Translated from *Uspekhi Khimii*, **57**, 1087-1109 (1988) U.D.C. 541.141

Photonics of the Triplet States of Molecular Complexes

E.I.Kapinus and I.I.Dilung

The review surveys the results of studies on the photophysical and photochemical reactions of triplet exciplexes and triplet-excited molecular complexes which are stable in the ground state. These two groups of excited molecular compounds are compared and the influence of the electronic structure on the kinetics and mechanisms of the elementary photoprocesses is analysed. The formation reactions and properties of the triplet exciplexes of various classes of organic substances are examined in detail.
The bibliography includes 110 references.

CONTENTS

I. Introduction 620
II. Photonics of triplet-excited electron donor-electron acceptor complexes 622
III. Triplet exciplexes 624
IV. Formation of the triplet states of molecular complexes as a result of intersystem crossing 629

I. INTRODUCTION

Many photochemical reactions—oxidation-reduction, isomerisation, addition, etc. reactions—proceed with participation of excited organic donor—acceptor molecular compounds. Complex formation keeps the reactant molecules near one another and orients them appropriately in space, thereby promoting the occurrence of the process.

Electron donor—electron acceptor (EDA) complexes or, in other words, charge-transfer complexes (CTC) are formed on charge transfer from an occupied donor orbital to an unoccupied electron acceptor orbital, which results in a decrease in the energy of the molecular system and a chemical bond is formed. According to Mulliken,[1] the molecular complex is a resonance hybrid of the so called non-bonded (AD) and ionic (A^-D^+) structures†:

$$AD \leftrightarrow A^-D^+ , \qquad (1)$$

In the hypothetical non-bonded state AD, there is no interaction between the molecules forming part of the complex. A dissociative potential surface corresponds to the complex (Fig.1). A potential surface of the bonding type corresponds to the "pure" ionic state A^-D^+. In this state, the components are held together by Coulombic attraction forces. If the structures A and D and A^-D^+ are capable of interconversion (1), then a mixed state arises and is described by the wave function

$$\psi_N = a_1\psi(AD) + a_2\psi(A^-D^+) , \qquad (2)$$

and has less energy than AD or A^-D^+. The new state has a potential surface with a minimum corresponding to the equilibrium configuration of the real complex.

In describing the excited states of molecular compounds, one must also take into account the locally excited structures—hypothetical structures without interaction between the components with the excitation localised on A or D (A^*D or AD^*):[2]

$$^1\psi_E = b_1^1\psi(AD) + b_2^1\psi(A^-D^+) + b_3^1\psi(A^*D) + b_4^1\psi(AD^*) . \qquad (3)$$

† The letter A denotes an electron acceptor molecule, D denotes an electron donor molecule, and an asterisk denotes an electronically excited species.

The contribution of each term in Eqns.(2) and (3) is determined by the energy of the corresponding state. The energies of the structures A^*D and AD^* are close to those of the corresponding excited molecules A^* and D^*. For the majority of organic CTC, the energies of the "pure" singlet and triplet charge-transfer states do not differ greatly. For gas-phase systems, they are estimated with the aid of the equation[1]

$$E(A^-D^+) = IP - EA - W$$

where IP is the ionisation potential of the electron donor, EA the energy of the electron affinity of the acceptor, and W the energy of the Coulombic interaction of the ions in the charge-transfer state. In the calculation of the energies of the structures A^-D^+ of the complexes in solutions, it is essential to take into account the solvation energy ΔH_s:

$$E(A^-D^+) = IP - EA - W - \Delta H, \qquad (5)$$

The difficulty of calculating the latter can be obviated by using the corresponding electrochemical potentials:

$$E(A^-D^+) = E_{1/2}^{ox} - E_{1/2}^{red} - W . \qquad (6)$$

Naturally, in this case $E(A^-D)$ refers to the solvent in which $E_{1/2}^{ox}$ and $E_{1/2}^{red}$ were determined. In order to convert it into the expressions for other media, it is necessary to introduce correction terms into Eqn.(6). The Coulombic interaction energy of two molecular ions in Eqns.(4)—(6) is usually substituted by the electrostatic interaction energy of two unlike points charges (e) separated by a distance equal to the sum of the molecular radii r (usually ~0.5 nm) in a medium with a dielectric constant ε:

$$W = \frac{e^2}{\varepsilon \cdot r} . \qquad (7)$$

In more accurate calculations of the attraction energy of the ions, account is taken of the distribution of charges in space.[3]

In those cases where $E(AD) \ll E(A^-D^+) \ll E(A^*D), E(AD^*)$, the charge-transfer state is the lowest excited state of the complex. For the opposite relations $E(A^-D^+) \gg E(A^*D), E(AD^*) \gg E(AD)$, the

locally excited state is the lowest. If the energies of the locally excited and charge-transfer state are similar, their effective mixing takes place.

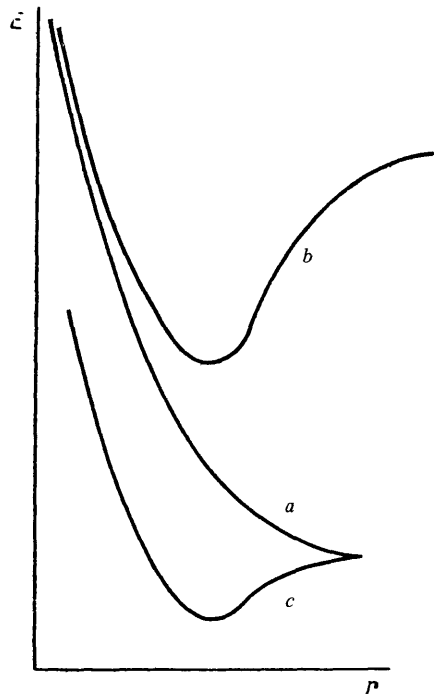


Figure 1. The potential energy (E) curves for the non-bonded state (a), the charge-transfer state (b), and the molecular complex (c); r is the distance between the species.[1]

Depending on the fraction of the charge-transfer state in the ground state, which to a large extent determines the stability of the donor–acceptor complex, it is possible to distinguish two limiting types: highly stable complexes with virtually complete charge transfer and complexes in which there is no charge transfer and no interaction of the components associated with it. Compounds of the latter group exist only at the instant of the collision of their reactant molecules (contact CTC). They are formed from the molecules of weak donors and weak acceptors.[4] Very powerful electron donors and electron acceptors give rise to complexes of the other extreme type mentioned above–radical-ion salts in which the energies of charge-tgransfer states are similar to or even lower than the energies of the non-bonding structures.[5]

The ground state of contact complexes involves repulsion for intermolecular distances corresponding to the equilibrium configurations of the molecular compounds. When the components are moved apart to a distance of approximately 0.3 nm, a small minimum appears on the potential surface for the system, which is due to relatively long-range but weak universal intermolecular forces.[6] Such van der Waals complexes have been detected and investigated with the aid of the special technique of cooled molecular beams.[7] However, in liquid solutions at room temperature, van der Waals forces are not able to ensure any appreciable stability of the molecular compounds formed on collision of the molecules of weak electron donors and weak electron acceptors.

The conversion of the contact complexes into a polar excited state greatly strengthens the bond between the components. Such donor–acceptor compounds, which exist virtually only in the excited state, have been called exciplexes or heteroexcimers.[8] Following the loss of the electronic excitation energy, the exciplexes pass to a state with a dissociative potential surface and decompose. As a consequence of the large difference between the energies $E(A^-D^+)$ and $E(AD)$, in exciplexes, in contrast to the excited CTC, there is no interaction between the structures AD and A^-D and the stabilisation of the ground state induced by such interaction is lacking (Fig.2).

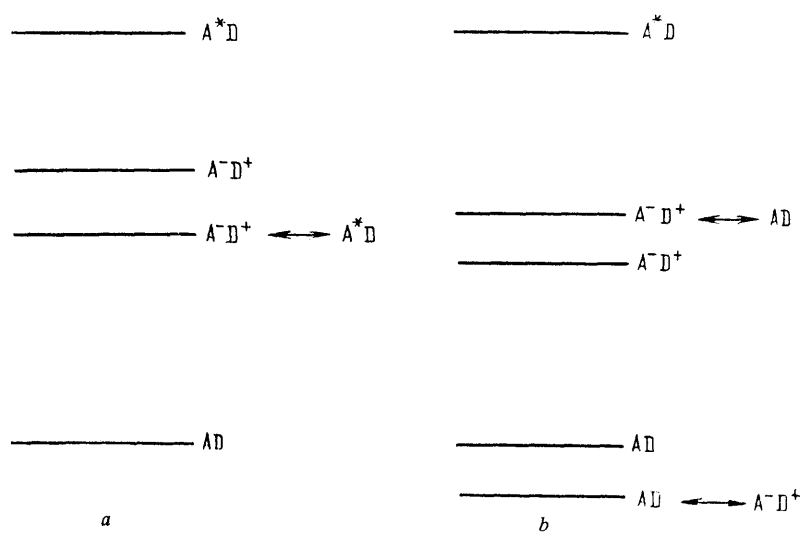


Figure 2. The energy level scheme for exciplexes (a) and CTC (b).

The rule of overall spin conservation of the system holds in electron exchange. Charge-transfer triplet states do not therefore interact with the AD state and the term containing AD does not enter into the expression for the wave function for the triplet-excited molecular state $^3\psi_E$:

$$^3\psi_E = c_1^3\psi(A^*D) + c_2^3\psi(A^-D^+) + c_3^3\psi(AD^*) \quad . \qquad (8)$$

Thus the triplet states of both exciplexes and CTC are not perturbed by the interaction with the non-bonded state AD. From this point of view, there are no differences between the triplet-excited EDA compounds, which are stable in the electronic ground state, and the triplet exciplexes. The study of both groups of molecular complexes yields mutually complementary information.

The excited CTC can be obtained on direct photoexcitation of molecular compounds:

$$AD \xrightarrow{h\nu} {}^1(A^{\delta-}D^{\delta+})^* \rightsquigarrow {}^3(A^{\delta-}D^{\delta+})^* \quad .$$

In liquid solutions, complex formation reactions also take place between excited and unexcited molecules

$$^1A^* + D \rightleftarrows {}^1(A^{\delta-}D^{\delta+})^* \quad ,$$
$$^3A^* + D \rightleftarrows {}^3(A^{\delta-}D^{\delta+})^* \quad .$$

Both complexes with a dissociative ground state and molecular compounds, which are fairly stable in the unexcited form, are formed via a dynamic pathway.

Systematic studies on the photonics of molecular compounds have been carried out since the beginning of the 1950's. Initially organic CTC having a stable ground state were investigated.[8-11] The study of Leonhard and Weller[12] initiated an avalanche of publications devoted to singlet exciplexes. The triplet exciplexes, discovered at the beginning of the 1970's,[13,14] have been studied much less than the singlet exciplexes. This is due to the complexity of their experimental detection and investigation: in liquid solutions, the triplet exciplexes do not as a rule luminesce. These excited compounds evidently play an important role in many photochemical processes. Their photophysical properties differ significantly from those of the singlet exciplexes. The insufficiency of experimental data is fully compensated by data obtained in studies on CTC. As already stated, the electronic structures of the triplet exciplexes and triplet-excited EDA complexes are identical, which makes it possible to construct an integral picture of this important group of excited species on the basis of seemingly unrelated facts.

II. PHOTONICS OF TRIPLET-EXCITED ELECTRON DONOR–ELECTRON ACCEPTOR COMPLEXES

1. Luminescence-spectroscopic Properties

The phosphorescence spectra of molecular complexes, whose triplet state is locally excited, are very similar to the corresponding spectra of the "free" electron acceptors or donors. An example of such molecular compounds is provided by the complexes of trinitrobenzene, tetracyanobenzene, and tetrachlorophthalic anhydride with aromatic hydrocarbons – benzene, toluene, and naphthalene.[16-19]

Detailed analysis of the phosphorescence spectra[16-19] nevertheless reveals distinctive features of the complex formation. For example, the vibrational structure of the phosphorescence spectra of the CTC is more closed compared with the phosphorescence spectra of the corresponding components and furthermore vibrations with lower frequencies are manifested in them.[18] In many cases a small but nevertheless appreciable bathochromic shift of the phosphorescence spectra of the electron donor, depending on the donor–acceptor parameters of the components of the EDA complexes, is observed.[18] For example, the 0–0 transition in the phosphorescence of naphthalene occurs in the region of 21.3×10^{-3} cm^{-1}, while for the complex of naphthalene with dichloro-*o*-phthalic anhydride it occurs in the region of 21.37×10^3 cm^{-1} (Table 1).

Table 1. The positions of the bands ($\tilde{\nu}_{phosph}$) and the phosphorescence quenching times (τ_{phosph}) for the EDA complexes of naphthalene in frozen solutions.

Electron acceptor	Solvent	$\tilde{\nu}_{phosph}$, 10^{-3} cm^{-1}	τ_{phosph}, s	Refs.
Dichloro-*o*-phthalic anhydride	PEI	21.37	2.1	[26]
Tetrachloro-*o*-phthalic anhydride	PEI	21.3	1.65	[26]
Tetrabromo-*o*-phthalic anhydride	PEI	21.2	0.29	[26]
Pyromellitic anhydride	n-propyl ether	21.3	1.8	[23]

Note: PEI is a 3 : 1 mixture of isopropyl ether and isopentane.

The lifetimes of the phosphorescent locally excited states of molecular complexes are usually shorter than the lifetimes of the corresponding states of the "free" components of the CTC,[16-18] which may serve, together with spectroscopic data, as evidence for complex formation. However, if the acceptor contains no heavy atoms, then complex formation does not affect greatly the phosphorescence lifetimes. As for the usual organic molecules, the introduction of heavy atoms into the complex shortens appreciably the duration of the phosphorescence.[20]

Thus the electronic transitions in the locally excited triplet states of molecular compounds can be regarded as electronic transitions perturbed by complex formation and occurring in the photoexcited component. Complex formation intensifies the spin–orbit coupling, which fixes in its turn the single S_1 and the triplet T_0 states, and the radiative transitions to the ground state $S_1 \rightarrow S_0$ and $T_0 \rightarrow S_0$.[21] This results in the acceleration of intersystem processes, which is manifested by a shortening of the lifetimes of the phosphorescent states of the photoexcited components.

The triplet–triplet absorption spectra of the CTC of this group resemble the triplet–triplet absorption spectra of the corresponding "free" CTC components. However, in these spectra too one can observe distinct features of complex formation—the broadening of the absorption bands and the appearance in the long-wavelength part of the spectrum of bands due to charge transfer from the excited triplet state localised on one of the components to the unoccupied level of the electron acceptor.[22]

Complexes with the lowest triplet charge transfer states have completely different phosphorescence spectra. These spectra consist of structureless bands due to reverse charge transfer, whose maxima undergo a hypsochromic shift with increase in the electron affinity of the acceptor.[16-19] The duration of the phosphorescence of the EDA complexes of this group is shorter, as for the previous

group, then the duration of the phosphorescence of the "free" component with the lowest triplet state energy when this is closest to the energy of the triplet state of the complex.[23] The shortening of the phosphorescence lifetime as a result of complex formation is caused, according to Hayashi et al.,[23] by a change in the rates of both radiative and non-radiative transitions.

The triplet–triplet absorption spectra of complexes of this group have been studied in detail in relation to the CTC of tetracyanobenzene with durene and hexamethylbenzene.[25] The absorption spectra of molecules in the charge transfer state do not resemble the triplet–triplet absorption spectra of the "free" components. They manifest electronic transitions involving reverse charge transfer and transitions leading to locally excited states of the ion:[25]

$$A^-D^+ \begin{cases} \longrightarrow AD^* \\ \longrightarrow A^{-*}D^+ \\ \longrightarrow A^-D^{+*} \end{cases}$$

The triplet locally excited complexes and the triplet complexes in the state involving virtually complete charge transfer between the components can be regarded as corresponding to extreme points in the series of excited complexes in which the degree of charge transfer can vary from 0 to 100% depending on the nature of the reactants. The change in the degree of polarity of the excited CTC influences strongly the luminescence-spectroscopic properties. As the degree of charge transfer is altered, the lifetimes and the positions of the phosphorescence bands change, and the absorption bands of the triplet-excited complexes are displaced.[2,23–25] These effects are strongest when the degree of charge transfer exceeds 50%.[24]

2. Dissociation of Triplet-Excited CTC into Ions

The products of the total electron transfer can be formed on dissociation of both singlet- and triplet-excited EDA complexes. Each of these mechanisms has its specific features.

The degree of involvement of states of different multiplicity in ionic dissociation processes of the CTC is determined in the first place by the thermodynamic conditions. In solvents with a high dielectric constant ε, the energy of the charge-transfer state is close to the energy of the state with dissociated ions. The EDA complexes in the charge-transfer state can therefore dissociate into free ions in highly polar solvents. On the other hand, locally excited complexes are unable to decompose spontaneously into ions.

The numbers of the free radical-ion species formed on dissociation of singlet- and triplet-excited states are determined by the rates of internal conversion, ionic dissociation, and intersystem processes involving the formation and deactivation of triplet states. However, the kinetics of these reactions have been scarcely investigated.

It is usually regarded as fully demonstrated that radical-ions are formed as a result of the dissociation of the triplet-excited CTC if the test system satisfies the following features.

1. The increase in the concentration of the radical-ion products occurs in the microsecond range parallel to the decrease in the intensity of the phosphorescence or the triplet–triplet absorption. For example, the photoexcitation in the charge transfer band of the complex of tetracyanobenzene with tetrahydrofuran in dichloroethane is accompanied by the formation of the radical-ion of the electron acceptor in the course of 300 μs. The time during which the concentration of the products of the ionic dissociation of the CTC increases then corresponds to the quenching time of the phosphorescence of the complex.[27]

2. Oxygen is an effective quenching agent for triplet states[21] and the yield of the products of the ionic dissociation of the triplet-excited CTC therefore diminishes as the solutions are saturated with oxygen. However, in the analysis of the influence of oxygen on the formation of radical-ion species it is essential to take into account the fact that this criterion is less rigorous, because oxygen can also quench a singlet-excited state and can accelerate intersystem crossing. For this reason, the data concerning the influence of oxygen on the yields of the radical-ions formed on photoexcitation of CTC require in general a careful kinetic analysis.[28]

3. If the radical-ion species arise as a result of the dissociation of the CTC in the triplet state, then the introduction into the solution of sensitisers, which are capable, after the transition to the triplet state, of transferring their energy to the complexes and of exciting their triplet states, increases the yield of the products of the total electron transfer.[29,30]

The triplet mechanism of the formation of radical-ion species operates only in the case of complexes whose lowest triplet states are charge-transfer states. The complexes of tetracyanoethylene, tetracyanobenzene, and pyromellitic dianhydride with π- and *n*-type electron donors, such as mesitylene, α-methylstyrene, dioxan, tetrahydrofuran, etc. serve as examples.[29,30]

If the lowest triplet states of the CTC belong to the class of locally excited states, then the ionic dissociation of the triplet-excited complexes does not take place. However, even in this case radical-ions may be formed following the absorption by the triplet-excited complexes of a second light quantum,[34–36] which converts the complex into a high-lying charge-transfer state:

$$AD \xrightarrow{h\nu} {}^1(AD)^* \rightarrow {}^3(A^*D) \xrightarrow{h\nu} {}^3(A^-D^+)^* \rightarrow A^- + D^+ .$$

Two-quantum CTC photodissociation processes have been observed experimentally from the quadratic dependence of the yield of radical-ions on the intensity of the exciting light. Analysis of such relations shows that the photoreaction of the complexes of tetracyanobenzene, pyromellitic and tetrachlorophthalic anhydrides with ether proceeds via a two-quantum mechanism, while the reaction of the complexes of the same acceptors with methyltetrahydrofuran, which is a stronger electron donor, involves a one-quantum mechanism.[35] In both the former and the latter group of complexes, the lowest triplet states belong to the locally excited type. The characteristics of the photochemical behaviour of molecular compounds of the first group are determined by the fact that in their molecules the first singlet excited states belong to the class of locally excited states. The dissociation of such molecular compounds is possible only after excitation to high-lying charge-transfer states.

Cases where both singlet- and triplet-excited states of EDA complexes are charge-transfer states are of considerable interest. As already stated, the energies of these compounds are similar and radical-ions can therefore form on dissociation of the CTC in either state. However, this most complex case has been scarcely investigated. It is only known that the relative efficiencies of the singlet and triplet channels leading to the formation of the products of the total electron transfer depend on the polarity of the medium. For example, in moderately polar solvents, the ionic dissociation of excited CTC of tetracyanobenzene and pyromellitic-dianhydride with ether, dioxan, and tetrahydrofuran takes place after the conversion of the complex to the triplet state, while in highly polar solvents—acetonitrile and butyronitrile—it occurs as a result of the decomposition of the singlet-excited CTC.[33]

III. TRIPLET EXCIPLEXES

The interaction of the triplet molecules of porphyrins, carbonyl compounds, dyes, and compounds of other classes with electron donor or electron acceptor molecules results in the formation of excited intermediates, which are frequently referred to in the literature as triplet exciplexes. Nevertheless, these excited molecular compounds are in essence triplet-excited CTC, which have a bonding ground state. This is manifested by the fact that the components of the majority of the so-called triplet exciplexes in the electronic ground state are capable of reacting with one another to form relatively stable molecular compounds. Specific examples will be given below. The application of the term exciplex to triplet-excited CTC is justified, because these excited species are formed via a dynamic mechanism, like the "true" exciplexes. Furthermore, the triplet states of both groups of molecular compounds are not perturbed as a result of the interaction with the non-bonded state.

1. Triplet Exciplexes of Porphyrin Compounds

The tetrapyrrole pigments undergoing reversible oxidation-reduction reactions in the cells of living organisms fulfil a series of key functions in photobiological processes. Studies under model conditions, including solutions and photochemical oxidation-reduction reactions with participation of tetrapyrrole pigments of all types—porphyrins, phthalocyanines, chlorines, etc.—have therefore developed widely.[38] The triplet states of the pigments play the main role in these photoreactions,[39] which is due to the long lifetime of the triplet states of many porphyrin compounds, the high quantum yields of the intersystem crossing, the pronounced electron-donating properties of the triplet-excited molecules, and the spin rules prohibiting the recombination of the primary radical-ion pairs formed. The interaction of the triplet molecules of the tetrapyrrole pigments with electron donors or acceptors shortens the lifetime of the triplet molecules and leads to the formation of "free" products of the total electron transfer in polar media.[38,39] In non-polar solvents, quenching may be accompanied by the appearance of triplet exciplexes.

The formation of a triplet exciplex was first observed in a study[13] in which the products of the pulse excitation of the solution of Zn-tetraphenylporphin in benzene containing *p*-benzoquinone were investigated. As a result of the action of the light pulse in this system, a variable absorption appeared, the kinetics of the disappearance of which were described by a complex two-component curve. It was suggested[13] that one of the components describes the destruction of a triplet exciplex. Subsequently analogous data were obtained in the study of the interaction of the triplet molecules of certain other porphyrins,[14,40-42] phthalocyanines,[42] and chlorophyll[43,44] with electron acceptors.

The hypothesis of the formation of triplet exciplexes on quenching of the triplet states of porphyrin molecules by electron acceptors has been confirmed by the study of the absorption spectra of the intermediates and of their deactivation by energy acceptors, in the study of the slow fluoroescence and pulse photoconductivity of the solutions, and by careful analysis of the kinetic curves.

It has been established[40] that the absorption spectrum of the "long-lived" component of the kinetic curve differs appreciably although not very greatly from the absorption spectra of triplet molecules. The spectra of these intermediates differ also from the absorption spectra of the corresponding radical-ions. The lifetime of the intermediate species shortens after the introduction into the solution of oxygen, azulene, tetracene, and perylene—substances whose molecules have low energies of the triplet states and which can therefore serve as energy acceptors in relation to the triplet porphyrin exciplexes. The rate constants for the quenching of the triplet exciplexes via these substances are close to the diffusion rate constants. The formation of the triplet chlorophyll exciplexes by reaction with organic electron acceptors is accompanied by the appearance of a slow fluorescence, whose spectrum agrees with the well known fast fluorescence spectrum of chlorophyll.[43,44] The appearance of the slow fluorescence in solutions where there are virtually no free triplet chlorophyll molecules can be caused only by processes involving triplet exciplexes. When electron acceptors are added to weakly polar chlorophyll solutions at concentrations sufficient for the complete quenching of the triplet states, an increase in photoconductivity is not observed.[40]

The triplet exciplexes of porphyrin compounds can be regarded as locally excited complexes with a relatively small contribution by the state involving charge transfer from the porphyrin to the oxidant. This is indicated by the absorption spectra of the complexes, which resemble the absorption spectra of the corresponding porphyrins in the triplet state.[40,42-44] This fact may at first sight appear to be unexpected because porphyrins are powerful electron donors.[45] However, together with very pronounced electron-donating properties, porphyrins are characterised by low energies of the triplet states (~ 150 kJ mol^{-1}),[38] so that the lowest triplet state of the EDA complexes of porphyrins with many electron acceptors is a locally excited state.

The contribution of the wave functions of the polar states to the wave function of the excited complex depends on the nature of the reactants, as stated above. With increase in the electron-accepting capacity of the oxidant forming part of the exciplex, the absorption spectrum of the latter becomes increasingly different from the absorption spectrum of the triplet molecules and begins to resemble increasingly the absorption spectrum of the corresponding radical-cation.[46] Even in the case of powerful electron acceptors such as dinitrobenzenes and dinitronaphthalenes, the absorption spectrum of the exciplex nevertheless differs from that of the corresponding radical-cation. Naturally, bands resembling the absorption bands of the radical-anions should also be present in the absorption spectra of the exciplexes. Owing to their low intensity, they are masked by the bands of the radical-cation.

The conclusion that the lowest triplet states of the exciplexes of many tetrapyrrole pigments formed by reaction with electron acceptors have a predominantly locally excited character has been confirmed by thermodynamic calculations.[47] Thus in non-polar media the energy of the triplet state of chlorophyll is lower than the energy of the triplet charge-transfer states of its complexes with nitrobenzene, dinitrobenzene, and *p*-benzoquinone. The triplet chlorophyll exciplexes are therefore locally excited complexes with a small admixture of the charge-transfer state.

With increase in solvent polarity, the energy of the charge-transfer state diminishes owing to its stabilisation by the dipoles of the medium. As a result of this, the formation of radical-ions becomes easier in highly polar solvents than that of exciplexes, which has been confirmed by flash photolysis data: the photoexcitation of solutions of chlorophyll and organic oxidants in highly polar media leads to the formation of a high yield of chlorophyll radical-cations with a characteristic absorption spectrum.[38,39,47]

The inversion of the levels of the locally excited state and the charge-transfer state can occur also without a significant change in solvent polarity after the introduction into non-polar solutions of

polar additives, which are capable of solvating selectively the exciplexes, inducing a decrease in the energy of the charge-transfer states. As an example, one may quote the results of a study[48] in which the influence of added ethanol, acetonitrile, and *N*-methylformamide on the lifetimes and spectroscopic properties of the triplet exciplexes of Zn-aetioporphyrin I with *p*-nitrotoluene was investigated. It was found that the presence of *N*-methylformamide in the solution at a concentration of 0.01 M shortens greatly the lifetime of the triplet exciplex. The increase in the concentration of the additive to 0.02 M is accompanied by the appearance in the spectrum of the variable-absorption bands of the radical-cations. Since such low concentrations of polar substances hardly increase the dielectric constant of the medium, the formation of free radical-ions in these solutions is therefore unlikely. The spectral changes can be explained by the inversion of the energy levels of the locally excited state and the charge-transfer state.

It has also been observed[49] that the quenching of the photo-induced absorption of chlorophyll solutions containing an electron acceptor has two-component kinetics. However, the authors of the above publication were not able to detect any intermediate products with a lifetime greater than 20 ns on interaction of the triplet molecules of the zinc complexes of porphyrins with *p*-benzoquinone and *p*-dinitrobenzene.[49,50] This served as a basis for the conclusion that the kinetic and spectral changes, explained by the formation of triplet exciplexes, are in fact due to the presence of impurities in the specimens consisting most probably of the metal-free pigments. It has to be said that, with the aid of the traditional methods of purification, it is easy to obtain spectroscopically pure preparations of tetrapyrrole pigments in which the content of the main substance is greater than 99.5%. Since metalloporphyrins have characteristic absorption spectra, it follows that extraneous coloured substances can be readily detected spectroscopically. The problem of the genesis of the two-component curves described can be solved by careful analysis of the kinetic curves. This problem will be considered in the next Section. It is possible to identify tentatively the causes of the failure of Renge and co-workers[49,50] to detect the triplet exciplexes of zinc-porphyrins with oxidants. It may be that the solvents or the metalloporphyrins themselves contained polar impurities capable of quenching the exciplexes via the mechanism considered by Roy and Whitten.[48] This may be promoted by the tendency of metalloporphyrins to form complexes.

2. Kinetics of the Quenching Processes with Participation of the Triplet Exciplexes of Porphyrin Compounds

The interaction of triplet-excited porphyrin molecules with electron acceptors is described, like the reactions of the singlet-excited molecules of aromatic substances, by a kinetic scheme which takes into account the possible occurrence of induced quenching—a process first proposed by Nakashima et al.[51] and Kuz'min and Sadovskii[52]—in parallel with the formation of exciplexes:

$$D^* + A \underset{k_{-1}}{\overset{k_1}{\rightleftarrows}} (AD)^* \xrightarrow{k_2} D + A \ , \tag{9}$$

$$D^* + A \xrightarrow{k_4} D + A \ , \tag{10}$$

$$D^* \xrightarrow{k_3} D \ . \tag{11}$$

The standard formal kinetic treatment of this scheme shows[41,42,46] that, subject to the condition $[A] \gg [D^*]$, the time variations of D^* and $(AD)^*$ are described by

$$[D^*] = a_1 \exp(-\lambda_1 t) + a_2 \exp(-\lambda_2 t) \ , \tag{12}$$

$$[(AD)^*] = b[\exp(-\lambda_1 t) - \exp(-\lambda_2 t)] \ . \tag{13}$$

Since the absorption spectra of both components of the kinetic curve usually overlap, the overall absorption is recorded under the conditions of flash photolysis:

$$D = D_t + D_e = \epsilon_t l[D^*] + \epsilon_e l[(AD)^*] = F_1 \exp(-\lambda_1 t) + F_2 \exp(-\lambda_2 t) \ . \tag{14}$$

In Eqns.(12)–(14), we have

$$\lambda_{1,2} = B/2 \pm (B^2/4 - C)^{1/2} \ ,$$

$$B = k_2 + k_{-1} + (k_1 + k_4)[A] = \alpha + \beta[A] \ ,$$

$$C = k_3(k_2 + k_{-1}) + (k_1 k_4 + k_2 k_4 + k_{-1} k_4)[A] = \gamma + \delta[A] \ ,$$

where ε_t and ε_e are the molar extinction coefficients of the triplet molecules and exciplexes respectively and l is the length of the cuvette. The pre-exponential factors a_1, a_2, b, F_1 and F_2 can be found by the usual procedures from the initial conditions.[46] In Eqn.(14), D_e and D_t are the optical densities due to the absorption of the triplet-excited molecules and the triplet exciplexes.

The lifetimes of the triplet exciplexes τ_e can be found from the dependence of λ_2 on the concentration of the quenching agent A:[42]

$$1/\tau_e = \lambda_{lim} = \lim_{[A] \to \infty} \lambda_2 = k_2 + k_{-1} k_4/(k_1 + k_4) \tag{15}$$

Eqn.(15) shows that the deactivation of the triplet exciplex can take place in two ways: via the direct intersystem degradation of the electronic excitation energy and as a result of the dissociation of the exciplex with subsequent deactivation of the triplet molecules induced by the quenching agent. The efficiency of each of these channels is characterised by the corresponding terms of Eqn.(15).

If the quenching process proceeds via a state involving the formation of an intermediate excited complex, then it follows from Eqns.(12)–(14) and (1), over a wide range of quenching agent concentrations, the dependences of λ_1 and λ_2 on [A] do not obey the Stern–Volmer equation,[42] which can be written in the form

$$\lambda_{1,2} = \frac{1}{\tau_0} + k_q[A] \ ,$$

where k_q is the quenching rate constant, and (2), as the quenching agent concentration is varied, the intensities of the first and second components of the kinetic curve vary in such a way that $A_1 + A_2 = \text{const}$.[46]

For systems where $k_4 \ll k_1$, the lifetimes of the triplet exciplexes of porphyrins with electron acceptors hardly differ from the lifetimes of the triplet molecules of the corresponding porphyrins in liquid degassed solutions.[42,53] The latter is entirely understandable, because the processes leading to the deactivation of the localy excited complexes can be regarded, as stated above, as weakly perturbed electronic transitions in the photoexcited component of the exciplex. If the rate of deactivation of the locally excited component is high, for example, as a consequence of the spin–orbit coupling, then the lifetime of the corresponding locally excited exciplex is short. Exciplexes of the ruthenium complexes of phthalocyanine with certain organic electron acceptors can serve as confirmation of this.[54] Depending on the axial ligand, the lifetimes of the triplet molecules of the "free" metallophthalocyanine range from 0.43 to 0.32 μs, while the lifetimes of the exciplexes range from 0.77 to 0.18 μs. Like the majority of the exciplexes examined above, these exciplexes are characterised by a low contribution of the charge transfer states. It is of interest that in certain cases the lifetime of the exciplex of the ruthenium complex of phthalocyanine was several times longer than the lifetime of the triplet molecules under the same conditions, which can be explained by the change in the rates of the non-radiative transitions as a result of complex formation.

If the second term in Eqn.(15) is sufficiently large compared with the first, then the lifetimes of even locally excited exciplexes can depend on the nature of the oxidant involved in the complex formation. The data in Table 2, which presents the values of λ_{lim} found from the dependences of λ_2 and τ_e on the oxidant concentration, serve as an illustration of this finding. In the table, the quenching agents are arranged in order of weakening electron accepting properties, while the porphyrins are arranged in order of weakening electron-donating properties. It can be seen that, for each metalloporphyrin, exciplexes with both strong and weak electron acceptors can have high values of λ_{lim}. The values of λ_{lim} which do not differ greatly from the rate constants for the pseudounimolcular deactivation of triplet porphyrin molecules ($\sim 10^3$ s^{-1}) lie in an intermediate region. The lifetimes of such triplet exciplexes, like those of the majority of triplet molecules,[9,21] are determined by the rates of quenching by residual oxygen, impurities, and the solvent. The region of long-lived exciplexes is differentiated in Table 2, an arbitrary boundary being designated by a dashed line.

Table 2. The rate constants for the deactivation of the triplet exciplexes (10^{-3} λ_{lim}, s^{-1}) of metalloporphyrins with electron acceptors in toluene solutions.[53,56]

Quenching agent	TPPMg	TPPAlOH	TPP GaOH	PhcMg	PhcAlCl	TPPInOH
2,5-Dichloro-*p*-benzoquinone	—	6.2	—	—	—	—
2,4,7-Trinitrofluorenone	1.1	10	—	—	—	10
Chloro-*p*-benzoquinone	2.2	4.2	—	—	—	—
Picryl chloride	1.2	—	12	—	—	7.2
p-Benzoquinone	2.1	1.2	—	5.8	4.8	
Toluquinone	1.8	1.5	—	7.7	3.1	15
1,4-Naphthoquinone	—	1.1	—	2.2	1.5	14
9,10-Phenanthrenequinone	—	1.0	—	—	—	—
2,6-Di-t-butyl-*p*-benzoquinone	1.9	0.7	—	3.6	—	30
o-Dinitrobenzene	1.0	1.2	1.2	—	—	8.2
Trinitrotoluene	—	—	0.9	—	—	—
Duroquinone	1.4	1.2	—	—	—	—
m-Dinitrobenzene	—	—	1.2	—	—	—
o-Chloronitrobenzene	1.2	—	4.5	—	—	—
o-Nitrotoluene	2.9	—	13	—	—	—
3-Nitro-*o*-xylene	4.3	—	—	—	—	—
NN-Dimethyl-*p*-nitroaniline	4.7	—	—	—	—	—

Note: TPP = mesotetraphenylporphin and Phc = tetra-t-butylphthalocyanine.

The size of the region of reduction potentials of the quenching agent $E_{1/2}^{red}$ for which low values of λ_{lim} are observed ($\sim 10^3$ s^{-1}) is determined by the electron-donating properties of the porphyrin. The tabulated data show a tendency towards a narrowing of the region of long-lived exciplexes as the electron-donating capacity of the excited molecules diminishes. The greatest number of long-lived exciplexes are therefore formed by the magnesium complex of mesotetraphenylporphin—one of the metalloporphyrins with the most pronounced electron-donating properties.

The complex dependence of the rate of deactivation of triplet exciplexes on the reduction potential of the quenching agent described above can be explained by the fact that the triplet exciplex can be deactivated not only by direct intersystem degradation but also as a consequence of dissociation with subsequent quenching agent-induced deactivation of the triplet-excited molecules formed. The relative efficiencies of these channels are determined by the ratios of the constants for the formation of the triplet exciplex, the induced quenching, and dissociation. This problem has been analysed in detail.[53,55]

In systems which exist in regions along the boundary of the "peninsula" (Table 2) of the long-lived exciplexes, we have $k_4 \gtrsim k_1$[53] and therefore the two terms of Eqn.(15) are comparable and both mechanisms of the deactivation of triplet molecules described are important in the description of the process.

The size of the quenching agent concentration range in which distinct two-component quenching curves are observed depends on λ_{lim}. For systems with high λ_{lim}, the quenching times for the first and second components of the kinetic curve can remain close to one another even if the concentration of the quenching agent changes appreciably (by several orders of magnitude). Bearing in mind also that the intensity of the first component diminishes with increase in the concentration of the quenching agent, the kinetics of the disappearance of the induced absorption in such systems remain virtually monoexponential over the entire accessible range of variation of the quenching agent concentration. In this case, the process proceeds in a quasi-stationary manner. The characteristic time of such a curve varies with increasing quenching agent concentration in accordance with a hyperbolic law:[53]

$$1/\tau = \frac{\alpha + \beta [A]}{\gamma + \delta [A]} , \qquad (16)$$

tending to the limiting value defined by Eqn.(15).

In a study of systems which are remote from the peninsula of the long-lived exciplexes, the formation of triplet-excited complexes cannot be observed by kinetic methods. Evidently the exciplexes in such systems have such short lifetimes that the dependence of $1/\tau$ on [A] becomes linear over the entire accessible range of quenching agent concentrations. Such short lifetimes of the triplet exciplexes can be caused solely by high dissociation and deactivation rate constants, because even for systems in the boundary regions the ratio $k_4/(k_1 + k_4)$ does not differ greatly from unity—its maximum value.

The hyperbolic form of the relation between $1/\tau$ and [A] [Eqn.(16)] can be explained by the fact that, with increase in the quenching agent concentration, the equilibrium in the exciplex formation reaction (9) shifts towards the excited complex. Such relations can be regarded as evidence for the reversible formation of the excited complexes when triplet molecules are quenched.[56,57] The equilibrium character of the formation by triplet-excited molecules of complexes with the quenching agent was observed in a study of the quenching of the triplet-excited states of the palladium complex of mesotetraphenylporphin by *NN*-dimethylaniline in liquid degassed solutions.[58] It has to be said that Pd-porphyrins have the fairly rarely encountered property of an intense phosphorescence in liquid deaerated solutions.[38] In a study of the quenching of the above system, characteristic negative deviations from the linear Stern–Volmer relation, associated with the formation of triplet exciplexes, were observed. Calculations showed that the equilibrium stability constant of the triplet exciplex of the above porphyrin with *NN*-dimethylaniline is approximately 10 litre mol^{-1}.[58] It is of interest that Mercer-Smith et al.[58] failed to observe a change in the phosphorescence spectra of the porphyrin after the introduction of an amine into the solution, which can be due to the fact that the triplet exciplex does not phosphoresce or, if it does phosphoresce, then it is locally excited. As already stated, the spectra of such complexes are virtually identical with the spectra of the corresponding components.

Being in the ground state, the molecules of the porphyrins and the electron acceptors can form relatively stable molecular complexes with one another.[58] Taking this factor into account, the majority of

the triplet exciplexes considered in the present Section should be included among excited EDA complexes, using the terminology proposed in the introductory Section. In the triplet-excited state, organic CTC are much more stable than in the ground state: the corresponding equilibrium constants for the excited states are 3 – 5 orders of magnitude greater than for the ground state.[42,46,60] The above triplet exciplexes are much more stable than the stable highly polar singlet exciplexes of aromatic compounds with oxidants or reductants.[61,62]

The high stability of the triplet exciplexes of porphyrins is somewhat unexpected, because, like other locally excited complexes, they cannot have high enthalpies of formation. Charge transfer stabilises them only slightly. The exciton interaction is also negligibly weak, because the energy of the triplet state of porphyrin is smaller by at least 100 kJ mol^{-1} than the energies of the lowest triplet states of the electron acceptors listed in Table 2.

The high stability of the triplet exciplexes is due to their high positive entropies of formation,[60,63] whose origin can be accounted for by a change in the structure of the solvation shells of the reactant molecules. The thermodynamic parameters of the exciplexes satisfy the following general compensation relations regardless of their multiplicity[60,63] (Fig.3):

$$\Delta H = \Delta H_0 + \beta_K \Delta S \ , \qquad (17)$$

where ΔH and ΔS are the enthalpy and entropy of the complex formation reaction, ΔH_0 = –17.7 kJ mol^{-1}, and β_K = 244 K. In plotting Fig.3 and in the calculation of the parameters of Eqn.(7), use was made of virtually all the literature values of ΔH and ΔS for excited complexes known to us. For exciplexes, the isoequilibrium temperature β_K is much lower than the isoequilibrium temperature for donor-acceptor complexes in the electronic ground state, which has been stated[64] to be 337 K. This may indicate that the excited complexes differ from the unexcited ones by a greater sensitivity of the structure to changes in the interaction energy. According to Lefler,[65] where there is a linear relation between ΔH and ΔS, the Gibbs free energy of the chemical reaction ΔG is expressed by the equation

$$\Delta G = \Delta H_0 - (T - \beta_K)\Delta S \ .$$

Since the isoequilibrium temperature for exciplexes lies below room temperature at which the stability constants are usually measured, the transition to more positive ΔS is accompanied in changes in ΔH, which increase the stability of the complex.

The rate constants for the formation of triplet exciplexes of porphyrin compounds with electron acceptors increase with increase in the reduction potential of the quenching agent and reach the diffusion region, where k_1 is almost independent of the nature of the oxidant.[53,66] The slope of the "vertical" branch of the relation between k_1 and the reduction potential of the oxidant is close to $-1/RT$, which is a characteristic feature of electron transfer processes, although the reaction leads to the formation of a locally excited complex with a small admixture of the charge-transfer state. In order to account for this contradiction, it has been suggested[53,66] that the formation of the exciplex involves an electron transfer stage. the entire process can be described by the scheme

$$D^* + A \rightleftarrows \underset{\text{collision complex}}{D^* \cdots A} \rightleftarrows \underset{\text{radical-ion pair}}{D^{+\cdot} \cdots A^{-\cdot}} \rightleftarrows \underset{\text{exciplex}}{(AD)^*} \rightarrow D + A \ .$$

After the mutual approach of the reactant molecules through diffusion, an electron is transferred with formation of the primary radical-ion pair. The species then continue to approach one another under the influence of Coulombic forces. This is accompanied by the partial neutralisation of the charges and the solvation environment and the mutual orientations of the molecules in the solvent cage are rearranged. This in fact results in the appearance of structures responsible for the high stability of the triplet exciplexes.

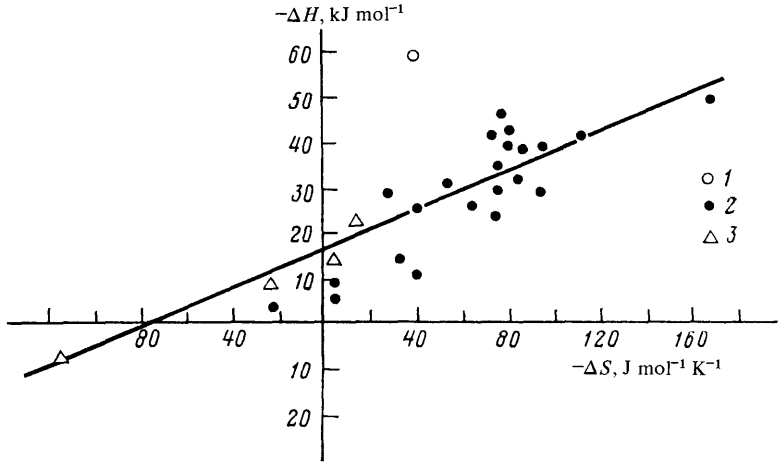


Figure 3. The isoequilibrium relation for exciplexes: *1*) singlet exciplexes in the vapour phase; *2*) singlet exciplexes in liquid solutions; *3*) triplet exciplexes; all the available thermodynamic literature data were used to plot the figure; the ΔH and ΔS for the triplet exciplexes were taken from Refs.60, 63, and 81.

3. Triplet Exciplexes of Carbonyl Compounds

The molecules of carbonyl compounds (quinones, ketones, aldehydes, and others) as a rule undergo photochemical reactions after transition to the triplet state.[67] Depending on the characteristics of their chemical structure, the lowest triplet state of carbonyl compounds can be $\pi\pi^*$, $n\pi^*$ or one of a mixed type. The most important photochemical reactions of organic compounds of this class are in one way or another related[68] to electron transfer, i.e.

$$\left(\rangle C{=}O\right)^* + D \rightarrow \left(\rangle C{=}O\right)^{\cdot-} + D^{\cdot+}$$

or the transfer of a hydrogen atom, i.e.

$$\left(\rangle C{=}O\right)^* + RH \rightarrow \rangle C^{\cdot}{-}OH + R^{\cdot}.$$

In those cases where the reactant RH molecule can serve as both an electron and hydrogen donor, the mechanism of the chemical reactions of the carbonyl compounds occurring under the influence of light is determined by the electronic structure of the excited state.[69]

In the early studies devoted to the photochemical reactions of carbonyl compounds, it was already suggested that these reactions proceed with participation of intermediate excited complexes.[70] However, until the end of the 1970's there were no experimental data of any kind confirming this view. It was first justified experimentally in a study[71] of the quenching of the phosphorescence of benzil PhCOCOPh by anisole and benzonitrile in liquid solutions. In these systems, the quenching of the phosphorescence was exponential, but the dependence of the quenching rate constants on the quenching agent concentration was non-linear. As in the quenching of the triplet molecules of porphyrins, these kinetics are determined by the formation of triplet exciplexes with a lifetime shorter than that of the triplet benzil molecules. The stability constants of these complexes are low (0.12–0.13 litre mol^{-1}).

The quenching of the triplet benzil molecules by triethylamine in moist acetonitrile has been investigated[72] using the method of laser photolysis. The bands of the benzil radical-anions were observed in the variable absorption spectrum. The rate of accumulation of this product proved lower than the rate of deactivation of the triplet molecules of the carbonyl compound, which provided the authors with justification to claim[72] that the electron phototransfer products are formed as a result of the dissociation of a highly polar relatively long-lived triplet exciplex.

The spectrum of the triplet exciplex of the carbonyl compound was first described in communications[74,75] reporting the results of the investigation of the quenching of triplet 2,6-diphenyl-1,4-benzoquinone molecules by tertiary amines. Excited molecular complexes of this type were examined in detail in a recently published review[73] and for this reason they will be only briefly characterised in the present communication.

The excited EDA compounds of ketones and quines can be both highly polar[74–78] and local excited.[78,79] the contribution of the wave function of the ionic state to the molecular wave function of the triplet exciplex is determined by the donor–acceptor properties of the reactant molecules. This question has been investigated in detail in relation to the triplet exciplexes of various quinones and aromatic electron donors.[73] In conformity with the treatment in the introductory Section, in those cases where the energy of the charge-transfer state is greater than or close to the energy of the triplet state of the quinone, locally excited complexes are formed. Their absorption spectra, like those of other locally excited molecular compounds, are close to the absorption spectra of the corresponding locally excited components—in the given instance quinones. The decrease in the energy of the charge-transfer state gradually increases its contribution to the excited complex state. The absorption spectra of such exciplexes, in which the charge transfer state has a lower energy than the energy of the locally excited state, consist of a superposition of the spectra of the corresponding radical-anion and radical-cation. The charge transfer energy is determined also by the solvating properties of the medium and for this reason the addition of even relatively small amounts of methanol (approximately 5%) leads to spectral changes indicating a marked increase in the polarity of the intermediate species.[78] An analogous phenomenon occurs also for triplet exciplexes of porphyrins with electron acceptors.[48]

The nature of the quenching agent determines the lifetimes of the triplet exciplexes. For complexes with the lowest locally excited state, the deactivation rate constants are close to those for the corresponding quinone molecules.[78] This feature is evidently a manifestation of the general feature, already examined, of locally excited molecular compounds. The lifetimes of highly polar triplet exciplexes of carbonyl compounds depend on the energy of the charge-transfer state: the smaller this energy, the higher the rate of deactivation.[77,78] This is apparently a manifestation of the energy gap law,[80] according to which the rate of the non-radiative transition increases with decrease in the difference between the energies of the corresponding energy levels.

A detailed kinetic analysis of the quenching of the triplet states of acetone by durene, which takes place with formation of a weakly polar triplet exciplex as an intermediate, has been carried out.[81] The rate constant for its formation is approximately two orders of magnitude smaller than the rate constant for the diffusion-controlled process. Like the locally excited complexes of porphyrin compounds, the triplet exciplex of acetone with durene has a low enthalpy of formation ($\sim$23 kJ mol^{-1}) and a less negative entropy of formation (–14 J mol^{-1} K^{-1}) than the typical singlet exciplexes. It is important that thermodynamic parameters of this triplet exciplex satisfy the thermodynamic compensation relation examined above.

4. Triplet Exciplexes of Dyes and Related Compounds

The triplet exciplexes formed by representatives of other classes of organic compounds have been much less investigated. In the literature, it is possible to find only individual scattered data concerning the triplet exciplexes of aromatic hydrocarbons, dyes, and heterocyclic compounds.

It has been reported[82] that the pulse photoexcitation of degassed toluene solutions containing *NN*-dimethylaniline apart from a phenazine compound leads to the apperance of a relatively long-lived variable absorption signal, whose spectrum differs from that of the triplet–triplet absorption spectrum of the initial phenazine compound. The authors[82] suggested that the observed intermediate species are triplet exciplexes. Data indicating complex quenching kinetics have been confirmed in a communication[83] where it was reported that the quenching of the long-lived component of the kinetic curve is non-exponential and, furthermore, that these signals are observed in oxygen-saturated solutions. However, later careful studies demonstrated[84] that the intermediates produced on quenching the triplet molecules of phenazine compounds by amines are nevertheless deactivated by oxygen with rate constants which do not differ greatly from the rate constants for diffusion-controlled processes. These intermediates are most probably triplet exciplexes.

Triplet exciplexes are evidently formed also on pulse photoexcitation of the 9-phenylacridinium cation in the presence of organic electron donors in liquid solutions.[85] These exciplexes have an unusual electronic structure: they represent, as it were, the complexes of the uncharged 9-phenylacridine radical and the radical-cation of the corresponding electron donor. Such triplet exciplexes are extremely stable even in polar media. The corresponding equilibrium complex formation constants are approximately 10^5 litre mol^{-1}. Such high stability of the triplet 9-phenylacridinium exciplexes also apparently cannot be accounted for by energy factors, because there is virtually no Coulombic interaction between the components in these excited molecular compounds. Their characteristic feature is that they are formed as a result of the intersystem crossing in the corresponding singlet exciplex, since the quantum yield of the triplet state of the 9-phenyl-acridinium cation is extremely low. This mechanism of the formation of the triplet states of molecular complexes will be examined in the next Section.

Usacheva et al.[96] investigated the intermediates formed on quenching the triplet state of eosin by an electron acceptor (methylviologen) in water. It was found that the quenching is accompanied by the formation of a short-lived intermediate whose absorption spectrum differs appreciably from that of the triplet eosin molecules. At the same time, it was shown that "free" radical species are not formed in the given system. On this basis, one can conclude that the observed intermediate is a triplet exciplex with a significant contribution by the charge-transfer state.

The question of the formation of triplet exciplexes on quenching of the triplet states of aromatic hydrocarbons by electron acceptors is controversial. The formation of triplet exciplexes of anthracene with organic nitro- and halogeno-compounds in benzene has been reported,[40] but this result could not be reproduced by other workers.[87] The latter were unable to detect the formation of triplet exciplexes even on quenching of the triplet 1,2-benzopyrene and 1,2-benzanthracene molecules by electron acceptors. Apparently, if the triplet exciplexes are in fact formed in these systems, they have extremely short lifetimes. The difficulty of studying the products of the pulse photoexcitation of aromatic hydrocarbons is due to the factor that electron acceptors also quench effectively the singlet-excited states, reducing the quantum yield of the triplet molecules and lowering thereby the intensity of the variable absorption signals.

IV. FORMATION OF THE TRIPLET STATES OF MOLECULAR COMPLEXES AS A RESULT OF INTERSYSTEM CROSSING

The triplet states of both EDA complexes and exciplexes can be formed as a result of the intersystem reactions of singlet-excited states on radical-ion pairs. The mechanisms of these processes will be considered in the present Section.

1. Intersystem Crossing in Excited EDA Complexes

On the basis of the study of molecular complexes by nanosecond laser photolysis, it has been concluded[88,89] that in frozen solutions an appreciable if not the main fraction of the triplet states of molecular complexes are produced during the laser flash as a result of intersystem transitions from the unrelaxed Franck–Condon singlet-excited state. Almost simultaneously, an analogous mechanism was put forward also for the intersystem crossing in exciplexes.[90] However, subsequent studies carried out using picosecond laser spectroscopy[91] disproved this mechanism. Although CTC have not been investigated by this method, nevertheless one can postulate that, in donor–acceptor compounds which are stable in the electronic ground state, the intersystem period in liquid solutions should involve mainly the classical mechanism i.e. the relevant transition should be from the thermalised fluorescent state. In frozen solutions the intersystem crossing can take place from the Franck–Condon state, because the structural rearrangements of the complexes in frozen solutions are greatly hindered and the Franck–Condon state is fluorescent.[92,93]

The rates and hence the yields of the intersystem crossing depend on the degree of charge transfer between the components of the complex in the triplet state. The following selection rules have been formulated[94] for the intersystem crossing in EDA complexes: the non-radiative transition between the singlet and triplet charge-transfer states must take place at low rates in contrast to the intersystem transitions from singlet charge-transfer states to the triplet states with a locally excited nature. These postulates were based on the fact that the matrix elements of the spin–orbit coupling of the singlet and triplet charge-transfer states are zero,

$$\langle {}^1\psi(A^-D^+)\,|H_{co}|\,{}^3\psi(A^-D^+)\rangle = 0\ , \qquad (18)$$

in contrast to the matrix elements of the spin–orbital coupling of the singlet-excited charge-transfer states and triplet locally excited states:

$$\langle {}^1\psi(A^-D^+)\,|H_{co}|\,{}^3\psi(D^*A)\rangle = -\langle \pi_a|H_{co}|\pi_d\rangle\ . \qquad (19)$$

In Eqns.(18) and (19), π_a is the highest unoccupied orbital of the acceptor, π_d the highest occupied orbital of the donor, and H_{SO} the Hamiltonian of the spin–orbital coupling. The selection rules formulated by Lim et al.[94] agree with the qualitative estimation of the role of the non-radiative transitions

$$S_1 \rightsquigarrow T \text{ and } S_1 \rightsquigarrow S_0$$

in the deactivation of singlet-excited states of various molecular complexes.[94] The main pathway to the deactivation of singlet-excited states of the CTC of tetracyanoethylene with benzene and its alkyl derivatives, whose triplet states are charge-transfer states, is internal conversion. The lowest triplet states of the complexes of the same donors with tetracyanobenzene are of the locally excited type. In conformity with the selection rules formulated, the rate of interconversion for such molecular compounds exceeds the rate of the internal degradation of the electronic excitation energy of the EDA complex. We may note that the conclusions by Lim et al.[94] concerning the pathways followed in the transformation of the electronic excitation energy were made on the basis of indirect data concerning the influence of the deuteriation of the electron donor molecules on the fluorescence quantum yields of the molecular complexes. The introduction of deuterium into the methyl group induces the strongest effects, because their C–H vibrations have the role of promoting modes in internal conversion proceses. For intersystem transitions between close-lying states, the high-frequency C–H vibrations do not fulfil this role. The influence of their isotope substitution on the rates of the transitions

$$S_1 \rightsquigarrow T$$

should therefore be small. the study of the usual and deuteriated complexes makes it possible to determine which of the non-radiative processes—non-radiative degradation or intersystem crossing—deactivates the singlet-excited CTC states. The conclusions reached

from the analysis of the isotope effects are confirmed by phosphorescence measurements, as shown by the analysis of Nagakura's data.[2]

2. Intersystem Crossing Processes Involving Exciplexes

The photoexcitation of solutions of fluorophors containing quenching agent concentrations for which only the bands of exciplexes are observed in the fluorescence spectrum is accompanied by the appearance of relatively intense absorption bands of the triplet molecules of one of the components of the exciplex. In many cases, the calculated interconversion yields proved to be the same or even higher than in the solutions of the same fluorophors without specially introduced quenching agents.[95] It is important that these effects were observed in systems where there were no heavy atoms intensifying the spin–orbit coupling and accelerating the intersystem transitions.

The triplet–triplet absorption bands under discussion are apparently due to the "free" triplet molecules or locally excited triplet exciplexes. It is usually assumed that the primary products of the intersystem transformations of singlet exciplexes are triplet-excited complexes, but the latter are unstable owing to the low enthalpies of formation and decompose immediately (see, for example, Goldschmidt et al.[95]). This postulate, which has become generally accepted, requires an experimental test in each individual case. This is indicated by the data, discussed above, demonstrating the high stability of the locally excited triplet exciplexes of porphyrin compounds, acetone, quinones, and the 9-phenylacridinium cation, which cannot have high enthalpies of formation. Furthermore, relatively stable triplet exciplexes are formed by phenazine compounds with tertiary amines.[82,84] Singlet fluorescent exciplexes, which may undergo intersystem crossing, are also observed in these systems.[96]

However, despite some uncertainty in the question of the form—"free" or as part of a complex—in which the excited triplet molecule exists, the triplet–triplet absorption recorded in exciplex systems indicates relatively high intersystem crossing yields of the singlet-excited exciplexes.

Studies carried out by the laser photolysis methods have shown that the intersystem crossing in exciplexes takes place after the formation of thermalised fluorescent states. For example, it has been established[97–99] that, as the variable absorption of the exciplex of *NNNN*-tetramethyl-*p*-phenylene-diamine with naphthalene and biphenyl and of anthracene with *NN*-dimethylaniline is quenched, an increase in the intensity of the triplet–triplet absorption band is observed. The kinetics of the accumulation of the triplet molecules then also correspond to the kinetics of the relaxation of the optical density of the absorption band of the singlet-excited complexes. Agreement between the rates of these processes has also been noted in a study[100] of exciplexes of anthracene and pyrene with *NN*-diethylaniline in hexane using the picosecond technique. During the first 200 ps after the laser flash, there were no bands due to triplet molecules in the variable absorption spectrum. This period was sufficient for virtually all the excited species to enter into complex formation and for the excited complexes to pass to the thermalised state. After long periods, an increase in the triplet–triplet absorption, accompanying the destruction of the exciplexes, was observed. These results demonstrated that in non-polar media the intersystem crossing and the fluorescence of the exciplexes are consecutive and not parallel processes.

The formation of triplet states from relaxed exciplexes takes place also in complexes formed as a result of the conformational changes in photoexcited bichromophoric $A-(CH_2)_n-D$ molecules, in which the donor and acceptor groups are linked by a flexible aliphatic chain.[101]

Thus it can now be regarded as established that in non-polar solvents the triplet states are formed as a result of intersystem transitions from relaxed charge-transfer states of the molecular complexes. On this basis, the rate of the intersystem crossing in the exciplex k_T' can be calculated from the formula[102]

$$\frac{k_T'}{k_T} = \frac{(\varphi_T/\varphi_T^0)\,(\varphi^0/\varphi) - 1}{(\varphi^0/\varphi) - 1} \cdot \frac{\tau_0}{\tau_0'} \quad ,$$

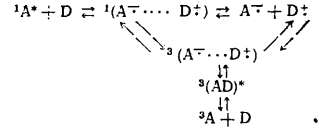
where τ_0 is the lifetime of the excited fluorophor in the absence of quenching agents, τ_0' the lifetime of the exciplex, φ^0 and φ are the fluorescence quantum yields, and φ_T^0 and φ_T are the quantum yields of the triplet molecules in the absence and presence of the quenching agent respectively.

The rate constants and quantum yields of the intersystem crossing in exciplexes are determined by the nature of the reactants. For example, quenching of the fluorescence of pyrene and anthracene by amines increases the yield of the triplet state of the hydrocarbons.[95] The formation of exciplexes of *NN*-dimethyl-β-naphthylamine with dimethyl isophthalate lowers the yields of the triplet molecules compared with the yield of the triplet molecules of the above amine in the absence of a quenching agent.[103] We may quote yet another example. The rate constants for the intersystem crossing in the exciplexes of 9,10-dicyanoanthracene with aromatic hydrocarbons are approximately 10^7 s^{-1} and those for the exciplexes with tertiary amines are approximately 10^9 s^{-1}.[102] Many of the features of the intersystem crossing in exciplexes can apparently be explained using the selection rules formulated in the previous Section, according to which the intersystem transitions in molecular complexes take place between charge-transfer and locally excited triplet states. The quantum yields in the formation of the triplet molecules diminish as a result of complex formation if the triplet locally excited states have a higher energy than the fluorescent state of the exciplexes. Another factor influencing the yield of the triplet molecules can be a change in the structure of the exciplex. This postulate has been confirmed by the results of a study on the intersystem transitions in intramolecular exciplexes.

The structures of the intramolecular exciplexes are known to be determined by the length of the chain linking the electron donor and electron acceptor groups.[104] For $n = 3$, there is a possibility of the formation of sandwich structures with a parallel arrangement of the planes of the donor and acceptor components. In such exciplexes, the intersystem transitions take place at relatively low rates close to the rates of the intersystem transitions in the majority of aromatic molecules (approximately 10^7 s^{-1}).[101] For $n = 1$ or 2 in singlet exciplexes, the molecules are arranged in planes which are almost perpendicular with respect to one another.[105] The transition from the sandwich to the "perpendicular" structure induces a marked increase in the rate of intersystem crossing.[101] These changes are explained by an increase in the matrix elements of the spin–orbit coupling of the corresponding states, whose values determine the rates of the intersystem transition. The rate of intersystem crossing can evidently be influenced, apart from the factors indicated, also by the charge distribution in the complexes and by the distance between the donor and acceptor groups. As a consequence of this, the rates of the intersystem transitions in exciplexes are extremely sensitive to

various structural factors. It is therefore not surprising that solvents capable of influencing appreciably the structures of excited molecular complexes alter the rates of the transitions from the single-excited to the triplet-excited states. As an example, one may quote again intramolecular exciplexes. An increase in solvent polarity weakens the Coulombic attraction of the charged parts of the exciplex. This alters the structure of the excited complex, which is reflected in the absorption spectra of the exciplexes.[106] Pronounced solvation induces conformational transitions and alters thereby the spin–orbital coupling and the rate of intersystem processes.[101] However, in the study of the influence of the solvent on the spin evolution of the intermolecular exciplex systems, it is essential to take into account the fact that in highly polar media there is a possibility of the operation of completely different mechanisms of intersystem crossing. In this connection, we shall characterise briefly the mechanisms of the formation of triplet-excited molecules in polar media.

In polar solvents, the quenching agent interacting with a singlet-excited molecule can also induce its transition to the triplet state. For example, the flash photoexcitation of acetonitrile solutions of aromatic hydrocarbons and electron donors (or acceptors) induces the appearance of triplet hydrocarbon molecules apart from the radical-ion products.[95] The mechanism of these photoprocesses has been established with the aid of nanosecond and picosecond laser photolysis.[107,108] In highly polar solvents, triplet states are formed as a result of at least two main types of reactions—the relatively slow recombination of the free radical-ions and the rapid intersystem crossing in the geminal radical-ion pairs. It is quite possible that the primary products of the geminal recombination of the radical-ion pairs are triplet exciplexes:[109,110]



It has been suggested that the intersystem transition from a singlet radical-ion pair to a triplet pair takes place via the so called hyperfine interaction mechanism, which is indicated by data concerning the influence of weak magnetic fields on the yields of triplet states.[101]

REFERENCES

1. R.S.Mulliken, J.Amer.Chem.Soc., 1952, **74**, 811.
2. S.Nagakura, in "Excited State", Acad.Press, New York, 1975, Vol.2, p.328.
3. M.A.T.Tavares, J.Chem.Phys., 1980, **72**, 43.
4. M.Tamres and R.L.Strong, "Molecular Association", Acad. Press, London, 1979, Vol.2.
5. L.J.Andrews and R.M.Keefer, "Molecular Complexes in Organic Chemistry" (Translated into Russian), Izd.Mir, Moscow, 1967.
6. I.G.Kaplan, "Vvedenie v Teoriyu Mezhmolekulyarnykh Vzaimodeistvii" (Introduction to the Theory of Intermolecular Interactions), Izd.Nauka, Moscow, 1982.
7. B.L.Blaney and G.E.Ewig, Ann.Rev.Phys.Chem., 1976, **27**, 553.
8. M.Gordon et al. (Editors), "The Exciplex", Acad.Press, New York, 1970.
9. J.B.Birks, "Photophysics of Aromatic Molecules", Wiley Intersci., London, 1970.
10. J.B.Birks (Editor), "Organic Molecular Photophysics", Acad. Press, London, 1975.
11. G.Briegleb, "Elektronen-Donator-Akzeptor-Komplexe", Springer Verlag, Berlin, 1961.
12. H.Leonhard and A.Weller, Ber.Bunsenges.phys.Chem., 1963, **61**, 971.
13. P.A.Shakhverdov, Optika i Spektrosk., 1971, **30**, 81.
14. J.K.Roy and D.G.Whitten, J.Amer.Chem.Soc., 1971, **93**, 7093.
15. G.Briegleb and J.Czecalla, Angew.Chem., 1960, **72**, 401.
16. S.Iwata, J.Tanaka, and S.Nagakura, J.Chem.Phys., 1967, **47**, 2203.
17. R.Foster, "Organic Charge-transfer Complexes", Acad.Press, London, 1969.
18. J.Czekalla, G.Briegleb, W.Herre, and H.J.Vahlensieck, Z.Elektrochem., 1959, **63**, 715.
19. N.Christodouleas and S.P.McGlynn, J.Chem.Phys., 1964, **40**, 166.
20. K.B.Eisenthal and M.A.El-Sayed, J.Chem.Phys., 1965, **42**, 794.
21. S.McGlynn, T.Azumi, and M.Kinoshita, "Molecular Spectroscopy of the Triplet State" (Translated into Russian), Izd.Mir, Moscow, 1972.
22. Z.Teitelbaum, R.Potashnik, and M.Ottolenghi, Mol.Photochem., 1971, **3**, 107.
23. H.Hayashi, M.Yagi, and N.Nishi, J.Luminescence, 1976, **12/13**, 169.
24. K.Kobayashi and S.Nagakura, Bull.Chem.Soc.Japan, 1972, **42**, 987.
25. S.Matsumoto, S.Nagakura, S.Iwata, and J.Nakamura, Mol. Phys., 1973, **26**, 1465.
26. J.Czekalla and K.J.Mager, Z.Elektrochem., 1962, **66**, 65.
27. Y.Achiba, S.Matsumoto, and K.Kimura, Chem.Phys.Lett., 1972, **13**, 213.
28. D.Mauzeral and S.G.Ballard, Ann.Rev.Phys.Chem., 1982, **33**, 377.
29. M.Irie, S.Tomimoto, and R.H.Hayashi, J.Phys.Chem., 1972, **76**, 1419.
30. Y.Achiba and K.Kimura, Chem.Phys.Lett., 1972, **19**, 45.
31. R.Potashnik, C.R.Goldschmidt, and M.Ottolenghi, J.Phys. Chem., 1969, **73**, 3170.
32. M.Shimada, H.Masuhara, and N.Mataga, Chem.Phys.Lett., 1972, **15**, 364.
33. M.Shimada, H.Masuhara, and N.Mataga, Bull.Chem.Soc. Japan, 1973, **46**, 1909.
34. K.Kimura, Y.Achiba, and S.Matsumoto, J.Phys.Chem., 1973, **77**, 2520.
35. Y.Achiba and K.Kimura, J.Luminescence, 1976, **12/13**, 871.
36. Y.Achiba, S.Matsumoto, and K.Kimura, Bull.Chem.Soc.Japan, 1972, **45**, 1272.
37. H.Masuhara and N.Mataga, Acc.Chem.Res., 1981, **14**, 312.
38. I.I.dilung and E.I.Kapinus, Uspekhi Khim., 1978, **47**(1), 83 [Russ.Chem.Rev., 1978(1)].
39. A.K.Chibisov, Uspekhi Khim., 1981, **50**(7), 1169.

40. J.K.Roy, F.A.Carrol, and D.G.Whitten, J.Amer.Chem.Soc., 1974, **96**, 6349.
41. E.I.Kapinus, V.P.Staryi, and I.I.Dilung, Dokl.Akad.Nauk SSSR, 1981, **261**, 907.
42. E.I.Kapinus, V.P.Staryi, and I.I.dilung, Dokl.Akad.Nauk SSSR, 1982, **18**, 450.
43. N.E.Andreeva and A.K.Chibisov, Teor.Eksper.Khim., 1979, **15**, 668.
44. N.E.Andreeva and A.K.Chibisov, Biofizika, 1976, **21**, 24.
45. V.G.Mairanovskii, "Porfiriny: Spektroskopiya, Elektrokhimiya, Primenenie" (The Porphyrins: Spectroscopy, Electro-chemistry, and Applications), Izd.Nauka, Moscow, 1987, p.187.
46. E.I.Kapinus, M.M.Aleksankina, and I.I.dilung, J.Photochem., 1983, **21**, 125.
47. A.K.Chibisov, in "Vozbuzhdennye Molekuly. Kinetika Prevrashchenii" (Excited Molecules. Reaction Kinetics), Izd.Nauka, Leningrad, 1982, p.160.
48. J.K.Roy and D.G.Whitten, J.Amer.Chem.Soc., 1972, **94**, 7162.
49. I.V.Renge, V.A.Kuzmin, and Yu.E.Borisevich, J.Photochem., 1985, **31**, 67.
50. I.V.Renge, V.A.Kuz'min, A.F.Mironov, and Yu.E.Borisevich, Dokl.Akad.Nauk SSSR, 1982, **263**, 143.
51. N.Nakashima, N.Mataga, and C.Yamanaka, Int.J.Chem. Kinet., 1973, **5**, 833.
52. M.G.Kuz'min and N.A.Sadovskii, Khim.Vys.Energii, 1975, **9**, 291.
53. E.I.Kapinus, M.M.Aleksankina, V.P.Staryi, et al., J.Chem.Soc. Farad.Trans.II, 1985, **81**, 631.
54. D.R.Prasad and G.Ferraud, Inorg.Chem., 1983, **22**, 1672.
55. E.I.Kapinus, M.M.Aleksankina, V.P.Staryi, and I.I.Dilung, Dokl.Akad.Nauk SSSR, 1984, **278**, 1165.
56. E.I.Kapinus, V.P.Staryi, and I.I.Dilung, Teor.Eksper.Khim., 1981, **17**, 100.
57. L.S.Degtyarev, E.I.Kapinus, and E.Yu.Skuridin, Khim.Vys. Energii, 1984, **18**, 56.
58. J.A.Mercer-Smith, C.R.Sutcliffe, R.H.Schmehl, and B.Whitten, J.Amer.Chem.Soc., 1979, **101**, 3995.
59. H.O.Hill, A.P.Macfarlane, and R.J.P.Williams, J.Chem.Soc.A, 1969, 1704.
60. E.I.Kapinus, M.M.Aleksankina, and I.I.Dilung, Chem.Phys. Lett., 1985, **114**, 507.
61. B.Steavens, Adv.Photochem., 1971, **8**, 161.
62. D.V.O'Connor and W.R.Ware, J.Amer.Chem.Soc., 1976, **98**, 4706.
63. E.I.Kapinus, M.M.Aleksankina, and I.I.Dilung, Dokl.Akad. Nauk Ukrain.SSR, Ser.B, 1984(9), 36.
64. E.N.Gur'yanova, I.P.Gol'dshtein, and I.P.Romm, "Donorno-Aktseptornaya Svyaz'" (The Donor–Acceptor Bond), Izd. Khimiya, Moscow, 1973, 397 pp.
65. J.E.Lefler, J.Org.Chem., 1955, **20**, 120.
66. E.I.Kapinus and M.M.Aleksankina, Khim.Fiz., 1985, **4**, 793.
67. N.J.Turro, "Modern Molecular Photochemistry", The Benjamin, Melo Park, 1978, 628 p.
68. A.I.Kryukov, V.P.Sherstyuk, and I.I.Dilung, "Fotoperenos Elektrona i Ego Prakticheskie Aspekty" (Electron Photo-transfer and Its Practical Aspects), Izd.Naukova Dumka, Kiev, 1982.
69. D.N.Shigorin, Zhur.Vses.Khim.Obshch.im.Mendeleeva, 1975, **20**, 32.
70. S.G.Cohen, A.H.Parolla, and G.H.Parsons, Chem.Rev., 1973, **73**, 141.
71. T.S.Fang, R.E.Brown, C.L.Kwan, and L.A.Singer, J.Phys. Chem., 1978, **82**, 2489.
72. M.V.Encinas and J.C.Scaiano, J.Amer.Chem.Soc., 1979, **101**, 7740.
73. P.P.Levin and V.A.Kuz'min, Uspekhi Khim., 1987, **56**(3), 527 [Russ.Chem.Rev., 1987(3)].
74. V.A.Kuz'min, A.B.Darmanyan, and P.P.Levin, Dokl.Akad. Nauk SSSR, 1979, **245**, 1150.
75. H.Kobashi, T.Kondo, and M.-A.Funabashi, Bull.Chem.Soc. Japan, 1986, **59**, 2347.
76. P.P.Levin, T.A.Kokrashvili, A.P.Darmanyan, and V.A.Kuz'-min, Dokl.Akad.Nauk SSSR, 1982, **262**, 1180.
77. P.P.Levin, T.A.Kokrashvili, and V.A.Kuz'min, Izv.Akad.Nauk SSSR, Ser.Khim., 1982, 521.
78. P.P.levin, Izv.Akad.Nauk SSSR, Ser.Khim., 1981, 2390.
79. P.P.Levin, A.S.Tatikolov, and V.A.Kuz'man, Izv.Akad.Nauk SSSR, Ser.Khim., 1982, 1005.
80. E.S.Medvedev and V.A.Osherov, "Teoriya Bezyzluchatel'nykh Perekhodov v Mnogoatomnykh Molekulakh" (Theory of Non-radiative Transitions in Polyatomic Molecules), Izd.Nauka, Moscow, 1983, 280 pp.
81. L.J.Johnston, J.C.Scaiano, and T.Wilson, J.Amer.Chem.Soc., 1987, **109**, 1291.
82. V.A.Osipov, M.N.Usacheva, and I.I.Dilung, Dokl.Akad.Nauk SSSR, 1980, **254**, 407.
83. V.A.Kuz'min, I.V.Renge, and Yu.E.Borisevich, Izv.Akad.Nauk SSSR, Ser.Khim., 1982, 2009.
84. V.A.Osipov, M.N.Usacheva, and I.I.Dilung, Khim.Vys.Energii, Khim.Vys.Energii, 1985, **19**, 523.
85. V.L.Ivanov, Sami Abu Al-Ainen, and M.G.Kuz'min, Dokl. Akad.Nauk SSSR, 1977, **237**, 1400.
86. A.M.Vinogradov, P.P.Levin, and V.A.Kuz'min, Izv.Akad.Nauk SSSR, Ser.Khim., 1982, 2818.
87. V.A.Kuzmin, I.V.Renge, and Yu.E.Borisevich, Chem.Phys. Lett., 1980, **70**, 257.
88. H.Masuhara, N.Tsujino, and N.Mataga, Chem.Phys.Lett., 1972, **12**, 481.
89. N.Tsujino, H.Masuhara, and N.Mataga, Chem.Phy.Lett., 1972, **15**, 357.
90. M.Ottolenghi, Acc.Chem.Res., 1973, **6**, 153.
91. N.Nakashima and N.Mataga, Chem.Phys.Lett., 1975, **35**, 487.
92. K.Egava, N.Nakashima, N.Mataga, and C.Yamanaka, Bull.Chem.Soc.Japan, 1971, **44**, 3287.
93. N.Masuhara and N.Mataga, Chem.Phys.Lett., 1973, **22**, 305.
94. B.T.Lim, S.Okajima, A.K.Chandra, and E.C.Lim, Chem.Phys. Lett., 1981, **79**, 22.
95. C.R.Goldschmidt, R.Potashnik, and M.Ottolenghi, J.Phys. Chem., 1971, **75**, 1021.
96. M.N.Usacheva, V.A.Il'yushonok, M.G.Kuz'min, and I.I.Dilung, Teor.Eksper.Khim., 1975, **11**, **64**.
97. C.R.Goldschmidt, J.Chem.Phys., 1975, **75**, 1025.
98. N.Orbach, J.Novros, and M.Ottolenghi, J.Chem.Phys., 1973, **77**, 2831.
99. E.J.Land, J.T.Richards, and J.K.Thomas, J.Chem.Phys., 1972, **76**, 3805.
100. T.Nishimura, N.Nakashima, and N.Mataga, Chem.Phys.Lett., 1977, **46**, 334.
101. T.Okada, I.Karaki, E.Matsusava, et al., J.Phys.Chem., 1981, **85**, 3957.
102. I.V.Soboleva, N.A.Sadovskii, and M.G.Kuz'min, Dokl.Akad. Nauk SSSR, 1978, **238**, 400.

103. H.Yamashita, H.Kokubun, and M.Koizumi, Bull.Chem.Soc. Japan, 1968, **41**, 4231.
104. F.C.De Schryver, N.Boens, and J.Put, Adv.Photochem., 1977, **10**, 359.
105. A.M.Swinnen, M.Van der Auweraer, F.C.De Schryver, et al, Chem.Phys.Lett., 1983, **95**, 467.
106. N.Mataga, T.Okada, H.Masuhara, et al. J.Luminescence, 1976, **12/13**, 159.
107. N.Orbach, R.Potashnik, and M.Ottolenghi, J.Phys.Chem., 1972, **76**, 1133.
108. N.Mataga and N.Nakashima, Spectroscopy Lett., 1975, **8**, 275.
109. M.E.Michel-Beyerle, R.Haberkorn, and W.Bude, Chem.Phys., 1976, **17**, 139.
110. K.Shulten, H.Staerk, A.Weller, et al., Z.Phys.Chem. N.F., 1976, **101**, 371.

Pisarzhevskii Institute of
Physical Chemistry,
Academy of Sciences of
the Ukrainian SSR,
Kiev