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Electron Transfer in Photochemical Reactions

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Modern ideas concerning the mechanism of electron transfer in photochemical reactions in solution are discussed. The quenching of the excited state via the electron transfer mechanism, the intermediate states and the role of the medium in the formation of radical-ions, the reactivity of excited states in the electron transfer reaction, and the energetics of this reaction are examined.
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I. INTRODUCTION

Among different types of photochemical reactions, the electron transfer process is one of the most common. Electron transfer processes constitute the basis of many reactions in organic photochemistry (for example, heterolytic substitution reactions[1-4]) and the photochemistry of coordination compounds[5-8], the photochemical methods for recording information[9,10] and in the first place spectral sensitisation in photography[11-14], the photodegradation of dyes[15], and many photobiological processes, for example, photosynthesis[16,17]. Photochemical oxidation-reduction reactions with participation of aromatic, carbonyl, and heterocyclic compounds[4,18], dyes of different classes[15,19-21], pigments[22-25], and coordination compounds[5-8], and inorganic ions[26-28] are widely investigated.

Definite advances, due primarily to progress in the development of experimental technique, have been achieved in recent years in this field of photochemical reactions. The application of nano- and pico-second lasers made it possible to investigate in detail the mechanism of electron transfer and the properties of the intermediates of oxidation-reduction photoreactions. Numerous studies, whose aim was to establish a correlation between the efficiency of the electron transfer and the properties of the reacting molecules and also studies devoted to the investigation of the energetics and kinetics of the electron transfer reaction, the elucidation of the role of the medium, etc. have been published recently.

This review deals with the current ideas about the mechanisms of electron transfer in photochemical reactions in solutions. Modern views on the mechanism of oxidation-reduction photoreactions are to some extent based on the

available theories of electron transfer[29-32] and also on the characteristic features of the behaviour of excited molecules.

II. ENERGETICS OF THE ELECTRON TRANSFER REACTION

Photochemical reactions (including electron transfer reactions) begin with the absorption of light by the molecular system, which leads to the formation of electronically excited states. The properties of molecules in the excited state can differ from their properties in the ground (unexcited) state, which is manifested by changes in the dipole moment, polarisability, and geometry of the molecules, by changes in the position of the acid–basic equilibrium, and also by changes in the ionisation potential, electron affinities, etc.[1,4,21,25,33-37].

The free energy ΔG of an electron transfer reaction in the gas phase between donor (D) and acceptor (A) molecules is defined fairly accurately by the relation

$$\Delta G = I_D - E_A, \tag{1}$$

where I_D is the ionisation potential of the donor and E_A the electron affinity of the acceptor.

On photoexcitation, the ionisation potential I_D diminishes by the excitation energy of the donor $E(^{1,3}D^*)$†, while the electron affinity E_A increases by the excitation energy of the acceptor $E(^{1,3}A^*)$.[33] Thus the free energy ΔG of the photochemical electron transfer, for example between $^{1,3}A^*$ and D, namely

$$^{1,3}A^* + D \rightarrow A^{\bar{}} + D^{+}, \tag{I}$$

is defined by the relation

$$\Delta G = I_D - [E_A + E(^{1,3}A^*)]. \tag{2}$$

If the photoreaction takes place between electrically neutral molecules, the electron transfer results in the formation of the radical-ion pair $A^{\bar{}}D^{+}$ stabilised by the Coulombic interaction:

$$^{1,3}A^* + D \rightarrow A^{\bar{}}D^{+}. \tag{II}$$

In this case the free energy change is

$$\Delta G = I_D - [E_A + E(^{1,3}A^*)] - e^2/R, \tag{3}$$

where e is the electronic charge and R the distance between the centres of the molecules A and D. Electron transfer in reactions (I) and (II) becomes possible when $\Delta G < 0$.

When the energetics of a photoreaction in solution is considered, one must take into account the energy of the transfer of the molecules $^{1,3}A^*(^{1,3}D^*)$ and A(D), the radical-ion pair $A^{\bar{}}D^{+}$, and the radical-ions $A^{\bar{}}$ and D^{+} from the gas to the condensed phase. The energy of the transfer (solvation) of ions (radical-ions) from a vacuum into a medium with a dielectric constant ε is given by the following expression according to Born:

$$\Delta G(A^{\bar{}}) + \Delta G(D^{+}) = -\frac{e^2}{2}\left(\frac{1}{R_{A^{\bar{}}}} + \frac{1}{R_{D^{+}}}\right)\left(1 - \frac{1}{\varepsilon}\right), \tag{4}$$

where $R_{A^{\bar{}}}$ and $R_{D^{+}}$ are the radii of the radical-ions $A^{\bar{}}$ and D^{+} respectively. Consequently the free energy of the photochemical electron transfer reaction in solution, leading to the formation of solvated radical-ions as the final products [reaction analogous to reaction (I)] is

$$\Delta G = I_D - [E_A + E(^{1,3}A^*)] - \frac{e^2}{2}\left(\frac{1}{R_{A^{\bar{}}}} + \frac{1}{R_{D^{+}}}\right)\left(1 - \frac{1}{\varepsilon}\right). \tag{5}$$

†The superscript 1,3 denotes the multiplicity of the state (singlet, triplet).

The energy of the transfer of an ion (radical-ion) pair, having an effective radius r and a dipole moment μ, from a vacuum into a medium with a dielectric constant ε is given by the following expression according to Kirkwood[38]:

$$\Delta G(A^{\bar{}}D^{+}) \simeq -\frac{\mu^2}{r^3}\left(\frac{\varepsilon - 1}{2\varepsilon + 1}\right). \tag{6}$$

If the photochemical electron transfer involves the formation of a solvated radical-ion pair (exciplex) as the final product, then the free energy of the reaction, analogous to reaction (II), is

$$\Delta G = I_D - [E_A + E(^{1,3}A^*)] - \frac{e^2}{R} - \frac{\mu^2}{r^3}\left(\frac{\varepsilon - 1}{2\varepsilon + 1}\right). \tag{7}$$

For the electron transfer reaction in solution, it is convenient to replace the values of I_D and E_A known for the gas phase by the half-wave potentials for the polarographic reduction of the donor $E_{1/2}(D/D^{+})$ and the polarographic reduction of the acceptor $E_{1/2}(A^{\bar{}}/A)$:[39-42]

$$I_D = E_{1/2}(D/D^{+}) - \Delta G(D^{+}) + \text{const}, \tag{8}$$

$$E_A = E_{1/2}(A^{\bar{}}/A^{+}) + \Delta G(A^{\bar{}}) + \text{const}. \tag{9}$$

The half-wave potentials are known for many aromatic hydrocarbons[43-48], inorganic compounds[49-52], dyes[53,54], and pigments[25]. The free energy of electron transfer in the photochemical reaction analogous to reaction (I), formulated in terms of the $E_{1/2}$ potentials, is

$$\Delta G = E_{1/2}(D/D^{+}) - [E_{1/2}(A^{\bar{}}/A) + E(^{1,3}A^*)], \tag{10}$$

and for a photochemical electron transfer reaction analogous to reaction (II) the free energy is

$$\Delta G = E_{1/2}(D/D^{+}) - [E_{1/2}(A^{\bar{}}/A) + E(^{1,3}A)] + \frac{e^2}{2}\left(1 - \frac{1}{\varepsilon}\right)\left(\frac{1}{R_{D^{+}}} + \frac{1}{R_{A^{\bar{}}}}\right) - \frac{e^2}{R} - \frac{\mu^2}{r^3}\left(\frac{\varepsilon - 1}{2\varepsilon + 1}\right). \tag{11}$$

The electrochemical potentials of the molecules in the ground, excited singlet, and excited triplet states.

Substance	$E_{1/2}(D/D^{+})$, V	$-E_{1/2}(A^{\bar{}}/A)$, V	$^1E^*$, eV	$^3E^*$, eV	$-[E_{1/2}(D/D^{+}) - E(^1D^*)]$, V	$-[E_{1/2}(D/D^{+}) - E(^3D)]$, V	$-E_{1/2}(A^{\bar{}}/A) + E(^1A^*)$, V	$E_{1/2}(A^{\bar{}}/A) + E(^3A^*)$, V
Biphenyl	—	2.65 [48]	4.09 [15]	2.82 [15]	—	—	1.44	0.17
Naphthalene	—	2.58 [48]	3.93 [15]	2.62 [15]	—	—	1.35	0.04
Phenanthrene	—	2.51 [48]	3.58 [15]	2.68 [15]	—	—	1.07	0.17
Anthracene	—	1.96 [48]	3.26 [15]	1.85 [15]	—	—	1.30	−0.11
Tetracene	—	1.53 [48]	2.62 [15]	1.27 [15]	—	—	1.09	−0.26
Chlorophyll *a*	0.54 [25]	1.11 [25]	1.85 [25]	1.33 [25]	1.31	0.79	0.74	0.22
Chlorophyll *b*	0.65 [25]	1.05 [25]	1.91 [25]	1.39 [25]	1.26	0.74	0.86	0.34
Phaeophytin *a*	0.92 [25]	0.84 [25]	1.84 [25]	1.33 [25]	0.92	0.41	1.00	0.49
Bacteriochlorophyll	0.40 [25]	1.08 [25]	1.58 [25]	1.00 [25]	1.18	0.60	0.50	−0.08
Porphin	0.93[25]	1.18 [25]	2.02 [25]	1.56 [25]	1.09	0.63	0.84	0.38
Riboflavin	—	0.61 [25]	2.50 [25]	2.02 [25]	—	—	1.89	1.41
Indole	1.26 [25]	—	4.28 [25]	3.09 [25]	3.02	1.83	—	—
Eosin	0.89 [53]	1.09 [53]	2.33 [53]	1.84 [15]	1.44	0.95	1.24	0.75
Acridine Orange	1.04 [53]	1.13 [53]	2.52 [53]	2.07 [15]	1.48	1.03	1.39	0.94
Thionine	1.27[53]	0.43 [53]	2.05 [53]	1.69 [55]	0.78	0.42	1.62	1.26
Phenosafranine	1.32[53]	0.67 [53]	2.34 [53]	1.77 [22]	1.02	0.45	1.67	1.10
$Ru(bipy)_3^{2+}$	1.29 [25]	1.33 [25]	—	2.10 [25]	—	0.81	—	0.77

Note. The numbers in square brackets denote references (Ed.of Translation).

In particular, it follows from Eqn.(10) that the polarographic reduction potential increases (the polarographic oxidation potential decreases) by the electronic excitation energy.

The Table lists the values of $E_{1/2}$ and $E(^{1,3}A^*, {}^{1,3}D^*)$ for a series of compounds. Thus the condition for reaction (I) in solution is the inequality

$$E_{1/2}(D/D^+) - E_{1/2}(A^-/A) - E(^{1,3}A^*) < 0. \quad (12)$$

The above relation is convenient for assessing the possibility of the electron transfer reaction in a specific system $^{1,3}A^*$–D.

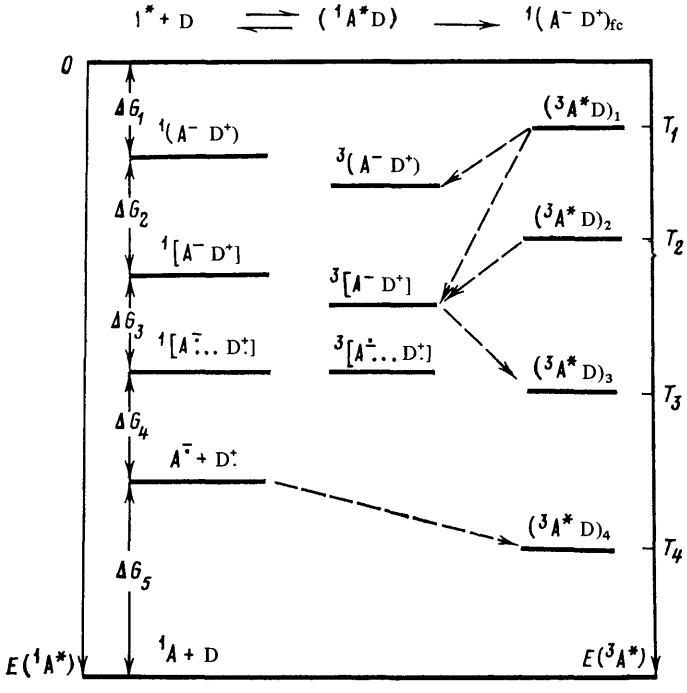


Figure 1. The energy scheme for electron transfer in a photochemical reaction between an acceptor A* and a donor D (for explanation, see text).

The efficiency of the formation of the final products of the electron transfer reaction is determined mainly by the energetics of the intermediate stages. Fig.1 presents a generalised energy scheme for electron transfer between the molecules of the acceptor $^{1,3}A^*$ and the donor D#. The electron transfer process involving the formation of solvated radical-ions includes the following sequence of stages.

1. The formation of a collision complex $^1A^*D$ between the excited singlet molecule $^1A^*$ and the molecule D in the ground state as a result of diffusional collisions between $^1A^*$ and D:

$$^1A^* + D \rightleftharpoons (^1A^*D). \quad (III)$$

Reaction (III) competes with the intersystem crossing into the triplet state $^3A^*$ and also with fluorescence and internal conversion processes. The free energy of reaction (III) is

$$\Delta G = -RT \ln \Delta V, \quad (13)$$

where ΔV is the relative change in the volume on formation of the complex[48].

2. Adiabatic electron transfer in the complex ($^1A^*D$) with formation of a vibrationally excited charge transfer state $^1(A^-D^+)_{fc}$ (the Franck–Condon state).

3. Vibrational relaxation from $^1(A^-D^+)_{fc}$ to the thermalised state $^1(A^-D^+)$ which takes place over a period of 10^{-12} s with retention of the initial orientation of the solvent molecules. The thermalised radical-ion pair in the triplet state $^3(A^-D^+)$ can be formed under the following conditions: (1) the transition to the triplet state T_1 competes effectively with the quenching of the fluorescence of $^1A^*$ by the donor molecules D; (2) the triplet level T_1 lies above the level corresponding to the charge transfer state $^3(A^-D^+)$. The free energy change ΔG_1 (Fig.1) is

$$\Delta G_1 = E_{1/2}(D/D^+) - [E_{1/2}(A^-/A) + E(^1A^*)] + \frac{e^2}{2}\left(\frac{1}{R_{D^+}} + \frac{1}{R_{A^-}}\right)\left(1 - \frac{1}{\varepsilon}\right) - \frac{e^2}{R} - \frac{\mu^2}{r^3}\left(\frac{n^2-1}{2n^2+1}\right), \quad (14)$$

where n is the refractive index of the medium. Thus a necessary condition for the quenching of the fluorescence (or the triplet state) of the acceptor by the electron donor is $\Delta G_1 < 0$.

4. The reorientation of the solvent molecules around the radical-ion pair $^1(A^-D^+)$ over a period 10^{-11}–10^{-10} s with formation of a radical-ion pair $^1[A^-D^+]$ (exciplex) stabilised by solvent molecules. The radical-ion pair $^3[A^-D^+]$ can be formed via the triplet state, pathways involving both $(^3A^*D)_1$ and $(^3A^*D)_2$ being energetically feasible under these conditions. However, electron transfer via the T_2 state is less probable, because it requires a definite orientation of the solvent molecules around the radical-ion pair $^3[A^-D^+]$. The solvation process can lead to the formation of solvate-separated radical-ion pairs $^1[A^-...D^+]$ and $^3[A^-...D^+]$ stabilised by the Coulombic interaction arising between the radical-ions A and D. The free energy changes ΔG_2 and ΔG_3 are

$$\Delta G_2 = -\frac{\mu^2}{r^3}\left(\frac{\varepsilon-1}{2\varepsilon+1} - \frac{n^2-1}{2n^2+1}\right), \quad (15)$$

$$\Delta G_3 = -\frac{e^2}{2}\left(\frac{1}{R_{D^+}} + \frac{1}{R_{A^-}}\right)\left(1 - \frac{1}{\varepsilon}\right) - \frac{e^2}{\varepsilon a} + \frac{e^2}{R} + \frac{\mu^2}{r^3}\left(\frac{\varepsilon-1}{2\varepsilon+1}\right), \quad (16)$$

where a is the distance between A^- and D^+ in the solvate-separated radical-ion pair.

5. In polar media the solvate-separated radical-ion pair dissociates into solvated radical-ions and the free energy of the reaction is

$$\Delta G_4 = e^2/\varepsilon a. \quad (17)$$

6. The formation of radical-ion pairs in the triplet state $^3[A^-D^+]$ and $^3[A^-...D^+]$ from the triplet state T_3 is energetically unlikely and requires an activation energy.

7. The recombination of radical-ions can lead to the population of the triplet level T_4 subject to the condition that

$$E_{1/2}(D/D^+) - E_{1/2}(A^-/A) > T_4. \quad (18)$$

The above relations (14)–(18) make it possible to find the free energies of the corresponding processes and hence to reach a conclusion about their feasibility.

III. THE QUENCHING OF THE EXCITED STATE AS A RESULT OF ELECTRON TRANSFER

The electron transfer in photochemical reactions between molecules, for example, those of the acceptor ($^{1,3}A^*$) and donor (D), can occur both as a result of diffusional collisions between $^{1,3}A^*$ and D and within the excited

#The reasoning remains the same when one considers the electron transfer reaction between $^{1,3}D^*$ and A.

complex formed beforehand by non-excited molecules A and D. The mechanism of the electron transfer reactions occurring as a result of the diffusional collisions between $^{1,3}A^*$ and D is considered below, it being assumed that a complex between A and D is not formed.

The electron transfer in a photochemical reaction between organic compounds can proceed both via excited singlet and the triplet state of the partners. The interaction between $^{1,3}A^*$ and D inevitably leads to the appearance of an additional pathway to the degradation of the excitation energy of the molecule $^{1,3}A^*$ and electron transfer results in a decrease of the lifetime of the excited molecules in the presence of a quenching additive. For the reaction between excited singlet acceptor molecules $^1A^*$ and non-excited donor molecules D,

$$^1A^* + D \xrightarrow{k_q^S} A^- + D^+, \qquad (IV)$$

the decrease of the lifetime of the molecules $^1A^*$ in the presence of D obeys the Stern–Volmer equation

$$\tau_S^0/\tau_S = 1 + k_q^S \tau_S^0 [D], \qquad (19)$$

where τ_S^0 and τ_S are the lifetimes of the excited singlet molecules $^1A^*$ in the absence and presence of the donor molecules respectively. For the reaction between triplet acceptor molecules $^3A^*$ and non-excited donor molecules D,

$$^3A^* + D \xrightarrow{k_q^T} A^- + D^+, \qquad (V)$$

the decrease of the lifetime of the triplet acceptor molecules in the presence of the quenching additive D is described by an equation analogous to Eqn.(19), k_q^S and k_q^T being the quenching rate constants for the corresponding states.

Thus the experimental observation of a linear relation between the relative decrease of the lifetime of excited molecules and the concentration of the quenching additive indicates directly the feasibility of the electron transfer. However one should note that not every quenching process of the excited states $^{1,3}A^*$ under the influence of the additive D, described quantitatively by Eqn.(19), is due to the electron transfer reaction (IV) or (V). A relation of the Stern–Volmer type holds also for many other processes, for example, for the triplet–triplet energy transfer between the acceptor and donor and the transfer of a hydrogen atom between $^{1,3}A^*$ and D. The electron transfer reaction is characterised, firstly, by the formation of an exciplex (in media of low polarity), secondly, by the formation of solvated radical-ions (in polar media), and, thirdly, by the existence of a correlation between the efficiency of the quenching of the excited state and the electron-donating (electron-accepting) properties of the quenching agent.

A definite relation can be established between the quenching rate constants $k_q^S(k_q^T)$ and the electron-donating properties of the quenching agent. In polar media the electron transfer in the collision complex between the excited acceptor molecule and the molecule of the donor quenching agent leads to the formation of a solvate-separated radical-ion pair and is described by the following scheme[56]:

Scheme 1

$$\begin{array}{ccccc} ^{1,3}A^* + D & \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} & (^{1,3}A^*D) & \underset{k_{32}}{\overset{k_{23}}{\rightleftharpoons}} & ^{1,3}[A^- \ldots D^+], \\ {\scriptstyle 1/\tau_{S,T}^0}\downarrow & & & & \downarrow{\scriptstyle k_{30}} \end{array}$$

where k_{12}, k_{21}, k_{23}, k_{32}, and k_{30} are the rate constants for the corresponding processes. It follows from Scheme 1 that

$$k_q^S \ (\text{or} \ k_q^T) = \frac{k_{12}}{1 + (1 + k_{32}/k_{30})\, k_{21}/k_{23}}. \qquad (20)$$

Eqn.(20) can be formulated in the following way:

$$k_q^S, k_q^T = k_{12}/\left[1 + \frac{k_{12}}{K_p k_{30}}\left(e^{\Delta G_{23}^{\ddagger}/RT} + e^{\Delta G_{23}/RT}\right)\right], \qquad (21)$$

where $\Delta G_{23}^{\ddagger}$ is the free energy of activation, ΔG_{23} the free energy of electron transfer in the collision complex, and $K_p = k_{12}/k_{21}$ the equilibrium constant.

$\Delta G_{23}^{\ddagger}$ and ΔG_{23} are related:

$$\Delta G_{23}^{\ddagger} = \Delta G_{23}/2 + [(\Delta G_{23}/2)^2 + (\Delta G_{23}^{\ddagger}(0))^2]^{1/2}, \qquad (22)$$

where $\Delta G_{23}^{\ddagger}(0)$ is the free energy of activation for $\Delta G_{23} = 0$.

Eqn.(21) can be simplified in the following two cases.

1. $\Delta G_{23} \ll 0$ and $\Delta G_{23}^{\ddagger} \cong 0$, whereupon

$$k_q^S \ (\text{or} \ k_q^T) = k_{12}/(1 + k_{21}/k_{30}). \qquad (23)$$

In this case the quenching rate constants k_q^S and k_q^T are invariant and independent of the nature of the donor quenching agent. It has been shown[56] that the ratio $k_{21}/k_{30} < 1$ for the electron transfer reaction between excited singlet molecules of a number of aromatic hydrocarbons (anthracene, 3,4-benzacridine, etc.) and electron donor molecules (tetramethyl-*p*-phenylenediamine, diethylaniline, methyldiphenylamine, etc.) and, in conformity with Eqn.(23), the rate constant for the quenching of the fluorescence is virtually identical with the constant k_{12} determined by the diffusion of the reacting molecules.

2. $\Delta G_{23} \gg 0$ and $\Delta G_{23}^{\ddagger} \cong \Delta G_{23}$, whereupon

$$k_q^S (\text{or} \ k_q^T) = \frac{K_p k_{30}}{2} e^{-\Delta G_{23}/RT}; \qquad (24)$$

according to Eqn.(24), there should be a linear relation between $\ln k_q^S$, $\ln k_q^T$, and ΔG_{23}. Figs.2*a* and 2*b* present the relations between k_q^S and ΔG_{23} for the reaction between aromatic hydrocarbons and electron donors[56] and between k_q^T/k_{12} and ΔG_{23} for the reaction between thionine and electron donors[57]. Fig.2 shows, firstly, that the values of k_q^S and k_q^T are constant over a wide range of values of ΔG_{23}, starting from $\Delta G_{23} < 10$ kcal mol^{-1} and, secondly, that the values of $\ln k_q^S$ and $\ln k_q^T$ are directly proportional to ΔG_{23}, starting from $\Delta G_{23} > 3$ kcal mol^{-1}. Thus Fig.2 illustrates a satisfactory agreement between the experimental data and the results of the theoretical study of Eqns.(21) to (24).

Relations similar to those presented in Fig.2 have also been obtained for the quenching of the fluorescence of pyrene and anthracene by a number of electron acceptors[58], of rubicene and acridine by certain amines[59,60], of substituted naphthalenes by dienes[61], of aromatic hydrocarbons and azastilbenes by inorganic anions[49,52,62], of bipyridyl complexes of ruthenium by nitro-compounds[63] and organic electron donors[64], of uranyl ions by metal cations[65], etc. The quenching of triplet states via the electron transfer mechanism [in conformity with Eqns.(23) and (24)] has been demonstrated for 2-naphthol[66], benzophenone[67], duroquinone[68], Methylene Blue[69,70], a number of aromatic hydrocarbons and carbonyl compounds[71], and also chlorophyll[72,73].

In non-polar media electron transfer also takes place in the collision complex between an excited molecule, for example, an acceptor molecule, and a non-excited donor molecule and

leads to the formation of a solvated radical-ion pair (exciplex). In this case the electron transfer is analogous to Scheme 1 (the difference consists in the replacement of the solvate-separated radical-ion pair by the exciplex) and the expressions for the rate constants for the quenching of the excited singlet and triplet states are analogous to Eqns.(20), (21), (23), and (24). The relations between $\ln k_q^S$ and $\ln k_q^T$, on the one hand, and ΔG_{23}, on the other ($\Delta G'_{23}$ is the free energy of the electron transfer reaction in the collision complex with formation of an exciplex), are similar to those presented in Fig.2.[73-75]

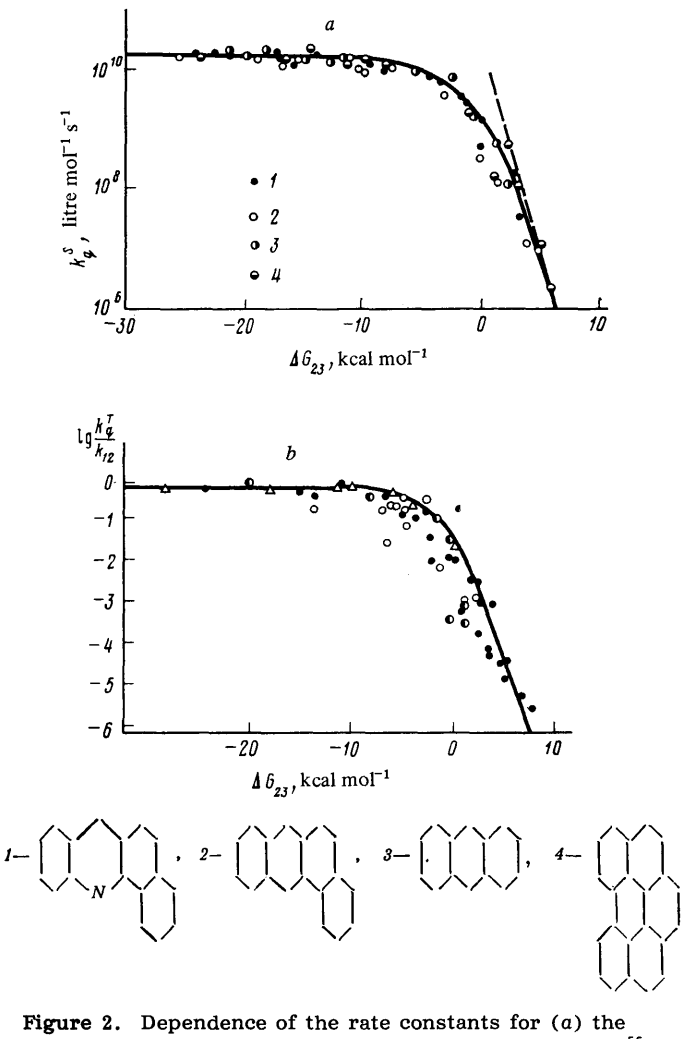


Figure 2. Dependence of the rate constants for (*a*) the quenching of the fluorescence of aromatic hydrocarbons[56] and (*b*) the quenching of the triplet state of Thionine[57] on the change in the free energy ΔG_{23}.

ΔG_{23} can be expressed in terms of the polarographic oxidation potential of the donor and the polarographic reduction potential of the acceptor:

$$\Delta G_{23} = E_{1/2}(D/D^+) - E_{1/2}(A^-/A) - E(^{1,3}A^*) - e^2/\varepsilon a. \quad (25)$$

The variation of the quenching rate constant with the donor oxidation potential (or the acceptor reduction potential for the photochemical oxidation of the donor) is analogous to that shown in Fig.2.

Two consequences which follow from an examination of Eqn.(23) and (24) must be mentioned. Firstly, according to Eqn.(23), the constants k_q^S and k_q^T can differ as a consequence of the difference between the rate constants for the destruction of the singlet and triplet radical-ion pairs (k_{30}). For the triplet pair, k_{30} should be appreciably smaller than for the singlet pair because the transition from the triplet pair to the ground state of the initial reaction products is forbidden[76-78]. Secondly, it follows from Eqn.(24) that the constants k_q^S and k_q^T must differ because of the difference between the values of ΔG_{23} for the reaction proceeding via the excited singlet and triplet states respectively:

$$\ln(k_q^S/k_q^T) = \ln(k_{30}^S/k_{30}^T) + \frac{1}{RT}[E(^1A^*) - E(^3A^*)]. \quad (26)$$

Thus the study of the kinetics and thermodynamics of the electron transfer process in photochemical reactions makes it possible to account for the quenching of the excited state by electron donors and acceptors as a consequence of electron transfer and to find the oxidation (reduction) potentials of the quenching agent molecules from the rate constant for the quenching of the excited state.

IV. THE NATURE OF THE EXCITED STATE OF THE MOLECULES INVOLVED IN THE ELECTRON TRANSFER REACTION

Electron transfer with participation of both excited singlet and triplet molecular states is energetically feasible.

1. Electron Transfer with Participation of the Triplet State

In liquid solutions electron transfer takes place as a result of diffusional collisions between the excited molecule and the other molecule involved in the reaction. The number of "acceptor" collisions is determined by the number of collisions between the reacting species during the lifetime of the excited states. The relation between the relative yield of the electron transfer reaction product, the lifetime of the excited state, and the concentration of the reactant D can be established for the reactions

$$^{1,3}A^* + D \xrightarrow{k_r} A^- + D^+, \quad (VI)$$

$$^{1,3}A^* \xrightarrow{k_0} A, \quad (VII)$$

where k_r is the effective rate constant for the electron transfer and k_0 the rate constant for the deactivation of the excited state $^{1,3}A^*$.

If the lifetime of the product exceeds significantly the duration of the electron transfer reaction, then the following relation exists between the initial concentration of the excited molecules $[^{1,3}A^*]_0$ and the maximum concentration $[A^-]_{max}$:

$$[A^-]_{max} = [^{1,3}A^*]_0(1 + k_0/k_r[D])^{-1}, \quad (27)$$

from which it follows that the maximum concentration of A^- is greatest for the condition $k_0 \ll k_r[D]$ and smallest for $k_0 \gg k_r[D]$. Typical rate constants for the excited singlet states of the molecules of many organic substances are $k_r \cong 10^9$ litre mol^{-1} s^{-1} and $k_0 \cong 2 \times 10^8$ s^{-1}. In this case the maximum yield of the electron transfer reaction products is

attained at concentrations of the quenching agent [D] > 1 M. Typical rate constants for the triplet states of molecules are $k_T \cong 10^8$ litre mol^{-1} s^{-1} and $k_0 \cong 10^3$ s^{-1}; for these values, the maximum yield of $A^{\mp}$ (or $D^{\pm}$) is attained at donor concentrations [D] > 10^{-4} M.[15,21]

Thus it follows from the results presented that, as a consequence of the significant difference between the lifetimes of the excited singlet and triplet molecules, the electron transfer at low concentrations of the quenching agent can proceed only via the triplet state. The proof of the involvement of the triplet state in the electron transfer reaction is based on a series of experimental data.

1. The quenching of the T state by electron acceptors (donors). To some extent, the quenching rate constant reflects the reactivity of the triplet states. The constant is found from data for the quenching of the triplet–triplet absorption.

2. Comparison of the emission times of a pulsed photoexcitation source and the time required for the accumulation of the electron transfer products. If the reaction proceeds via the triplet state and, according to the experimental conditions, the pulsed photoexcitation time τ_{pep} is significantly shorter than the lifetime of the triplet state τ_T, then the time of the attainment of the maximum concentration τ_{max} of the radical-ions at low concentrations of the quenching agent (electron acceptor or donor) must satisfy the condition

$$\tau_{pep} < \tau_{max} \leqslant \tau_T. \qquad (28)$$

If the radical-ions are formed with participation of the excited singlet state, then the maximum concentration of the radical-ions is attained during the photopulse ($\tau_{max} \cong \tau_{pep}$).

3. The competitive quenching of the triplet state. It follows from Eqns.(VI) and (VII) that, in the presence of a competitive quenching agent for the T state, the quantum yield of the radical-ions $\phi_{A^{\mp},D^{\pm}}$ decreases in accordance with the equation

$$\varphi_{A^{\mp},D^{\pm}} = \varphi^0_{A^{\mp},D^{\pm}} (1 + k_Q \tau^0_T [Q])^{-1}, \qquad (29)$$

where $\phi^0_{A^{\mp},D^{\pm}}$ and τ^0_T are quantities determined in the absence of the competitive quenching agent Q. The competitive quenching agents can be compounds with heavy atoms as well as compounds which function as acceptors of the triplet excitation energy, for example, oxygen, etc.[79].

Extensive factual data, demonstrating convincingly that the electron transfer takes place via the triplet states of the molecules of many organic compounds, have now accumulated. The involvement of triplet states has been demonstrated in the reduction of pyrene by radical-anions ($CO_2^{\mp}$, $CH_2O^{\mp}$, $CH_3CHO^{\mp}$),[80] of 2-naphthol and 1-anthrol by quinoline and 4-methylpyridine,[81] of 4-nitropyridine by isopropyl alcohol[82], of benzophenone and 2-naphthaldehyde by amines[83–86], and of quinones by amines and Fe^{2+},[87,88] and in the photochemical oxidation of phenothiazine by nitrobenzene[89] and Eu^{3+}.[90] The important role of the triplet state has also been demonstrated in one-electron reduction and oxidation reactions of dyes and photosynthetic pigments: Thionine[91–95], Methylene Blue[60,69,96–104], fluorescein[105–108], eosin[109–111], erythrosin[21], safranine T,[112] phenosafranine[113], oxonin[114], Acridine Orange[115], rhodamine 6G,[116–118], polymethine dyes[119,120], chlorophyll[22,121–130], phaeophytin[131], Mg-phthalocyanine[132], porphyrins[133], etc.

The above examples illustrate the electron transfer reaction occurring as a result of diffusional collisions between a triplet donor (acceptor) molecule and a non-excited molecule of the other reactant (exogenic electron acceptor or donor respectively). At the same time electron transfer can proceed with participation of molecular triplet states also in the absence of extraneous electron donor or acceptor molecules. In this case the other reactant may be a molecule in the triplet state (triplet–triplet interaction) or in a non-excited state (concentration-dependent quenching):

$$^3A^* + {}^3A^* \rightarrow A^{\mp} + A^{\pm}, \qquad (VIII)$$

$$^3A^* + {}^1A \rightarrow A^{\mp} + A^{\pm}. \qquad (IX)$$

Measurements of the rate of accumulation of radical-ions formed via reactions (VIII) and (IX) have shown that the rate constants for the accumulation of $A^{\mp}$ are always smaller than the rate constants for the quenching of the triplet state as a result of the triplet–triplet interaction and the concentration-dependent quenching[19,21,111]. Consequently the electron transfer reactions (VIII) and (IX) are accompanied by processes involving the "physical" deactivation of the triplet states:

$$^3A^* + {}^3A^* \rightarrow {}^1A^* + {}^1A, \qquad (X)$$

$$^3A^* + {}^1A \rightarrow {}^1A + {}^1A. \qquad (XI)$$

The feasibility of electron transfer via reactions (VIII) and (IX) can be assessed with the aid of the relations

$$E_{1/2}(A/A^+) - E_{1/2}(\bar{A}/A) - 2E(^3A^*) < 0, \qquad (30)$$

$$E_{1/2}(A/A^+) - E_{1/2}(A^-/A) - E(^3A^*) < 0. \qquad (31)$$

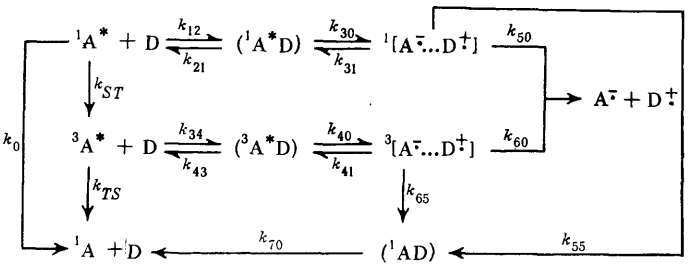
For example, the polarographic oxidation and reduction potentials are respectively +0.76 and −0.99 V for chlorophyll *a* in the $^3E^* = 1.33$ eV triplet state (see Table). Thus, in conformity with Eqns.(30) and (31), the electron transfer can occur only when two triplet chlorophyll *a* molecules interact. The detection of the pigment radical-ions has been confirmed by[134] measurements of the transient conductivity arising on pulsed photoexcitation of chlorophyll solutions. The occurrence of electron transfer via reactions (VIII) and (IX) has been established for fluorescein[105], eosin[135], rhodamine 6G,[116,118] and thiazine[97,111] and polymethine dyes[120,136].

2. Kinetic Analysis of the Electron Transfer Reaction Mechanism

With increase in the concentration of the quenching additive, the number of "successful" collisions not only between triplet and quenching agent molecules but also between excited singlet and quenching agent molecules also increase. Consequently at certain concentrations of the quenching agent there is a possibility of electron transfer involving the excited singlet states of the molecules and leading to the formation of radical-ions. The formation of radical-ions as a result of electron transfer between the excited molecule of, for example, the acceptor and the non-excited molecule of the donor occurs only in polar media. The dependence of the quantum yield in the formation of radical-ions on the concentration of the quenching agent in the electron transfer reaction, proceeding through excited

singlet and triplet states of the acceptor in conformity with Scheme 2, is analysed below:

Scheme 2



It is suggested that a complex is not formed between the acceptor and donor molecules; k_0 and k_{ST} are the rate constants for the fluorescence (including internal conversion) and the intercombination conversion to the triplet state respectively and k_{TS} is the rate constant for the intercombination degradation.

For a reaction proceeding similarly via the excited singlet state, there is a linear relation between the reciprocal of the quantum yield in the formation of solvated radical-ions ($A^{\bar{\cdot}}$ or $D^{+\cdot}$) and the reciprocal of the donor concentration:

$$\frac{1}{\varphi^{S}_{A^{\bar{\cdot}},D^{+\cdot}}} = 1 + \frac{k_{55}}{k_{50}} + \left(1 + \frac{k_{55}}{k_{50}}\right)\frac{1}{k_q^S \tau_S^0 [D]}, \qquad (32)$$

where

$$k_q^S = k_{12}/\left[1 + \frac{k_{21}}{k_{30}}\left(1 + \frac{k_{31}}{k_{50} + k_{55}}\right)\right], \qquad (33)$$

$$\tau_S^0 = (k_0 + k_{ST})^{-1}. \qquad (34)$$

For a reaction proceeding solely via the triplet state (when the excited singlet state is quenched), the dependence of the quantum yield in the formation of solvated radical-ions ($A^{\bar{\cdot}}$ or $D^{+\cdot}$) on 1/[D] passes through a minimum in conformity with the relation

$$1/\varphi^{(T)}_{A^{\bar{\cdot}},D^{+\cdot}} = \left(\frac{1 + k_{65}/k_{60}}{\varphi_T}\right)\left(1 + \frac{k_q^S \tau_S^0}{k_q^T \tau_T^0} + k_q^S \tau_S^0 [D] + \frac{1}{k_q^T \tau_T^0 [D]}\right). \qquad (35)$$

where

$$k_q^T = k_{34}/\left[1 + \frac{k_{43}}{k_{40}}\left(1 + \frac{k_{41}}{k_{60} + k_{65}}\right)\right], \qquad (36)$$

$$k_q^S = k_{12}/\left[1 + \frac{k_{21}}{k_{30}}\left(1 + \frac{k_{31}}{k_{55}}\right)\right], \qquad (37)$$

$$\varphi_T = \frac{k_{ST}}{k_0 + k_{ST}}, \qquad (38)$$

$$\tau_T^0 = k_{TS}^{-1}. \qquad (39)$$

Relations (32) and (35) have been obtained for the electron transfer reaction between an excited acceptor molecule and a non-excited donor molecule. Exactly the same expressions for the reciprocals of the quantum yield in the formation of the radical-ions can be obtained for the electron transfer reaction between an excited donor molecule and a non-excited acceptor molecule. Fig.3 illustrates the the relations between $1/\phi^{(S,T)}_{A^{\bar{\cdot}},D^{+\cdot}}$ and 1/[D] expected according to Eqns.(32) and (35) and corresponding to the values $\phi_T \cong 0.5$, $k_q^S \cong 10^{10}$ litre mol^{-1} s^{-1}, $k_q^T \cong 10^9$ litre mol^{-1} s^{-1} (it is suggested that $\Delta G_{30,40} \ll 0$), $\tau_S^0 \cong 10^{-9}$ s, $\tau_T^0 \cong 10^{-4}$ s, $k_{65}/k_{60} \cong 1$, and $k_{55}/k_{50} \cong 10-10^2$ typical for dyes and pigments. Fig.3 also presents experimental data obtained for the photochemical oxidation of chlorophyll *a* by nitrobenzene. Comparison of the experimental relation with relations (32) and (35) shows that radical-ions are formed solely via the triplet state.

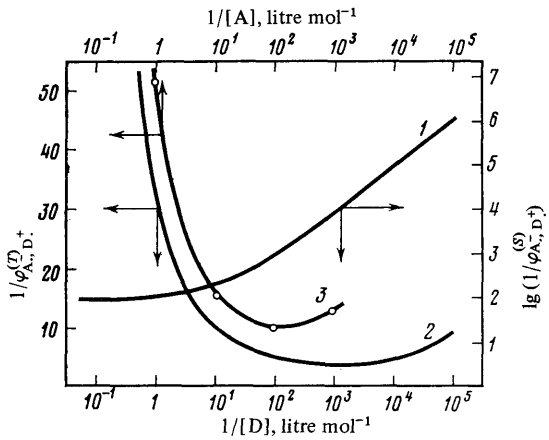
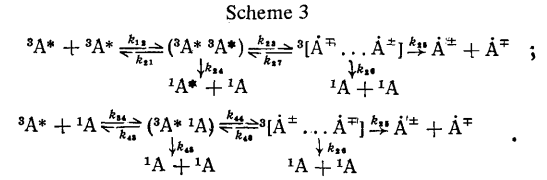


Figure 3. Dependence of the reciprocal of the quantum yield for the formation of radical-ions on the reciprocal of the concentration of the excited state quenching agent: *1*) and *2*) according to Eqns.(32) and (35); *3*) experimental data for the photochemical oxidation of chlorophyll with nitrobenzene[128].

Thus the conclusion that the triplet state plays an important role in the formation of electron transfer products is based on the kinetic analysis of the reaction mechanism postulating the quenching of both the excited singlet and triplet states. This conclusion has been confirmed in direct experiments on the electron transfer between an excited bacteriophaeophytin molecule and *p*-benzoquinone by the method of picosecond spectrophotometry[137].

As stated above, electron transfer can occur as a result of the interaction of both two triplet molecules with one another and of a triplet molecule with a non-excited molecule. The electron transfer reactions and the competing processes are presented in Scheme 3 below:

Scheme 3



Measurements of the rate constants for the quenching of the triplet state as a result of the triplet–triplet interaction [$k_q^{(T-T)}$] and the concentration-dependent quenching [$k_q^{(T-S)}$] have shown that $k_q^{(T-T)}$ exceeds $k_q^{(T-S)}$: in terms of order of magnitude, $k_q^{(T-T)} \cong 10^9$ litre

mol^{-1} s^{-1} and $k_q^{(T-S)} \cong 10^7-10^8$ litre mol^{-1} s^{-1}.[19,21,111,118,120] The difference between $k_q^{(T-T)}$ and $k_q^{(T-S)}$ can be explained in terms of Scheme 3, from which it follows that

$$k_q^{T-T} \simeq k_{12}/(1+k_{21}/k_{23}) + k_{12}/2(1+k_{23}/k_{21}). \quad (40)$$

Eqn.(40) has been obtained on the assumption that $k_{27} < (k_{25}+k_{26})$, since $\Delta G_{23} < -20$ kcal mol^{-1} [in conformity with tabulated data and Eqn.(30)] and $k_{24} < k_{23}$, k_{21}. It also follows from Scheme 3 that

$$k_q^{(T-S)} \simeq \frac{k_{34}}{2k_{43}/k_{44}} + \frac{k_{34}}{k_{43}/k_{45}}. \quad (41)$$

Eqn.(41) has been obtained on the assumption that $k_{46} \cong k_{25}+k_{26}$ [$\Delta G_{44} > 2-5$ kcal mol^{-1} in conformity with the tabulated data and Eqn.(31)], and $k_{43} > k_{45}$, k_{44}. Since $k_{12}=k_{34}$ and $k_{21}=k_{43}$, the differences between $k_q^{(T-T)}$ and $k_q^{(T-S)}$ are due to the fact that $k_{44} < k_{23}$. Measurements of the rate constants for electron transfer as a result of the triplet–triplet interaction [$k_r^{(T-T)}$] and the concentration-dependent quenching [$k_r^{(T-S)}$] have shown that $k_r^{(T-T)}$ exceeds $k_r^{(T-S)}$.[21,118,120] The explanation of this finding follows from an examination of Scheme 3.

When account is taken of the above assumptions, Scheme 3 leads to

$$k_r^{(T-T)} = \frac{k_{12}}{(1+k_{21}/k_{23})(1+k_{26}/k_{25})}, \quad (42)$$

$$k_r^{(T-S)} = \frac{k_{34}}{2(k_{43}/k_{44})(1+k_{26}/k_{25})}. \quad (43)$$

Thus the efficiency of electron transfer via the triplet–triplet interaction and concentration-dependent quenching mechanisms is determined by processes occurring in the radical-ion pairs.

Radical-ion pairs are formed in the electron transfer reaction (Scheme 2) exclusively via the triplet state. The explanation of the important role of the triplet state consists in the different rates of the recombination processes occurring in the singlet and triplet radical-ion pairs respectively. According to Scheme 2, electron transfer takes place in the collision complexes formed by the donor molecule with an excited singlet or triplet acceptor molecule. This leads to the formation of radical-pairs in the singlet and triplet states respectively. The probability of the dissociation of the radical-ion pairs into solvated radical-ions is determined by the ratios $k_{50}/(k_{31}+k_{50}+k_{55})$ (for the pair in the singlet state) and $k_{60}/(k_{41}+k_{60}+k_{65})$ (for the pair in the triplet state). For exothermic electron transfer reactions ($\Delta G < -10$ kcal mol^{-1}), the constants k_{31} and k_{41} make a small contribution to the overall rate constant for the destruction of radical-ion pairs and in addition it is evident that $k_{50} \cong k_{69}$.

Thus the ratio of the probabilities of the dissociation of the singlet and triplet radical-ion pairs into radical-ions is $(k_{60}+k_{65})/(k_{50}+k_{55})$. As a consequence of the prohibition of transitions between states of different multiplicity, it is to be expected that $k_{55} \gg k_{65}$ and in addition that $k_{50} < k_{55}$, since the dissociation of the ion pair into radical-ions involves the overcoming of Coulombic interaction forces. Consequently the recombination process, taking place effectively in the singlet pair, significantly suppresses the dissociation of the singlet pair, in contrast to the pair in the triplet state. Thus, according to Gouterman and Holten[77], radical-ions are formed in the photochemical oxidation of bacteriophaeophytin by *p*-benzoquinone exclusively via the triplet state, which has been confirmed in the study of the rate constants for the processes: $k_{55} \cong 10^{12}$, $k_{50} \cong k_{60} \cong 4 \times 10^9$, and $k_{65} \ll 4 \times 10^9$ s^{-1}.

V. THE REACTIVITY OF THE EXCITED STATE IN THE ELECTRON TRANSFER REACTION

The formation of radical-ions in the photochemical electron transfer reaction is a multistage process. The electron transfer takes place in the collision complex formed by excited molecules and a non-excited molecule of the other reactant and leads to the formation of a radical-ion pair. The rate constant k_{23} in Scheme 1 can serve as a measure of the reactivity of the excited state in the electron transfer reaction.

The reactivities of the excited singlet and triplet states are compared below. According to Scheme 2, the electron transfer rate constants can be expressed in the form

$$k_{30} \propto \exp(-\Delta G_{30}^{\neq}/RT), \quad (44)$$

$$k_{40} \propto \exp(-\Delta G_{40}^{\neq}/RT), \quad (45)$$

where $G_{30,40}^{\neq}$ is the free energy of activation for electron transfer via the excited singlet and triplet states respectively.

It follows from Eqns.(44) and (45) that the expression

$$\ln(k_{30}/k_{40}) = (\Delta G_{40} - \Delta G_{30})/RT, \quad (46)$$

is valid for endothermic reactions ($\Delta G_{30,40} \gg 0$) when account is taken of Eqn.(22), whereupon $\Delta G_{30,40}^{\neq} \cong \Delta G_{30,40}$. Since

$$(\Delta G_{40} - \Delta G_{30}) = E(^1A^*) - E(^3A^*) \equiv \Delta E, \quad (47)$$

we have

$$\ln(k_{30}/k_{40}) = \Delta E/RT. \quad (48)$$

Thus the greater energy of the excited singlet state of the molecule compared with that of the triplet state is responsible for the greater reactivity of the excited singlet molecules. For an exothermic reaction, where $\Delta G_{30,40} \ll 0$ and $\Delta G_{30,40}^{\neq} \cong 0$, the difference between k_{30} and k_{40} is significantly reduced.

1. Protonation of the Excited State and Comparative Reactivity

Electron transfer can proceed with participation of both protonated (for example, $^{1,3}A^*H^+$) and deprotonated ($^{1,3}A^*$) molecules. The rate constant for the quenching of the excited state is related to the free energy of reaction; consequently there is a relation between the free energy of the electron transfer reaction and the protolytic equilibrium constant for molecules in the excited state. The electron transfer reactions involving deprotonated and protonated excited molecules are presented in Scheme 4:

Scheme 4

$$\begin{array}{ccc} ^{1,3}A^*H^+ + D & \rightarrow & A^{\cdot}H + D^+ \\ \downarrow\uparrow H^+ & & \downarrow\uparrow H^+ \\ ^{1,3}A^* + D & \rightarrow & A^- + D^+ \end{array}$$

The expressions for the free energy of the electron transfer reaction are

$$\Delta G_b = E_{1/2}(D/D^+) - [E_{1/2}(A^-/A) + E(^{1,3}A^*)], \quad (49)$$

$$\Delta G_a = E_{1/2}(D/D^+) - [E_{1/2}(AH/AH^+) + E(^{1,3}A^*H^+)]; \quad (50)$$

where subscripts a and b denote the protonated and deprotonated states of the acceptor molecules respectively. It follows from Eqns.(49) and (50) that

$$\Delta\Delta G = (\Delta G_b - \Delta G_a) = [E_{1/2}(\mathrm{AH/AH^+}) - E_{1/2}(\mathrm{A^-/A})] + [E(^{1,3}\mathrm{A^*\,H^+}) - E(^{1,3}\mathrm{A^*})]. \quad (51)$$

Scheme 5 below (the Forster cycle)

Scheme 5

$$\begin{array}{ccc} ^{1,3}\mathrm{A^*} + \mathrm{H^+} & \overset{pK^*}{\rightleftharpoons} & ^{1,3}\mathrm{A^*\,H^+} \\ \uparrow h\nu_1 & & \uparrow h\nu_2 \\ \mathrm{A} + \mathrm{H^+} & \overset{pK}{\rightleftharpoons} & \mathrm{AH^+} \end{array}$$

leads to the relation

$$E(^{1,3}\mathrm{A^*\,H^+}) - E(^{1,3}\mathrm{A^*}) = 2.3RT(pK - pK^*), \quad (52)$$

where pK and pK^* refer to the acid–base equilibria involving the non-excited and excited (singlet and triplet) molecules (according to Scheme 5)[15]. Scheme 6

Scheme 6

$$\begin{array}{ccc} \mathrm{A^-} + \mathrm{H^+} & \overset{pK_R}{\rightleftharpoons} & \mathrm{\dot{A}H} \\ \uparrow e & & \uparrow e \\ \mathrm{A} + \mathrm{H^+} & \overset{pK}{\rightleftharpoons} & \mathrm{AH^+} \end{array}$$

also leads to

$$E_{1/2}(\mathrm{AH/AH^+}) - E_{1/2}(\mathrm{A^-/A}) = 2.3RT(pK_R - pK); \quad (53)$$

we finally have

$$\Delta\Delta G = 2.3RT(pK_R - pK^*). \quad (54)$$

Thus it follows from Eqn.(54) that the increase of the rate constant for the quenching of the excited state of the protonated acceptor molecules by the electron donor molecules is determined by the condition $pK_R > pK^*$. For the photochemical reduction of Thionine by aromatic hydrocarbons[57], the Thionine triplet state quenching constant is higher in an acid medium, which is consistent with the conclusion which follows from Eqn.(54), since $pK_R = 10.4$ and $pK^* = 7.0$ for Thionine.

At the same time, according to Eqns.(44) and (45), the rate constant for electron transfer within the collision complex can be expressed in terms of the changes in the free energy of activation. In the case of an endothermic electron transfer reaction the ratio of the electron transfer rate constant for the reactions of protonated ($k^a_{30,40}$) and deprotonated ($k^b_{30,40}$) excited molecules can be expressed in terms of pK_R and pK^* in the following way:

$$\ln\frac{k^a_{30.40}}{k^b_{30.40}} = 2.3(pK_R - pK^*). \quad (55)$$

Consequently a conclusion concerning the comparative reactivities of the protonated and deprotonated excited molecules can be based on the values of pK_R and pK^*.

2. Relation between the Reactivity and the Nature of the Electronic Excitation

For photochemical electron transfer reactions, the excited electronic n,π^* and π,π^* states are of greater interest. The n,π^* state is populated as a result of the $n \to \pi^*$ transition in which the n electrons of the heteroatom pass to the antibonding π orbital. The maximum information about the involvement of the T_{n,π^*} states in photochemical reactions has been obtained in relation to carbonyl compounds[34,138,139]. The high reactivity of the T_{n,π^*} states in the electron transfer reaction is due to the appearance of an electron density deficit at the oxygen atom of the carbonyl group as a result of the $n \to \pi^*$ transition. Thus the photochemical reduction of benzophenone and acetophenone in aqueous solutions as a result of electron transfer from a carbonate ion has been investigated[140].

A high reactivity of triplet n,π^* states has been observed also for aromatic quinones (benzo-, naphtho-, and anthra-quinones) with the lowest T_{n,π^*} level. A number of studies have been made[140–146] in which semiquinone radicals were formed as a result of electron transfer from a series of inorganic anions (CO_3^{2-}, SO_4^{2-}, Cl^-, SCN^-, PO_4^{3-}, OH^-, etc.). Quantitative measurements of the electron transfer rate constant in photochemical reduction reactions have been made for anthraquinones in aqueous solutions[145,147,148] by the method of competition kinetics. The rate constants for electron transfer to the T_{n,π^*} state of anthraquinone-2,6-disulphonic acid are 1.8×10^6 litre mol^{-1} s^{-1} for HCO_3^- and 7.1×10^6 litre mol^{-1} s^{-1} for OH^-.

As shown above, the rate constant for electron transfer in the collision complex is a measure of the reactivity of the excited state, but it can be by no means always determined or estimated. The quantum yield of the electron transfer products γ can also serve as a relative measure of reactivity. Measurements have been made[140] of γ for the formation of $CO_3^{\bullet-}$ in the photochemical oxidation of carbonate by different quinone derivatives. It follows from the results of this study that naphtho- and anthra-quinones can be separated into two groups: those which oxidise carbonate with a quantum yield γ close to unity (1,4-naphthoquinone, 8-methyl-1,4-naphthoquinone, and anthraquinonesulphonic acid) and those which do not oxidise carbonate ($\gamma < 10^{-3}$; hydroxy- and amino-derivatives of naphtho- and anthraquinones).

This difference between reactivities can be associated with the different positions of the triplet n,π^* and π,π^* levels in the anthraquinone molecules[149,150]. The much lower reactivity of the triplet π,π^* states compared with the n,π^* states of aromatic carbonyl compounds is associated with the absence of a deficiency of electron density at the oxygen atom of the carbonyl group. The lack of data for the electron transfer rate constants involving carbonyl T_{π,π^*} states hinders a quantitative estimate of the reactivity of such states. The principal conclusions on this subject have been reached by comparing the yields γ of the products of the photochemical reduction of carbonyl compounds with different positions of the triplet n,π^* and π,π^* levels.

Despite the considerable differences between the reactivities of the T_{n,π^*} and T_{π,π^*} states, it has been noted that the acetophenone derivatives, which have a lowest T_{π,π^*} level, are capable of photochemical reduction with an appreciable yield[151,152]. For the alkyl phenyl ketones investigated, it is known that (a) $\Delta E \cong 1000$ cm^{-1} and (b) the wave function of the T_{π,π^*} state becomes "mixed" with that of the T_{n,π^*} state. Thus the photochemical reduction of phenyl ketones proceeds via a lowest triplet π,π^* state, which has partial n,π^* character and which is responsible for the appreciable quantum yield of the reaction. The reaction can also proceed via a highest T_{n,π^*} state (with a lowest T_{π,π^*} state) populated on thermal excitation[153].

Thus, examination of the data presented reveals a significant difference between the reactivities of the molecules of carbonyl compounds and quinones in the T_{n,π^*} state (compared with T_{π,π^*}) in the electron transfer reaction.

VI. THE INTERMEDIATE STATES IN THE FORMATION OF RADICAL-IONS

As stated above, solvated radical-ions are formed in the photochemical electron transfer reaction between the donor and acceptor molecules via a series of intermediate states including the exciplex and the solvate-separated radical-ion pair. The exciplex or the complex in the excited state are formed as a result of the interaction of the excited (singlet, triplet) donor (acceptor) molecule with a non-excited acceptor (donor) molecule[154-158]. The formation of an exciplex has been observed in non-polar (weakly polar) media on the basis of the appearance of a structureless luminescence band or of a transient absorption[159,160]. The existence of singlet exciplexes has been established reliably for atomatic hydrocarbons[48,161-171], aminopyridine[172], fluorene[173], transition metal complexes[174], etc. Triplet exciplexes have been investigated in less detail, mainly due to the extremely low phosphorescence quantum yields in the liquid solutions. The existance of triplet exciplexes is therefore established on the basis of the appearance of a transient absorption. The formation of triplet exciplexes has been observed between metalloporphyrins and aromatic nitro-compounds[175-177], chlorophyll and *p*-benzoquinone[178], phaeophytin and *p*-benzoquinone[179], benzene (and its methyl derivatives) and tetracyanobenzene[180], etc. The formation of triplet exciplexes has also been postulated in a number of studies of the mechanism of the quenching of the triplet state of thiazine[94,95] and polymethine dyes[120].

Measurements of the absorption spectra of the exciplexes by the method of laser photolysis[160] showed that the exciplexes have in many instances the structure of an ion pair[164-167,181]. At the same time it also follows from spectroscopic and thermodynamic data that the triplet exciplexes of many metalloporphyrins in the chlorophyll have the structure of an ion pair with partial charge transfer[177,178]. The wave function of the exciplex can be represented by a combination of the wave functions of states with complete charge transfer and states with excitation localised at one of the components of the complex[61,182]:

$$\psi_{exc} = \alpha\psi_1(\bar{A}D^+) + \beta\psi_2(A^*D) + \gamma\psi_3(AD^*). \qquad (56)$$

For singlet exciplexes comprising aromatic hydrocarbons and amines and also heterocyclic compounds and amines, which have the ionic structure A^-D^+, measurements have been made of the dipole moments μ, the heats of formation ΔH, and the molecular volumes ΔV. Thus $\mu = 13.3 \pm 1.7$ D for the exciplex of 3,4-benzacridine and diethylaniline[170]. The heats of formation $-\Delta H$ vary from 6.6 to 10.2 kcal mol^{-1} on passing from the exciplex of biphenyl and diethylaniline to the exciplex of anthracene and diethylaniline[48]. The change in molecular volume on formation of the exciplex relative to the initial components is $-\Delta V = 15.5$ cm^3 litre mol^{-1} for the pyrene–diethylaniline pair[170].

As stated above, in contrast to charge-transfer complexes, exciplexes are formed only in the excited state and this leads to the quenching of the fluorescence of the initial molecules (for singlet exciplexes) or to the quenching of the triplet–triplet absorption (for triplet exciplexes) and is accompanied by the appearance of a new luminescence or transient absorption. The mechanism of the electron transfer reactions leading to the formation of an exciplex is in broad outline analogous to Scheme 1. The application of picosecond laser excitation made it possible to obtain a series of data on the kinetics of the formation of exciplexes[183-185]. It has been shown for the exciplex of anthracene and diethylaniline that the exciplex formation rate constant is equal to the diffusional constant $(10 \pm 1) \times 10^{10}$ litre mol^{-1} s^{-1}. The formation of an exciplex of anthracene and diethylaniline in pure diethylaniline is slower than in hexane, since the rate-limiting stage of the reaction is orientational relaxation whose period is longer in diethylaniline than in hexane.

In non-polar and weakly polar media the formation of solvated radical-ions is usually not observed and the excitation energy is degraded as a result of a set of radiative and non-radiative processes. The solvated radical-ions can be formed in non-polar media as a result of two-quantum reactions, in which the second quantum is absorbed by the exciplex[160]. The non-radiative processes occurring in singlet exciplexes can be represented by a set of the following reactions[186-188]:

$$^1A^* + D \rightleftharpoons (^1A^*D) \rightarrow {}^1(A^-D^+)_{fc}, \qquad (XII)$$

$$^1(A^-D^+)_{fc} \rightarrow {}^1(A^-D^+), \qquad (XIII)$$

$$^1(A^-D^+)_{fc} \rightarrow {}^3A^* + D, \qquad (XIV)$$

$$^1(A^-D^+) \rightarrow A + D + (D)_{fl}, \qquad (XV)$$

$$^1(A^-D^+) \rightarrow {}^3A^* + D, \qquad (XVI)$$

$$^1(A^-D^+) \rightarrow {}^1[A^-D^+] \qquad (XVII)$$

$$^1[A^-D^+] \rightarrow A + D + h\nu_{fl}, \qquad (XVIII)$$

$$^1[A^-D^+) \rightarrow A + D. \qquad (XIX)$$

The electron transfer takes place in a collision complex and leads to the formation of a Franck–Condon state of the exciplex [reaction (XII)] which is followed by the vibrational relaxation process (XIII). When the exciplex passes to a thermalised state, a "fast" intercombination transition to the triplet state [reaction (XIV)] competes. The subsequent deactivation processes include fluorescence from a vibrationally relaxed state [reaction (XV)], a "slow" intercombination transition to triplet states [reaction (XVI)], and a transition to a fully relaxed state as a result of the reorientation of the solvent molecule [reaction (XVII)], which is followed by fluorescence [reaction (XVIII)] and recombination [reaction (XIX)] processes. According to a series of data[163-165,189], the ratio of the rate constant for the radiative deactivation of the exciplex to the overall rate constant for the non-radiative deactivation process is in the range 0.01 to 1.5 for the perylene–dimethylaniline, 1,12-benzoperylene–*p*-chloro-*N*,*N*-dimethylaniline, etc. complexes.

In polar media the lifetime of the exciplex is shortened and this is accompanied by a decrease of the fluorescence yield and the appearance of solvated radical-ions. It has been shown[190] for the exciplex of anthracene and diethylaniline that the solvate radical-ions can be formed via the exciplex. According to a study[191] by the method of laser photolysis, an increase in the dielectric constant of the medium alters the electronic structure of the exciplex.

In weakly polar and polar media a solvate-separated radical-ion pair is an intermediate in the formation of solvated radical-ions. The formation of a solvate-separated radical-ion pair was demonstrated[192] on the basis of absorption spectra measured 50 ns after the laser excitation of pyrene in the presence of an electron acceptor–dicyanobenzene in dichloromethane. Parallel photoconductivity measurements demonstrated the absence of solvated radical-ions in the course of 50 ns after photoexcitation.

The processes occurring in the singlet radical-ion pairs can be represented by the following reactions:

$$^1A^* + D \rightleftharpoons (^1A^*D) \rightarrow {}^1(A^- \ldots D^+), \qquad (XX)$$

$$^1(A^- \ldots D^+) \rightarrow A + D, \qquad (XXI)$$

$$^1(A^- \ldots D^+) \rightarrow {}^3(A^- \ldots D^+), \qquad (XXII)$$

$$^1(A^- \ldots D^+) \rightarrow {}^1[A^- \ldots D^+], \qquad (XXIII)$$

$$^1[A^- \ldots D^+] \rightleftharpoons A^- + D^+. \qquad (XXIV)$$

The electron transfer takes place in the collision complex and leads to the formation of a "primary" radical-ion pair $^1(A^{\bar{\cdot}}...D^{+\cdot})$ [reaction (XX)], which is apparently similar to the Franck–Condon state of the exciplex[193]. The dissociation of the solvate-separated radical-ion pair $^1[A^{\bar{\cdot}}...D^{+\cdot}]$ into solvated radical-ions [reaction (XXIV)] precedes the recombination [reaction (XXI)] and intercombination conversion [reaction (XXII)] processes and the orientational relaxation of the solvent [reaction (XXIII)] in the pair $^1(A^{\bar{\cdot}}...D^{+\cdot})$.[193–195]. According to a number of studies[195–197], the recombination process takes place over a period of ~10 ns. The intercombination transition can be extremely effective as a consequence of the interaction between the electron spins and nuclei and can take place over a period of several nanoseconds[197–199].

The processes in triplet radical-ion pairs are fundamentally analogous to the processes in the singlet pairs. The main difference consists in the times of the recombination processes. Thus according to Gouterman and Holten[77], the recombination time in the singlet radical-ion pair formed by bacteriophaeophytin and *p*-benzoquinone is 5 ps, while the recombination time in the triplet pair is significantly greater than 230 ps. The difference between the recombination times is responsible for the difference between the quantum yields in the formation of solvated radical-ions via the excited singlet and triplet states.

VII. THE ROLE OF THE MEDIUM IN ELECTRON TRANSFER PROCESSES

As mentioned above, solvated radical-ions are formed as the final electron transfer products in photochemical reactions only in polar media, which has been manifested experimentally by the transient absorption of the radical-ions or the transient conductivity of the solution. In non-polar media there is no photoinduced absorption or photoinduced conductivity. Studies of the electron transfer mechanism[25,69–71] in media of different polarity have demonstrated the relation between the intermediate states in electron transfer. Scheme 7 presents the fundamental processes in the photochemical oxidation of a donor $^{1,3}D^*$:

Scheme 7

$$^{1,3}D^* + A \underset{k_{21}}{\overset{k_{12}}{\rightleftharpoons}} (^{1,3}D^*A) \begin{cases} \overset{k_{23}}{\underset{k_{32}}{\rightleftharpoons}} {}^{1,3}[D^+A^-] \\ \overset{k_{34}}{\underset{k_{43}}{\rightleftharpoons}} {}^{1,3}[D^{+\cdot}...A^{\bar{\cdot}}] \overset{k_{56}}{\underset{k_{65}}{\rightleftharpoons}} D^{+\cdot} + A^{\bar{\cdot}} \end{cases} \qquad k_{45} \downarrow \uparrow k_{54}$$

The pathway followed in the electron transfer reaction can be traced from the changes in free energy as a function of the dielectric constant of the medium[200]. The change in the free energy of formation of the exciplex ΔG_{23} (notation of Scheme 7) is given by the following expression according to Eqns.(14) and (15) and Knibbe[48]:

$$\Delta G_{23} = \Delta G_{23}(\text{hexane}) - \frac{\mu^2}{r^3}\left(\frac{\varepsilon - 1}{2\varepsilon + 1} - 0.186\right). \qquad (57)$$

The change in the free energy of formation of the solvate-separated radical-ion pair ΔG_{34} is given by the following equation according to Eqns.(14)–(16):

$$\Delta G_{34} = [E_{1/2}(D/D^+) - E_{1/2}(A^-/A)]_{\varepsilon_0} - \frac{e^2}{\varepsilon a} + \Delta G_{\text{solv}} - E(^{1,3}D^*), \qquad (58)$$

where

$$\Delta G_{\text{solv}} = \frac{e^2}{2}\left(\frac{1}{R_{D^+}} + \frac{1}{R_{A^-}}\right)\left(\frac{1}{\varepsilon} - \frac{1}{\varepsilon_0}\right) \qquad (59)$$

is the change in the free energy of solvation on passing from a medium with a dielectric constant ε_0 (in which the polarographic oxidation-reduction potentials are measured) to a medium with a dielectric constant ε. The change in the free energy of formation of solvated radical-ions $\Delta G_{34} + \Delta G_{56}$ is described by an expression analogous to Eqn.(10).

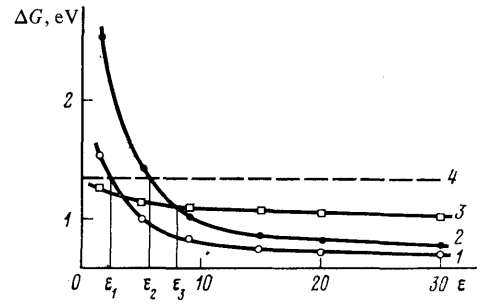


Figure 4. Dependence of the change in the free energy ΔG of formation of a solvate-separated radical-ion pair (curve *1*), solvated radical-ions (curve *2*), and the exciplex (curve *3*) for the chlorophyll *a*–*p*-benzoquinone system on the dielectric constant of the medium ε; curve *4* represents the position of the triplet level of chlorophyll *a*.[201]

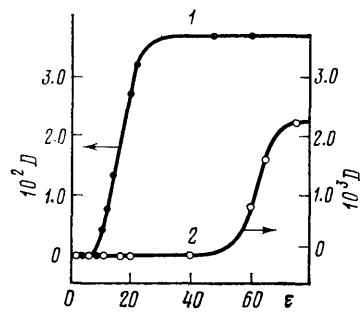


Figure 5. Dependence of the optical density *D* of the chlorophyll *a* radical-cation on the dielectric constant of the medium in the presence of *p*-benzoquinone (curve *1*) and nitrobenzene (curve *2*).[202]

Fig.4 presents the variation of the changes in the free energies of formation of the exciplex, the radical-ion pair, and solvated radical-ions based on the data of Andreeva and Chibisov[201]. Examination of the relations in Fig.4 shows, firstly, that in non-polar media the values of ΔG_{34} and $\Delta G_{34} + \Delta G_{56}$ are significantly positive in relation to the donor excitation energy, while ΔG_{23} is negative. This explains the possibility of the formation of the exciplex alone and hence the absence of solvated radical-ions. Secondly, with increase of ε for the medium, both ΔG_{34} and $\Delta G_{34} + \Delta G_{56}$ decrease, changing sign at dielectric constants ε_1 and ε_2 respectively. Consequently radical-ions are formed when $\varepsilon > \varepsilon_2$. Thirdly, ΔG_{34} becomes more negative than ΔG_{23} when $\varepsilon > \varepsilon_3$, as a consequence of which the radical-ion pair is formed effectively directly via the collision complex.

The results of the study of the dependence of the yield of the radical-ions on ε for the medium have shown that it is described by an S-shaped curve[202,203]. This type of relation can be understood by referring to Figs.5 and 6. At low dielectric constants of the medium the yield of radical-ions is virtually zero owing to the energetically unfavourable electron transfer process in the collision complex and also the necessity to overcome the Coulombic interaction forces in the radical-ion pair when the latter dissociates into radical-ions. With increase in the dielectric constant of the medium, a monotonic increase of the concentration of radical-ions to a maximum is observed. For higher values of ε, the free energies $\Delta G'$ and $\Delta G''$ become significantly negative; furthermore, the energy of the Coulombic interaction in the ion pair diminishes, which significantly facilitates its dissociation into solvated radical-ions.

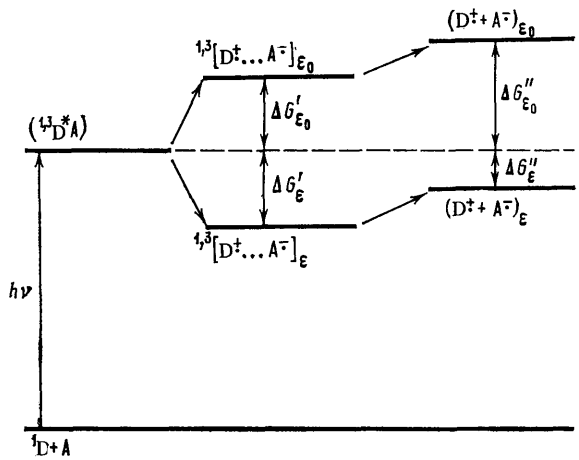


Figure 6. Schematic illustration of the arrangement of the energy levels of the intermediate states for low (ε_0) and high (ε) dielectric constants of the medium.

A quantitative expression for the dependence of the quantum yield in the formation of radical-ions on the dielectric constant of the medium can be obtained as follows. It is assumed that the quenching of the fluorescence of the acceptor by the electron donor can be neglected. It then follows from Eqn.(35) that

$$\varphi_{A^{\mp},D^{\pm}} = \varphi_T\left(\frac{k_{60}}{k_{60}+k_{65}}\right)\left(\frac{k_q^T\tau_T^0[D]}{1+k_q^T\tau_T^0[D]}\right). \qquad (60)$$

The dependence of $\phi_{A^{\mp},D^{\pm}}$ on ε is determined by the relations $k_{60}(\varepsilon)$ and $k_q^T(\varepsilon)$. The expression for $k_{60}(\varepsilon)$ assumes the form[203]

$$k_{60}(\varepsilon) = \frac{\text{const}}{\eta\varepsilon^{3/2}}\exp\left(-\frac{e^2}{\varepsilon aRT}\right), \qquad (61)$$

where η is the solvent viscosity.

The dependence of k_q^T on ε is determined, according to Eqn.(36), by the quantities $k_{40}(\varepsilon)$, $k_{41}(\varepsilon)$, and $k_{60}(\varepsilon)$. In the case where $\Delta G_{40} \ll 0$ (Scheme 2) the quenching rate constant $k_q^T(\varepsilon)$ can be expressed in a form analogous to that of Eqn.(23):

$$k_q^T(\varepsilon) = k_{34}/[1 + k_{43}/(k_{65} + k_{60}(\varepsilon))]. \qquad (62)$$

In the case where $\Delta G_{40} > 0$ the expression for $k_q^T(\varepsilon)$ is analogous to Eqn.(24):

$$k_q^T(\varepsilon) = \frac{k_{34}(k_{65}+k_{60}(\varepsilon))}{2k_{43}}\exp\left(-\frac{\Delta G_{40}(\varepsilon)}{RT}\right), \qquad (63)$$

while the expression for $\Delta G_{40}(\varepsilon)$ is analogous to Eqn.(58).

The formation of intermediates in electron transfer and their subsequent transformations depend significantly on the ratios of the excitation energies of one of the reactants, the electrochemical oxidation-reduction potentials, and the dielectric constant of the medium. By varying these parameters, it is possible to alter the efficiency of the formation of intermediates in the electron transfer reaction.

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