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Electron-transfer reactions in polymer matrices

A V Vannikov, A D Grishina
Frumkin Institute of Electrochemistry, USSR Academy of Sciences, Moscow

ABSTRACT. This paper discusses the dark reactions and photoreactions that occur with transfer of an electron from a donor to an acceptor in polymer matrices under electron tunnelling conditions and when forming change-transfer complexes. The main emphasis is on an analysis of the factors that determine the rate of electron transfer, which, in accordance with the advanced theory of electron transfer, are the magnitude of the exchange interaction, the free energy of the process, and the reorganisation energies of the medium and the reacting donor and acceptor molecules.

The existing models for the movement of charge carriers between single-type transport sites are discussed. The limits of applicability of the different models have been determined. The reorganisation energy of a polymer matrix is shown to have a considerable effect on the rate of movement of charge carriers on introduced transport molecules. The effect of the dielectric properties and free volume of polymer matrices on the characteristics of electron phototransfer in donor-acceptor complexes is discussed.

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I. Introduction

With the production of polymeric materials for electrophotography and films for photochemical recording of optical information, and with the development of solar energy converters and the synthesis of conductive and semiconductive polymers, electron-transfer reactions in polymer matrices have started to stimulate an increasing interest among research workers in recent years.[1–13] Moreover, polymer matrices with transport sites constitute an effective model system for the study of charge transfer in disordered media.

In the present study we shall restrict ourselves to an examination of dark and photolytic electron-transfer processes in systems involving a polymer matrix as the dielectric medium and donor (D) and acceptor (A) components distributed in it.

In this case D and A components can be chemically bonded to polymer chains. An analysis of the factors that determine the rate of electron transfer in polymer donor-acceptor systems is given below together with the quantum yield of products of electron phototransfer and the effect of temperature, the concentration of the transport sites, electric field, and characteristics of the polymer matrix on the mobility of the charge carriers (electrons or holes) in polymers.

An examination will be made of systems in which the distance between the components (R) is greater than the sum of the van der Waals radii of the molecules (the notation D ... A is given for such systems) and electron transfer is due to a quantum effect— tunnelling,[14,15] and also of composites based on charge-transfer complexes (CTC, denoted as D·A) in which the value of R as a result of efficient packing can be less than the van der Waals radii of the components.[16]

A common feature of these systems is the fact that electron transfer in them under dark conditions and with photoexcitation is due to overlap of the wave functions of the states without electron transfer— ψ_0(D, A)—and the states that correspond to complete electron transfer from D to A—$\psi_1(D^+, A^-)$.[16–19]

$$\psi_i(DA) = \psi_0(D, A) + \lambda\psi_1(D^+, A^-), \quad (1)$$

$$\psi_{f,ex}(D^+A^-) = \psi_1(D^+A^-) - \lambda\psi_0(D, A), \quad (2)$$

Here ψ_i(DA) and $\psi_f(D^+, A^-)$ are the wave functions of the initial and final states of the system with thermal electron transfer; ψ_i(DA) and $\psi_{ex}(D^+, A^-)$ represent the ground and excited state of the system with electron phototransfer; $\lambda = V_{01}/\Delta G$, where V_{01} is the energy of the exchange interaction; ΔG is the free energy of electron transfer.

$$\Delta G = E_0 - E_1, \quad (3)$$

where E_0 and E_1 are the energies of the states without bonding and with complete electron transfer respectively:

$$E_0 = \int\psi_0^*(D, A)H\psi_0(D, A)dv,$$

$$E_1 = \int\psi_1^*(D^+A^-)H\psi_1(D^+A^-)dv,$$

where ψ^*(D, A) and $\psi^*(D^+, A^-)$ are complex associated wave functions, v is a combination of the spatial and spin coordinates of the electron.

The thermal reaction

$$D ... A \rightleftarrows D^+ ... A^- \quad (4)$$

occurs as a result of "horizontal" electron transfer.

The transition between the two equilibrium states D ... A and $D^+ ... A^-$ involves surmounting the potential barrier $G^{\neq}$ (Fig. 1*a*). According to two analyses,[17,18] with values of $V_{01} < 20$ cm^{-1} (i.e., 2.48×10^{-3} eV) electron transfer occurs under nonadiabatic conditions when the D ... A system, existing in the transition state (near the point $q^{\neq}$, see Fig. 1*a*), repeatedly crosses the $q^{\neq}$ point along its own potential curve before undergoing transfer to a lower trajectory corresponding to the $D^+ ... A^-$ state. Adiabatic conditions (Fig. 2), in other words, transfer of the D ... A system to the $D^+ ... A^-$ state at each crossing of the $q^{\neq}$ point, correspond to the values $20 < V_{01} < 400$ cm^{-1} ($\sim$0.05 eV).

The convergence of the components on conversion to D·A complexes gives rise to an exponential increase in V_{01} from 0.05 to 0.5 eV. The rate of electron transfer corresponds to the value $\nu = V_{01}/h \sim 10^{13}$ s^{-1} (h is Planck's constant). In this case we are dealing with the dipole $D^{+\delta}A^{-\delta}$ (D·A $\rightleftarrows$ ($D^+ \cdot A^-$).[16,19] As a result of mixing the states

without bonding and with complete charge transfer [$\lambda > 0$ in expressions (1) and (2)], an optical transition with charge transfer is possible in both systems

$$D...A \text{ (or } D.A) \xrightarrow{h\nu_{et}} D^{+}...A^{-} \text{ (or } D^{+}A^{-})$$

(Fig. 1*a* or Fig. 2).[16–19]

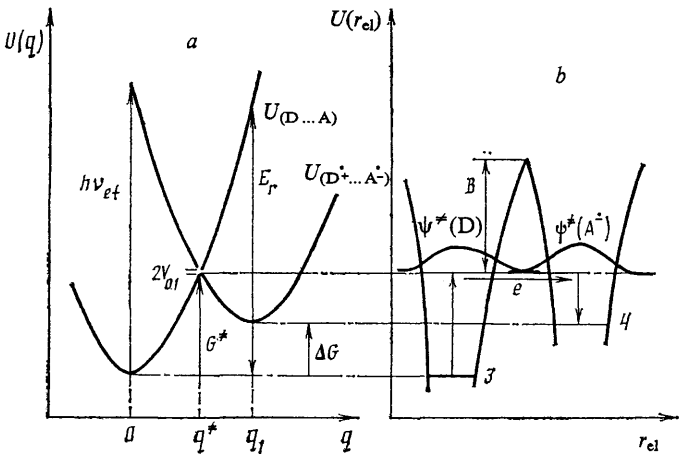


Figure 1. *a*) Dependence of the potential energies $U_{(D...A)}$ and $U_{(D^{+}...A^{-})}$ on the generalised coordinate q. The parameters that determine the rate of thermal reaction (4) and electron phototransfer under non-adiabatic conditions ($V_{01} < 20$ cm^{-1}) are given. *b*) Dependence of the electron energy $U(r_{el})$ on the coordinate r_{el}. The levels cor-respond to: *3*) equilibrium potential $E_{1/2}(^{1}D_0/D^{+})$; *4*) $E_{1/2}(A^{-}/A)$. For further explanation, see text.

II. Thermal electron transfer

The polaron theory of electric conductivity[20] has been developed in relation to ionic semiconductors. According to this theory the movement of an electron can be represented as the successive transfer between lattice points (by a distance R) when there is strong polarisation of the lattice. Polaron theory proposes that the energy barrier for movement of an electron is determined by the change in polarisation of the lattice on transfer of the electron from one transport site to another $M^{+}...M \rightarrow M...M^{+} \rightarrow$ etc. The main conclusions of the polaron theory were used to develop the quantum-chemical theory of thermal electron transfer in liquid media (the model of the dielectric continuum).[17,21–29] The latter model extends the polaron theory by taking into account the expenditure of energy on intramolecular reorganisation in the change from a molecule to a radical ion. This model is becoming more common because it is suitable for a wide range of donor-acceptor systems $D...A \rightarrow D^{+}...A^{-}$ for which the driving force of electron transfer is the free energy of this process.

According to the Marcus–Levich–Dogonadze–Kuznetsov model of the dielectric continuum, the rate of charge transfer is determined by a combination of processes that take place in a "supermolecule" consisting of the D...A system and the neighbouring sphere of the surrounding dielectric continuum (in our case the polymer medium). As a result of thermal motion there is a fluctuation of such parameters as the mutual orientation of the D...A components and the molecules of the medium, the distance between the D...A components, and the internuclear distances in the D and A molecules, and a redistribution of charge occurs in the D...A system and the molecules of the medium, etc. This causes fluctuations in the generalised coordinate q, which characterises the interaction between D...A and the dielectric medium and inside the D...A system.

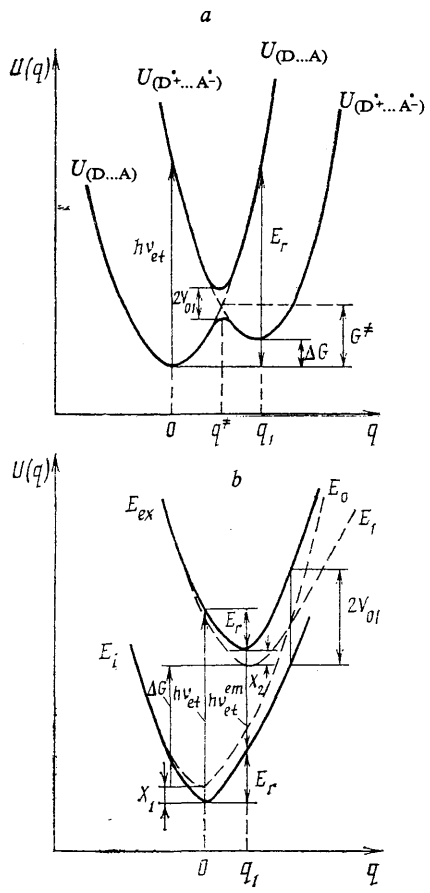


Figure 2. *a*) Dependence of the potential energies $U_{(D...A)}$ and $U_{(D^{+}...A^{-})}$ on the generalised coordinate q. The parameters that determine the rate of thermal reaction (4) and electron phototransfer under adiabatic conditions ($20 < V_{01} < 400$ cm^{-1}) are given. *b*) Relative position of the ground E_i ($\equiv U_{(D.A)}$) and excited E_{ex} ($\equiv U_{(D^{+}.A^{-})}$) levels of the D.A complex. The parameters that determine electron phototransfer are given. For further explanation, see text.

The potential energies of the fluctuating system that occurs in the initial (D...A) and final ($D^{+}...A^{-}$) states are represented as two parabolae (see Fig. 1):

$$U_{(D...A)}(q) = aq^{2}, \tag{5}$$

$$U_{(D^{+}...A^{-})}(q) = b(q - q_1)^{2} + \Delta G, \tag{6}$$

where q_1 is the equilibrium coordinate of the final state. The

coefficient a corresponds to the potential energy value of the initial state at the equilibrium coordinate of the final state ($q = q_1$):

$$U_{(D...A)}(q_1) = aq_1^2 \equiv E_r,$$
$$a = E_r/q_1^2,$$

where E_r is the reorganisation energy of the "supermolecule" brought about by electron transfer in the D ... A system. The coefficient b corresponds to the potential energy of the final state at the equilibrium coordinate of the initial state ($q = 0$):

$$U_{(D^{\cdot+}...A^{\cdot-})}(0) = b(-q_1)^2 + \Delta G = E_r + \Delta G.$$

In reversible reactions $E_r = E_r'$ and correspondingly $a = b$. Thus, for reversible reactions we obtain

$$U_{(D...A)}(q) = E_r(q/q_1)^2, \quad (5a)$$
$$U_{(D^{\cdot+}...A^{\cdot-})}(q) = E_r\left(\frac{q - q_1}{q_1}\right)^2 + \Delta G,$$
$$E_r = E_{in} + E_s, \quad (6a)$$

where E_{in} is the energy expended on the transition from D ... A to D^{+}... A^{-} ion radicals, resulting from the change in distance between the components of the complex as well as the distances between the nuclei and the bond angles in these same molecules D and A (the "inner-sphere" energy, including intramolecular reorganisation); E_s is the reorganisation energy of the medium (the "outer-sphere" reorganisation).

(a) Rate of electron transfer in condensed media

The rate constant of thermal electron transfer (k_{et}) in the reaction $D...A < D^{+}...A^{-}$ under nonadiabatic conditions (na) is determined by the relationship

$$k_{et}(na) = (2\pi/\hbar)|V_{01}|^2 FC, \quad (7)$$

where FC is the Franck–Condon factor.

Necessary conditions for electron transfer in accordance with reaction (4) are: 1) adherence to the Franck–Condon principle; and 2) overlap of the wave functions of the donor and the acceptor radical anion in a Franck–Condon state (see Fig. 1*b*); then

$$V_{01} = \int \psi^{\neq}(D...A) H \psi^{\neq}(D^{+}...A^{-}) dv > 0. \quad (8)$$

A Franck–Condon state conforms to the isoenergetic condition (Fig. 1*b*):

$$\int \psi^{*\neq}(D...A) H \psi(D...A) dv = \int \psi^{*\neq}(D^{+}...A^{-}) H \psi^{\neq}(D^{+}...A^{-}) dv.$$

In accordance with the Franck–Condon principle, electron transfer occurs with an unchanged nuclear configuration as a result of the high rate of the act of electron transfer ($t < 10^{-13}$ s). Only the electronic polarisation of the medium is synchronous to this process whereas the other forms of polarisation, which are related to the movement of nuclei (atomic, configurational) are established much more slowly in $> 10^{-13}$ s and $10^{-12}-10^{-9}$ s respectively.[24] Consequently, electron transfer from molecule D to A will only occur after the "supermolecule" acquires from thermal fluctuations a nonequilibrium configuration (along the $q^{\neq}$ coordinate) in which the potential energies of the initial and final states coincide; i.e., when

$$E_r(q^{\neq}/q_1)^2 = E_r\left(\frac{q^{\neq} - q_1}{q_1}\right)^2 + \Delta G.$$

hence

$$q^{\neq}/q_1 = (E_r + \Delta G)/2E_r.$$

According to equation (5a) the energy of activation for transfer of the D ... A system to the Franck–Condon state ($G^{\neq}$, see Fig. 1) is equal to:

$$U_{(D...A)}(q^{\neq}) \equiv G^{\neq} = (E_r + \Delta G)^2/4E_r. \quad (9)$$

Hence the FC factor in equation (7) is given by

$$FC = A\exp(-G^{\neq}/kT) = A\exp[-(E_r + \Delta G)^2/4E_r kT], \quad (10)$$

where

$$A = (4\pi E_r kT)^{-1/2}.$$

Equation (10) represents the state of the system in the classical approximation, i.e., when $\hbar\omega \ll kT$, where ω is the effective angular frequency of the fluctuations in the "supermolecule" (related to E_r by the relationship $E_r = \hbar\omega q_1^2/2$). The FC factor has a maximum value $FC = A$ when there is a negative free energy $-\Delta G = E_r$.

According to expression (10), in isoenergetic systems (when $\Delta G = 0$) $G^{\neq} \equiv G^{\neq}(0) = E_r/4$.

The free energy of the thermal reaction (4) is equal to

$$\Delta G = E_0 - E_1 = e[E_{1/2}(D/D^{\cdot+}) - E_{1/2}(A^{\cdot-}/A)] + e^2/\varepsilon R, \quad (11)$$

where $E_{1/2}(D/D^{\cdot+})$ and $E_{1/2}(A^{\cdot-}/A)$ are the equilibrium potentials of oxidation of the donor and reduction of the acceptor respectively, $e^2/\varepsilon R$ is the Coulomb attraction energy of the radical ions $D^{\cdot+}$ and $A^{\cdot-}$, having their own solvation shells; ε is the dielectric constant of the medium.

The reorganisation energy of the medium due to electron transfer is calculated from the equation of Marcus:[21,25]

$$E_s = e^2(1/n^2 - 1/\varepsilon) f(r, R), \quad (12)$$

where n is refractive index of the medium, $f(r, R)$ is a function that depends on the radius of the components and on the distance of electron transfer R. For exchange reactions

$$M^{\cdot+} ... M \overset{k_{et}}{\rightleftharpoons} M ... M^{\cdot+}, \quad (13a)$$
$$M^{\cdot-} ... M \overset{k_{et}}{\rightleftharpoons} M ... M^{\cdot-} \quad (13b)$$

function $f(r, R) = (1/r - 1/R)$, which for reaction (4): $f(r, R) = (1/2r_D - 1/2r_A - 1/R)$. Here r, r_D, and r_A are the radii of the transport site M, the donor molecule, and acceptor molecule respectively.

The "inner-sphere" reorganisation energy E_{in}, such as for reaction (13a), can be determined experimentally from the difference in gas-phase ionisation potentials:[30–33]

$$E_{in} = I^V - I, \quad (14)$$

where I^V is the vertical or Franck–Condon ionisation potential, which is equal to that quantum of energy ($I^V = h\nu_{max}$) at which are formed the maximum number of electrons from photodecomposition; I is the adiabatic ionisation potential. In two studies[30,31] I was calculated from the equation $I = h\nu + 0.15$ eV, where $h\nu$ is that quantum of energy at which the number of electron from photodecomposition is 1% of those that are formed at $h\nu_{max}$. The value of E_{in} determined thus for a series of 25 alkylamines is 0.6–0.7 eV.

The complete reorganisation energy of a "supermolecule" is given by the difference

$$E_r = E^V - [eE_{1/2}(M/M^{\cdot+}) + E_0], \quad (15)$$

where E^V is that quantum of energy which corresponds to photoionisation of molecules in the liquid phase when the energy of the electrons emitted into the gas phase is close to zero. $E_{1/2}(M/M^{\cdot+})$ is the equilibrium oxidation potential of the molecule compared to a reference electrode (S.H.E.). E_0 is the energy level of the reference

electrode relative to vacuum [E_0 = 4.43 eV for a standard hydrogen electrode (S.H.E.)].[34] Thus, [$eE_{1/2}(M/M^+)$ + E_0] is the energy of the radical cation M^+ relative to vacuum in a completely relaxed state, namely, after completion of both "inner-sphere" and "outer-sphere" reorganisation. The value of E_r was determined from the experimental values of E^V and $E_{1/2}(M/M^+)$ for a number of alkylamines[32] (Table 1) and for all methyl-substituted benzenes.[32,33] The "intramolecular" reorganisation energy, calculated from the expression $E_{in} = E_r - E_s$, is also given in Table 1.[31] In the calculation of E_s it was suggested that $r = r_{eff} = R/2$. The effective radius r_{eff} of M molecules was determined from the experimentally determined electron polarisation energy, taken as equal to $P_e = [(I^V + I)/2] - E^V$ and related to r_{eff} by the expression $P_e = e^2(1-1/n^2)/2r_{eff}$.[31,32] Thus

$$r_{eff} = e^2(1 - 1/n^2)/(I^V + I - 2E^V).$$

Table 1. Reorganisation energy E_r of a "supermolecule" and the medium E_s for exchange reaction (13a) of a number of alkylamines in acetonitrile calculated from equations (15) and (12) and the intramolecular reorganisation energy $E_{in} = E_r - E_s$.[31]

Compound	E_r, eV*	E_s, eV	E_{in}, eV*
Butylamine	1.67	1.17	0.5
Isobutylamine	1.64	1.23	0.41
t-Butylamine	1.6	1.22	0.38
Dibutylamine	1.3	1.07	0.23
Tributylamine	1.23	0.82	0.41
Tetramethyl-*p*-phenylenediamine			0.365**

*The value of E_0 = 4.5 eV used by Watanabe et al[31] has been replaced by 4.43 eV for a S.H.E.[34]
**Value taken from two studies.[35,36]

It was shown[31] that values of r_{eff} calculated from this expression agree with the values that are calculated from the volume occupied by the molecule: $4\pi r_{eff}^3/3 = MW/dN_A$, if the coefficient 0.5 is used instead of $(3/4\pi)^{1/3}$ (MW is the molecular weight of alkylamine, d is the density of alkylamine, N_A is the Avogadro number).

The most common method for determining E_r, and hence E_{in}, is a determination of the energy of activation $G^{\neq}$ of exchange reactions, for which, as has already been mentioned, $G^{\neq} \equiv G^{\neq}(0) = (E_{in} + E_s)/4$. The energy E_{in} thus obtained for the exchange reaction of *N,N,N',N'*-tetra-methyl-*p*-phenylenediamine (TMPD) in different solvents is given in Table 1. The value of E_{in} was determined by extrapolating the dependence of $4G^{\neq}$ on $(1/n^2 - 1/\varepsilon)$ to $(1/n^2 - 1/\varepsilon) = 0$, i.e., when $E_s = 0$ [see (equation 12)].[35,36] The value of E_{in} obtained for TMPD by this method (0.365 eV, see Table 1) is close to that calculated by the Pariser–Parr–Pople method (0.337 eV). For methyl-substituted benzenes $(C_6H_{6-n}(CH_3)_n$, $n = 1-6)$ the experimental value E_{in} = 0.26 eV.[32,33]

It should be mentioned in addition that the total polarisation energy of the medium by a radical cation $M^+(D^+)$ is determined from the adiabatic ionisation potential:

$$p^+ = e^2(1 - 1/\varepsilon)/2r_{eff} = \{I - [eE_{1/2}(M/M^+) + E_0]\}.$$

The energy of the exchange interaction in a Franck–Condon state (8) is given by the equation[37,38]

$$V_{01} \equiv V(R) = V(R_0)\exp[-(R - R_0)/\alpha], \quad (16)$$

where R_0 is the sum of the van der Waals radii of D and A^-, α is the attenuation factor of the wave function in the Franck–Condon state.

$$\alpha = 1/0.511B^{1/2}, \text{ Å}. \quad (17)$$

here B is the height of the barrier or difference between the position of the highest occupied orbital of the donor and the energy of the lowest conducting state of the medium (in eV) (see Fig. 1*b*).

Thus the rate constant of electron transfer under nonadiabatic conditions in accordance with equations (7), (10), and (16) can be written in the general form

$$k_{et}(na) = (2\pi/\hbar)(4\pi E_r kT)^{-1/2} V^2(R_0)\exp[-2(R - R_0)/\alpha] \cdot \exp[-(E_r + \Delta G)^2/4E_r kT]. \quad (18)$$

It is necessary to bear in mind that because of steric hindrance in the formation of molecular conformations with minimum potential energies in polymer matrices, a nonuniform distribution of ionisation potentials and electron affinities (i.e., ΔG), steric variation in the dielectric constant of the medium ε (i.e., E_r), and other factors giving rise to a variation in k_{et} are possible.

In organic systems there is a common situation when the frequency of the "outer-sphere" fluctuations ω_s ($E_s = \hbar\omega_s q^2/2$) conforms with the inequality $\hbar\omega_s \ll kT$, while the distance between the vibrational levels in the donor and acceptor molecules conforms with the inequality $\hbar\omega_{in} \gg kT$. Under these conditions, the lowest vibrational level is occupied in the initial system D ... A, while the final state $(D^+ ... A^-)$ is represented by a set of parabolae, given by equation (6a), separated from each other on the y-axis by a quantum of vibrational energy $\hbar\omega_{in}$.[17,39] Electron transfer can occur by conversion to different vibrational levels of the acceptor [$n_i\hbar\omega_{in}$, where $v_i = (v + 1/2)$] (v is the vibrational quantum number, equal to 0, 1, 2, 3...). The overall constant results from summation of the rate constants of electron transfer to different vibrational levels and is given by:[39]

$$k_{et} = (2\pi/\hbar)V_{01}^2(4\pi E_r kT)^{-1/2}\sum_{v_i=0}^{\infty}\frac{\exp(-S)S^{v_i}}{v_i!}\times \exp\left[-\frac{(\Delta G + v_i\hbar\omega_{in} + E_s)^2}{4E_s kT}\right]. \quad (18a)$$

where $S = E_{in}/\hbar\omega_{in}$. For large negative values of ΔG (when $|\Delta G| > E_s$) the main channel for electron transfer reduces to a vibrational term corresponding to the value $G^{\neq} = 0$, i.e., $v_i = (\Delta G - E_s)/\hbar\omega_{in}$.

At the adiabatic (a) limit (Fig. 2*a*)[40,41]

$$k_{et}(a) = \frac{\varepsilon}{\tau_D n^2}\left(\frac{E_s}{4\pi kT}\right)^{1/2}\exp\left[-\frac{G^{\neq} - V_{01}}{kT}\right]. \quad (19)$$

where τ_D is the dielectric relaxation time of the medium after electron transfer. In contrast to nonadiabatic conditions, in which the rate of electron transfer is controlled by the exchange interaction V_{01}^2, under adiabatic conditions k_{et} is mainly determined by the longitudinal relaxation time of the medium $\tau_L : \tau_L = \tau_D n^2/\varepsilon$.

In contrast to liquid media in which an electron transfer reaction mainly occurs after the diffusional approach of components to the distance R_0, equal to the sum of the van der Waals radii, in polymer systems D and A are either fragments of a polymer chain and are separated by a fixed distance or are dissolved in the polymer matrix

and have a random distribution with an interaction radius R. In this case the pattern of electron transfer can be complicated by the effect of the free volume and other polymer effects.

Donor-acceptor compounds with bridging groups (B) constitute a model of dielectric polymer media. Charge transfer along the saturated bonds $-CH_2-$ is caused by hyperconjugation[42,43] (superexchange interaction), namely, by overlap of the π-orbitals of the organic aromatic groups D and A with the atomic $p\sigma$-orbital of an unsaturated $-CH_2-$ fragment. The extent of this overlap depends on the rotation angle of the aromatic rings relative to the bridging group.[42,44] The $-CH_2-Ar-CH_2-$ groups are regarded as bridges (Ar is aromatic fragment).[44,45] The stepwise transfer of an electron via bridging groups can occur with complete reorganisation of the "supermolecule" at each transition step as well as a dynamic transfer when short-lived bridging states participate in electron transfer.[17] The energy of the exchange interaction for bridging systems is determined from the equation:[44,45]

$$V_{01}=\sum_{B}V_{0B}V_{B_1}/(G_1^{\neq}-E_B),$$

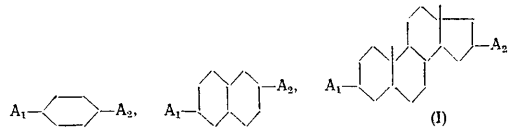
where the index B relates to a bridging group; E_B is the energy at the minimum of the potential curve of the bridging group; $G_1^{\neq}$ is the energy of the initial state of the D...A system at the point of intersection of the initial potential curve of $U_{(D...A)}$ with the potential curve of the bridging fragment; V_{0B} and V_{B1} are the energies of the exchange interaction of the orbitals of D and B^- and B^- and A^- respectively.

Under conditions of superexchange the attenuation factor α in expression (16) takes the form

$$\alpha=\frac{1}{R}\ln\left(\frac{B}{V_{B^-B}}\right),$$

where R and V_{B^-B} (or V_{B^-B}) are respectively the distance and exchange integral between bridging groups on which the movement of a charge occurs.

Electron transfer has been studied[28,46,47] in compounds of the type A_1-B-A_2 such as substituted cyclohexanes, decalins, and steroids:



(I)

where A_1 is biphenyl (electron affinity 2.4 eV), A_2 are aromatic compounds with different values of the equilibrium potential $E_{1/2}(A_2^-/A_2)$ corresponding to a free energy of electron transfer

$$\Delta GT=e[E_{1/2}(A_1^-/A_1)-E_{1/2}(A_1^-/A_2)]=0 \text{ to } -0.25 \text{ eV}.$$

Pulsed radiolysis was used to study the reaction

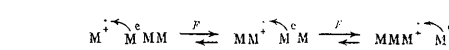
$$A_1-B-A_2 \xrightarrow{e} \begin{cases} \rightarrow A_1^- - B - A_2 \\ \rightarrow A_1 - B - A_2^- \end{cases} \quad (20)$$

The first step in reaction (20) is capture by an A_1-B-A_2 molecule of an electron formed during pulsed irradiation of solvents such as methyltetrahydrofuran (MTHF), tetrahydrofuran, and isooctane at 296 K.

The interconversion of the optical spectra of A_1^- and A_2^- is an indication of electron transfer, in accordance with reaction (20), via saturated $-CH_2-$ (or $>CH-$) bonds. When substituted steroids (I) are used, the dependence of k_{et} on $-\Delta G$ acquires a bell-shaped form. The experimentally determined dependence is in agreement with that calculated from expression (18a) when E_{in} = 0.45 eV, $\hbar\omega_{in}$ = 1500 cm^{-1}, V_{01} = 6.2 cm^{-1}, E_s = 0.75 eV in MTHF and 0.15 eV in isooctane. In the calculation of E_s from equation (12) it is assumed that $r_{A_1}=r_{A_2}$ = 2.95 Å, R = 17.3 Å. The value of the constant k_{et} decreases from 5×10^9 to 10^6 s^{-1} on increasing the number of saturated bonds (n) that separate A_1 and A_2 from 4 to 10. A relationship was established[47] between the energy of the exchange interaction V_{01} and n when $V_0=1.1\times10^3$ cm^{-1}: $2\ln V_{01}=2\ln V_0-1.15(n-1)$.

(b) Electron transfer between single-type transport sites

Electron transfer between single-type transport sites that are situated in a disordered manner in a solid dielectric medium is of particular interest from a theoretical viewpoint and important for practical application. Polymers with a glass transition temperature (T_g) that exceeds the temperature at which the electron transfer measurements are carried out are usually chosen as the medium. An important feature of these systems is the participation of the oxidised (or reduced) form of the neutral transport site (M) in electron transfer and the occurrence of fixed distances between the transport sites [reaction (13a) and (13b)]. When an external electric field F is applied, these reactions determine the flow of hole (or electron) current through the sample:



etc.

The transport of holes is simpler to study experimentally in systems with transport sites that are characterised by low ionisation potentials I_M (or low oxidation potentials of M), while the transport of electrons is simpler to study in systems with high values of electron affinity E_M. This is related to the fact that in polymer matrices there are chemical impurities and structural defects which in the case of electron transport are electron traps if their electron affinity is higher than E_M. Capture of electrons in traps considerably complicates their transport through a sample. The effect of additional traps on the transport of charges has been studied experimentally and theoretically.[48] In the present review this question is not considered as it is possible to select experimental conditions that exclude the effect of additional traps.

In this section four types of systems will be examined: 1) polymers in which the transport sites are substituents in the main chain, for example, the carbazolyl group in polyvinylcarbazole (PVCA), polyepoxypropylcarbazole (PEPCA), etc.; 2) polymers in which the transport sites occur in the main chain, for example, polyimides,[49] polyphenylene sulphides,[50] polyepoxyamino adduct,[51] and others; 3) molecularly doped polymers, namely, inert polymer matrices [polystyrene (PS), polycarbonate (PC), and others] in which are dissolved low-molecular weight transport molecules such as triphenylmethane (TPM) and its derivatives, triphenylamine (TPA), isopropylcarbazole (IPCA), and others; 4) mixed systems, for example, PVCA in which TPA is dissolved, PC containing IPCA and TPA in different proportions, and also the system that has been the most studied—PVCA + trinitrofluorenone (TNF).

The electron transfer reaction in the systems is the simplest of those considered above, it is completely reversible, and the composition of the reaction products is no different from that of the initial reactants. Serious problems in the theoretical treatment arise because the distances between the neighbouring transport sites are fixed but

differ over quite a wide range. The result of this is that the energy of the bond between the electron and the transport site, which depends on the local environment, also varies for specific transport sites, the distribution of energy of the bond reaching a width of several magnitudes of kT.

This electron transfer process determines the electron conductivity of photoconductive organic materials by nonequilibrium charge carriers. These materials are extensively used as electron-transport media in electrophotographic films, high energy transformers, etc. An experimental study of these reactions for the determination of k_{et} and the kinetic mechanisms presents certain difficulties because of the identification of the chemical composition of the reactants and the reaction products, the spin state, and spectroscopic characteristics. However, charge transfer in an external field F has the result that the charge acquires an additional drift rate in the direction of the field, and a current arises in the electric circuit which includes the polymer sample; the charge mobility μ is determined by analysing the current. The rate constant k_{et} and charge mobility μ are related through the diffusion coefficient

$$\mu = De/kT; \quad D = \rho^2 k_{et}$$

by the relationship

$$\mu = \rho^2 k_{et} e/kT, \tag{21}$$

where ρ is the length of electron hop.

In accordance with expression (21) all subsequent treatment of electron mobility in polymer matrices is also fully related to a study of the rate constant of the electron transfer reaction between identical sites. The most informative method for studying electron (hole) transport is the measurement of transit times. A packet of nonequilibrium charge carriers is produced on the surface of a polymer film at the time $t = 0$ (by injection from a catalyst or by direct photoexcitation with strongly absorbed light). If the transport sites are arranged in an ordered manner, the packet of charge carriers will move in the external field through the polymer film to the collector electrode, spreading out through drift but retaining a Gaussian form. In the process the distribution of charge carriers on the coordinate (σ) increases its width according to the principle $\sigma \sim t^{1/2}$. In this case the transport is called Gaussian and the current in the external circuit (i) has a constant value during drift (transit) of the packet through the film and rapidly decreases when it reaches the collector electrode at time t_{tr}. The drift mobility is determined here as $\mu = l/F t_{tr}$ (l is thickness of sample), and the current during drift can be expressed as

$$i = \mu e N \text{ (for } t < t_{tr}), \tag{22}$$

where N is the concentration of drifting charges. If the transport sites are arranged in a disordered manner, the hopping times between neighbouring sites vary over a wide range. Because of this, the packet of charges loses its Gaussian form, the plateau on the $i-t$ curve disappears, and it takes the form of a diminishing curve with a considerably elongated tail. In this case a determination of t_{tr} from the relationship $i = f(t)$ becomes impossible. However, in the logarithmic coordinates $\log i - \log t$ the current curve is converted into two linear sections which correspond to the relationships

$$i(t) \sim t^{-(1-\beta_1)} \text{ when } t < t_{tr},$$

$$i(t) \sim t^{-(1+\beta_2)} \text{ when } t > t_{tr}, \tag{23}$$

where β_1 and β_2 are constants which are independent of t; they have values within the limits $0 \leqslant (\beta_1, \beta_2) \leqslant 1$. The transit time occurs at the point of intersection of the linear segments, but in this case it corresponds to the arrival at the collector electrode (and mobility) of the fastest charges. The prolonged decrease after the break point can only be accounted for if it is assumed that there is a sufficiently large scatter (deviation) of t_{tr} for different groups of drifting charges. Hence charge transfer with the cited anomalous current characteristics is called dispersive. It is possible to determine the value of the current if the average displacement $\bar{x}$ of the packet of charges in relation to t is known. For Gaussian transport, $\bar{x} \sim t$, in accordance with equation (22), we obtain $i \sim d\bar{x}/dt = \text{const}$. If it is assumed that the displacement of the packet does not occur at a constant rate but gradually slows down, so that $\bar{x} \sim t^{\beta_1}$, for the current we obtain the dependence[52] $i(t) \sim d\bar{x}/dt \sim t^{-(1-\beta_1)}$, which is in agreement with equation (23).

It should be mentioned that the rate of movement of the packet $d\bar{x}/dt$ is proportional to the rate constant k_{et}; therefore, if Gaussian transport occurs, k_{et} is independent of t, but if dispersive transport takes place, $k_{et} = At^{-(1-\beta_1)}$, where A is a constant independent of t. A rate constant that varies with time in accordance with this relationship correlates well with a number of experimental results on the fate of captured electrons in vitreous matrices at 77 K.[53]

Relationships (23) were first obtained by Sher and Montroll[54] using the continuous time random walk (CTRW) model. In order to take account of the dispersion of t_{tr} occurring as a result of the dispersion in hopping times between neighbouring transport sites in the CTRW model, a disordered medium is broken down into single units composing a regular lattice. Each unit contains a sufficiently large number of transport sites so that the units have an equivalent concentration of M. The distribution of hopping times for the neighbouring sites in each unit is expressed as a prolonged distribution function for the probability of hops between units [$\psi(t) \sim t^{-(1+\beta)}$], which leads to dependence (23) with $\beta_1 = \beta_2 = \beta$. In Gaussian transport the distribution function decreases exponentially with time and has a single characteristic time τ_0:

$$\psi(t) = (1/\tau_0) \exp(-t/\tau_0).$$

It was originally supposed that the CTRW model represents electron hops between neighbouring sites by a tunnel mechanism. In this case it is clear that the relationship $h' > \rho$ holds true between the linear dimensions of a unit (h') and ρ. Subsequent analysis showed[15,55] that the condition for the CTRW model to be applicable was the inequality with an opposite form: $h' \ll \rho$. This indicates that the transport of electrons occurs in a conduction zone (a zone mechanism) with repeated capture on traps with an energy distribution in a certain range.

Dispersive current with the decreasing curve (23) must occur during nonequilibrium transport of electrons, namely, in the absence of thermal equilibrium between mobile (electrons in the conduction zone) and localised (electrons in localised states) fractions. In this case the time of electron motion in the conduction zone determines the probability of their being trapped, while the dispersive characteristics of transport determine the energy distribution of trap depths. For example, for an exponential distribution of trap depths:

$$g(E) = (N_t/E_0) \exp(-E/E_0),$$

(N_t is trap density), the relationships $\beta_1 = \beta_2 = \beta$ and $\beta = kT/E_0$ are fulfilled.[56]

A condition for nonequilibrium transport is that the relationship $\tau_l(E) > t_{tr}$, where $\tau_l(E)$ is the distribution of charge localisation times in traps of varying depth E, holds for a substantial fraction of the traps. After generation (injection or photoexcitation of the surface

layer of the film sample) the charges are localised in traps according to their concentration and independent of depth. In order to establish thermal equilibrium repeated escape of the charges from the traps into the conduction zone is necessary. If the condition $\tau_t(E) \ll t_{tr}$ is fulfilled for all traps, during the time of drift of a packet through the sample the current has a constant value and on reaching t_{tr} it falls more or less abruptly.

The temperature dependence of μ is determined by trap depth, and by extrapolating the dependence $\mu - T$ in the Arrhenius curve to $T^{-1} \to 0$ it is possible to determine the charge mobility in the conduction zone μ_0. For organic polymer systems (in contrast to, for example, chalcogenide glasses) μ_0 has the value $\mu_0 \sim 1$ cm^2 V^{-1} s^{-1}, and this corresponds to the limiting value that determines the applicability of the zone model, since when $\mu_0 < 1$ cm^2 V^{-1} s^{-1} the length of the electron path becomes comparable with or less than R in the polymer. Therefore, even though direct simulation of the transient current $i(t)$ using Monte Carlo curves for the zone model with repeated capture of charges by traps effectively represents the characteristics of hole transfer in PVCA[57,58] (including the lack of dependence of μ on l, the disappearance of the inflection on the transient current curve when the temperature is decreased, the prolonged decrease of transient current when $t > t_{tr}$, etc.), the suitability of the zone model for representing charge transfer in a polymer matrix is in doubt.

This difficulty can be overcome in the percolation of model of dispersive transport, developed in several studies,[15,55,59,60] which can be used to replace the CTRW approximation when the condition $h' \gg \rho, \rho = R - R_0$, is fulfilled, namely, when tunnel electron transfer occurs between transport sites. The rate of electron transfer between neighbouring sites depends exponentially on R and the height of the energy barrier.

In the percolation model it is considered that in an amorphous solid with a considerable concentration of transport sites it is possible to distinguish "rapid" trajectories of the movement of electrons through sites, the distance between which is less than a given optimum distance R_m, and "slow" trajectories for which $R > R_m$. On increasing the concentration of transport sites to a threshold concentration C_0, the rapid trajectories combine to form an endless cluster on which rapid electron transfer through the sample from electrode to electrode occurs. A further increase in the concentration of transport sites leads to an increase in density of the endless cluster, so that $i = (C - C_0)^\gamma$, where γ is a constant.

If the energy of the bonding between the electrons and the sites is distributed over the range δE and $kT > \delta E$ (quite high temperatures), it may be assumed that the energy of the electron on hopping does not vary and the only variable that determines the rate of transit is R. As a result, as analysis has shown,[15] when $t < t_{tr}$ the current remains constant, but when $t > t_{tr}$ the current displays a prolonged non-exponential decay. If the important role played by the energy scatter of the bond between the electrons and sites when $\delta E > kT$ is taken into account in the percolation model, the current is given by expression (23), $\beta_1 = \beta_2 = \beta$.

Thus, in measurements of electron transfer, the percolation model predicts the possibility when the measurement temperature is increased of changing from a purely dispersive transport to a Gaussian one with a constant current when $t < t_{tr}$. However, such a change is also predicted by the zone model with repeated capture on replacing nonequilibrium transport with quasi-equilibrium (with an increase in temperature), which is due to the decrease of $\tau_t(E)$ so that for all depths $\tau_t(E) < t_{tr}$. Such a change has been observed more than once experimentally, for example, in PVCA it occurs at 424 K,[61] while in poly(*p*-phenylene sulphide) it occurs at 310 K.[62] It should be emphasised that in the initial CTRW model, transport is regarded as dispersive, regardless of the temperature and other factors, which is at variance with the results obtained for these systems.

The percolation model effectively accounts for the kinetic characteristics of electron transfer between transport sites, the dependence of μ on the width of the sample (l), and other phenomena, but it follows from it that

$$i(t, T, F) = (eF\mu/l) f(T, t), \tag{24}$$

namely, that the mobility μ is independent of F. This is at variance with the experimental data, according to which the dependence μ on F is almost exponential. A similar situation occurs in the CTRW model.

The discrepancies between the theoretical models and experiment that have been detected are so serious that, in order to simplify the interpretation of the experimental results, in recent years measurements have been conducted on polymer systems in which dispersive transport is absent and i = const when $t < t_{tr}$. In this case the mobility does not depend on the width of the film sample. It is these systems, mainly polymer dielectric matrices (PC, PS) doped with aromatic amines and diamines,[63] which are examined below. In such systems the average distances between the neighbouring sites can readily be varied by changing the concentration of transport sites. In the majority of the experiments carried out the dependence of μ on the three main parameters—R, T, and F—has been studied. All of the experimental results are effectively related by the equation

$$\mu = \frac{eR^2}{kT} \exp[f_1(R)] \exp[f_2(T, R)] \exp[f_3(F, T, R)], \tag{25}$$

when $F \to 0$, $f_3(F, T, R) \to 0$, and the absence of the cofactor $[f_3(F, T, R)]$ in expression (25) gives a zero-field approximation. Attention was drawn for the first time by Gill[65] to the fact that in amorphous polymer systems the mobility μ is related to R by:

$$\mu \sim R^2 \exp[-2(R - R_0)/\alpha]. \tag{26}$$

Hence it follows that $f_1(R) = -2(R - R_0)/\alpha$. Thus, $\exp[f_1(R)]$ in expression (25) is the factor for overlap of wave functions of the neighbouring sites [see equations (8) and (16)]. In the majority of cases an activation dependence of μ on T occurs. On Arrhenius coordinates when measurements are made over a wide temperature range, a reduction in the energy of activation ΔE_a sometimes occurs in the high-temperature region (above 300 K). Furthermore, ΔE_a usually increases with an increase in R, in other words, it may be assumed that $f_2(T, R) = -\Delta E_a(R)/kT$. In all of the experimental and theoretical models[66,67] the cofactor $f_3(F, T, R)$ reflects the reduction in the energy barrier for electron transfer in an electric field and is usually written as $f_3(F, T, R) = e(R - R_0)F/kT$.

As a result, in representing the experimental data use is made of a simple relationship of the form:

$$\mu = \frac{eR^2}{kT} \exp[-(R - R_0)/\alpha] \exp\{-[\Delta E_a - e(R - R_0)F]/kT\}. \tag{27}$$

For a more complete representation of the experimental data it is necessary to find more exact relationships and to select the most realistic models of charge transfer in polymer systems.

The exponential dependence of μ on F in the model of repeated capture on traps in the case of quasi-equilibrium transport is due to the Frenkel–Poole effect; in this case $f_3 = \eta F^{1/2}/kT$, where η is the Frenkel–Poole constant. However, the suitability of this model for polymer systems, as has already been mentioned, raises serious

objections and the Frenkel–Poole effect itself assumes the existence of a large concentration of charged traps in which charges are captured during transport. The latter is not likely for the single-component systems doped with molecules that are commonly studied such as PC + TPA, and also for PVCA and other transport polymers without added components.

Bassler et al.[66,68] used the Monte Carlo method to resolve the problem of electron transfer in a transport system that meets the following conditions:

1) the energy distribution of the bonding of the charges on sites is Gaussian:

$$\varphi(E) = (2\pi\sigma)^{-1/2} \exp(-E^2/2\sigma^2);$$

2) the factor for overlap of wave functions of the neighbouring transport sites is written in the form

$$\exp[f_1(R)] = \exp[-2(R - R_0)/\alpha];$$

3) the probability of a hop from the ith transport site to the jth site when $E_j > E_i$ is taken into account using the Boltzmann constant:

$$W_{ij} = \nu_0 \exp[-2(R - R_0)/\alpha] \exp[-(E_j - E_i)/kT]$$
$$W_{ji} = \nu_0 \exp[-2(R - R_0)/\alpha],$$

i.e.

$$W_{ij} \exp(-E_j/kT) = W_{ji} \exp(-E_i/kT).$$

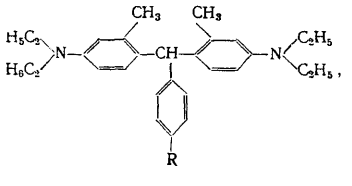
4) the electric field increases the number of transport sites on to which an electron can hop without activation; this occurs when $E_i + e(R - R_0)F > E_j$.

It was shown that the temperature dependence of mobility in such systems does not follow the Arrhenius equation, but in expression (25) $f_2 = -(T_0/T)^2$ and $f_3 = F/F_0$. Here $T_0 = K\sigma$ and

$$F_0 = \frac{T^2 R_0}{2B' eK^2 \sigma},$$

where K and B' are constants.

An analytical solution of this problem [69,70] leads to similar results: in this case K = 7400 Kl eV^{-1}, B' = 0.15. The values of T_0 and F_0 were calculated for different TPM derivatives–PC (TPM concentration of 40 wt.%) from the experimental dependences of μ on T and F determined by Pai et al.[71] and Bassler.[72]



where R = N$(C_2H_5)_2$; H; OH; Br; OCH_3; CN; NO_2.

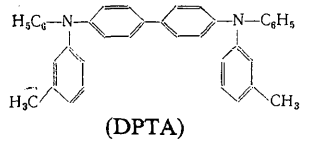
It was found for this series of derivatives that as the electron affinity of substituent R increases, the mobility of the charge carriers decreases by a factor of 10^4. It was suggested[72] that with an increase in electron affinity of substituent R, there is an increase in dopole moment (κ) of the TPM derivative, and consequently an increase in the polarity of the medium (ε).

According to Bassler[72] the spread of distances between neighbouring transport sites M results in a scatter (σ) of interaction energies between a charge on a site and the medium, and σ increases as ε increases, changing the values of F_0 and T_0. Even though the values of T_0 and F_0 vary considerably for the different TPM derivatives, their product remains constant $T_0/F_0 \simeq 310 \pm 4$ mV K cm^{-1} when T = const; this accords with the model under consideration: $T_0F_0 = T^2R_0/(2B'eK)$, and does not depend on σ. We should emphasise that the increase in the slope of the temperature dependences of $T_0 = K\sigma$ with an increase in κ does not unequivocally prove that there is a direct relationship between κ and σ. The slope may also depend on the intramolecular reorganisation energy (E_{in}) of the transport site M during an electron hop. This reorganisation energy naturally depends on the structure of M. Moreover, according to the Bassler model, for different values of F, straight lines on the coordinates of $\log\mu = f(T_0/T)^2$ should intersect at the same point on the y-axis [when $(1/T)^2 \to 0$] in accordance with equation (25). In fact, this characteristic was found for PVCA + TNF (1 : 0.2) systems.[72,73]

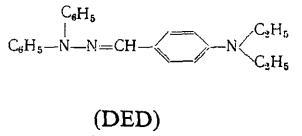
However, this model is not valid for polymers doped with aromatic amines since the relationships between μ, T and F do not hold in this case.

It should be mentioned that the relationship $\log\mu \sim (1/T)^2$ can reflect the temperature change of the energy of activation, which is possible for a Gaussian distribution of energy of the bonding of the charges on the transport sites; at which values of σ it ceases to be observed and what form it takes with other types of distribution is not clear at the present time (further investigation of this problem is required). Moreover, as has been indicated above, deviations from an Arrhenius relationship may be due to a change in the state of the polymer matrix as T increases and thus the relationship $f_2 = -(T_0/T)^2$ may be regarded as a special case of the temperature dependence of μ. A more general case is the Arrhenius dependence of μ on T with ΔE_a = const.

Interesting results were obtained for two systems based on PC doped with di (*N*-phenyl-*N*-*m*-tolyl)-*p*-aminobiphenyl (DPTA)[63] and *p*-diethylaminobenzaldehyde diphenylhydrazone (DED).[64]



(DPTA)



(DED)

It transpired that in DED the energy of activation (ΔE_a) does not depend on the distance R between the dopant molecules on changing R from 8 to 18 Å, while in DPTA it increases from 0.35 to 0.53 on changing R from 10 to 15.5 Å. The distance was determined from the equation $R = 3 \times 10^{27}/(4\pi \times N_A C^{1/3})$ Å, where C is the molar concentration of dopant. Values of μ [extrapolated to $F = 0$ ($f_3 = 0$)] and the energies of activation ΔE_a determined at different concentrations of C were used to calculate $f_1(R)$ from equation (25).[64] The result was that with these limits for varying R in DPTA, f_1 = const, namely, the $\exp(f_1)$ term in equation (25) does not depend on R, while in DED $f_1(R) = -2(R - R_0)/\alpha$ (where α = 1.7 Å). These results may be accounted for using a simple model of activated hops by polarons of small radius,[64,74] for which, as has been mentioned above, $\Delta G = 0$, $E_{in} = 0$, $G^{\neq} = E_s/4$.[20] For a nonadiabatic case in a zero-field approximation the mobility of a polaron of small radius is given by the expression:[64,74]

$$\mu = (eR^2/kT)\nu_0 \exp[-2(R - R_0)/\alpha] \exp(-G^{\neq}/kT). \quad (28)$$

where ν_0 is the frequency of optical phonons (without taking into account dispersion within the simple model), $G^{\neq} = e^2(1/r - 1/R)/4\varepsilon_p$, r is the radius of localisation if the charge, $1/\varepsilon_p = (1/n^2 - 1/\varepsilon)$. On comparing expressions (25) and (28) it is clear that

$$\exp(f_1) = \nu_0 \exp[-2(R - R_0)/\alpha]; \quad f_2 = -G^{\neq}/kT.$$

For small-sized DED molecules, for which $1/R < 1/r$, the effect of R on $G^{\neq}$ is small, which is in line with experiment. For the large DPTA

molecules, at all of the concentrations used R was comparable with $2r$ (i.e., there was contact between the molecules) and adiabatic electron transfer can be assumed. In this case

$$\exp(f_1) \approx \nu_0; \quad f_2 = -(G^{\neq} - V_{01})/kT. \tag{29}$$

Namely, in accordance with experiment f_1 does not depend on R, while the energy of activation in f_2 varies with R. This treatment is qualitative, but we should mention that, in accordance with (21), the rate constant of electron transfer $k_{et} = \exp(f_1)\exp(f_2)$ enters into the equations for μ [(25), (28) and (29)]. Expressions for the rate constant in the model for small-radius polaron hops constitute a special case of relationships (18) and (19) (when $\Delta G = 0$ and $E_{in} = 0$) for the rate constant of electron transfer between donor and acceptor components in a dielectric medium (model of the dielectric continuum).

The possibility of using the Marcus–Levich–Dogonadze–Kuznetsov[17] theory for the elucidation of electron transport in polymer media was demonstrated by Sahyun,[4] and the experimental proof was obtained by Vannikov et al.[75,76] in studying the effect of the polarity of the matrix on charge transport in a TPA + PC system. In this case the polarity was varied not by replacing the substituents in transport sites, as was carried out by Pai et al.,[71] but by the introduction of added components with different κ values that did not participate in transport. The added components were *p*-, *m*-, and *o*-dinitrobenzenes (DNB), which have dipole moments of 0.5, 4, and 6 D respectively. The concentration of TPA was 33 wt.% and that of DNB varied from 0 to 6 wt.%. It can be seen in Fig. 3 that at the same concentrations of DNB, *o*-DNB had the greatest effect on μ and ΔE_a and *p*-DNB had no effect.

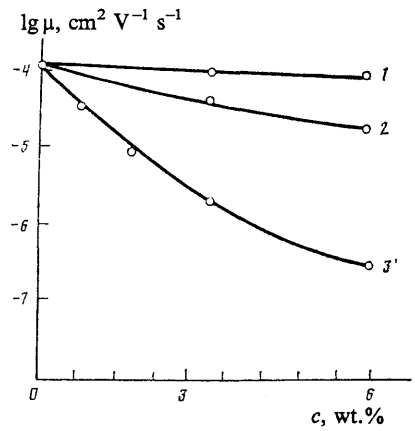


Figure 3. Dependence of the drift mobility of holes μ in the system PS + TPA on the concentration of added quantities of: *1*) *p*-DNB; *2*) *m*-DNB; *3*) *o*-DNB. TPA concentration = 33 wt.%.[75,76]

The ionisation potential of DNB in the gas phase is 10.5 eV, which is considerably higher than the ionisation potential of TPA (6.8 eV), therefore DNB molecules cannot be traps for holes, the transport of which occurs in TPA + PC systems. On increasing the concentrations of *o*-DNB to a value of 6 wt.%, the dielectric constant increases from 2.9 to 4.9 (in this system, $n^2 = 2.4$). The energy of activation for electron transfer may be determined, in accordance with what has been stated above, as

$$\Delta E_a \equiv G^{\neq} = \frac{(E_s + E_{in} + \Delta G)^2}{4(E_s + E_{in})}, \tag{30}$$

where ΔG is given by expression (11), $E_r = (E_s + E_{in})$, and E_s and E_{in} are determined from equations (15), (12), and (14) respectively.

For electron transfer through identical sites in an electric field F we can write $\Delta G = e(R - R_0)F$.

When the concentration of TPA is equal to 33 wt.%, $R = 10$ Å. In electron transfer from a neutral TPA molecule to a TPA^+ radical cation, a change in valence state of the nitrogen atom occurs. In TPA the nitrogen atom has a tetrahedral structure while in TPA^+ it is planar. The "inner-sphere" reorganisation energy E_{in} of the molecule, namely, the energy required for converting TPA to a TPA^+ form in the gas phase is 0.8–1.0 eV.[4] The experimental results of the dependence of μ and ΔE_a on the dielectric constant ε of the polymer matrix are shown in Fig. 4.[75,76] As can be seen, when ε increases from 2.9 to 4.9 μ decreases by a factor of 320 while ΔE_a increases from 0.18 to 0.46 eV. The curve of ΔE_a against ε, calculated from equation (30) [in calculating E_s from equation (12) it was assumed that $R = 25$, $r = 3$ Å, $E_{in} = 0.6$ eV, $F = 3 \times 10^5$ V cm^{-1}), is also given on Fig. 4. This value of E_{in} (less than that calculated in the gas phase) may occur because in the polymer matrix conformations of TPA^+ with different bond angles of the nitrogen atom are frozen,[77] resulting in a reduction in magnitude of E_{in}. On the whole the form of the curve agrees with the experimental results. The value of μ_1/μ_2, calculated from the equation

$$\mu_1/\mu_2 = \left[\exp\left(-\frac{\Delta E_{a1}}{kT}\right) \Big/ \exp\left(-\frac{\Delta E_{a2}}{kT}\right)\right] \simeq 320,$$

agrees with that obtained experimentally. Here the values of ΔE_{a1} and ΔE_{a2} are calculated from equation (30) when $\varepsilon = 2.9$ and 4.9 respectively. The difference between the experimental value of ΔE_a and that calculated for a maximum $\varepsilon = 4.9$ (see Fig. 4) may be due to the above-mentioned effect of the polarity of the medium on the energy spread of the bonding between a hole and M.

It should be mentioned that the models considered above (with the exception of the models of the polaron of small radius and the dielectric continuum) do not take into account the effect of the polarity of the medium on electron transfer in a polymer matrix. The cited experiment that involved a varying polarity of the medium showed that there is a dependence of the mobility of the charge carriers on the dielectric properties of the medium and also on the intramolecular reorganisation energy, which can only be explained on the basis of the dielectric continuum model of Marcus–Levich–Dogonadze–Kuznetsov.

II. Electron phototransfer

1. Tunnel electron phototransfer during exchange interaction in the ground state

The interaction of the wave functions [see (1) and (2)] results in stabilisation of the ground state of the system ($X_1 = E_i - E_0$) and destabilisation of the excited state ($X_2 = E_1 - E_{ex}$) by the amount (see Fig. 2*b*):[16,78–80]

$$X_{1,2} = \mp [\Delta G/2 - (\Delta G^2/4 + V_{01}^2)^{1/2}|], \tag{31}$$

where E_i and E_{ex} are the energies of the ground and excited states of the D ... A system respectively (Fig. 2*b*); ΔG is given by equations (3) and (11). When $V_{01} \ll \Delta G/2$, expression (31) frequently reduces to the form:[16,79,80]

$$X_{1,2} = \mp\left\{\frac{\Delta G}{2} - \left[\frac{\Delta G}{2}\left(1 + \frac{4V_{01}^2}{\Delta G^2}\right)^{1/2}\right]\right\} = \pm\frac{V_{01}^2}{\Delta G}. \qquad (32)$$

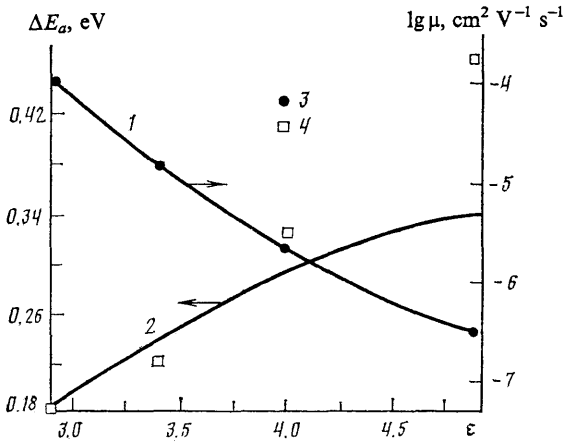


Figure 4. Dependence of the drift mobility of holes μ (curves *1* and *3*) and the energy of activation ΔE_a (curves *2* and *4*) on the dielectric constant of the polymer matrix ε. *1*) Calculation from expression (28); *2*) calculation from expression (30). Curves *3* and *4* are experimental results.[75,76]

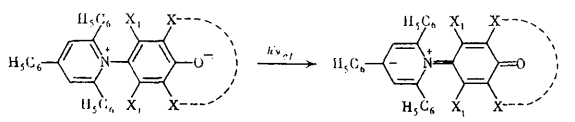
The spectroscopic distribution of the optical density $D(\nu)$ of the charge-transfer band (Fig. 1) is determined by the *FC* factor:[17,18]

$$D(\nu) = D(\nu_{max}) \exp\left[-\frac{(E_r + \Delta G - h\nu_{et})^2}{4E_r kT}\right], \qquad (33)$$

where $D(\nu_{max}) \sim V_{01}^2$ is the optical density at the maximum of the charge-transfer band, namely, when $h\nu_{et}^{max} = E_r + \Delta G$. According to expression (33), the width of the charge-transfer band is given by

$$h\Delta\nu_{1/2} = (2\ln 2)^{1/2}(2E_r kT)^{1/2}. \qquad (34)$$

The dependence of the position and shape of the charge-transfer band on E_r in liquid media has been studied experimentally.[83–86] In aqueous solution containing a high concentration of ferri- and ferrocyanide ions the shape of the electron-transfer band ($\lambda_{max} \sim 800$ nm) is determined by the "outer-sphere" reorganisation, to which the reorganisation energy of the solvent and the reorganisation of the ionic atmosphere make contributions.[83] Kjaer and Ulstrup[84,85] have studied the solvatochromism of intramolecular charge transfer in *N*-substituted 2,4,6-triphenylpyridines (betaines):



The position of the maximum of the charge-transfer band $h\nu_{et}^{max}$ in solutions of the betaines forms the basis for developing a polarity scale of the solvents.

In accordance with their effect on the width of the charge-transfer band, the solvents were divided into three groups: polar aprotic solvents, alcohols, and nonpolar aprotic solvents. In polar aprotic solvents, in accordance with equation (34), the shape of the band is determined by the relationship $E_r = E_s + E_{in}$, where the energy of intramolecular reorganisation results from the change in the C–O, N–C, and C–C bond lengths ($E_{in} = 0.2$ eV) on changing the distribution of charge by exposure to light with energy $h\nu_{et}$. In alcohols the change in vibrational frequencies of the hydrogen bonds formed between an alcohol and betaine makes an additional contribution to E_r. In nonpolar aprotic solvents the width of the charge-transfer band is determined not by E_r but by other forms of electrostatic interaction between the betaines and the solvent (dispersion forces, etc.).

A temperature-dependent ($\sim T^{1/2}$) broadening of the charge-transfer band in a mesitylene–tetracyanoethylene complex in hexane was established by Novikov et al.;[86] this was in complete agreement with expression (34).

According to Hopfield[18] the dipole moment of an optical transition $h\nu_{et}$ is given by

$$\mu_{ex,i} = \int \psi_{ex}^* \mu_{0d} \psi_i d\tau \simeq eRV_{01}/\Delta G,$$

Here μ_{0d} is the dipole moment operator. The molar extinction coefficient of the $h\nu_{et}$ band is proportional to $(\mu_{ex,i})^2$.[16]

$$\varepsilon_{max} \sim \nu_{et}^{max}\mu_{ex,i}^2/\Delta\nu_{1/2}.$$

Where ε_{max} is the extinction coefficient at the charge-transfer band maximum (at ν_{et}^{max}), $\Delta\nu_{1/2}$ is the width of the spectrum or the distance between the points at which $\varepsilon_{1/2} = \varepsilon_{max}/2$. Thus,

$$\varepsilon_{max}^{na} : \varepsilon_{max}^{a} : \varepsilon_{max}^{DA} = (R^{na}V_{01}^{na})^2 : (R^{a}V_{01}^{a})^2 : [R_0 V(R_0)]^2.$$

The values of ε_{max}^{na} and ε_{max}^{a} can be determined from the above-mentioned values of V_{01} of ~20 and 400 cm^{-1} respectively for non-adiabatic and adiabatic conditions of charge transfer and also from expression (16) for R, for example, in the approximation $V(R_0) = 1100$ cm^{-1}, $\alpha = 1$ Å, $R_0 = 7.4$ Å.[12] (For D·A complexes $R \simeq R_0$, i.e., $V_{01} \simeq V(R_0)$. After substitution we obtain

$$\varepsilon_{max}^{na} : \varepsilon_{max}^{a} : \varepsilon_{max}^{DA} = (11{,}4^2 \cdot 4 \cdot 10^2) : (8.4^2 \cdot 16 \cdot 10^4) : (7.4^2 \cdot 1.1^2 \cdot 10^6).$$

For D·A complexes $\varepsilon_{max}^{DA} \sim 10^3$ dm^3 mol^{-1} cm^{-1}, hence $\varepsilon_{max}^{a} \simeq 170$ and $\varepsilon_{max}^{na} \simeq 0.78$ dm^3 mol^{-1} cm^{-1}. The latter value agrees with the estimate obtained in two studies,[18,87] in which it is observed that ε usually does not exceed 1 dm^3 mol^{-1} cm^{-1}.

2. Tunnel phototransfer of electrons in the absence of an exchange interaction in the ground state

In the absence of a D·A interaction in the ground state, overlap of the orbitals of the components which gives rise to electron transfer can occur through photoexcitation of one of the components (Fig. 5). In contrast to a liquid, in which electron transfer mainly occurs after diffusion convergence of the components, in a solid (including a polymer) matrix noncontact exciplexes $(D \ldots A)^* \rightarrow (D^{\dot{+}} \ldots A^{\dot{-}})$, where $(D \ldots A)^*$ means $(^{1,3}D_1 \ldots {}^1A_0)$ or $(^1D_0 \ldots {}^{1,3}A_1)$, can participate in electron-transfer reactions. The wave functions of the initial excited and ionic state have the form [by analogy with expressions (1) and (2)]:

$$\psi_1(D \ldots A)^* = \psi_0(D \ldots A)^* + \lambda\psi_1(D^{\dot{+}} \ldots A^{\dot{-}}),$$

$$\psi_{11}(D^{\dot{+}} \ldots A^{\dot{-}}) = \psi_1(D^{\dot{+}} \ldots A^{\dot{-}}) - \lambda\psi_0(D \ldots A)^*.$$

The free energy $\Delta G'$ (Fig. 5) and λ are given by expression (3) when E_0 is replaced by $E_{0'}$ and V_{01} is replaced by $V_{01'}$.

$$E_0' = \int \psi_0^*(\mathrm{D}\ldots\mathrm{A})^* H \psi_0(\mathrm{D}\ldots\mathrm{A}) d\tau,$$

$$V_{01}' = \int \psi_0^*(\mathrm{D}\ldots\mathrm{A})^* H \psi_1(\mathrm{D}^{\dot{+}}\ldots\mathrm{A}^{\dot{-}}) d\tau.$$

The transformation of a noncontact exciplex into a contact form when the D and A components are brought closer together, i.e., when V_{01}' is increased, is similar to that shown in Figs. 1 and 2 for donor-acceptor systems interacting in the ground state.

In the present section we shall consider systems in which the distance R between the D ... A components is greater than the van der Waals radii. In these systems when component D or A undergoes photoexcitation in solid matrices, reactions leading to formation of the radical ion pair $^{1,3}[\mathrm{D}^{\dot{+}}\ldots\mathrm{A}^{\dot{-}}]$ can occur:

$$\left.\begin{array}{l} {}^{1,3}\mathrm{D}_1 + {}^1\mathrm{A}_0 \rightarrow {}^{1,3}\mathrm{D}_1 \ldots {}^1\mathrm{A}_0 \\ {}^1\mathrm{D}_0 + {}^{1,3}\mathrm{A}_1 \rightarrow {}^1\mathrm{D}_0 \ldots {}^{1,3}\mathrm{A}_1 \end{array}\right\} \rightarrow {}^{1,3}(\mathrm{D}^{\dot{+}}\ldots\mathrm{A}^{\dot{-}}) \rightarrow \left\{\begin{array}{l} \mathrm{D}^{\dot{+}} + \mathrm{A}^{\dot{-}} \\ \text{products} \\ {}^1\mathrm{D}_0 + {}^1\mathrm{A}_0 \end{array}\right. \quad (35)$$

$$({}^2(\mathrm{D}^{\dot{+}}\ldots{}^2\mathrm{A}^{\dot{-}}) \quad {}^2\mathrm{D}^{\dot{+}}\ldots{}^2\mathrm{A}^{\dot{-}} \text{ or } {}^2[\mathrm{D}^{\dot{+}}\ldots\mathrm{A}^{\dot{-}}])$$

(The equilibrium $^{1,3}[\mathrm{D}^{\dot{+}}\ldots\mathrm{A}^{\dot{-}}] \rightleftharpoons [{}^2\mathrm{D}^{\dot{+}}\ldots{}^2\mathrm{A}^{\dot{-}}]$ corresponds to a weak spin correlation (or its absence) of radical ions that are separated by a distance greater than the van der Waals radii.)

In reactions (35) a photoexcited charge-transfer complex involving a bridging molecule (B) can act as one of the components:

$$\left.\begin{array}{l} {}^{1,3}(\mathrm{D.B})_1 + {}^1\mathrm{A}_0 \rightarrow {}^{1,3}(\mathrm{D.B})_1 \ldots {}^1\mathrm{A}_0 \\ {}^1\mathrm{D}_0 + {}^{1,3}(\mathrm{B.A})_1 \rightarrow {}^1\mathrm{D}_0 \ldots {}^{1,3}(\mathrm{B.A})_1 \end{array}\right\} \rightarrow {}^1\mathrm{B}_0 + \left\{\begin{array}{l} {}^{1,3}[\mathrm{D}^{\dot{+}}\ldots\mathrm{A}^{\dot{-}}] \\ {}^2[\mathrm{D}^{\dot{+}}\ldots\mathrm{A}^{\dot{-}}] \end{array}\right.$$

and subsequently as in reaction (35). Reactions of this type have been studied in detail in a review,[12] in which various classes of dyes that can cause spectroscopic sensitization of electron transfer in donor-acceptor systems are used as a bridging molecule. The free energy of electron transfer according to reaction (35) is given by (Fig. 5):

$$\Delta G' = eE_{1/2}({}^{1,3}\mathrm{D}_1/\mathrm{D}^{\dot{+}}) - eE_{1/2}(\mathrm{A}^{\dot{-}}/{}^1\mathrm{A}_0) + e^2/\varepsilon_s R \quad (36)$$

or

$$\Delta G' = eE_{1/2}({}^1\mathrm{D}_0/\mathrm{D}^{\dot{+}}) - eE_{1/2}(\mathrm{A}^{\dot{-}}/{}^{1,3}\mathrm{A}_1) + e^2/\varepsilon_s R. \quad (36a)$$

Here

$$E_{1/2}({}^{1,3}\mathrm{D}_1/\mathrm{D}^{\dot{+}}) = E_{1/2}({}^1\mathrm{D}_0/\mathrm{D}^{\dot{+}}) - E({}^{1,3}\mathrm{D}_1),$$

$$E_{1/2}(\mathrm{A}^{\dot{-}}/{}^{1,3}\mathrm{A}_1) = E_{1/2}(\mathrm{A}^{\dot{-}}/{}^1\mathrm{A}_0) + E({}^{1,3}\mathrm{A}_1),$$

where $E(^{1,3}\mathrm{D}_1)$ or $E(^{1,3}\mathrm{A}_1)$ is the distance from the ground to excited singlet or triplet level of molecule D or A; $E(^1\mathrm{D}_1)$ and $E(^1\mathrm{A}_1)$ are the energies that correspond to unrelaxed Franck–Condon or relaxed excited states of the molecules. When excited molecules of D or A participate in phototransfer of an electron in a Franck–Condon state [reactions (35)], the probability of a radical ion pair being formed is determined from the difference $E_e - G^{\neq}$ (see Fig. 5*a* and 5*b*), where E_e is the excess energy of the (D ... A) system that occurs in a Franck–Condon state above the energy at the minimum of the potential curve. In the region $E_e < G^{\neq}$, the probability of electron transfer increases exponentially as E_e increases

$$P_{et} = A' \exp\left[-\frac{-E_e + G^{\neq}}{c}\right],$$

and reaches a maximum value at $G^{\neq} - E_e = 0$. (In this equation $c = kT$ if $\hbar\omega \ll kT$ and $c = \hbar\omega$ if $\hbar\omega \gg kT$.) Under nonadiabatic conditions P_{et} decreases as the kinetic energy $\Gamma = E_e - G^{\neq}$ increases in the region $E_e > G^{\neq}$ because of the increased probability of passing through the intersection point of the potential curves on its pathway, i.e., without electron transfer (Fig. 5*a*).[88]

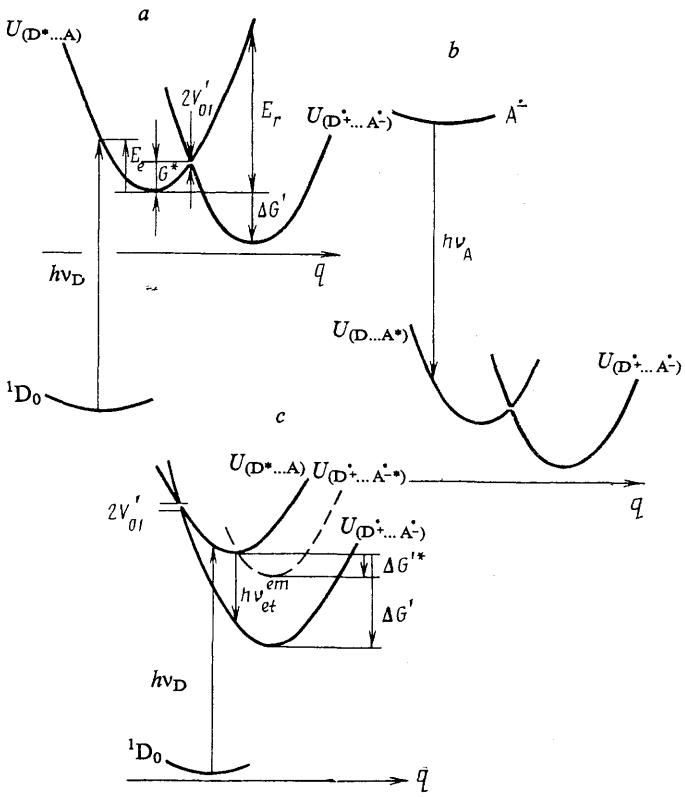


Figure 5. Dependence of the potential energies $U_{(D^*\ldots A)}$ (*a* and *c*), $U_{(D\ldots A^*)}$ (*b*), $U_{(D^{\dot{+}}\ldots A^{\dot{-}})}$, and $U_{(D^{\dot{+}}\ldots A^{\dot{-}*})}$ on the generalised coordinate q. The parameters that determine the probability of electron phototransfer under nonadiabatic conditions without an exchange interaction in the ground state during photoexcitation of the donor $h\nu_D$ (*a* and *c*) or acceptor $h\nu_A$ (*b*) are given. $^1D_0$ (*a* and *c*) and $A^{\dot{-}}$ (*b*) correspond to the energies of the donor in the ground state and of the radical anion of the acceptor respectively. The free energy $\Delta G'^*$ corresponds to the transfer of an electron to an electronically or vibrationally excited energy level of the acceptor.

When relaxed $^{1,3}(\mathrm{D}\ldots\mathrm{A})_1$ states participate in electron transfer the probability of electron transfer corresponds to the relationship $P_{et} = A' \exp(-G^{\neq}/c)$. In systems with a large negative free energy $-\Delta G'$ (Fig. 5*c*) the rate constant may be determined by electron transfer not to the lowest unfilled acceptor orbital but to a higher level that corresponds to formation of an acceptor radical anion in an electronically excited or vibrationally excited state. In both cases

$$k_{et} = A' \exp\{-[(\Delta G' - E') + E_s]^2/4E_s c\}.$$

In the first case $E' = E(\mathrm{A}^{\dot{-}*})$, in the second $E' = \nu\hbar\omega_{in}$; E_s is calculated from equation (12).

With high negative values of $-\Delta G'$ an emissive charge-transfer transition is to be expected (Fig. 5*c*)

$$(D \ldots A)^* \rightarrow (D^{+} \ldots A^{-}) + h\nu_{et}^{em}$$

and also emission from an excited A^{-}* state:

$$(D^{+} \ldots A^{-*}) \rightarrow (D^{+} \ldots A^{-}) + h\nu_{A}^{em}.$$

It should be mentioned that electron transfer by route (35) can occur with local excitation of one of the components of the D ... A system in which there is an exchange interaction in the ground state (Fig. 6). Under nonadiabatic conditions this route is more effective than electron transfer on exposure to light $h\nu_{et}$, since, as was mentioned above, the charge-transfer band has a low extinction coefficient. Under these conditions light with energy $h\nu_D$ (or $h\nu_A$) accelerates the charge-transfer reaction.[3]

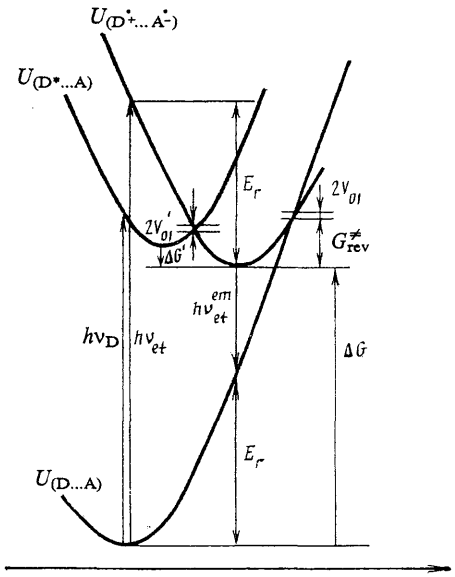


Figure 6. Dependence of the potential energies $U_{(D...A)}$, $U_{(D^{*}...A)}$, $U_{(D^{+}...A^{-})}$ on the generalised coordinate q. The parameters that determine the probability of electron phototransfer under nonadiabatic conditions when there is an exchange interaction in the ground state during photoexcitation of the donor $h\nu_D$ or the D ... A system $h\nu_{et}$; $G^{\neq}_{rev}$ is the energy of activation of the reverse reaction of (4).

When there is an exchange interaction (V_{01}) in the ground state (Fig. 6), reverse electron transfer can occur both by a route that involves surmounting the potential barrier $G^{\neq}_{rev}$ and with emission of $h\nu^{em}_{et}$:[89,90]

$$D^{+} \ldots A^{-} \rightarrow D \ldots A + h\nu_{et}^{em}.$$

It follows from the positions of the levels shown in Fig. 6 that $h\nu_{et} + h\nu_{et}^{em} = 2\Delta G$ and the Stokes shift is given by $h\nu_{et} - h\nu_{et}^{em} = 2E_r$.[89,90]

A number of studies[91–101] examine the factors that determine the tunnelling distance during photoexcitation of the D (or A) components over a wide temperature range, including room temperature, in higher alcohols[91,92] and polymer matrices [polycarbonate,[93] cellulose,[94–97] polyvinylpyrrolidone (PVP),[98] polystyrene,[99] polyvinyl acetate (PVA) and polymethylstyrene (PMS)[100,101]]. The tunnelling distance was determined from the dependence of the intensity (I) of luminescence of the excited component in a D ... A system on the concentration of quencher Q (where Q ≡ D or A).

The quenching of luminescence, which occurs by an electron-transfer mechanism in these systems, is given by the Perrin model:

$$I/I_0 = \exp(-N_A V[Q]), \qquad (37)$$

where V is the volume of the "active" sphere containing a quencher molecule. According to this model, excitation of a molecule is either quenched or not quenched at all depending on whether the molecule is within the "active" sphere or outside it. The radius of the "active" sphere R_q is determined from the relationship:

$$N_A V [Q]_0 = (4\pi/3) R_q^3 N_A [Q]_0 = 1, \qquad (38)$$

where $[Q]_0$ is the concentration of quencher at which the intensity of luminescence calculated from (37) is e times weaker than in the absence of quencher. Hence

$$R_q = (3 \cdot 10^{27}/4\pi N_A [Q]_0)^{1/3}, \text{ Å}.$$

The relationship between R_q and the energy characteristics of electron transfer was determined from equation (18) when $R = R_q$:[91]

$$(R_q - R_0) = \frac{\alpha}{2} [\ln(\nu_0/k_{et}) - (\Delta G' + E_r)^2/4E_r kT]. \qquad (39)$$

Here $R_q - R_0$ is the tunnelling distance. The constant k_{et} may be obtained experimentally from kinetic measurements of luminescence from the expression $k_{et} = (1/\tau_f) - (1/\tau_0)$, where τ_0 is the inherent lifetime of excitation and τ_f is the lifetime of excitation in the presence of a quencher at concentration $[Q]_0$.

The dependence of R_q on $\Delta G'$ in electron phototransfer reactions from excited ruthenium complexes with different types of ligands to a methyl viologen quencher (MV^{2+}) has been determined.[92] This dependence has a maximum ($R_q - R_0$) = 3 Å when $-\Delta G' = E_r = 0.7$ eV. In reactions involving the quenching of excited acceptors (rubrene, tetracene, perylene, 9-methylanthracene, 9,10-diphenylanthracene, fluoranthrene, acridinium) by amines (TMPD and diethylamine), the tunnelling distance determined from expression (39) is given by ($R_q - R_0$) = 7–10 Å and α = 0.75 Å. Expression (39) effectively represents the dependence of R_q on $\Delta G'$ obtained experimentally[98] in the quenching of the singlet excited dye rhodamine B by electron transfer to the dye from such donors as TMPD, 10-methylphenothiazine, ferrocene, pentamethylferrocene, ascorbic acid and also from the dye to acceptors such as dipyridinium salts with various substituents in a PVP matrix. It was established that ($R_q - R_0$) increases from 0 to 16 Å as $\Delta G'$ decreases from 0.2 to –1.0 eV.

Palazzotto et al.[100,101] have studied the fluorescence quenching of rhodamine 6G (R6G) by donor quenchers such as carbazole, triphenylamine (TPA), *N*,*N*-dimethyl-*p*-toluidine (DMT), phenothiazine (PT), *N*-methylphenothiazine (MPT), 1,4-diazabicyclo[2.2.2]octane, *N*,*N*'-diphenyl-*p*-phenylenediamine (DPPD), and *N*-phenyl-*p*-phenylenediamine (PPD) in PVA and PMS films. It has been shown[101] that R6G forms charge-transfer complexes with these donors (in the ground state). The complex formation constant (K, $dm^3\ mol^{-1}$) depends on the nature of the polymer matrix and for different donors (in brackets) is for PVA and PMS respectively: 2.8 and undetermined (TPA), 5.9 and 5.8 (DMT), 5.7 and 8.7 (MPT), 7.5 and 56.3 (PT), 9 and 35.9 (DPPD), 10.3 and 41.7 (PPD). Molecules of R6G that do not form a complex are responsible for fluorescence in this case; the

proportion of these is given by

$$([R6G]_0 - [D.R6G])/[R6G]_0 = 1/(1 + K[D])^{-1}.$$

where $[R6G]_0$ and [D·R6G] are the total concentration of dye and the final concentration of dye forming a complex respectively. When the radius R_q was calculated[101] from equation (38) the volume of the "active" sphere was determined from the experimental dependence of the intensity of fluorescence of R6G molecules on the concentration of donor (quencher) according to the equation:

$$I/I_0 = (1 + K[D])^{-1} \exp(-N_A V[D]). \quad (40)$$

The free energy $\Delta G'$ was calculated from expression (36a) (for the approximation $e^2\varepsilon_s R = 0$). It was found[101] that when $\Delta G'$ decreased from –0.55 to –1.11 eV, R_q increases from 3 to 10.9 Å in a PVA matrix and from 9.6 to 12.1 Å in a PMS matrix.

In several studies[93–97,99] a model[102,103] which takes into account the random distribution of interaction distances R was applied to polymer systems. According to this model

$$I/I_0 = \exp\{-k_0 t - A[\ln^3(\nu_0 t) + 1.73165\ln^2(\nu_0 t) + 5.9343\ln(\nu_0 t) + 5.44]\}.$$

Here $A = \alpha[Q]/R_q^3[Q]_0$.[93–97,99] The value of Q_0 is calculated from expression (38). The dependence of the tunnelling distance $(R_q - R_0)$ on the free energy $-\Delta G'$ calculated from this expression is given in Table 2. The increase in the disance $(R_q - R_0)$ as $-\Delta G'$ increases and as the temperature rises is demonstrated. This model satisfactorily represents the fluorescence quenching of TMPD and tetramethylbenzidine (TMB) with phthalic anhydride (PA)[99] and methyl viologen[97] respectively. Determinations of R_q (17 Å) and α (1.73 Å) have been made for the system $^3TMPD_1...^1PA_0$ in polystyrene[99] and also R_q = 38 Å and α = 3.4 Å for $^3TMB_1...^1(MV^{2+})_0$ in cellulose.[97] Unfortunately, in all of the studies mentioned above, in the calculation of $(R_q - R_0)$ and α, the possible increase in the size of the molecule (i.e. R_0) on going to an excited singlet and triplet state was not taken into account. The considerable tunnelling distances obtained in a number of systems are due to a superexchange mechanism, with fragments or defects in the polymer chains being regarded as bridging groups.[93]

3. Effects of the polymer matrix on the optical absorption properties of charge-transfer complexes

D ... A systems in which the distance between the components is greater than the sum of their van der Waals radii have been examined above. In these systems radical ions with separate solvation shells are formed through electron transfer. In the case of excited contact D·A complexes the point dipole model[19,81,89,104] has been used. The transformation of a two-sphere model, namely, a model with separate solvation shells in which the reorganisation energy of the medium is given by expression (12), into a single-sphere system that corresponds to a point dipole model has been reported.[89] The dipole κ [$\kappa \equiv e[r_D + r_A)$] produces an Onsager reaction field in the dielectric:

$$R(\varepsilon) = \frac{2\kappa}{a^3} F(\varepsilon) \quad \text{or} \quad R(n) = \frac{2\kappa}{a^3} F(n),$$

where $R(n)$ is the electronic component of the reaction field, $F(\varepsilon) = (\varepsilon - 1)/(2\varepsilon + 1)$ and $F(n) = (n^2 - 1)/(2n^2 + 1)$, a is the radius of the cavity occupied by the polarising dipole. The interaction energy of the dipole κ with the reactive field is given by

$$-\kappa R(\varepsilon) = -\frac{2\kappa^2}{a^3}\left(\frac{\varepsilon - 1}{2\varepsilon + 1}\right) \quad \text{or} \quad -\kappa R(n) = -\frac{2\kappa^2}{a^3}\left(\frac{n^2 - 1}{2n^2 + 1}\right). \quad (41)$$

As in the case of the two-sphere model the Stokes shift between the excitation maxima and fluorescence emission of the D·A complex is determined by the reorganisation energy ($E_r = E_{in} + E_s$) and is given by the Lippert–Mataga expression[19,104] (see Fig. 2*b* and Fig. 6):

$$h\nu_{et} - h\nu_{et}^{em} = 2E_r = 2E_{in} - [\kappa R(\varepsilon) - \kappa R(n)] = 2E_{in} + \frac{2\kappa^2}{a^3}\left(\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{n^2 - 1}{2n^2 + 1}\right). \quad (42)$$

Table 2. Increase in $(R_q - R_0)$ as $-\Delta G'$ increases in the fluorescence quenching of RuL_3^{2+} ruthenium complexes by methyl viologen (L = ligand).[93]

Ligand in RuL_3^{2+}	$-\Delta G'$, eV	$(R_q - R_0)$, Å at:	
		77 K	293 K
4,7-Dimethylphenanthroline	—0.13	6.4	10.6
2,2'-Bipyridine	—0.4*	—	10.0*
5-Chlorophenanthroline	—0.49	10.5	14.6
2,2'-Bipyridine 4,4'-diisopropyl ether	—0.88	15.9	18.9

*Reported value.[94]

Expression (42) has been successfully used for an experimental determination from the Stokes shift of the phase (ε, n) in which a D·A complex is formed in complex biological systems.[104]

A detailed analysis of the effect of dielectric properties in liquid media on the position of the maximum in the optical spectrum of D·A molecular complexes is given in a number of review articles (a general treatment of them is given by Davis[81]). In accordance with expression (33), in condensed media

$$h\nu_{et}^{max} = \Delta G' + E_r \equiv (\Delta G' + E_{in}) + E_s.$$

Since the optical absorption spectrum corresponds to a transition from the ground to an excited Franck–Condon state, the electronic polarisation of the medium $\kappa R(n)$ is synchronous with this process. Hence,

$$h\nu_{et}^{max} = h\nu_{et}^{max}(\text{gas}) - \frac{2\kappa^2}{a^3}\left(\frac{n^2 - 1}{2n^2 + 1}\right). \quad (43)$$

Here

$$h\nu_{et}^{max}(\text{gas}) = I_D - E_A - e^2/R + 2X + E_{in}, \quad (44)$$

where, according to (31) and (32), $2X = |X_1| + |X_2|$. The dependence of $h\nu_{et}^{max}$ on the dielectric properties of the medium (including polymer matrices) for the complexes $(C_5H_5)_2Fe.CBr_4$, $DPBA.CBr_4$, and $DPBA.CBr_3SO_2CBr_3$ (DPBA = diphenylbenzylamine) has been determined.[105] An analysis of the long-wavelength decrease in optical absorption of these complexes showed that in all the media studied the optical spectrum has a Gaussian form

$$D(\nu) = D(\nu_{max}) \exp[-(\nu_{max} - \nu)^2/2(\sigma \cdot 10^3)^2], \quad (45)$$

where $\sigma \times 10^3 = (\nu_{max} - \nu_{1/2}) \times (2\ln 2)^{1/2}$. It was established experimentally (Fig. 7) that the position of the maximum in the optical absorption spectrum of a $(C_5H_5)_2Fe.CBr_4$ complex conforms to a relationship which is common to liquid systems and solid polymer

matrices:

$$h\nu^{max} = 3.9 - 3.1\,(n^2 - 1)/(2n^2 + 1). \quad (46)$$

The degree of charge transfer (δ^*) in the excited state of the complex $[(C_5H_5)_2Fe^{+\delta^*}.CBr_4^{-\delta^*}]$ was determined approximately from the assumption that $r_D = r_A = r$, $R_0 = 2r$, $a = 2r$, i.e., according to expressions (43) and (46) $(2\kappa^2/a^3) = (e^2\delta^{*2}/r) = 3.1$. An estimated value of $e^2/r = 3.8$ was obtained[12] by correlating a large number of experimental results in the literature on the polarisation of liquid media by radical cations of aromatic hydrocarbons, radical anions and cations of different types of dyes, and radical anions of various acceptors. By using this value for $(C_5H_5)_2Fe.CBr_4$ complexes, the degree of charge transfer in the excited state $\delta^* = (3.1/3.8)^{1/2} \simeq 0.9$ was calculated. The degree of charge transfer in this complex in the ground state ($\delta = 0.1$) was determined from the reported[106] dependence of δ on $I_D - E_A$ for complexes of this type. The fulfillment of the relationship $\delta^* = 1 - \delta$ is an indication that the excited state of the $(C_5H_5)_2Fe.CBr_4$ complex corresponds only to electron transfer ($h\nu^{max} = h\nu_{et}^{max}$) and does not contain contributions from local excitations of the individual donor or acceptor components. The half-width of the optical spectrum of this complex has a constant value in all of the media studied (both liquid and polymer)

$$(\nu_{max} - \nu_{1/2}) = \sigma \cdot 10^3\,(2\ln 2)^{1/2} = 3850 \pm 140 \text{ см}^{-1}$$

and is due to an electronic-vibrational interaction.[77]

It may be noted that for exciplexes (which, as was mentioned above, do not have an optical absorption spectrum since they are only formed by photoexcitation of the D or A component) the emission energy from a relaxed state is given by the expression:[79,80,107]

$$h\nu_{et}^{em} = h\nu_{et}^{em}(\text{gas}) - \frac{2\kappa^2}{a^3}\left[\frac{\varepsilon - 1}{2\varepsilon + 1} - \frac{1}{2}\,\frac{n^2 - 1}{2n^2 + 1}\right],$$

from which the dipole moment κ and degree of charge transfer in a relaxed exciplex can be determined.[107] In this case the energy of the relaxed exciplex is assumed to be equal to

$$E^* = E^*(\text{gas}) - \frac{\kappa^2}{a^3}\left(\frac{\varepsilon - 1}{2\varepsilon + 1}\right).$$

A characteristic feature of the optical spectra of DPBA.CBr_4 and DPBA.$CBr_3SO_2CBr_3$ is their broadening on going from liquid media to polymer matrices (retaining a Gaussian form) and a subsequent increase in the width of the spectrum on reducing the generalised free volume V_E' of the polymer composite.[105] Table 3 gives the values of $(\nu_{max} - \nu_{1/2})$, the free volume V_E of the polymer, and the generalised free volume V_E' of the composite, calculated on the assumption that it is an additive function of the free volume of the components:

$$V_E' = \Sigma \Phi_i V_{E,i}.$$

Here Φ_i is the volume fraction of an individual component in the polymer and $V_{E,i}$ is its free volume.

It follows from Table 3 that the width of the optical spectrum of the DPBA.$CBr_3SO_2CBr_3$ complex remains constant on changing the liquid solvent. The increase in $(\nu_{max} - \nu_{1/2})$ in the series of polymers (Table 3) may be due to the reduction in generalised free volume V_E'.

It was established using PVC matrices that the optical spectrum of the DPBA.$CBr_3SO_2CBr_3$ complex contracts reversibly when the temperature is increased. The spectra recorded as the temperature was reduced from 80° to 77° and then 60 °C are shown in Fig. 8. It is clear that as a result of reducing the temperature the optical density decreases in the region of maximum absorption of the complex (about 365 nm) but increases at longer wavelengths in the spectrum (420–650 nm). In this case the change in optical density on reducing the temperature from 77 to 60 °C is comparable in magnitude with the change over the narrow temperature region (80 → 77 °C) of the glass transition temperature of PVC ($T_g \sim 78$ °C).

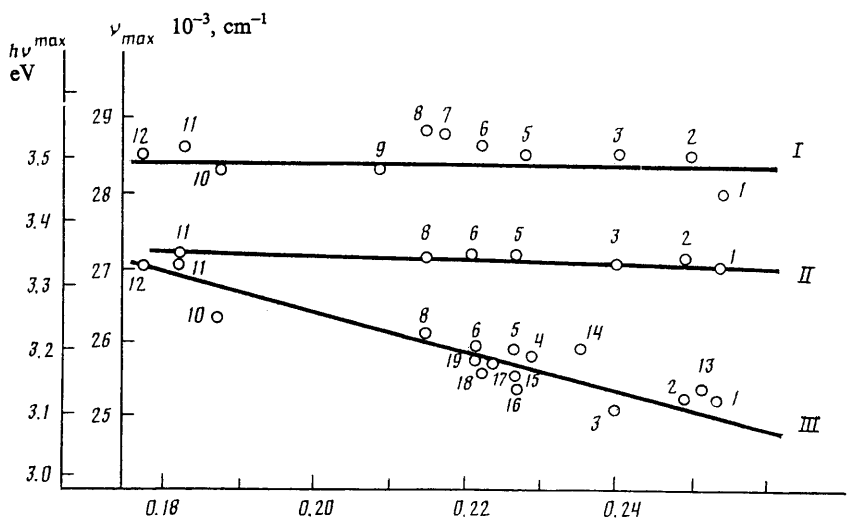


Figure 7. Dependence of ν_{max} and $h\nu_{max}$ on $(n^2 - 1)/(2n^2 + 1)$ in composites containing the following complexes: *I*) DPBA.CBr_4; *II*) DPBA.$CBr_3SO_2CBr_3$; *III*) $(C_5H_5)_2Fe.CBr_4$. The experimental results were obtained by Grishina et al.[105] The points correspond to: *1*) PS; *2*) CPVC; *3*) PVC; *4*) benzene; *5*) toluene; *6*) PMMA; *7*) dimethyl sulphoxide; *8*) PVA; *9*) dichloroethane; *10*) n-hexane; *11*) acetone; *12*) acetonitrile; *13*) PC; *14*) PVP; *15*) polyvinylethylal; *16*) polyvinylformalethylal; *17*) polybutyral; *18*) polybutyl metha-crylate; *19*) acetylcellulose.

It was suggested[108] that the broadening of the spectra of such complexes on going from liquid media to polymer matrices is due to the formation of mD·nA complexes with different ratios of m/n. In a polymer matrix the alteration in the ratio between complexes with different compositions when the temperature is varied is suppressed and it cannot be regarded as the only reason for the temperature dependence of the width of the optical spectrum.

Table 3. Free volume of liquid or polymer (V_E), generalised from volume of composite (V_E'), width of optical spectrum ($\nu_{max} - \nu_{1/2}$), calculated for a DPBA.$CBr_3SO_2CBr_3$ complex in liquid media and polymer matrices.[105]

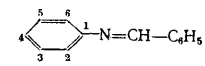
Medium	V_E, cm^3 mol^{-1}	V_E' cm^3 mol^{-1}	$(\nu_{max} - \nu_{1/2})$, cm^{-1}
	Liquid		
n-Hexane	62.5	62.5	2320
Toluene	43.7	43.7	2320
Benzene	35.9	35.9	2320
Acetone	34.5	34.5	2320
Acetonitrile	23.2	23.2	2320
	Polymer matrix		
PS	31.83	40.27	2850
PMMA	23.17	37.98	3040
PVA	24.51	36.83	3200
PVC*	18.56	35.22	3290
CPVC**	15.14	35.80	3350

*poly(vinyl chloride)
**chlorinated poly(vinyl chloride)

The combined experimental data, namely, the broadening of the optical spectra on going from liquid media to polymer matrices, the broadening as the free volume of a polymer is reduced, the temperature-dependent contraction of the spectrum in a polymer matrix (Fig. 8) have been accounted for[77,105] on the basis of the conformational isomerism of benzylanilines (including DPBA) and the freezing in a limited free volume of conformations which do not occur under equilibrium conditions in a liquid. Conformational isomerism is taken to mean the existence amongst benzylanilines of a "set" of structures which differ according to the rotation angle (φ) of the nonbonding orbital of the amino group relative to the plane of the benzene ring (Fig. 9).

Freezing out of isomers with a different angle of rotation φ (twist angle) account for the photophysical properties of substituted anilines that are introduced into the polymer matrix; donor (amino group) and, in a *para*-position relative to it, acceptor (cyano, ester, 9-anthryl, or other groups) fragments are combined in a single aniline molecule.[109–114] The slowing down in the reorientation of angle φ in polymer matrices at room temperature causes a nonuniform broadening of the fluorescence excitation spectrum of these compounds. This broadening appears as an enlargment of the spectrum at longer wavelength, at which there is no absorption in the liquid phase.[111,112] On exposure to light at longer wavelength isomers with an increased twist angle are selectively exicted, being converted with high probability to an excited charge-transfer state corresponding to $\varphi = 90°$.

The formation of molecular conformations with different equilibrium rotation angles of the aromatic ring about the C(1)–N bond in substituted *N*-benzylidenanilines



has an effect on a number of physicochemical properties of these compounds.,[115–117] Thus, introduction of a substituent into the 2-position (or 2- and 6-positions), which results in the aromatic ring being forced out of conjugation with the n orbital of the nitrogen ring, causes a decrease in ionisation potential (in the gas phase) from 8.25 (with no substituents) to 8.06 (or 8.00) eV.[116] It was established by NMR that introduction of an NO_2 group at a *para*-position relative to the C(1)–N bond increases the degree of conjugation of the aromatic ring with the nonbonding orbital of the nitrogen atom.[116] According to Akaba et al.[117] this results in an increase in ionisation potential of the molecule to 8.76 eV.

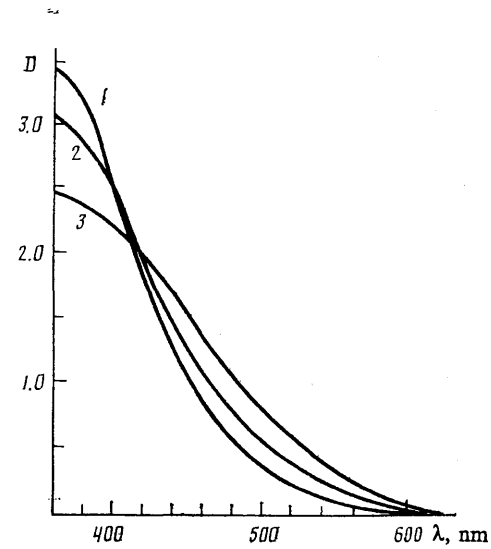


Figure 8. Optical spectra of the DPBA.$CBr_3SO_2CBr_3$ complex in a PVC matrix recorded as the temperature is decreased from 80 °C (1) to 77 °C (2) and 60 °C (3).

Benzylanilines (including DPBA) in polymer matrices where there is a limited free volume also exist in various conformations that differ according to the magnitude of their angle of rotation φ as a result of steric hindrance produced by the matrix (Fig. 9). These orientations of φ are frozen because of the long relaxation times of the polymer. It can be seen from Fig. 9 that a change in angle φ gives rise to a change in the degree of overlap of the π-electron orbitals of the aromatic ring and the n orbital of the unshared electron pair (UEP) of the nitrogen atom. This overlap is at minimum when $\varphi = 90°$ and increases as φ decreases to 0°.

In the formation of an intermolecular $n-\sigma^*$ complex in which the acceptor is coordinated with the nitrogen atom of benzylaniline, the n orbital of the nitrogen atom is involved as the donor in the interaction with the acceptor if $\varphi = 90°$, in other words, if the amino group is not conjugated with the benzene ring. If $\varphi = 0°$ the donor properties of benzylaniline are determined by the system of conjugated bonds that include the benzene ring and the UEP of the

nitrogen atom. For this reason,[44] instead of the statistically averaged gas-phase potential I_D it is necessary to use the inverse of the energy of that benzylaniline orbital (I_{BA}) which undergoes a donor-acceptor interaction.[77,105] Its magnitude is determined by the expression

$$I_{BA} = I_0 + I\cos^2\varphi. \quad (47)$$

When $\varphi = 0°$ $I_{BA} = I_0 + I$, where $I_0 + I$ is the ionisation potential of the system of conjugated bonds. It is close to the ionisation potential of aniline ($I_0 + I$) = 7.7 eV.[118] When $\varphi = 90°$ $I_{BA} = I_0$, where I_0 is the "ionisation potential" of the UEP orbital of the nitrogen atoms. It is presumed that I_0 is close to the ionisation potential of TPA (I = 6.88 eV), in which the aromatic groups are turned through 45° relative to the UEP of the nitrogen atom.[119]

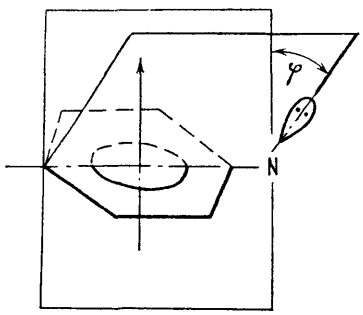


Figure 9. Angle of rotation φ of the nonbonding orbital of the nitrogen atom relative to the plane of the benzene ring in benzylanilines.[77]

In the possible formation of a $\pi-\sigma^*$ complex, namely, in coordination of the acceptor with the benzene ring of benzylaniline, when φ increases from 0 to 90°, i.e., as the UEP moves out of the system of conjugated bonds, the energy of the orbital involved in the D·A interaction varies in accordance with the relationship:

$$I_{BA} = (I_0 + I) + I'\sin^2\varphi,$$

from I_{BA} = (I_0 + I) = 7.7 eV to the value (I_0 + I) + I', which is close to the ionisation potential of benzene (9.25 eV[118]).

The calculations carried out by Novikov and Vannikov[77] showed that in compounds such as DPBA in which $\varphi \sim 45°$, the broadening of the optical spectra of the complex DPBA.$CBr_3SO_2CBr_3$ on transferring to polymer matrices by $\sim 10^{-3}$ cm^{-1} (Table 3) corresponds to a scatter in values of angle φ by $\sim 5-8°$ and that this scatter leads to a broadening of the long-wavelength region of the optical absorption in the case of $n-\sigma^*$ complexes but causes an extension of the spectrum to shorter wavelength when the acceptor is coordinated to the benzene ring of benzylaniline.

The series of results considered above corresponds to the relative position of the energy levels (shown in Fig. 10) in complexes based on DPBA, particularly in DPBA.CBr_4 and DPBA.$CBr_3SO_2CBr_3$ complexes. In a liquid medium the electron level corresponds to a single equilibrium conformation of DPBA. The broadening of the optical absorption band of a DPBA.A complex, as in the case of $(C_5H_5)_2Fe.CBr_4$, is due to an electronic-vibrational interaction.[77] The extensive set of energy levels of BA.A complexes in a polymer matrix is shown in Fig. 10; the levels correspond to the different rotation angles of the phenyl group relative to the UEP of the nitrogen atom, changes in which are regarded by the polymer matrix.

The position of the optical absorption maximum of DPBA.A complexes in all media has a constant value of $h\nu^{max}$ = 3.5 eV when A = CBr_4 and 3.38 eV when A = $CBr_3SO_2CBr_3$ (see Fig. 7). The 0.12 eV decrease in the position of the maximum for A = $CBr_3SO_2CBr_3$ is caused by a corresponding increase in the electron affinity of this acceptor.[120] The lack of dependence of $h\nu^{max}$ on the dielectric properties of the medium is consistent with a small degree of charge transfer in the excited Franck–Condon state of that group of complexes, which determines the position of $h\nu^{max}$. This may be due to the close position of the energy levels of the charge-transfer state

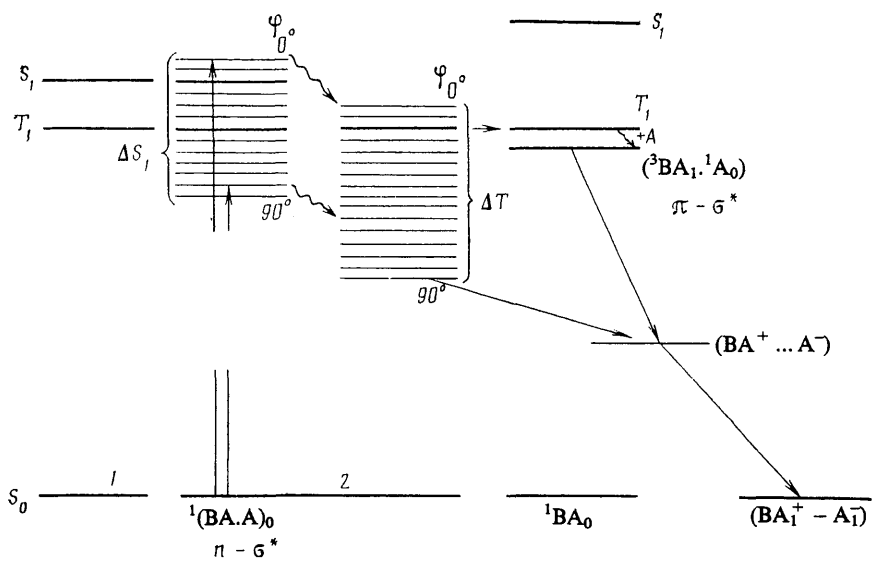


Figure 10. Position of energy levels and scheme for photoprocesses in complexes of benzylanilines (DPBA, dibenzylaniline) with acceptors (CBr_4, $CBr_3SO_2CBr_3$) in a liquid medium (*1*) and polymer matrix (*2*).

$(D^{+\delta^*}-A^{-\delta^*})$ and the local excitation of the donor ($^1D_1$.A), which causes a mixing of the wave functions of these states:

$$\psi^1(D^{+\delta_1}-A^{-\delta_1})_1 = a_1\psi(D^{+\delta^*}-A^{-\delta^*}) + b_1\psi(^1D_1.A),$$

where a_1 and b_1 are the contributions of the charge-transfer state $(D^{+\delta^*}-A^{-\delta^*})$ and the local excitation of the donor ($^1D_1$.A) respectively to the wave function. As a result of mixing the states the degree of charge transfer (δ_1) in the excited complex $^1(D^{+\delta_1}-A^{-\delta_1})_1$ is less than in the "pure" charge-transfer state (δ^*) and is given by $\delta_1 = \delta^* a_1^2/(a_1^2 + b_1^2)$. (It was shown above that $b_1 = 0$ and $\delta_1 = \delta^*$ for the complex $(C_5H_5)_2Fe.CBr_4$.)

The first stages of photolysis of the complex DPBA.$CBr_3SO_2CBr_3$ in a PVC matrix when exposed to laser irradiation with a wavelength of 353 nm were studied by Mal'tsev et al.[121,122] It was established that



the charge-transfer products $DPBA^+$ and $CBr_2=S(O)-CBr_3...Br^-$) and the excited triplet donor ($^3DPBA_1$) are formed at the same time, which is also an indication of the close relative position of the triplet levels of the locally excited donor and the charge-transfer state in the group of high-energy complexes. The wave function of the triplet state of this group can be represented as

$$\psi^3(D^{+\delta_2}.A^{-\delta_2})_1 = a_1'\psi^3(D^{+}.A^{-})_1 + b_1'\psi(^3D_1.A), \qquad (48)$$

where $\delta_2 = (a_1')^2/[(a_1')^2 + (b_1')^2]$, the degree of charge transfer. In this case the wave functions are represented by $\psi^3(D^+.A^-)_1$—the triplet charge-transfer state—and $^3D_1$.A—the locally excited triplet state of the donor. The magnitude of δ_2 is markedly dependent on small changes in the relative position of the levels of the states with complete charge transfer

$$E_1' = \int\psi^3(D^+A^-)H\psi^3(D^+A^-)dv$$

and the locally excited donor

$$E_2' = \int\psi(^3D_1.A)H\psi(^3D_1.A)dv.$$

For DPBA, $E_2' = E(^3D_1) = 3.00$ eV. The ratio (b_1'/a_1') may be determined from the expression

$$(b_1'/a_1') = V_{01}/(E_2' - E_1'), \qquad (49)$$

where V_{01} is the energy of the exchange interaction between the triplet charge-transfer state and the locally excited triplet donor

$$V_{01} = \int\psi^3(D^+A^-)_1H\psi(^3D_1.A)dv.$$

It is estimated that $V_{01} = 0.05-0.5$ eV. It was established[121,122] that when DPBA is replaced by diphenylamine (DPA, $E_2' = 3.14$ eV[123]), the excited triplet state of the donor is not formed on exposure to a laser with $\lambda = 353$ nm. This may be due to the corresponding decrease in contribution of b_1' from the locally excited triplet state of the donor to the wave function. (48) In fact, the energy $E_1' = h\nu_{et}^{max}$(gas) [see expressions (44) and (49)] in a DPA.A complex is ~0.34 eV less than in a DPBA.A complex (here A = $CBr_3SO_2CBr_3$). [Determined, in accordance with (44), from the difference E_1'(DPBA) – E_1'(DPA) = I_D(DPBA) – I_D(DPA) = $e[E_{1/2}$(DPBA/$DPBA^+$) – $E_{1/2}$(DPA/DPA^+)], where $E_{1/2}$(DPBA/$DPBA^+$) = 0.98 V[12] and $E_{1/2}$(DPA/DPA^+) = 0.64 V—the equilibrium oxidation potentials of DPBA and DPA respectively.]

From the dependence of the quantum yield of the products of ionic photodissociation of the DPBA.CBr_4 complex in the presence of an acceptor with triplet energy (1-naphthol, etc.) on the concentration of these components, it was concluded[124] that on exposure to light with λ = 365 nm the products of ionic dissociation are mainly formed by transfer of triplet energy from the complex to a molecule of amine (see scheme in Fig. 10) to form a $\pi-\sigma^*$ exciplex ($^3DPBA_1.CBr_4$), which dissociates to radical ions. It is to be expected that the probability of direct ionic photodissociation of excited triplet DPBA.CBr_4 complexes will increase with the wavelength of stimulating light since when I_{BA} decreases [see expressions (44)] the E_1' level decreases and hence the contribution of the locally excited triplet state of the DPBA donor diminishes [see expressions (48) and (49)].

Thus, the polymer effect, which consists of the freezing out of different conformations of benzylaniline molecules, results firstly in a bathochromic shift of the optical spectrum by about 10^3 cm^{-1} on going from liquid media to polymer matrices. It has been shown[105] that this causes the sensitivity of photographic materials based on benzylanilines to be extended into the visible region. Secondly, as the wavelength of stimulating light is increased, polymer matrices are probably responsible for a change in mechanism of the formation of ionic photodissociation products from mainly a primary transfer of triplet energy (see Fig. 10) in the case of high-energy complexes to direct dissociation into radical ions of low-energy complexes.

It has been pointed out[77] that in $(C_5H_5)_2Fe.CBr_4$ complexes the nonuniform broadening of the optical spectrum in polymers is absent as a result of the high symmetry for ferrocene molecules. It is because of the absence of specific polymer effects in these complexes that the dependence of $h\nu_{et}^{max}$ on the dielectric properties of the medium [see expression (46)] as predicted by electron-transfer theory is found to occur.

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It should be mentioned in conclusion that the basic concepts of electron-transfer theory developed for liquid media are applicable to donor-acceptor systems in polymer matrices.

However, in contrast to liquids, different conformations of complex organic molecules can occur in rigid polymer matrices when there is a limited free volume; this gives rise to a nonuniform distribution of parameters such as the ionisation potential or electron affinity, intramolecular reorganisation energy and reorganisation energy of the medium during electron transfer. The magnitudes of these effects depend on the size and symmetry of the donor and acceptor molecules as well as on the total magnitude and distribution of the free volume and mobility of the polymer chains.[125,126] These effects can completely mask the processes which accompany electron transfer in liquid media.

In turn, the disorder of a polymer matrix causes a spatial variation in dielectric constant and hence in reorganisation energy of the medium. Because of steric hindrance in a polymer matrix only partial intramolecular reorganisation can occur when the molecule changes to a radical cation or anion form. For a complete elucidation of the available experimental data it is necessary to develop a model which simultaneously takes into account these factors and also the form of energy distribution of the interaction between the reaction (transport) sites and the medium, the distribution of distances between neighbouring sites, and the effect of the dielectric properties of the medium on electron transfer between sites.

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