds according to the mechanism of reductive sensitization [reactions (6) and (10)]. The mechanism of reductive sensitization occurs for the above analogous ternary systems in which methylviologen is used as electron acceptor. The obtained data revealed that on the one hand addition of methylviologen results in quenching of \dot{R}^- for dye III and on the other hand leads to quenching of the triplets of the same dye. Thus in the given ternary system the sensitizer in the triplet state interacts not only with the donor, D_e , but also with the acceptor of electrons, A_e , determining by this both the reductive and the oxidative pathways of photosensitization. The k_{11} value for dye III is $1 \times 10^8 M^{-1} s^{-1}$ (D_e is ascorbic acid and A_e is methylviologen).

Thus, the results show that thiocarbocyanines are able to photosensitize electron transfer.

Acknowledgements

The author is pleased to acknowledge the helpful suggestions of Professor I. I. Levkoev and Dr. V. A. Kuzmin.

References

- 1 L. G. S. Brooker, in C. E. K. Mees and T. H. James (eds.), *The Theory of the Photographic Processes*, 3rd Edn, Macmillan, New York, 1966, p. 198.
- 2 H. Meier, *Spectral Sensitization*, Focal Press, London, 1968.
- 3 M. Bass, T. F. Deutsch and M. J. Weber, in A. K. Levine and A. J. de Maria (eds.), *Lasers*, Vol. 3, Marcel Dekker, New York, 1971.
- 4 E. P. Ippen, C. V. Shank and A. Dienes, *Appl. Phys. Lett.*, 21 (1972) 348.
- 5 M. Koizumi and Y. Usui, *Mol. Photochem.*, 4 (1972) 57.
- 6 F. Dörr, J. Kotschy and H. Kausen, *Ber. Bunseng. Phys. Chem.*, 69 (1965) 11.
- 7 P. J. McCartin, *J. Chem. Phys.*, 42 (1965) 2980.
- 8 A. K. Chibisov, *Teor. Eksp. Khim.*, 2 (1966) 825.
- 9 W. West, S. Pearce and F. Grum, *J. Phys. Chem.*, 71 (1967) 1316.
- 10 W. West and A. F. Buettner, *Int. Congr. Phot. Sci.*, Paris, 1965.
- 11 W. West, *Scientific Photography*, Pergamon Press, New York, 1962, p. 557.
- 12 W. West, *Dye Sensitization*, Focal Press, London, 1970, p. 105.
- 13 R. A. Pierce and R. A. Berg, *J. Chem. Phys.*, 51 (1969) 1267.
- 14 P. J. Wagner and G. S. Hammond, *Adv. Photochem.*, 5 (1968) 21.
- 15 A. K. Chibisov, *Usp. Khim.*, 39 (1970) 1886.
- 16 J. C. Dalton and N. J. Turro, *A. Rev. Phys. Chem.*, 21 (1970) 499.
- 17 A. K. Chibisov and A. V. Karyakin, in A. A. Krasnovsky (ed.), *Molecular photonics (Molekulyarnaya fotonika)*, Nauka, Moscow-Leningrad, 1970, p. 231.
- 18 A. V. Karyakin and A. K. Chibisov, in B. S. Neporent (ed.), *Elementary photoprocesses in molecules*, Nauka, Leningrad, 1966, p. 296.
- 19 A. K. Chibisov, V. A. Kuzmin and A. P. Vinogradov, *Dokl. Akad. Nauk S.S.S.R.*, 187 (1969) 142.
- 20 A. V. Buettner, *J. Phys. Chem.*, 68 (1964) 3253.
- 21 Yu. I. Lifanov, V. A. Kuzmin, A. V. Karyakin, A. K. Chibisov and I. I. Levkoev, *Izv. Akad. Nauk S.S.S.R., Ser. Khim.*, (4) (1973) 737.
- 22 V. L. Ermolaev, in B. S. Neporent (ed.), *Elementary photoprocesses in molecules*, Nauka, Leningrad, 1966, p. 147.
- 23 G. Porter and F. Wilkinson, *Proc. Roy. Soc.*, A264 (1961) 1.
- 24 A. K. Chibisov, V. A. Kuzmin, G. P. Roitman, I. I. Levkoev and A. V. Karyakin, *Izv. Akad. Nauk S.S.S.R., Ser. Fis.*, 34 (1970) 1288.
- 25 Yu. I. Lifanov, V. A. Kuzmin, A. K. Chibisov and I. I. Levkoev, *Khim. Vys. Energ.*, 7 (1973) 321.
- 26 W. Cooper and K. A. Rome, *J. Phys. Chem.*, 78 (1974) 16.
- 27 E. J. Land, *Proc. Roy. Soc.*, A305 (1968) 457.
- 28 P. G. Bowers and G. Porter, *Proc. Roy. Soc.*, A299 (1967) 348.
- 29 N. J. L. Roth and A. C. Craig, *J. Phys. Chem.*, 78 (1974) 1154.
- 30 E. B. Lifshits, *Dokl. Akad. Nauk S.S.S.R.*, 179 (1968) 596.
- 31 V. I. Permogorov, L. I. Seryukova, E. B. Lifshits and I. I. Levkoev, *Opt. Spektros.*, 31 (1971) 890.
- 32 Yu. I. Lifanov, V. A. Kuzmin, A. K. Chibisov, I. I. Levkoev and A. V. Karyakin, *Zh. Prikl. Spektros.*, 20 (1974) 221.
- 33 A. K. Chibisov, V. A. Kuzmin and Yu. I. Lifanov, *Opt. Spektros.*, 36 (1974) 919.
- 34 K. Kikuchi, H. Kokubun and M. Koizumi, *Bull. Chem. Soc. Japan*, 44 (1971) 1527.
- 35 Yu. I. Lifanov and A. K. Chibisov, *Khim. Vys. Energ.*, 8 (1974) 418.