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Journal of Photochemistry and Photobiology A: Chemistry 102 (1996) 51–57

Journal of
PHOTOCHEMISTRY
AND
PHOTOBIOLOGY
A: CHEMISTRY

Exciplex mechanism of excited state electron transfer reactions in polar media

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Abstract

Experimental data provide strong evidence for the transient formation of exciplexes in excited state electron transfer reactions, even in polar media. The exciplex mechanism of excited state electron transfer involves the reversible formation of low polarity exciplexes from excited molecules at positive or slightly negative free energies of electron transfer (i.e. in the kinetic region). This means that the mechanism of electron transfer involves a gradual electron shift from electron donor to acceptor and conjugated simultaneous reorganization of the reactants and media, rather than an electron jump after preliminary reorganization.

The apparent quenching rate depends on the equilibrium constant of formation and lifetime of the exciplex rather than on the reorganization energy of the reactants and media. Transient exciplex formation provides new pathways for excitation decay (internal conversion and intersystem crossing) which compete with the formation of the products of electron transfer and lead to a decrease in their yield and, at the same time, produce an increase in the total rate of excited state quenching.

Keywords: Exciplex mechanism; Excited state electron transfer reactions; Polar media

1. Introduction

The classical mechanism of electron transfer, based on the model proposed in 1956 by Marcus [1,2], assumes a diabatic electron jump from electron donor to acceptor after preliminary reorganization of the reactants and media (which provides degenerate electronic terms for the reactants and products) and subsequent relaxation of the products and media. This mechanism has been used in numerous discussions of excited state electron transfer reactions. Experimental data on the rate constants of fluorescence quenching by electron donors and acceptors have been used as electron transfer rate constants in discussions of various modifications of this mechanism, since excited state quenching rate constants can be obtained much more easily than ground state rate constants.

Several years ago, it was concluded [3–6] that the real mechanism of excited state electron transfer between organic molecules in the kinetic region (i.e. for endergonic and slightly exergonic reactions with Gibbs' energies of electron transfer of $\Delta G_{et} > -15$ kJ mol^{-1}) involves the transient formation of exciplexes, even in polar media, and a gradual concerted shift of the electron density from electron donor to acceptor and changes in the nuclear coordinates of the reactants and media, rather than a diabatic electron jump. In this paper, we discuss new evidence for this mechanism and its consequences.

2. Exciplexes in polar solvents

Exciplexes are formed in non-polar solvents [7–13], but were believed to be unstable in polar solvents ($\epsilon > 20$) due to dissociation to free radical ions. Only in the last few years has weak emission from exciplexes been observed in acetonitrile and other polar solvents [4,5,14–18] for donor–acceptor pairs at $\Delta G_{et} > -15$ kJ mol^{-1}. Surprisingly long lifetimes (10–100 ns) were observed [3–6,14–19] for some exciplexes in polar media, much longer than the lifetimes of radical ion pairs (10–500 ps) [19,20]. At the same time, relatively low dipole moments (1–6 D) were found [5,18] from the solvent shift of the exciplex emission band for exciplexes formed by electron donor–acceptor pairs at $-3 > \Delta G_{et} > 5$ kJ mol^{-1}, much lower than the typical dipole moments (about $15 \text{ D} = 6 \times 10^{-29}$ C m) known for regular exciplexes (whose structures are close to contact radical ion pairs $M^{\cdot -\delta}D^{\cdot +\delta}$, $\delta \cong 1$) formed by electron donor–acceptor pairs at $\Delta G_{et} < -15$ kJ mol^{-1} [21,22]. The small values of the dipole moments indicate a lesser extent of electron transfer ($\delta \leq 0.3$) in such exciplexes.

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PII S1010-6030(96)04462-0

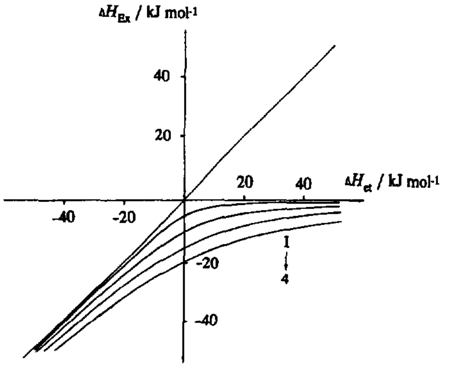

Fig. 1. Dependence of the enthalpy of exciplex formation ΔH_{Ex} on the energy gap between locally excited and charge transfer states (enthalpy of electron transfer ΔH_{et}) for various β values (kJ mol^{-1}) (Eq. (2)): 5 (1), 10 (2), 15 (3), 20 (4).

The explanation for these peculiarities is clear from a consideration of the dependence of the electronic structure of the exciplex on ΔG_{et}. Even a simplified representation of the electronic wavefunction of an exciplex in the form of a linear combination of wavefunctions of locally excited (M*D) and complete charge transfer (M^-D^+) states

$$\Psi = a\psi(M^*D) + b\psi(M^-D^+) \qquad (1)$$

shows that the ratio of the coefficients a and b depends on the energy gap between (M*D) and (M^-D^+) states (i.e. the enthalpy of excited state electron transfer ΔH_{et}) and the exchange interaction β. The enthalpy of exciplex formation ΔH_{Ex} and degree of electron transfer δ in the exciplex can be approximately expressed (neglecting solvent polarization) as

$$\Delta H_{Ex} \cong \Delta H_{et}/2 - [(\Delta H_{et}/2)^2 + \beta^2]^{1/2} \qquad (2)$$

$$\delta \cong 1/\{1 + [\Delta H_{et}/2\beta + (1 + (\Delta H_{et}/2\beta)^2)^{1/2}]^2\} \qquad (3)$$

The enthalpy of exciplex formation ΔH_{Ex} can be negative even at positive ΔH_{et} (Fig. 1). In the region $-\beta < \Delta H_{et} < \beta$, the stabilization of an exciplex is provided substantially by exchange interaction rather than by the difference between the orbital energies of donor and acceptor and the electrostatic interaction. Consequently, in this region, a considerable contribution to the electronic structure of the exciplex comes from the locally excited state (coefficients a and b are comparable or even $a > b$) and the dipole moment of such an exciplex is much lower than the dipole moment of a contact radical ion pair. At the same time, the stabilization energy constitutes significant hindrance to the dissociation of the exciplex to free radical ions in polar media and hence prolongs its lifetime. In some respects, such exciplexes are similar to ground state charge transfer complexes when the complete charge transfer state has a much higher energy than the corresponding ground state ($\Delta G_{et} > 100$ kJ mol^{-1}) and $\Psi = a\psi(MD) + b\psi(M^-D^+)$, with $a \gg b$.

The majority of previously studied exciplexes have been observed for strongly exergonic excited state electron transfer reactions ($\Delta H_{et} < -15$ kJ mol^{-1}) in non-polar solvents for two reasons which facilitate the observation of the exciplex emission band: the relatively high enthalpy and equilibrium constant of exciplex formation and the strong shift of the exciplex emission relative to the parent excited molecules ($h\Delta\nu \cong 2\Delta H_{Ex}$).

The exciplex fluorescence quantum yields φ'_0 in acetonitrile (Table 1) are rather small (0.01–0.1) [5,18]. The emission rate constant k'_f is about 10^6 s^{-1}. This is an order of magnitude smaller than for regular polar exciplexes, e.g. k'_f for exciplexes of 9,10-dicyanoanthracene with strong electron donors is in the range $(0.6–3.0) \times 10^7$ s^{-1}, decreasing with decreasing ionization potential of the electron donor [23,24].

Similar results have been obtained recently by Gould et al. [15,16] who studied the emission and absorption spectra of exciplexes of 9,10-dicyanoanthracene and 2,6,9,10-tetracyanoanthracene with weak electron donors (methyl-substituted benzenes) in solvents of various polarity. The electronic structure of these exciplexes (i.e. the percentage of charge transfer) was found to be substantially dependent on the oxidation potential of the electron donor and on the solvent polarity. The lifetimes of these exciplexes were in the range 1–100 ns. Correlations between the emission, intersystem crossing and internal conversion rate constants, the mean emission frequency of the exciplex and the contribution of the charge transfer state were found and discussed [15–17]. The exciplex emission rate constant falls from 22 to 1 μs^{-1}

Table 1
Exciplex fluorescence quantum yields (φ'_0), dipole moments (μ') and apparent quenching rate constants (K_{SV}/τ_0) in acetonitrile and toluene [18]

M	Q	ΔG_{et} (kJ mol^{-1})	φ'_0	μ' (D)	K_{SV}/τ_0 (M^{-1} ns^{-1}) (in CH_3CN)	K_{SV}/τ_0 (M^{-1} ns^{-1}) (in toluene)
DCA	*p*-Xylene	−11	0.001	<1	0.5	0.007
Pyr	TMeOB	−11	0.0003	4.4	6.6	0.24
BA	TMeOB	−9	0.04	6.3	11	0.12
DCA	Biphenyl	−6	0.03	6.0	3	0.6
CA	DMN	−6	0.01	1.6	5	
BP	TMeOB	−1	0.01	5.2	3.5	0.08
CA	Naphth	+12	0.2	<1	0.07	
BP	TPhE	+12		<1	0.3	

DCA, 9,10-dicyanoanthracene; CA, 9-cyanoanthracene; Pyr, pyrene; BA, 1,2-benzanthracene; BP, 1,12-benzperylene; TMeOB, 1,2,4-trimethoxybenzene; DMN, 1,6-dimethylnaphthalene; TPhE, tetraphenylethylene; Naphth, naphthalene.

Table 2
Kinetic parameters of exciplex formation and decay [5,18,27]: Gibbs' energy of electron transfer (ΔG_{et}) and exciplex formation (ΔG_{Ex}), exciplex formation enthalpy (ΔH_{Ex}) and entropy (ΔS_{Ex}), exciplex lifetime (τ'_0), rate constants of exciplex formation (k_1), emission (k'_f), intersystem crossing (k'_{isc}) and radical ion formation (k'_R), apparent activation energies of quenching (E_Q) and radical ion (E_R) and triplet (E_T) formation

Parameter	BP + DCB	CA + DMN	BP + TMeOB	Pyr + DBP	BP + DETP
ΔG_{et} (kJ mol^{-1})	−9	−6	−1	0	+1
k_1 (M^{-1} ns^{-1})	33	8	16		34
ΔG_{Ex} (kJ mol^{-1})	< −20	−10	−8		< −20
τ'_0 (ns)	< 10	21	10	17	< 10
k'_f (μs^{-1})		0.5	1		
k'_{isc} (μs^{-1})				25	
k'_R (μs^{-1})				22	
ΔH_{Ex} (kJ mol^{-1})		−30	−40		
ΔS_{Ex} (J mol^{-1} K^{-1})		−60	−100		
E_Q (kJ mol^{-1})	6		0		−12
E_R (kJ mol^{-1})	1		10		6
E_T (kJ mol^{-1})	2		3		0

CA, 9-cyanoanthracene; Pyr, pyrene; BP, 1,12-benzperylene; TMeOB, 1,2,4-trimethoxybenzene; DMN, 1,6-dimethylnaphthalene; DETP, diethyl terephthalate.

following an increase in contribution from the charge transfer state. This indicates a decrease in the transition moment on going from the locally excited to the charge transfer state. In contrast, the intersystem crossing rate constant increases in the same range with increasing contribution of the charge transfer state.

3. Exciplex kinetics

Double-exponential fluorescence kinetics, with lifetimes of τ_1 and τ_2, are observed in the emission bands of the fluorescer and exciplex in polar solvents [5,16,18]. This proves the formation of exciplexes, which are in equilibrium with the parent excited molecules [25,26]

$$\begin{tikzcd}
M^* + Q \arrow[rr, shift left, "k_1"] \arrow[d, shift left, "1/\tau_0"] & & {}^1(M^{-\delta}Q^{+\delta}) \arrow[ll, shift left, "k_{-1}"] \arrow[d, "1/\tau'_0"] \\
{} \arrow[u, shift left, "h\nu"] & & {}
\end{tikzcd}$$

Here we neglect the induced deactivation of the excited molecules by the electron donor or acceptor [25], which competes with the formation of the exciplex and can decrease its yield of formation substantially in some cases. All the rate constants involved above (Table 2) were found from the dependence of both the fluorescence lifetimes and the quantum yields on the quencher concentration [6,18].

When the exciplex emission is too weak and cannot be observed, the dependence of the apparent lifetime of M* on the quencher concentration can be used to estimate the exciplex lifetime τ'_0 and the equilibrium constant of exciplex formation $K_{Ex} = k_1/k_{-1}$. In the case of reversible exciplex formation ($k_{-1} \gg 1/\tau'_0$) at $\tau_0 \gg \tau'_0$, the plot of τ_0/τ_2 vs. [Q] is sublinear (τ_1 can be very short and invisible in real kinetic curves at $k_1\tau_0[Q] \gg 1$)

$$\tau_0/\tau_2 \cong (1 + (\tau_0/\tau'_0)K_{Ex}[Q])/(1 + K_{Ex}[Q]) \quad (5)$$

$$[Q]/(\tau_0/\tau - 1) = (1/K_{Ex} + [Q])/(\tau_0/\tau'_0 - 1) \quad (6)$$

$$\varphi_0\tau/\varphi\tau'_0 = 1 + K_{Ex}[Q] \quad (7)$$

Under these conditions, the initial slope of the dependence τ_0/τ_2 vs. [Q] is different from the Stern–Volmer quenching constant, obtained from the dependence φ_0/φ vs. [Q], and the value of τ_0/τ_2 at large [Q] tends to the limit equal to τ_0/τ'_0. The observed lifetime of M*, which is in equilibrium with the exciplex, changes with increasing quencher concentration and tends to a limit equal to the exciplex lifetime τ'_0. A plot of $1/\tau_2$ vs. [Q] can have a negative initial slope, i.e. the observed lifetime is longer in the presence of the quencher, when $\tau_0 < \tau'_0$ [26] (although Eq. (5) is not valid in this case).

Several anomalies are observed [3,5,6,28] for the total (apparent) quenching rate constants $k_Q = K_{SV}/\tau_0$, formally obtained from a Stern–Volmer plot of the fluorescence quantum yield vs. the quencher concentration, which contradict the classical model for direct complete electron transfer in an encounter complex

$$M^* + Q \underset{k_{21}}{\overset{k_{12}}{\rightleftarrows}} M^*Q \underset{k_{32}}{\overset{k_{23}}{\rightleftarrows}} M^-Q^+ \overset{k_{30}}{\rightarrow} \quad (8)$$

According to this model, the rate of electron transfer is controlled by the reactant and media reorganization energies [1,2,29].

The dependence of the apparent quenching rate constant on the temperature and on ΔG_{et} indicates the formation of exciplexes even for systems in which exciplex emission is too weak to be observed. A non-Arrhenius temperature dependence for log k_Q vs. $1/T$ was found in the region -15 kJ mol^{-1} < ΔG_{et} < 15 kJ mol^{-1} [3,5,6]. This dependence shows a bell-shaped plot with a very low or even negative temperature coefficient for higher temperatures. Since the reorganization energy cannot be negative, this provides evi-

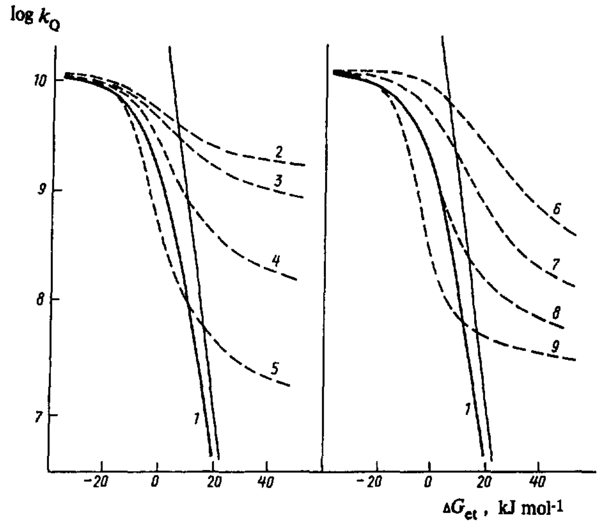

Fig. 2. Simulated plots of the apparent quenching rate constant k_Q vs. the Gibbs' energy of electron transfer ΔG_{et} in acetonitrile for kinetic schemes of transient exciplex formation and direct electron transfer [5]: 1, direct electron transfer, $\Delta G_0^{\ne} = 10$ kJ mol^{-1}, $\tau'_0 = 0.1$ ns; 2–9, transient exciplex formation; $\beta = 10$ kJ mol^{-1}, $\tau'_0 = 0.01$ ns (2), 1 ns (3), 10 ns (4), 100 ns (5); $\tau'_0 = 30$ ns, $\beta = 20$ kJ mol^{-1} (6), 15 kJ mol^{-1} (7), 10 kJ mol^{-1} (8), 5 kJ mol^{-1} (9).

dence for transient complex formation with a negative enthalpy of formation. It is important that a negative temperature coefficient can only be obtained when the activation enthalpy for transient complex decay is lower than ΔH_{Ex}.

Furthermore, the sublinear dependence of τ_0/τ on [Q] corresponds to Eq. (5) rather than to the Stern–Volmer equation, because the observed maximum slope is smaller than K_{SV} obtained from the fluorescence quantum yield Stern–Volmer plot [3].

The slope of the dependence of log k_Q vs. ΔG_{et} in the kinetic region (which is considered to be an important criterion for the comparison of electron transfer mechanisms) is usually much lower than that ($2.3/RT$) corresponding to the Marcus or Weller equations [2,30]. An S-shaped dependence of log k_Q vs. ΔG_{et} is observed in several cases [28,31].

To compare the dependence of log k_Q vs. ΔG_{et} and $1/T$ arising from the classical model for direct complete electron transfer and the exciplex model, we simulated [3,5] these dependences for the various parameters β and τ'_0 (Fig. 2). A significant difference between these two mechanisms is obtained in the region where $\Delta G_{et} > -15$ kJ mol^{-1}. Substantially greater values of k_Q are found for the exciplex mechanism than for the direct electron transfer mechanism, and k_Q fails to depend on ΔG_{et} at $\Delta G_{et} > 50$ kJ mol^{-1}. In this region, the quenching of M* arises from transformation into an exciplex, which decays mainly by internal conversion and intersystem crossing rather than by dissociation to radical ions. The exciplex mechanism also fits the temperature dependence of log k_Q well [3]. The apparent activation energy of quenching varies from negative to positive values depending on β, τ'_0 and ΔG_{et}.

Therefore the considerable variations observed for the dependence of log k_Q vs. ΔG_{et} (especially in the kinetic region near the bend of the Rehm–Weller plot) for different types of compounds may be attributed to the effects of the chemical structures of the excited molecules and quenchers on β and τ'_0. The multiple Rehm–Weller plots observed for the quenching of 9-cyanoanthracene by amines, aromatic compounds and olefins [32] are also probably related to the effects of different electron delocalization in the donor molecules on the energy of coupling and the lifetimes of the exciplexes formed by these classes of quenchers.

Experimental data on the quenching rate constants in various solvents show that the classical Rehm–Weller plot shifts slightly to smaller ΔG_{et} values in solvents of low polarity. For example, the difference between hexane and acetonitrile solutions for the quenching of 9-cyanoanthracene by amines, aromatic compounds and olefins is about 0.1 eV [32]. However, evaluation of the electrostatic energy difference for ion pairs in these solvents gives a much greater value (about 1 eV). This difference cannot be explained easily by the classical model of direct complete electron transfer and has always caused surprise. However, the exciplex model provides clear reasons for the very small solvent effect on k_Q, related to the small dipole moment of the exciplex formed. For example, the spectral shift of the exciplex emission spectrum (which reflects the solvation energy difference) for the exciplex of 9-cyanoanthracene with 1,6-dimethylnaphthalene ($\Delta G_{et} = -6$ kJ mol^{-1}), which has a dipole moment of 1.6 D [18], is 700 cm^{-1} or 0.09 eV from acetonitrile to toluene. This value is very close to the shift of the Rehm–Weller plot in these solvents.

4. Formation of radical ions and triplet states

Singlet exciplex decay in polar media can, in principle, yield radical ions (by dissociation accompanied by the completion of electron transfer), a triplet state ^{3}M (by intersystem crossing accompanied by dissociation) or relaxation to the ground state (by internal conversion accompanied by dissociation to parent molecules). The last two processes are usually activationless and their rates are determined by Franck–Condon and spin factors. Triplet exciplexes are less stable because of thermodynamic factors and dissociate to ^{3}M and Q much more easily than singlet exciplexes.

The quantum yields of radical ion and triplet formation were studied [6,33,27] in several donor–acceptor systems in polar solvents by flash photolysis and laser photolysis (Fig. 3). The radical ion quantum yield depends on the quencher concentration

$$\varphi_R = k'_R\tau'_0/(1 + 1/K_{SV}[Q]) = k'_R\tau'_0(1 - \varphi/\varphi_0) \qquad (9)$$

where k'_R is the rate constant for exciplex dissociation to radical ions. Values of k'_R (Table 2), obtained from the dependence of the radical ion yield on φ/φ_0, are much lower than the rate constants for the dissociation of contact radical ion pairs to free radical ions. For example, the contact radical ion pair formed from pyrene and N,N-dimethylaniline has a

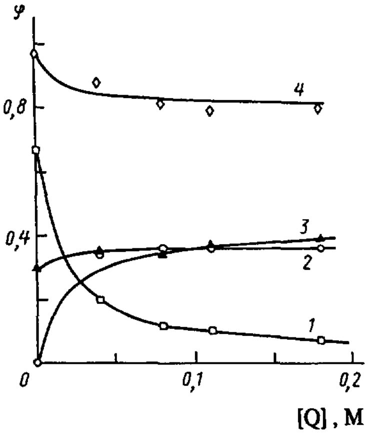

Fig. 3. Dependence of the quantum yields of fluorescence (1), radical ions (2) and triplet states (3) of pyrene on the concentration of dibutyl phthalate; (4) is the total quantum yield of emission, triplets and radical ions [6].

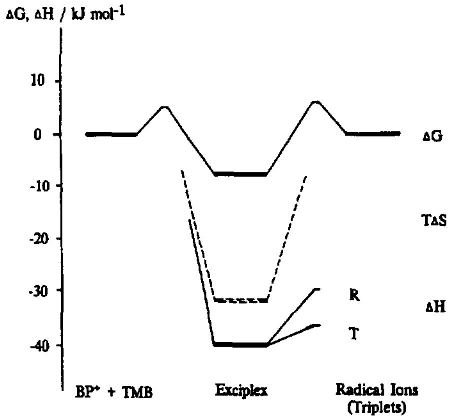

Fig. 4. Gibbs' energy, enthalpy and entropy of formation and decay of the exciplex of 1,12-benzperylene with 1,2,4-trimethoxybenzene in acetonitrile [27].

dissociation rate constant in acetonitrile of 5×10^8 s^{-1} [34]. The smaller rates of exciplex dissociation compared with contact radical ion pairs gives further evidence for exciplex stabilization by coupling of locally excited and charge transfer states. Unfortunately, the range of variation of k'_R studied is too small to discuss the probable dependence of k'_R on the energy gap between an exciplex and charge transfer state ($\Delta G_{et} - \Delta G_{Ex}$). Nevertheless, k'_R is rather low at $\Delta G_{et} > 20$ kJ mol^{-1}.

The total yield of triplets (which are formed in two ways: from excited molecules M* and from the exciplex) and the fluorescence quantum yield depend on the quencher concentration in different ways

$$\varphi_T = k_{isc}\tau_0\{1 + (k'_{isc}\tau'_0/k_{isc}\tau_0)K_{SV}[Q]\}/(1 + K_{SV}[Q]) = k'_{isc}\tau'_0 + (k_{isc}\tau_0 - k'_{isc}\tau'_0)(\varphi/\varphi_0) \quad (10)$$

The triplet yield changes with changing concentration of the quencher and tends to the value $k'_{isc}\tau'_0$. It may decrease or increase in the presence of a quencher depending on the ratio $k'_{isc}\tau'_0/k_{isc}\tau_0$. The intersystem crossing rate constants in exciplexes (Table 2) [5,18,27] are close to values typical of k_{isc} in other aromatic molecules. However, Gould et al. [16,17] came to the conclusion that intersystem crossing in exciplexes can be considered as back electron transfer coupled with spin inversion.

The activation enthalpies for exciplex dissociation to radical ions (Table 2), obtained from the temperature dependence of the radical ion quantum yields, are in the range 1–10 kJ mol^{-1}. The activation entropy of this dissociation is strongly negative. Fig. 4 presents the energy diagram for the formation of the exciplex of 1,12-benzperylene with 1,2,4-trimethoxybenzene and its decay processes. Similar values of the activation enthalpy (less than 4 kJ mol^{-1}) and entropy (about -60 J mol^{-1} K^{-1}) were obtained for the dissociation of contact radical ion pairs [34] and for electron exchange between radical ions and neutral molecules (2–10 kJ mol^{-1} and $-(50–70)$ J mol^{-1} K^{-1} respectively) [35–37]. A larger activation enthalpy, 15 kJ mol^{-1}, was found recently for the dissociation of the triplet geminate (contact) radical ion pair formed from 9,10-anthraquinone and 1,2,4-trimethoxybenzene in 1,1,2,2-tetrachloroethane [38]. An evaluation of the electrostatic contribution to the entropy of dissociation of a neutral molecule into oppositely charged ions, obtained from the temperature dependence of the permittivity of acetonitrile ($\Delta S_{es} = \Delta G_{es}\partial(\ln \epsilon)/\partial T$), gives a similar value ($\Delta S_{es} = -57$ J mol^{-1} K^{-1}).

5. Conclusions

The above discussion shows that the exciplex mechanism of excited state electron transfer reactions fits the experimental data observed in both polar and non-polar media much better than the conventional model of direct complete electron transfer (especially in the kinetic region, when $\Delta G_{et} > -15$ kJ mol^{-1}, which is frequently called the "normal Marcus region"). Evidence of exciplex formation in polar solvents may be subdivided into direct evidence (exciplex emission band observed in some systems; double-exponential kinetics observed in the emission bands of the parent excited molecules and the exciplex) and indirect evidence (sublinear Stern–Volmer plot for the lifetimes of the excited molecules (when the exciplex emission band cannot be observed); non-Arrhenius temperature dependence of k_Q with negative temperature coefficient; enhancement of the triplet yield in the presence of quenchers; deviations from the Rehm–Weller plot; small solvent effect on k_Q).

Exciplexes with only a small degree of electron transfer are formed at $\Delta G_{et} > -15$ kJ mol^{-1}, and ΔG_{Ex} can be negative even for positive ΔG_{et} due to electron coupling of locally excited and charge transfer states. Dissociation of these exciplexes to radical ions (which requires complete electron transfer during dissociation) is hindered by substantial coupling energy and the lifetimes may reach 10–100 ns even in polar solvents.

The total (apparent) quenching rate is controlled by the exciplex formation equilibrium constant and its lifetime rather than by the reorganization energy. Nevertheless, a cor-

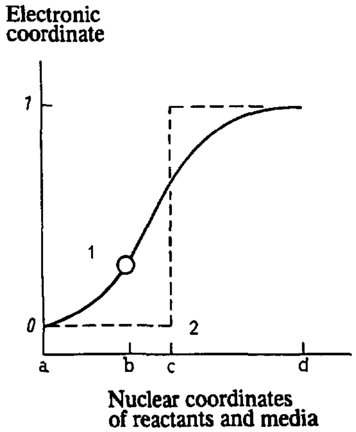

Fig. 5. Electronic and nuclear coordinates of reactants and media along the reaction coordinate according to the exciplex mechanism (1) and the classical mechanism of electron jump after reactant and media reorganization (2). Parent reactant state (a), exciplex (b), transition state for electron jump (c) and final product state (d) are marked.

relation between the apparent quenching rate constants and ΔG_{et} is still observed for excited state electron transfer reactions because of the dependence of ΔG_{Ex} on ΔG_{et}.

An important feature of excited state electron transfer reactions is the competition between radiationless deactivation (yielding ground and triplet states) and complete electron transfer (yielding radical ions). In contrast with ground state reactions, the formation of the exciplex provides new pathways for the decay of excitation (internal conversion and intersystem crossing), which lead to a decrease in the yield of the electron transfer products and, at the same time, an increase in the total rate for excited state quenching. Therefore fluorescence quenching rate constants cannot be used with any confidence to verify theories of electron transfer reactions and to determine accurately the redox potentials of excited molecules and quenchers.

The transient formation of low polarity exciplexes in excited state electron transfer reactions indicates the principal difference between this mechanism and the classical mechanism of complete electron transfer in the encounter complex. The latter assumes that an electron jumps from the electron donor to the acceptor after preliminary reorganization of the nuclear configuration of the reactants and media (necessary to achieve the degeneracy of the electronic levels in the initial and final states). Such a separation of electronic and nuclear coordinates implies very weak electron coupling in these states. In contrast, the formation of exciplexes (with partial electron transfer) indicates strong coupling of these states, which is sufficient for the stabilization of the exciplexes ($\Delta H_{Ex} < -15$ kJ mol^{-1}), and gives reasonable values for their equilibrium constants of formation. The transient formation of low polarity exciplexes means that a gradual electron shift takes place simultaneously and synchronously with the nuclear reorganization of the reactants and media rather than a diabatic electron jump after preliminary reorganization of the reactants and media (Fig. 5).

Similar transient charge transfer complex formation can also be assumed for ground state electron transfer reactions of organic molecules in polar media. In contrast with small metal ions, in which the solvation energies are very high, organic molecules have a larger size and require a much smaller solvation energy for the stabilization of their ions. The goal of further investigations is to determine which electron transfer reactions follow which mechanisms.

Acknowledgements

This work was supported by ISF grant MDW000, INTAS grant 93-0751 and RFBR grant 93-03-4987.

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