Exciplex mechanism of fluorescence quenching in polar media

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Abstract. The formation of exciplexes (non-emitting or poorly emitting) is suggested as one of the causes for deviations of experimental data on fluorescence quenching in polar solvents from the classical model of excited-state electron transfer yielding radical ion pairs. Several evidences for the formation of such exciplexes were found for fluorescence quenching of aromatic compounds by weak electron donors and acceptors. For cyano-substituted anthracenes exciplex emission can be observed in the presence of quenchers even in polar solvents. In other systems, indirect evidences of exciplex formation were observed: nonlinear dependence of the inverse value of excited pyrene lifetime on the concentration of the quencher; very small and, in some cases, even negative experimental activation energies of pyrene fluorescence quenching, which are much less than activation energies, calculated from the experimental values of the quenching rate constants etc.

The proposed model explains the difference between theoretical and experimental dependencies of $\log k_Q$ vs. Gibbs energy of electron transfer ΔG_{ET} and other experimental features known for fluorescence quenching by electron donors and acceptors. This model states that the exciplex is in equilibrium with the encounter complex and apparent quenching rate constants are controlled by two main factors – the lifetime of the exciplex and the enthalpy of its formation. Experimentally observed dependence of apparent quenching rate constant on ΔG_{ET} is caused by the dependence of the exciplex formation enthalpy on ΔG_{ET} , which is quite different from the dependence of electron transfer activation energy on ΔG_{ET} predicted by the theoretical models. Simulations of the dependencies of $\log k_Q$ vs. ΔG_{ET} according to the exciplex formation model confirms its agreement with the experimental data.

Electronic structure of the exciplex involved may be close to contact radical-ion pair only at $\Delta G_{ET} < 0$, when the rate of quenching is limited mainly by the diffusion, but for $\Delta G_{ET} > 0$, the structure of the exciplex should be much less polar.

Keywords. Fluorescence quenching; polar media; exciplex mechanisms; excited-state electron transfer.

1. Introduction

Electron transfer photoreactions are very important in chemistry and biology. Excited-state electron transfer is supposed to be a general mechanism of fluorescence quenching in the absence of energy transfer and heavy atom effects. It is necessary to know the real mechanism of this process prior to the discussion of various theoretical models of electron transfer.

The classical kinetic scheme proposed by Rehm and Weller (1969, 1970) assumes

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that the electron transfer step yields contact radical-ion pairs which dissociate very fast in polar solvents (k_{30} is about 10^{11} s^{-1}):

$$k_Q = k_{12} / [1 + (1 + k_{32}/k_{30})k_{21}/k_{23}], \quad (2)$$

$$\varphi_0/\varphi = \tau_0/\tau = 1 + k_Q\tau_0[\text{Q}], \quad (3)$$

where φ_0 , φ and τ_0 , τ are fluorescence quantum yields and lifetimes in the absence and in the presence of a quencher Q, respectively ($1/\tau_0 = k_f + k_d$).

A number of experimental investigations (Fox and Chanon 1988) showed the existence of the typical dependence of the quenching rate constants k_Q in polar solvents on the Gibbs energy of electron transfer ΔG_{ET} which has a diffusion limit for $\Delta G_{\text{ET}} \ll 0$ and kinetic limit for $\Delta G_{\text{ET}} \geq 0$. This experimental dependence is in good agreement with the kinetic scheme (1), if one assumes that activation energy of an electron transfer step depends on ΔG_{ET} according to the empirical Weller's equation (Rehm and Weller 1969, 1970),

$$\Delta G_{23}^* = \Delta G_{\text{ET}}/2 + [(\Delta G_{\text{ET}}/2)^2 + (\Delta G_0^*)^2]^{1/2}, \quad (4)$$

or theoretical Marcus' equation (Marcus 1956).

$$\Delta G_{23}^* = \Delta G_0^* (1 + \Delta G_{\text{ET}}/a\Delta G_0^*)^2. \quad (5)$$

But numerous experimental data obtained in recent years for various systems (Hishimura *et al* 1977, Baggott and Pilling 1983, Kitamura *et al* 1987, Avila *et al* 1991, Carrera *et al* 1991, Neumann and Pastre 1991 etc.) have shown that such correlation is qualitative rather than quantitative. Wide scatter is observed for k_Q at $\Delta G_{\text{ET}} \geq 0$. Even values of k_Q greater than thermodynamically permitted for electron transfer were observed.

To find out the origin of these deviations we investigated fluorescence quenching kinetics and determined the activation energies of quenching from the temperature dependence of the apparent quenching constants in several systems. Fluorescence quenching of pyrene and 9-cyanoanthracene by some weak electron donors and acceptors was studied in acetonitrile ($\Delta G_{\text{ET}} \approx 0$) and in other solvents (Kuzmin and Soboleva 1986; Kuzmin *et al* 1992). We found several evidences that fluorescence quenching even in polar solvents can proceed by the formation of exciplexes rather than by direct electron transfer mechanism:

In the case of equilibrium between the excited molecules and the exciplex the value of the apparent quenching rate constant is controlled by the lifetime of the exciplex and equilibrium constant of its formation rather than by the rate constant of electron transfer.

Exciplexes are well known to be formed in electron transfer photoreactions in non-polar media (Gordon and Ware 1975). But in polar media no exciplex emission was observed in most cases and electron-transfer reactions are usually assumed to yield radical-ion pairs which dissociate very fast ($\sim 10^{-10} - 10^{-11}$ s) and produce free radical-ions.

Kinetics of exciplex formation in non-polar solvents were studied in various systems (Kuzmin and Soboleva 1986):

Fluorescence quenching follows the Stern–Volmer equation, but the observed Stern–Volmer quenching constant has completely different sense:

$$\varphi_0/\varphi = 1 + K_{sv}[Q] = 1 + k_1\tau_0[Q]/(1 + k_{-1}\tau'_0). \quad (8)$$

The ratio of exciplex (φ') and initial molecule (φ) fluorescence quantum yields linearly depends on the quencher concentration:

$$\varphi'/\varphi = k_f k_1 \tau_0 [Q] / k_f (1 + k_{-1} \tau'_0). \quad (9)$$

Initial molecule fluorescence decay kinetics ($f(t)$) is biexponential and exciplex fluorescence kinetics ($f'(t)$) is the difference of the same exponents:

$$f(t) = f_0 [\alpha \exp(-t/\tau_1) + \exp(-t/\tau_2)], \quad (10)$$

$$f'(t) = f'_0 [\exp(-t/\tau_2) - \exp(-t/\tau_1)]. \quad (11)$$

Dependence of the lifetimes of these exponents on the quencher concentration, in the general case, is nonlinear and can be expressed by the following expressions:

$$\begin{aligned} 1/\tau_{1,2} = & 1/\tau_0 + k_1[Q] + 1/\tau'_0 + k_{-1} \\ & \pm [(1/\tau_0 + k_1[Q] - 1/\tau'_0 - k_{-1})^2 + 4k_1k_{-1}[Q]]^{1/2}, \end{aligned} \quad (12)$$

$$\alpha = (1/\tau_0 + k_1[Q] - 1/\tau_2)/(1/\tau_1 - 1/\tau_0 - k_1[Q]). \quad (13)$$

In the case of reversible exciplex formation ($k_{-1} \gg 1/\tau'_0$), at $\tau_0 \gg \tau'_0$, the dependence of τ_0/τ_2 on $[Q]$ is sublinear (τ_1 is very short at $k_1\tau_0[Q] \gg 1$ and may be imperceptible)

$$\tau_0/\tau_2 \approx (1 + (\tau_0/\tau'_0)K_{Ex}[Q])/(1 + K_{Ex}[Q]), \quad (14)$$

($K_{Ex} = k_{23}/k_{32}$ is the exciplex formation equilibrium constant), and has initial slope different from the Stern–Volmer constant for φ_0/φ and reaches the limit equal to τ_0/τ'_0 . With the increase of concentration of the quencher, the observed lifetime of M^* (which is in equilibrium with the exciplex) falls to the limit determined by the exciplex

lifetime. For $\tau_0 \ll \tau'_0$, the dependence of $1/\tau_2$ on $[Q]$ can even have a negative initial slope.

2. Evidence for exciplex formation in polar solvents

Fluorescence quenching of pyrene and 9-cyanoanthracene by some weak electron donors and acceptors in acetonitrile and other polar solvents follows the Stern–Volmer equation (figure 1)

$$\varphi_0/\varphi = 1 + K_{sv}[Q]. \quad (15)$$

A weak new emission band was observed for 9-cyanoanthracene in the presence of 1,6-dimethylnaphthalene (DMN) (figure 2) but no new emission bands were observed in the presence of the quenchers in most of the other systems investigated. This means that exciplexes have low emission rate constants or very short lifetimes. The apparent quenching rate constant according to scheme (6) can be expressed as

$$k_Q = K_{sv}/\tau_0 = k_1/(1 + k_{-1}\tau'_0). \quad (16)$$

The ratio of the emission quantum yields of 9-cyanoanthracene and its exciplex linearly depends on the concentration of DMN (figure 3) according to (9). Fluorescence decay kinetics of 9-cyanoanthracene in the presence of DMN is biexponential and fluorescence kinetics of its exciplex is the difference between the same exponents, [(10)–(11)].

Pyrene fluorescence decays monoexponentially (at least two orders of magnitude) in the absence and the presence of the quenchers but the lifetimes do not follow the

Figure 1. Plots of pyrene relative fluorescence quantum yields φ_0/φ (1, 3) and lifetimes τ_0/τ (2, 4) vs. concentration of dibutylphthalate in acetonitrile (1, 2) and in butyronitrile (3, 4).

Figure 2. Uncorrected fluorescence spectra of 9-cyanoanthracene in the presence of various concentrations of 1,6-dimethylnaphthalene in acetonitrile (a) (1–6: 0, 2, 4, 9, 20, 40 mM), normalized fluorescence spectra (b) and exciplex emission spectra (extracted from overall spectra) (c).

Figure 3. Plots of relative fluorescence quantum yields of 9-cyanoanthracene (ϕ_0/ϕ , 1) and of the exciplex (ϕ'/ϕ , 2) vs. concentration of 1,6-dimethylnaphthalene in acetonitrile.

Stern–Volmer equation – $1/\tau$ sublinearly depends on the quencher concentration (figure 1), which is typical for exciplex formation, (14). Plots of $[Q]/(\tau_0/\tau - 1)$ and $\phi_0\tau/\phi\tau_0$ vs. $[Q]$ give K_{Ex} and τ_0/τ'_0 :

$$[Q]/(\tau_0/\tau - 1) = (1/K_{Ex} + [Q])/(\tau_0/\tau'_0 - 1), \quad (17)$$

$$\phi_0\tau/\phi\tau_0 = 1 + K_{Ex}[Q]. \quad (18)$$

The values of K_{Ex} and τ'_0 obtained are given in table 1.

To confirm the nature of the nonlinear dependence of $1/\tau$ on $[Q]$ we studied this dependence in the presence of additional quenchers (O_2 and dimethylfumarate which quench both excited pyrene molecules and the exciplexes and change τ_0 and τ'_0) and obtained the same values of K_{Ex} . The observed difference in τ_0 and τ'_0 show that both excited pyrene molecules and exciplex are quenched by oxygen and by dimethylfumarate with diffusion rate constants. It is important that exciplex lifetimes are relatively long – from 10 to 30 ns. This means that the reason for the absence of exciplex emission for these systems is the very low value of the emission rate constant ($k'_f < 10^6 s^{-1}$).

Another proof of exciplex formation is the very low (and in some cases even negative) value of experimental activation energy of quenching, determined from the temperature dependence of the apparent quenching rate constant in the range (-40) to $(+60)^\circ C$. Apparent activation energy determined this way according to (16) is a sum of the exciplex formation enthalpy (negative) and its decay activation energy (small and positive).

Table 1. Experimental data for pyrene and 9-cyanoanthracene. Stern-Volmer fluorescence quenching constants K_{sv} , apparent quenching rate constants k_Q (at 298 K), experimental activation energies E_{exp}^* and exciplex formation equilibrium constants K_{Ex} and lifetimes τ'_0 .

Quencher	Solvent	K_{sv} (M^{-1})	$k_Q/10^7$ ($M^{-1}s^{-1}$)	E_{exp}^* (kJ/mol)	K_{Ex} (M^{-1})	τ'_0 (ns)
<i>Pyrene</i>						
DBP	MeCN	57	18	−4.6	4 ± 2	17 ± 5
	MeCN + O ₂				6 ± 2	8 ± 3
	MeCN + Q'				3 ± 2	8 ± 3
	PrCN	2.6	0.9	5.9	0.6 ± 0.4	35 ± 20
	AcOEt	2.0	0.9	5.7		
	CH ₂ Cl ₂	7.2	2.9	3.8		
	Toluene	2.3	0.8	7.1		
DEP	MeCN	57	18	−6.7		
DMB	MeCN	14	4.7	−7.0		
Et ₂ NH	MeCN	99	33	10.5		
BuNH ₂	MeCN	1.2	0.4	5.0		
<i>9-Cyanoanthracene</i>						
DMN	MeCN	80	490		45	260

Abbreviations: DBP = dibutylphthalate; DEP = diethylphthalate; DMB = 1,4-dimethoxybenzene; Et₂NH = diethylamine; BuNH₂ = *tert*-butylamine; Q' = dimethylfumarate; DMN = 1,6-dimethylnaphthalene; MeCN = acetonitrile; PrCN = butyronitrile; AcOEt = ethylacetate.

Formal activation energies E_F^* , calculated from the ratio of the diffusion rate constant in the solvent and apparent quenching rate constant at a given temperature (supposing that it is the activation enthalpy which is responsible for their difference) are about 14–26 and 20–25 kJ/mol greater than the respective experimental ones.

3. The nature of the exciplex

The electronic structure of exciplexes is usually represented by a combination of the wavefunctions of locally excited and charge transfer states (if the excited state of the quencher can be neglected owing to much higher excitation energy):

$$\Psi(AD)^* = a\Psi(A^*)\Psi(D) + b\Psi(A^-D^+). \quad (19)$$

Coefficients a and b depend on the difference of the energies of the locally excited and charge transfer states (which can be approximated by the enthalpy of an electron transfer ΔH_{ET}) and on the exchange interaction parameter β . Enthalpy of the exciplex ΔH_{Ex} (neglecting the polarization of the solvent) and magnitude of electron transfer in the exciplex ${}^1(M^{-\delta}Q^{+\delta})^*$ depend on the same parameters:

$$\Delta H_{Ex} \approx \Delta H_{ET}/2 - [(H_{ET}/2)^2 + \beta^2]^{1/2}, \quad (20)$$

$$\delta \approx 1/\{1 - (\Delta H_{ET}/\beta) \cdot [(1 + (\Delta H_{ET}/2\beta)^2)^{1/2} - \Delta H_{ET}/2\beta]\}. \quad (21)$$

The enthalpy of exciplex formation will be negative not only for negative ΔH_{ET} but

Figure 4. Corrected emission spectra of the exciplexes of 9-cyanoanthracene with 1,6-dimethylnaphthalene in acetonitrile (1), butyronitrile (2), dichloromethane (3), and toluene (4).

also for ΔH_{ET} close to zero and even positive ΔH_{ET} . For strongly negative ΔH_{ET} , $\delta \approx 1$ and ordinary polar exciplexes are formed whose structure is close to radical-ion pair. But for positive ΔH_{ET} , $\delta \ll 1$ and low polar exciplexes are formed (their electronic structure is similar to ordinary ground-state charge transfer complexes). According to (20) the smaller ΔH_{ET} , the greater the exciplex formation equilibrium constant $K_{Ex} = \exp(-\Delta G_{Ex}/RT)$. Emission maxima of the exciplex of 9-cyanoanthracene with 1,6-dimethylnaphthalene only slightly depends on the polarity of the solvent (figure 4) which confirms the low polarity of such exciplexes.

The emission bands of these low polar exciplexes can be very weak for several reasons: the low value of the equilibrium constant K_F and the low probability of radiative transition to the ground state. The emission band can also be masked by the main fluorescence band of pyrene.

Decay of the exciplex can also proceed by several ways: by internal conversion to the ground state (encounter complex $M \cdot Q$), by intersystem crossing to the triplet state (triplet exciplex) and by dissociation on free radical-ions (solvated). All these processes should have sufficiently slow rates ($< 10^8 \text{ s}^{-1}$) to provide the relatively long lifetime of the exciplex ($> 10^{-8} \text{ s}$). For the latter process, this means that its activation energy is greater than 25 kJ/mol. Internal conversion and intersystem crossing can have low probability because of small values of Franck-Condon factor and spin-inversion factor respectively rather than because of high activation energy (which can be close to zero). All these four rate constants (including emission rate constant) should depend on the chemical nature of both fluorophore and quencher.

4. Simulation of the dependence of k_Q on ΔH_{ET}

We simulated the dependence of k_Q on ΔH_{ET} for both the kinetic models of fluorescence quenching, (1) and (6), using the following approximations.

Rate constants are expressed by the Arrhenius' equations

$$k_{ij} = k_{ij}^0 \cdot \exp(-E_{ij}^*/RT).$$

Encounter complex formation in acetonitrile

$$k_{12}^0 = 10^{11} \text{ M}^{-1} \text{ s}^{-1}; \quad E_{12}^* = 5 \text{ kJ/mol.}$$

Equilibrium constant of encounter complex formation

$$k_{12}/k_{21} = 0.5 \text{ M}^{-1}, \quad \Delta H_{12} = 0.$$

For (1):

Electron transfer in the encounter complex

$$k_{23}^0 = 10^{11} \text{ s}^{-1}; \quad \Delta G_{23}^* = (\Delta G_{ET}/2) + [(\Delta G_{ET}/2)^2 + (\Delta G_0^*)^2]^{1/2}, \\ \Delta G_0^* = 10 \text{ kJ/mol.}$$

Radical-ion pair decay

$$k_{30} = 10^{11} \text{ s}^{-1}; \quad E_{30}^* = 0$$

For (6):

Exciplex formation

$$k_{23}/k_{32} = \exp(-\Delta H_{Ex}/RT); \quad k_{23}^0 = 10^{11} \text{ M}^{-1} \text{ s}^{-1}; \\ \Delta H_{Ex} = (\Delta H_{ET}/2) - [(\Delta H_{ET}/2)^2 + \beta^2]^{1/2}; \quad \Delta H_{ET} \approx \Delta G_{ET}; \\ E_{23}^* = (\Delta H_{Ex}/2) + [(\Delta H_{Ex}/2)^2 + (\Delta H_0^*)^2]^{1/2}, \quad \Delta H_0^* = 10 \text{ kJ/mol};$$

β -variable parameter (initial value $\beta = E_F^* - E_{Exp}^* = -15 \text{ kJ/mol}$).

Exciplex decay

$$1/\tau_0' = k_{30}^0 \exp(-E_{30}^*/RT) \\ k_{30}^0 = A \text{ and } E_{30}^* = E \text{ are variable parameters.}$$

For (6) apparent quenching rate constants k_Q were calculated from

$$k_Q = 10^{11} \exp(-5/RT) / \{1 + 2 \times 10^{11} \exp(-5/RT) / (10^{11} \exp(-E_{23}^*/RT)) \\ + 2 \times 10^{11} \exp(-5/RT) \cdot \exp(\Delta G_{Ex}/RT) / (A \cdot \exp(-E/RT))\}. \quad (22)$$

Simulated dependence of $\ln k_Q$ on ΔG_{ET} according to the classical scheme (1) (curve 1) and the exciplex scheme (6) for various values of β and τ_0' (curves 2–9) are given in figure 5. For $\Delta G_{ET} \approx 0$, quenching rate constants according to (6) are smaller than those for (1). For $\Delta G_{ET} \gg 0$, the quenching rate constants do not depend on ΔG_{ET} and are greater than those expected according to the classical scheme (1). In this region of ΔG_{ET} values the quenching of excited molecules results from their

Figure 5. Plots of apparent fluorescence quenching rate constants ($\ln k_Q$) on Gibbs energy of electron transfer ΔG_{ET} according to kinetic schemes (1) and (6): 1 – simulation according to scheme (1); 2–9 – simulation according to scheme (6). 2–5 – $\beta = 10$ kJ/mol, $\tau'_0 = 0.01, 1, 10, 100$ ns; 6–9 – $\tau'_0 = 30$ ns, $\beta = 20, 15, 10, 5$ kJ/mol.

conversion to the exciplex. A limiting value of the apparent quenching rate constant and the slope of the plot of $\log k_Q$ vs. ΔG_{ET} are functions of τ'_0 and β .

At fixed τ'_0 values, the rise of β will result in the contraction of the range of the dependence of k_Q on ΔG_{ET} and increase in the limiting value of k_Q (curves 2–4). At sufficiently large values of β , the quenching rate constant does not depend on ΔG_{ET} in the whole range $\Delta G_{ET} > 5$ kJ/mol because of the irreversibility of the exciplex formation. This exciplex decays by internal conversion and/or by intersystem crossing.

At fixed values of β , the decrease of the exciplex lifetime τ'_0 results in the increase of the quenching rate constant (curves 5–7). The greater the value of β , the greater the stability of the exciplex and the smaller the effect of τ'_0 on the apparent quenching rate constant. At sufficiently large values of β , the lifetime of the exciplex does not affect the quenching because of the irreversibility of the exciplex formation.

Activation energy of quenching can vary in wide range from negative to positive values in accordance with the parameters β , ΔG_{ET} and τ'_0 .

The exciplex scheme (6) represents quite well the experimental data for temperature-dependence of the apparent rate constant of pyrene fluorescence quenching by dibutylphthalate in acetonitrile at the following values of the parameters: $\beta = -13.5$ kJ/mol, $A = 1.1 \times 10^9$ s $^{-1}$, $E = 10$ kJ/mol, $\Delta G_{ET} = -2$ kJ/mol (figure 5). In butyronitrile the best fit of the experimental data was obtained at $\beta = -10$ kJ/mol, $A = 0.9 \times 10^9$ s $^{-1}$, $E = 11$ kJ/mol, $\Delta G_{ET} = +9$ kJ/mol (figure 5). At 20°C k_{30} is equal to 5×10^7 M $^{-1}$ s $^{-1}$ in acetonitrile and 3×10^7 M $^{-1}$ s $^{-1}$ in butyronitrile which are close to the values determined directly from fluorescence kinetics (table 1). In less polar butyronitrile

the value of β is slightly smaller than in acetonitrile. The values of activation energy and pre-exponential factor of exciplex decay are close in both solvents.

5. Quenching dynamics

Let us consider the nature of the potential barriers, along with the reaction coordinate in the course of fluorescence quenching, taking into account exchange interactions between reactants (coupling of locally excited and charge transfer states) in the frame of very simple approximations (figure 6).

For positive ΔG_{ET} (figure 6, top) as the reactants D^* and A approach each other, the energy decreases according with increase of the overlap of the wavefunctions of the reactants (increase of the exchange interaction energy β) and decrease of the energy (E_2) of the charge transfer state ($D^+ A^-$).

$$E \approx [(E_1 + E_2)/2] - [(E_1 - E_2)^2/4 + \beta^2]^{1/2}, \quad (23)$$

Figure 6. Potential energy curves for exciplex formation and electron transfer at $\Delta G_{ET} > 0$ (top) and at $\Delta G_{ET} < 0$ (middle) for uncharged reactants, and for an uncharged and a charged reactant (bottom).

where E_1 is the energy of the locally excited state (D^*A). An exciplex with a modest degree of electron transfer is formed. The degree of electron transfer increases gradually as reactants approach each other and solvent reorganization also gradually follows the polarization of the encounter complex.

Three potential barriers along with the reaction coordinate for the exciplex formation and subsequent complete electron transfer can arise. The first one is the diffusion barrier which has the usual activation energy in the range 5–10 kJ/mol. The second is the activation energy of exciplex formation which can be formally approximated by:

$$E_{23}^+ = (\Delta H_{\text{Ex}}/2) + [(\Delta H_{\text{Ex}}/2)^2 + (\Delta H_0^+)^2]^{1/2}; \quad (24)$$

assuming $\Delta H_0^+ = 10$ kJ/mol, similar to Weller's model (this value was found to be unessential for the results of the simulations since equilibrium between the exciplex and the reactants is established at $\Delta G_{\text{ET}} > 0$).

Complete electron transfer in this exciplex needs activation energy of about $[\Delta H_{\text{ET}}^2 + 4\beta^2]^{1/2}$ and yields a contact radical-ion pair (which can dissociate on free (solvated) radical-ions). Therefore, dominant ways of decay of the exciplex formed are internal conversion, intersystem crossing and emission (which do not need substantial activation energy), rather than complete electron transfer and formation of radical-ions. The rates of the first two radiationless decay processes may be very responsive to the chemical nature of the reactants. Therefore the lifetime of the exciplex can vary in the wide range $\sim 10^{-12} - 10^{-7}$ s and may depend on the chemical nature of both excited molecule and quencher.

For negative ΔG_{ET} (middle part of figure 6), the approach of the reactants towards each other can also be followed by the gradual increase of the charge separation but (in contrast to $\Delta G_{\text{ET}} > 0$) it finally produces a radical-ion state. This is the most well-known kind of exciplex. Along with reaction coordinates, the exchange interaction and the magnitude of charge transfer increase gradually. The solvent reorganization also occurs gradually and reorganization energy is much smaller than is expected from the Marcus theory.

Completely different nature of the activation barrier can be expected for electron transfer charged and uncharged molecules (figure 6, bottom). In this case, electrostatic interaction does not exist in either the initial or the final states and the potential curves of both the states in the first approximation are parallel to each other. For exergonic ($\Delta G_{\text{ET}} < 0$) electron transfer the inclusion of exchange interactions will produce the repulsion of the potential curves (the rise of the energy of the initial state $D^* + A$ which can be expressed by the analog of (21) but with the positive sign ahead of the square root). This rise of energy will depend on the distance of electron transfer and will build up an additional potential barrier for electron transfer. Therefore, some additional contribution to the activation energy of electron transfer due to an exchange interaction between reactants must be taken into account in the models of electron transfer processes at negative ΔG_{ET} .

Conclusions

The model assuming the formation of sufficiently long-lived (up to 10–50 ns) exciplexes even in polar solvents is able to explain and quantitatively describe the experimentally observed abnormal temperature effect and lifetime dependence of fluorescence quenching

in polar solvents and also the deviations of the experimental dependence of the quenching rate constants on ΔG_{ET} from that predicted by the electron transfer theory of the quenching (especially in the kinetic region). The stabilization energy of the exciplex at positive ΔG_{ET} can arise from exchange interactions between reactants (similar to ground state CT complexes); such exciplexes may have a low contribution of charge transfer state. The radiationless decay of the exciplex does not need any activation energy. This mechanism does not suppose the necessity of complete electron transfer between reactants in the excited state. Therefore, fluorescence quenching cannot be used with confidence for the verification of the theories of electron-transfer processes and for the determination of the redox-potentials of quenchers.

The exciplex model of quenching supposes that there are two main parameters – exciplex formation equilibrium constant K_{Ex} and its lifetime τ'_0 – which determine the apparent value of the fluorescence quenching rate constant. The abnormal temperature effect arises from the negative enthalpy of the exciplex formation (in contrast to the positive activation energy of electron transfer).

The correlation between quenching rate constants and the free energy of electron transfer ΔG_{ET} has different origins in the classical Weller's model, (1), and in the exciplex model, (2). In the classical model, two parameters which control the value of the quenching rate constant are the activation energy of isoergonic reaction ΔG_0^+ and the lifetime of the radical-ion pair ($1/k_{30}$). The last one was supposed to be 0.01 ns and ΔG_0^+ was found to be 10 kJ/mol (Rehm and Weller 1970). The last one, ΔG_0^+ , was assumed to be variable to explain the variations in the $\log k_Q$ vs. ΔG_{ET} relationships.

In the exciplex model (6), the dependence of apparent quenching rate constants on ΔG_{ET} arises from the dependence of the exciplex formation enthalpy on ΔG_{ET} , (20). The lifetime of the exciplex may exceed by many orders of magnitude the lifetime of radical-ion pairs in polar solvents and can vary in a very wide range, depending on the chemical structure of both the excited molecule and quencher. Positive and negative deviations from classical Weller's curve $\log k_Q$ vs. ΔG_{ET} may arise from the variations of the dependence of K_{Ex} on ΔG_{ET} and from the variations of τ'_0 . In consistence with numerous experimental data the slope of $\log k_Q$ vs. ΔG_{ET} plot in the kinetic region in the frame of the exciplex model (6) as a rule is much smaller than for thermodynamic limit (which is 5.9 kJ per one logarithmic unit).

References

- Avila V, Cosa J J, Chesta C A and Previtali C M 1991 *J. Photochem. Photobiol.* **A62** 83
Baggott J E and Pilling M J 1983 *J. Chem. Soc., Faraday Trans.* **79** 221
Carrera A, Cosa J J and Previtali C M 1991 *J. Photochem. Photobiol.* **A56** 267
Fox M A and Chanon M (eds) 1988 *Photoinduced electron transfer* (Amsterdam: Elsevier) vol. A–D
Gordon M and Ware W R (eds) 1975 *The exciplex* (New York: Academic Press)
Hishimura T, Nakashima N and Mataga N 1977 *Chem. Phys. Lett.* **46** 334
Kitamura N, Obata R, Kim H -B and Tazuka S 1987 *J. Phys. Chem.* **91** 2033
Kuzmin M G, Sadovskii N A, Weinstein J A and Soloveichik O M 1992 *High Energy Chem.* **26** 522 (in Russian)
Kuzmin M G and Soboleva I V 1986 *Prog. React. Kinet.* **14** 157
Neumann M G and Pastre I A 1991 *J. Photochem. Photobiol.* **61** 91
Marcus R A 1956 *J. Chem. Phys.* **24** 966
Rehm D and Weller A 1969 *Ber. Bunsenges Phys. Chem.* **73** 834
Rehm D and Weller A 1970 *Israel J. Chem.* **8** 259