

Exciplex mechanism of the fluorescence quenching in polar media

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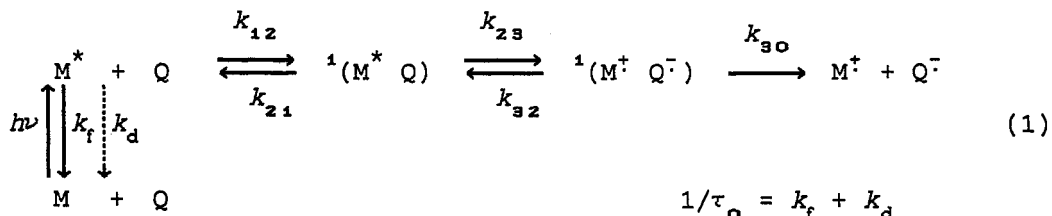
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Abstract

The formation of exciplexes (non-emitting or poorly emitting) is proposed as a cause of the deviations of the experimental data from the classical model of excited state electron transfer in polar solvents yielding radical ion pairs. Experimental evidences for the formation of such exciplexes are discussed. Simulation of the dependencies of the quenching rate constant vs. Gibbs energy of electron transfer according to the exciplex formation model confirms its consistence with the experimental data.

INTRODUCTION

Excited state electron transfer is commonly supposed to be a general mechanism of fluorescence quenching in the absence of energy transfer and heavy atom effects. Classical kinetic scheme proposed by A.Weller [1,2] assumes that electron transfer step yields contact radical-ion pair which dissociates in polar solvents very fast:



$$k = k_{12} / \{ 1 + (1 + k_{32}/k_{30}) k_{21}/k_{23} \} \quad (2)$$

$$\phi_o/\phi = \tau_o/\tau = 1 + K_{sv}[Q] = 1 + k_q \tau_o [Q] ; \quad (3)$$

where ϕ_o , ϕ and τ_o , τ are fluorescence quantum yields and lifetimes in the absence and in the presence of a quencher Q respectively.

A lot of experimental investigations [3-4] showed the existence of typical dependence of quenching rate constants k_q in polar solvents on Gibbs energy of electron transfer ΔG_{ET} . This dependence has diffusion limit at $\Delta G_{ET} \ll 0$ and thermodynamic limit at $\Delta G_{ET} > 0$. It is in consistence 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 equation [1,2]

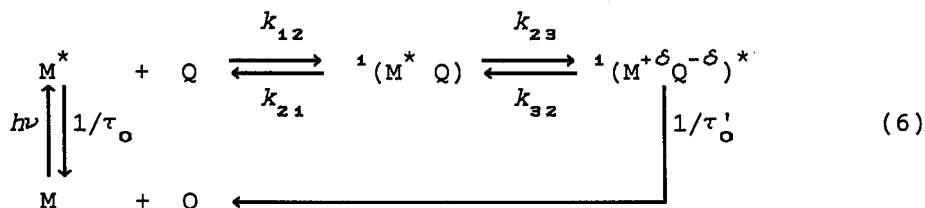
$$\Delta G_{23}^{\ddagger} = \Delta G_{ET} / 2 + \sqrt{(\Delta G_{ET} / 2)^2 + (\Delta G_o^{\ddagger})^2} , \quad (4)$$

or theoretical Marcus equation [5]

$$\Delta G_{23}^{\ddagger} = \Delta G_{0}^{\ddagger} (1 + \Delta G_{\text{ET}}/a\Delta G_{0}^{\ddagger})^2. \quad (5)$$

But numerous experimental data obtained in recent years for various systems have shown that such correlation is rather qualitative than quantitative [4,6]. Wide scatter is observed for k_{Q} at $\Delta G_{\text{ET}} \geq 0$. Even k_{Q} values greater than thermodynamically permitted for electron transfer were observed.

To find out the origin of these deviations we investigated fluorescence quenching kinetics and determined activation energies of quenching from the temperature dependence of the apparent quenching constants in several systems. Fluorescence quenching of pyrene by some weak electron acceptors and donors was studied in acetonitrile ($\Delta G_{\text{ET}} \approx 0$) and in other solvents [7]. We found several evidences that fluorescence quenching even in polar solvents can proceed rather by the formation of exciplexes than by direct electron transfer mechanism:



According to this scheme quenching of fluorescence of M also follows Stern-Volmer equation, but observed Stern-Volmer quenching constant K_{SV} has completely different sense. In the case of reversible exciplex formation ($1/\tau_0' \ll k_{32}$):

$$\varphi_0/\varphi = 1 + K_{\text{SV}}[\text{Q}] \approx 1 + K_{\text{Ex}}(\tau_0/\tau_0')[\text{Q}], \quad (7)$$

where $K_{\text{Ex}} = k_{12}k_{23}/k_{21}k_{32}$ is the exciplex formation equilibrium constant and τ_0' is the exciplex lifetime. Observed decay time of M^* which are in the equilibrium with the exciplex depend on the quencher concentration non-linearly:

$$\tau_0/\tau \approx (1 + (\tau_0/\tau_0')K_{\text{Ex}}[\text{Q}]) / (1 + K_{\text{Ex}}[\text{Q}]) . \quad (8)$$

Such plot has initial slope different from Stern-Volmer constant K_{SV} and reaches the limit equal to τ_0/τ_0' at high quencher concentrations.

EXPERIMENTAL EVIDENCES FOR EXCIPLEX FORMATION IN POLAR SOLVENTS

Quenching of pyrene fluorescence follows to Stern-Volmer equation (Fig. 1) [7]. No new emission band was found in the presence of the quenchers in the investigated systems. This means that exciplexes if they formed have low emission rate constants or very short lifetimes.

Pyrene fluorescence decays exponentially (at least two orders of magnitude) in the absence and in the presence of the quenchers and $1/\tau$ sub-linearly depends on the quencher concentration which is in

accordance to Eq. (8). Plots of $\phi_o\tau/\phi\tau_o$ and $[Q]/(\tau_o/\tau - 1)$ vs. $[Q]$ give K_{Ex} and τ_o/τ'_o :

$$\phi_o\tau/\phi\tau_o = 1 + K_{Ex}[Q] \quad (9)$$

$$[Q]/(\tau_o/\tau - 1) = (1/K_{Ex} + [Q]) / (\tau_o/\tau'_o - 1) \quad (10)$$

Obtained values of K_{Ex} and τ'_o are given in the Table. It is important to emphasize that exciplex lifetimes are relatively long - 10 to 30 ns. This means that the reason of the absence of exciplex emission for these systems is very low value of the emission rate constant ($k' \ll 10^5 \text{ s}^{-1}$).

TABLE

Stern-Volmer pyrene fluorescence quenching constants K_{sv} , apparent quenching rate constants k_q (at 298 K), experimental activation energies E_{exp}^{\ddagger} and exciplex formation equilibrium constants K_{Ex} and lifetimes τ'_o .

Quencher	Solvent	K_{sv} M^{-1}	$k_q/10^7$ $M^{-1}s^{-1}$	E_{exp}^{\ddagger} kJ/mol	K_{Ex} M^{-1}	τ'_o ns
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		4.7	-7.0		
Et ₂ NH	MeCN	99	33	10.5		

Note: DBP = Dibutylphthalate; DEP = Diethylphthalate;

DMB = 1,4-Dimethoxybenzene; Et₂NH = Diethylamine; Q' = Dimethylfumarate;

MeCN = Acetonitrile; PrCN = Buthyronitrile; AcOEt = Ethylacetate.

Another evidence for exciplex formation is very low (and in some cases even negative) values of the experimental activation energies of quenching which were determined from the temperature dependence of apparent quenching rate constant in the range (-20) - (+60) °C. Apparent activation energy determined by such a way is a sum of the exciplex formation enthalpy (negative) and its decay activation energy (small and positive).

THE NATURE OF EXCIPLEX

Electronic structure of exciplexes is usually represented by a combination of the wave functions of locally excited and charge transfer states. Enthalpy of the exciplex formation ΔH_{Ex} (neglecting the polarization of the solvent) and magnitude of electron transfer in the exciplex ${}^1(P^{-\delta}Q^{+\delta})^*$ depend on the difference of 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 energy β :

$$\Delta H_{Ex} \approx \Delta H_{ET}/2 - \sqrt{(\Delta H_{ET}/2)^2 + \beta^2} \quad (11)$$

$$\delta \approx 1/[1 - (\Delta H_{ET}/\beta) \cdot [\sqrt{1 + (\Delta H_{ET}/2\beta)^2} - \Delta H_{ET}/2\beta]] \quad (12)$$

Enthalpy of exciplex formation will be negative not only for negative ΔH_{ET} but also for ΔH_{ET} close to zero and even for positive ΔH_{ET} . For strongly negative ΔH_{ET} $\delta \approx 1$ and ordinary polar exciplexes are formed which 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).

Decay of the exciplex can proceed by several ways: by internal conversion to the ground state (encounter complex D·A), 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 to allow the relatively long lifetime of the exciplex ($> 10^{-8}$ s). For the dissociation to radical-ions this needs activation energy greater than 25 kJ/mol. Internal conversion and intersystem crossing can have low probability rather because of small values of Franck-Condon factor and spin-inversion factor respectively 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.

SIMULATION OF THE DEPENDENCE OF k_Q VS. ΔG_{ET}

According to the exciplex model the dependence of k_Q vs. ΔG_{ET} arises from the dependence of the exciplex formation enthalpy and equilibrium constant on ΔG_{ET} (Eq.11).

We simulated dependencies of k_Q vs. ΔG_{ET} for both kinetic models of fluorescence quenching (1) and (6) using standard parameters for diffusion and electron transfer rate constants [1,2] and Eq.(11) and (13) for the exciplex formation (assuming $\Delta H_O^\ddagger = 10$ kJ/mol):

$$E_{23}^\ddagger = \Delta H_{Ex}/2 + \sqrt{(\Delta H_{Ex}/2)^2 + (\Delta H_O^\ddagger)^2}; \quad (13)$$

Simulated dependencies of $\ln k_Q$ vs. ΔG_{ET} according to classical scheme (1) (curve 1) and exciplex scheme (6) for various values of β and τ' (curves 2-7) are given on Fig.2. According to exciplex model $\log k_Q$ depends on ΔG_{ET} much weaker than in classical Weller's model. For $\Delta G_{ET} \gg 0$ quenching rate constants fail to depend on ΔG_{ET} and it is greater than expected according to classical scheme (1) since in this region quenching of excited molecules results from their conversion to the exciplex. A limiting value of the apparent quenching rate constant and the slope of the dependence of $\log k_Q$ vs. ΔG_{ET} are functions of τ' and β .

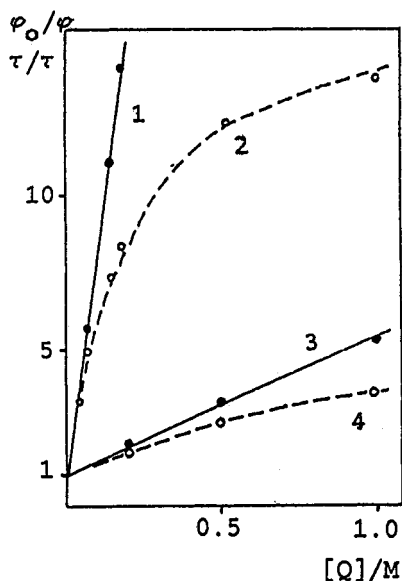


Fig. 1. Plots of relative quantum yields φ_0/φ (1,3) and lifetimes τ_0/τ (2,4) of pyrene vs. concentration of dibutylphthalate in acetonitrile (1,3) and in butyronitrile (3,4).

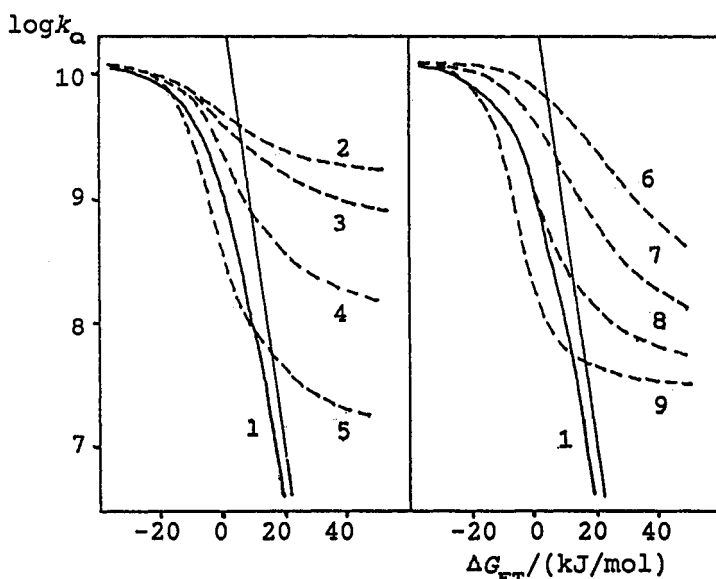


Fig. 2. Plots of apparent fluorescence quenching rate constant k_Q vs. Gibbs energy of electron transfer ΔG_{ET} according to kinetic schemes (1) and (6):
 1 - simulation by scheme (1);
 2 - simulation by scheme (6);
 2-5 - $\beta=10$ kJ/mol, $\tau'_0 = 0.01, 1, 10, 100$ ns;
 6-9 - $\tau'_0=30$ ns, $\beta=20,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

At fixed β the decrease of the exciplex lifetime τ' results in the increase of the quenching rate constant (curves 2-5) which tend at large positive ΔG_{ET} to the limit which can be approximated as $k_{12}/(1+k_{21}(\tau'_0+1/k_{23}^0))$.

At fixed τ' the increase of β will result in the narrowing of the range of the dependence of k_Q on ΔG_{ET} and decrease of the slope of $\log k_Q$ vs. ΔG_{ET} in this range (curves 6-9).

Activation energy of quenching can vary in wide range from negative to positive values depending on the parameters β , ΔG_{ET} and τ' . Exciplex scheme (6) represents also quite well experimental data for temperature dependence of apparent rate constant of pyrene fluorescence quenching in acetonitrile and butyronitrile at the following values of the parameters: $\beta = -(10 - 13.5)$ kJ/mol, $A = (0.9 - 1.1) \cdot 10^9$ s $^{-1}$, $E = 10 - 11$ kJ/mol, $\tau' = 20-30$ ns.

CONCLUSION

The exciplex model (6), assuming the formation of sufficiently long-lived (up to 10-50 ns) exciplex even in polar solvents, is able to explain and quantitatively describe experimentally observed abnormal temperature effects and lifetime dependence at fluorescence quenching

and also the deviations of the experimental dependence of the quenching rate constants vs. ΔG_{ET} from the predicted by 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 (similarly to ground state CT complexes); such exciplexes can have low contribution of charge transfer. Radiationless decay of the exciplex does not need activation energy.

Exciplex mechanism do not supposes the necessity of complete electron transfer between reactants in the excited state (in contrast to the ground state reactions). Therefore, fluorescence quenching cannot be used with confidence for the verification of the theories of electron transfer processes and for determination of redox-potentials of excited molecules and quenchers.

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