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Investigations on the nature of non-radiative transitions from excited singlet and triplet states of dimethyl substituted phenols in the presence of acceptor 2-nitrofluorene at 77 K

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Abstract

Steady state emission measurements are combined with time-resolved experiments to examine the nature of the different non-radiative transitions from the photoexcited donors (D) (3,5-dimethylphenol, 35DMP; 2,6-dimethylphenol, 26DMP; 3,5-dimethylanisole, 35DMA; 2,5-dimethylanisole, 25DMA) in the presence of the acceptor (A) 2-nitrofluorene (2NF) in ethanol (EtOH) rigid glassy matrix at 77 K. At such low temperature observations of large negative driving energy (ΔG^0) values (-1.42 eV to -2.03 eV) for the systems of present excited singlet (S_1) donors and ground state 2NF are indicative of the occurrence of highly exothermic electron transfer (ET) reactions in the singlet state S_1 whereas relatively lower values of ΔG^0 (-0.17 eV to -0.70 eV) for the excited triplet (T_1) donors and the acceptor 2NF in the ground state suggest the involvement of moderately exothermic ET reactions within these D–A pairs. Following the Weller equation, the destabilization energy (ΔG_d^0) has been computed (to estimate the driving energy for ET reactions in solid solution) for the ion pair states of the present donor–acceptor molecules. However, the computed value of ΔG_d^0 ($\sim$0.26 eV) for the present D–A systems indicate that though, the driving energy decreases in magnitude does not reduce to a large extent on going from polar acetonitrile (ACN) liquid to EtOH glass. It seems in EtOH solid solution at 77 K dipole rotations of the solvent may not be fully eliminated unlike the situation observed by Wasielewski et al. in the case of less polar methyltetrahydrofuran glass environment. From the energy gap dependence of ET rates and the observed relationships between λ, nuclear re-organization energy parameter and ΔG^0, it is apparent that singlet (S_1) ET reactions might be occurring in the Marcus inverted region (MIR) while such reactions between triplet donors and ground state acceptor 2NF seem to proceed through the normal/intermediate region. From the observations of the large spectral overlapping between the donor emission and electronic absorption spectra of the acceptor coupled with the high values of T (99%), the theoretical transfer efficiency of non-radiative energy transfer of Förster's type, and R_0 ($\sim$27 Å), Förster's critical energy transfer distance, it seemingly indicates that the combined effect of the concurrent processes of photoinduced ET and Förster's type energy transfer is primarily responsible for the observed fluorescence quenching of the present donors in the presence of the acceptor 2NF at 77 K. The same trend was observed at the ambient temperature as reported earlier. Moreover, steady state and time-resolved data reveal that triplet–triplet ($T_1^D \rightarrow T_1^A$) energy transfer along with triplet state ET reactions might be responsible for the observed donor phosphorescence quenching phenomena. Reaction schemes describing the various possible pathways for the non-radiative depletion of the excited (singlet and triplet) states of the donors effected through the interactions with the quencher (electron acceptor) 2NF have been proposed from the observed experimental results.

Keywords: 2-Nitrofluorene; Non-radiative transitions; Dimethylsubstituted phenols

1. Introduction

It was reported in our earlier paper [1] that at the ambient temperature (296 K) in highly polar ACN solvent the donor (35DMP; 26DMP; 35DMA and 25DMA) fluorescence emission intensity quenches remarkably in the presence of the acceptor 2-nitrofluorene (2NF). The measured apparent fluorescence quenching rate constant, k_q, was found to be about two orders of magnitude higher ($k_q \sim 10^{12}$ M^{-1} s^{-1}) than the diffusion-controlled rate. The large quenching was attributed to the concurrent occurrences of the two processes viz., (1) photoinduced electron transfer (ET) from an excited singlet donor to the ground state acceptor 2NF (from highly negative values of free energy change, ΔG_{ET}^0) and (2) Förster's type singlet–singlet energy transfer from the donor to the acceptor 2NF (as evidenced from large values of Förster's critical energy transfer distance, $R_0 \sim 25$ Å and

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theoretical transfer efficiency, $T\sim 99\%$). It was also reported in our earlier paper [1] that at 77 K in ethanol (EtOH) rigid glassy matrix significant quenching in both fluorescence and phosphorescence emission of the present donors were observed in the presence of the electron acceptor 2NF. This observation seemingly indicates that, even at 77 K, there is a large possibility of concurrent occurrences of the above two processes (1) and (2) within the present D–A pairs. Thus, in the present paper we reported the detailed studies, made in the present investigations, by using steady state and time-resolved techniques to reveal the exact mechanisms of the quenching processes involved within the D–A systems in EtOH rigid glassy matrix at 77 K. Our prime interest in the present work was to examine the role of the triplet states of the donors in electron and energy transfer mechanisms. The present paper deals with the results obtained from the above studies. It was also intended to measure various photophysical parameters and to propose a suitable reaction scheme for the quenching phenomena at 77 K.

2. Experimental details

2.1. Purification of chemicals

The samples 35DMP, 26DMP, 35DMA, 25DMA and 2NF supplied by Aldrich were purified by vacuum sublimation. The solvent EtOH (E. Merck) of spectroscopic grade, used as a rigid glassy matrix at low temperature (77 K) measurements, was distilled under reduced pressure.

2.2. Spectroscopic apparatus

The electronic absorption and steady state emission spectra of moderately dilute solid solutions ($\sim 10^{-3}$ to 10^{-5} M) of the samples were recorded at 77 K with the help of Shimadzu UV–VIS 2101PC spectrophotometer and Hitachi F-4500 fluorescence spectrophotometer, respectively. Measurements of low temperature (77 K) emission spectra and phosphorescence lifetimes (τ_p) were made by using a cylindrical dewar assembly. To study the phosphorescence decay of the samples with the Hitachi F-4500 fluorescence spectrophotometer the exciting radiation was cut off to have the dark decay on the recorder after the phosphorescence intensity achieved a steady state. Using the room temperature redox potential values obtained in ACN solvent from the electrochemical measurements made by using a PAR 370-4 electrochemistry system, whose details are given elsewhere [2], the free energy changes (ΔG^0_{ET}) for photoinduced ET reactions between the excited (singlet or triplet) donor and ground state acceptor 2NF at 77 K in EtOH rigid glassy matrix were estimated considering the necessary corrections for the change of solvation energy.

The fluorescence quantum yields (ϕ_f) of the present donor molecules in the absence of the acceptor 2NF at 77 K in EtOH rigid glassy matrix were measured relative to benzonitrile in EPA glass (ϕ_f=0.30±0.02) [3] as standard. The necessary corrections for different solvation effects were made in estimating the ϕ_f values.

3. Results and discussion

3.1. Quenching observed in fluorescence emission spectra of the donors in the presence of the acceptor 2NF at 77 K in EtOH rigid glassy matrix

In EtOH rigid glassy matrix at 77 K a regular decrement in the fluorescence emission band intensity of a present donor was noticed due to gradual addition of the electron acceptor 2NF (Fig. 1). Apart from intensity reduction no significant spectral shift of the donor fluorescence spectra was observed. It was reported in our earlier paper [1] that at room temperature the two basic quenching processes, for example, excitational energy transfer of Förster's type and photoinduced ET within the present D–A systems are primarily responsible for the donor fluorescence quenching phenomena. In the present study at 77 K an attempt was made to examine the possibilities of occurrences of the above non-radiative processes, which are found to be active at the room temperature, within the present D–A systems in EtOH rigid glassy matrix by steady state, time-resolved spectroscopic and electrochemical techniques. The details are given below:

3.2. Search for the possibilities of occurrences of photoinduced ET reactions within the present D–A systems at 77 K

(a) Within the excited singlet (S_1) donor and ground state acceptor:

The free energy change ΔG^0_{SET} (SET stands for excited singlet state electron transfer) associated with radical ion pair formation resulted from ET reactions between the

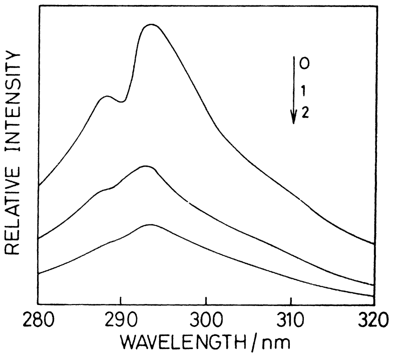


Fig. 1. Fluorescence emission spectra of 25DMA (C=7.2×10^{-5} M) in an EtOH rigid glassy matrix at 77 K (λ_{exc}=270 nm) in the presence of 2NF. Concentration of 2NF (M):(0) 0; (1) 1.9×10^{-4}; (2) 3.8×10^{-4}.

present excited singlet (S_1) donors and ground state acceptor was computed using the well-known Rehm–Weller relation [4,5] (Eq. (1)) in polar ACN fluid solution at 296 K.

$$\Delta G^0_{\mathrm{SET}}(\mathrm{ACN}) = E^{\mathrm{OX}}_{1/2}(\mathrm{D/D^+}) - E^{\mathrm{RED}}_{1/2}(\mathrm{A^-/A}) - E^*_{0,0} - e^2/(4\pi\varepsilon_0\varepsilon_s R) \tag{1}$$

Here, $E^{\mathrm{OX}}_{1/2}$ ($\mathrm{D/D^+}$) and $E^{\mathrm{RED}}_{1/2}$ ($\mathrm{A^-/A}$) are the half-wave oxidation potential of the donor and the half-wave reduction potential of the acceptor, respectively. The redox potentials were measured in polar ACN fluid solution at 296 K. $E^*_{0,0}$ is the energy of the lowest excited singlet (S_1) of the donor (or acceptor) where ET reactions occur. The other symbols have their usual meanings. However, in highly polar solvent like ACN ($\varepsilon_s\sim$ 37.5) the fourth term (Coulomb stabilization term) in Eq. (1) is often neglected [2,6].

For evaluating $\Delta G^0_{\mathrm{SET}}$ in the cases of the present D–A pairs in EtOH rigid glassy matrix at 77 K, a modification in Eq. (1) is essential due to the change in the polarity of the medium on going from ACN fluid solution to EtOH glass. Prior to this, we must have an idea about the polarity of the environment in EtOH rigid glassy matrix at 77 K.

Earlier in many cases, dielectric constant of a polar liquid was found to suffer a large drop at the freezing point [7]. This indicates that the degrees of freedom of orientation of the molecular dipoles may disappear on solidification. Though according to Harrison et al. [9], molecular reorientation is still possible in the solid phase, but to a lesser extent. Unfortunately, to our knowledge, there is no literature data regarding the polarity of EtOH glass at 77 K. However, we computed the dielectric constant of EtOH glass at 77 K by fitting the experimental data, obtained earlier by Ganguly et al. [10], to the following equation as defined by Liptay [11].

$$\Delta E = \Delta E^0 - \frac{2}{a^3}\frac{\varepsilon_s - 1}{2\varepsilon_s + 1}[\{\mu(^1L_a)\}^2 - \{\mu(^1L_b)\}^2 + \mu_g\{\mu(^1L_a) - \mu(^1L_b)\}] \tag{2}$$

Eq. (2) is particularly valid in rigid solutions as it does not distinguish between relaxed and non-relaxed (Franck–Condon) states [12]. Here, ΔE and ΔE^0 are the energy gaps between the ^1L_a and ^1L_b states of the molecule under investigation in EtOH glass at 77 K and in the gas phase, respectively; 'a' is the spherical cavity radius; ε_s is the static dielectric constant of EtOH at 77 K and $\mu(^1L_a), \mu(^1L_b)$ and μ_g are the dipole moments of the $^1L_a, ^1L_b$ and ground states, respectively. Using this procedure, the average value of the dielectric constant (ε_s) of EtOH at 77 K comes out to be ~4.4 which is much lower as compared to the room temperature (296 K) value. This sharp decrease in the value of ε_s on going from polar liquid to solid agrees reasonably well with the earlier observations made by Böttcher [7]. Moreover, this value of ε_s for EtOH at 77 K, obtained by using Eq. (2), is very similar to the value (3.7) reported earlier by Marcus [8] for the mixture of EtOH and methanol in the ratio of 4:1.

It seems that the photoinduced ET reactions should occur with less efficiency in EtOH rigid glass at 77 K than in ACN fluid solution at 296 K. This is because in polar ACN fluid solution, solvent dipoles can easily orient themselves around an ion pair thereby decreasing the energy of the ion pair state. But, in EtOH rigid glass environment, reorientation of solvent dipoles around an ion pair is somewhat hindered [13–15]. This increases the energy of the ion pair state in rigid glass than in the liquid. As a result, The free energy of the singlet excited ET reaction will be less negative (less exothermic) in EtOH rigid glassy matrix at 77 K which could be computed by using Eq. (3) [16,17].

$$\Delta G^0_{\mathrm{SET}}(\mathrm{EtOH}) = \Delta G^0_{\mathrm{SET}}(\mathrm{ACN}) + \Delta G^0_{\mathrm{d}} \tag{3}$$

Here, ΔG^0_{d} is the ion pair destabilization energy brought about by the decrease in the polarity of the environment on going from ACN fluid solution at 296 K to EtOH glass at 77 K.

Using the Born dielectric contiuum model of the solvent, Weller [18] derived Eq. (4) to calculate the value of ΔG^0_{d} in a solvent with a static dielectric constant ε_s, if the redox potentials of the donor and acceptor are measured in a medium with a high dielectric constant ε'_s.

$$\Delta G^0_{\mathrm{d}} = \frac{e^2}{\varepsilon_s}\left[\frac{1}{2r_D} + \frac{1}{2r_A} - \frac{1}{R}\right] - \frac{e^2}{\varepsilon'_s}\left[\frac{1}{2r_D} + \frac{1}{2r_A}\right] \tag{4}$$

Here, the symbols have their usual meanings.

For intermolecular ET reactions it is rather difficult to choose the proper value of the D–A separation distance, R. In the present investigations, we have chosen R=7 Å as was done in our earlier work [1]. This is based on the fact that for intermolecular D–A systems highly exothermic ET reactions should occur at $R\geq$7 Å as predicted by Kikuchi [19]. The same value of R=7 Å was also chosen by several other workers [20,21] in the cases of some highly exothermic intermolecular ET reactions.

From Eq. (4) the destabilization energy is found to be nearly 0.26 eV. Earlier working with some porphyrin–donor–quinone acceptor systems in less polar glassy 2-methyltetrahydrofuran (MTHF) at 77 K, Wasielewski et al. [16,17] found the value of ΔG^0_{d} to be quite high (~0.8 eV). But, in the present investigations, though the destabilization factor on going from ACN liquid to EtOH glass decreases the negativity of the value of the free energy change ($\Delta G^0_{\mathrm{SET}}$) for ET reaction but merely to a lesser extent. This is apparent from the values of $\Delta G^0_{\mathrm{SET}}$ for the present D–A systems observed in polar ACN fluid solution at 296 K and in EtOH rigid glassy matrix at 77 K as shown in Table 1. Table 1 also indicates that the nature of the ET reactions within the present D–A systems remains of highly exothermic type when the temperature is lowered down to 77 K.

Table 1
Gibbs free energy changes associated with ET reactions within the present D–A systems in ACN fluid solution at 296 K and in EtOH rigid glassy matrix at 77 K

Donor[a]	Acceptor	$\Delta G^0_{\mathrm{SET}}$ (ACN) at 296 K[b]	$\Delta G^0_{\mathrm{SET}}$ (EtOH) at 77 K[c]
25DMA *	2NF	−1.68	−1.42
26DMP *	2NF	−1.73	−1.47
35DMP *	2NF	−2.00	−1.74
35DMA *	2NF	−2.29	−2.03

[a] * denotes the first excited singlet state (S_1).

[b] Obtained from the electrochemical measurements of the present donor and acceptor molecules in ACN solvent at 296 K (see [1]).

[c] Computed by using Eq. (3) (see text). While evaluating ΔG^0_{d} from Eq. (4), values of r_{D} and r_{A} were calculated using the relation $r=(3M/4\pi\rho N_{\mathrm{A}})^{1/3}$. An average value of $r_{\mathrm{D}}\sim 3.6$ Å for the present donors and $r_{\mathrm{A}}\sim 4.4$ Å for 2NF were used (see text). For EtOH rigid glass at 77 K, $\varepsilon'_{\mathrm{s}}\sim 4.4$ was used (see text). Also, $R=7$ Å was assumed (see text).

(b) within the excited triplet (T_1) donor and ground state acceptor:

The values of $\Delta G^0_{\mathrm{TET}}$ (TET stands for excited triplet electron transfer) for photoinduced ET reactions between the excited triplet (T_1) donors and ground state acceptor in EtOH glass at 77 K were computed by using the relation 5 as shown below:

$$\Delta G^0_{\mathrm{TET}}(\mathrm{EtOH}) = \Delta G^0_{\mathrm{SET}}(\mathrm{EtOH}) + \Delta E_{\mathrm{S_1-T_1}} \tag{5}$$

In the above expression the term $\Delta E_{\mathrm{S_1-T_1}}$ has been included since the exothermicity of the reaction will be lowered (less negative) by the difference between the first excited singlet states of the donors and their triplets. The $-\Delta G^0_{\mathrm{TET}}$ values which are relatively much lesser in magnitude than the values observed for $-\Delta G^0_{\mathrm{SET}}$ of the D–A pairs studied in the present investigation are listed in Table 2. Nevertheless, from the observed negative values of $\Delta G^0_{\mathrm{TET}}$ (Table 2) it seemingly indicates that the occurrences of ET reactions in the triplet state should also be thermodynamically possible.

3.3. Search for the possibilities of occurrences of Förster's type singlet (S_1)–singlet (S_1) energy transfer processes within the present donor and acceptor systems in EtOH rigid glassy matrix at 77 K

From the considerable spectral overlapping of donor emission with the electronic absorption spectra of the acceptor 2NF at 77 K the values of R_0, Förster's critical energy transfer distance, were computed and are found to be around 27 Å. This large value of R_0 excludes the possibility of the occurrence of Dexter's type one-dimensional energy transfer and predicts Förster's type energy transfer process within the present D–A systems.

Further, the theoretical efficiency (T) of Förster's type non-radiative energy transfer was estimated from the relation 6 [21].

$$T = \frac{(R_0/R)^6}{1 + (R_0/R)^6} \tag{6}$$

While calculating T from Eq. (6), a value of $R=7$ Å was chosen, the reason of which has already been stated. The value of T was found to be 99% for the present D–A pairs. This value of T coupled with the large value of R_0 indicates the possibility of the occurrence of Förster's type singlet–singlet energy transfer process within the present D–A systems at 77 K. However, due to the non-fluorescent behavior of the acceptor 2NF spectral evidence in favor of such energy transfer is lacking.

3.4. Phosphorescence quenching of the donors in presence of the acceptor 2NF at 77 K in EtOH rigid glassy matrix

In EtOH rigid glassy matrix at 77 K significant quenching in the intensity of the entire phosphorescence band envelop of the present donors is found on addition of the acceptor 2NF (Fig. 2). Interestingly this quenching was accompanied by the concomitant appearance and augmentation of a

Table 2
Gibbs free energy changes associated with singlet excited ET reactions (SET) and triplet excited ET reactions (TET) and corresponding ET rate constants as well as Gibbs free energy changes associated with triplet–triplet energy transfer (TEN) for the present D–A pairs in EtOH rigid glassy matrix at 77 K

Systems[a]	$\Delta G^0_{\mathrm{SET}}$ (EtOH) (eV[b])	k_{SET} (S[c])	$\Delta G^0_{\mathrm{TET}}$ (EtOH) (eV[d])	k_{TET} (S[c])	$\Delta G^0_{\mathrm{TEN}}$ (EtOH) (eV[e])
25DMA *+2NF+EtOH	−1.42	8.2×10^{8}	−0.17	7.0×10^{8}	−0.60
26DMP *+2NF+EtOH	−1.47	3.6×10^{8}	−0.18	8.1×10^{8}	−0.52
35DMP *+2NF+EtOH	−1.74	1.6×10^{6}	−0.49	3.0×10^{10}	−0.60
35DMA *+2NF+EtOH	−2.03	6.1×10^{2}	−0.70	8.8×10^{10}	−0.52

[a] * denotes the excited singlet (S_1) or excited triplet (T_1) state as the case may be.

[b] See footnotes of Table 1.

[c] Computed using Eqs. (7)–(9) and assuming $A=1\times10^{11}\ \mathrm{s}^{-1}$ at 77 K (see text). In calculating λ at 77 K, $\lambda_{\mathrm{v}}=0.3$ eV has been chosen (see text). While calculating λ_{s} at 77 K, an average value of $r_{\mathrm{D}}\sim 3.6$ Å and $r_{\mathrm{A}}\sim 4.4$ Å have been used and $R=7$ Å has been assumed (see text). The computed value of λ is around 0.8 eV for the present D–A systems in EtOH glass at 77 K. For EtOH rigid glassy matrix at 77 K, $\varepsilon_{\mathrm{s}}\sim 4.4$ and $n\sim 1.3614$ have been used (see text).

[d] Computed using Eq. (5) (see text).

[e] Computed from the triplet energies of the present donor and acceptor molecules (see text).

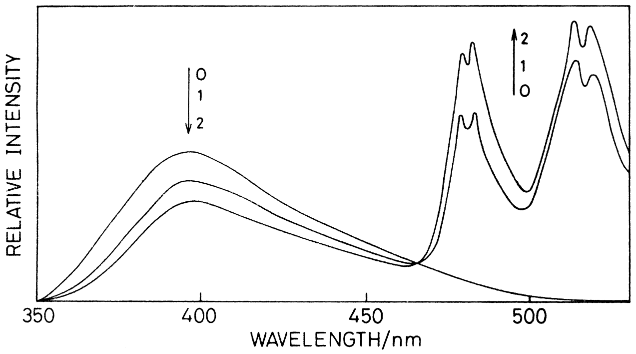


Fig. 2. Phosphorescence emission spectra of 25DMA (C=7.2×10^{-5} M) in an EtOH rigid glassy matrix at 77 K (λ_{exc}=270 nm) in the presence of 2NF. Concentration of 2NF (M):(0) 0; (1) 1.9×10^{-4}; (2) 3.8×10^{-4}.

longer wavelength emission band around 470–530 nm region. An isoemissive point was observed at 468 nm. It is apparent from the spectra (Fig. 2) that the longer wavelength phosphorescence band is developing at the expense of the phosphorescence spectra of the donor molecule with increase of the acceptor concentration. To examine the nature of the species responsible for the long wavelength phosphorescence band, phosphorescence decay times were measured by using the monitoring wavelengths of 480 and 510 nm of the longer wavelength phosphorescence band of the mixture of a present donor and acceptor 2NF in EtOH rigid glassy matrix at 77 K. From both the decays a lifetime of the order of 0.2 s (Table 3) was obtained. This phosphorescence lifetime, τ_{p}, corresponds to the lifetime of only acceptor 2NF at 77 K in EtOH rigid glassy matrix (Table 3). This observation indicates in favor of the occurrence of triplet (T_1)–triplet (T_1) ($T_1^D \rightarrow T_1^A$) energy transfer process within the present D–A systems.

The free energy changes, $\Delta G^0_{\mathrm{TEN}}$, associated with triplet–triplet energy transfer process ($T_1^D \rightarrow T_1^A$) within the present D–A systems were estimated from their triplet energies as it was done by Shizuka et al. [23]. These values are shown in the Table 2. The observed negative values of $\Delta G^0_{\mathrm{TEN}}$ (Table 2) support our proposition, made from the phosphorescence decay measurements, in favor of the occurrence of triplet–triplet energy transfer process. Thus, from the thermodynamic point of view, the possibility of the concurrent occurrences of both triplet–triplet energy transfer and triplet state ET reactions (from negative values of $\Delta G^0_{\mathrm{TET}}$, Table 2) could be inferred within the present D–A systems at 77 K. It seems that the combined effect of the above two processes might be responsible for the observed lowering of the donor phosphorescence band intensity in the presence of the acceptor molecules.

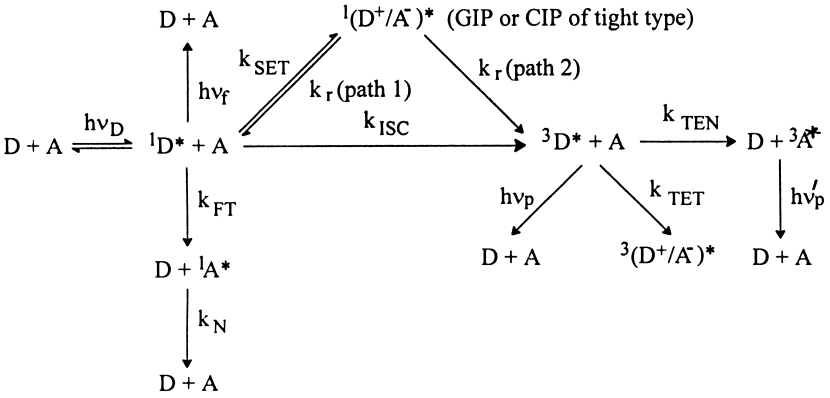
It was reported in our earlier paper [1] that at room temperature the contact ion pair (CIP) and solvent-separated ion pair (SSIP) or free radical ions resulted from photoinduced ET reactions fluoresce at around 355 and 390 nm regions in non-polar cyclohexane (CH) and polar ACN solvents, respectively. At 77 K such fluorescence bands of CIP or SSIP, if at all present, were rather difficult to observe due to the presence of the donor phosphorescence band envelop in this region. It appeared that by quenching this phophorescence band artificially the CIP or free radical ionic fluorescence band, if at all formed, could be detected easily. However, from the above phosphorescence quenching studies (Fig. 2) no such band in these regions was found at 77 K in EtOH rigid glassy matrix unlike the situation observed at the room temperature. Possibly the geminate ion pair (GIP) which is initially formed in the excited singlet state (S_1) just after excitation of the donor moiety may be of tight contact ion pair type from which the back ET (geminate recombination) process is highly probable, resulting in the formation of ground state (unexcited donor and acceptor) or triplet (T_1) state products (Scheme 1, vide infra). However, for a conclusive evidence more investigations with several similar systems seem to be necessary. It is relevant to point out here that at the room temperature, GIP complex, formed as a product of primary ET reactions, was proposed to be of loose type because formations of excited state charge transfer (CT) and ionic bands due to photoinduced ET reactions within the present D–A systems were clearly observed as it has been reported in our earlier paper [1].

Table 3
Values of the phosphorescence lifetime (τ_{p}) for the present D–A systems in EtOH rigid glassy matrix at 77 K

Systems[a]	Concentration of donor/M	Concentration of acceptor/M	τ_{p} (s[b]) at λ_{em} (nm)			
			400	417	480	510
2NF *+EtOH		3.6×10^{-4}			0.2	0.2
35DMP *+EtOH	2.0×10^{-5}		2.0			
35DMP *+2NF+EtOH	2.0×10^{-5}	3.6×10^{-4}	1.7		0.2	0.2
26DMP *+EtOH	1.6×10^{-4}			0.6		
26DMP *+2NF+EtOH	1.6×10^{-4}	1.9×10^{-4}		0.6	0.2	0.2
35DMA *+EtOH	7.2×10^{-5}		4.5			
35DMA *+2NF+EtOH	7.2×10^{-5}	1.5×10^{-3}	4.7		0.2	0.2
25DMA *+EtOH	4.3×10^{-5}			1.2		
25DMA *+2NF+EtOH	4.3×10^{-5}	3.6×10^{-4}		1.1	0.2	0.2

[a] * denotes the first excited triplet state (T_1).

[b] Percentage error in the measured values of τ_{p} lies in the range of 5–10%.



Scheme 1. Quenching phenomena within the present D–A systems in EtOH rigid glassy matrix at 77 K. GIP: geminate ion pair; CIP: contact ion pair; SET: excited singlet (S_1) electron transfer; TET: excited triplet (T_1) electron transfer; ISC: intersystem crossing; FT: Förster's type singlet–singlet ($S_1^D \rightarrow S_1^A$) energy transfer; TEN: triplet–triplet ($T_1^D \rightarrow T_1^A$) energy transfer; k_N denotes the non-radiative decay rate of the acceptor from its excited singlet to the ground state; k_r denotes the charge recombination (CR) rate. CR produces either excited singlet (path 1) or excited triplet (path 2) species of the donor molecules (* denotes the excited state).

3.5. Rate constants associated with photoinduced ET reactions within the present D–A systems both in the excited singlet (S_1) and triplet (T_1) states in EtOH rigid glassy matrix at 77 K

It has been inferred above from the observed highly negative ΔG^0_{SET} values and moderately negative values of ΔG^0_{TET} that there are favorable chances, from the thermodynamical point of view, for the occurrences of photoinduced ET reactions within the present donors and acceptor 2NF both in the excited singlet (S_1) and triplet (T_1) states at 77 K in EtOH rigid glassy matrix. An attempt was made in the present study to estimate the rate constants associated with ET reactions both in the excited singlet and triplet states.

The ET rate constant, k_{ET}, for the excited singlet (or triplet) donor and ground state acceptor was computed by using the Arrhenius relation 7 [22].

$$k_{ET} = A \exp(-\Delta G^{\dagger}/k_B T) \qquad (7)$$

The activation energy, $\Delta G^{\dagger}$, is given by [21]

$$\Delta G^{\dagger} = (\lambda/4)(1 + \Delta G^0/\lambda)^2 \qquad (8)$$

where λ is the nuclear re-organization energy parameter. This is the critical parameter for defining MIR. λ is the sum of the two re-organization energies, λ_v (for oscillations within the molecule) and λ_s (for oscillations of the solvent molecules). The value of λ_v was chosen as 0.3 eV. This value is the characteristic value for aromatic D–A systems [5,24,25]. λ_s was computed from the following well-known relation [5].

$$\lambda_s = e^2\left(\frac{1}{2r_D} + \frac{1}{2r_A} - \frac{1}{R}\right)\left(\frac{1}{n^2} - \frac{1}{\varepsilon_s}\right) \qquad (9)$$

For EtOH at 77 K, $\varepsilon_s \sim 4.4$ and $n \sim 1.3614$ (assuming that the value of n at 77 K is the same as that at the room temperature as exact temperature dependence of n is not known yet [26]). Using the room temperature values [1] of $r_D \sim 3.6$ Å and $r_A \sim 4.4$ Å, the value of λ for all the present D–A pairs comes out to be around 0.8 eV.

Comparing the value of λ with the values of ΔG^0_{SET} and ΔG^0_{TET} (Table 2) at 77 K, it was seen that $-\Delta G^0_{SET} > \lambda$ but $-\Delta G^0_{TET} < \lambda$. These observations indicate [27] that ET reactions between the excited singlet donors and ground state acceptor 2NF occur in MIR whereas the occurrences of ET reactions in the normal region might have resulted from the encounter between the excited triplet donors and ground state acceptor 2NF. As a corroborative evidence the energy gap dependences of the ET rates for the present excited (singlet and triplet) donor–ground state acceptor systems have been demonstrated in Fig. 3. It is to be admitted that in estimating k_{ET} values from Eq. (7) we have used the same value of A ($\sim 10^{11}$ s^{-1}) as was used at room temperature [1]. However, it should not affect our interpretations as we were primarily interested to observe the trend of the variation of k_{ET} with the exothermicity (ΔG^0_{SET} or ΔG^0_{TET} as the case may be) rather than on the absolute magnitudes of the rate constants associated with the ET reactions. From Fig. 3 it is apparent that in the intermediate region [19] where the values of ΔG^0_{TET} fall, ET rates increase with the increase of the exothermicity (more negative ΔG^0_{ET} values) whereas in highly exothermic region [19] where the values of ΔG^0_{SET} fall, ET rates decrease with the increase of exothermicity. Thus, from the energy gap dependence on ET rates and observed relationship between nuclear re-organization energy (λ) and exothermicity (ΔG^0_{SET} or ΔG^0_{TET}) it may be reasonably concluded that though the ET reactions seem to be occurring both in the excited singlet and triplet state of the donor molecules, but the nature of the ET reactions in the two excited states appears to be different. From all the observed results, discussed above, it seemingly indicates that the acceptor is involved in highly exothermic ET reactions with excited singlet donors and

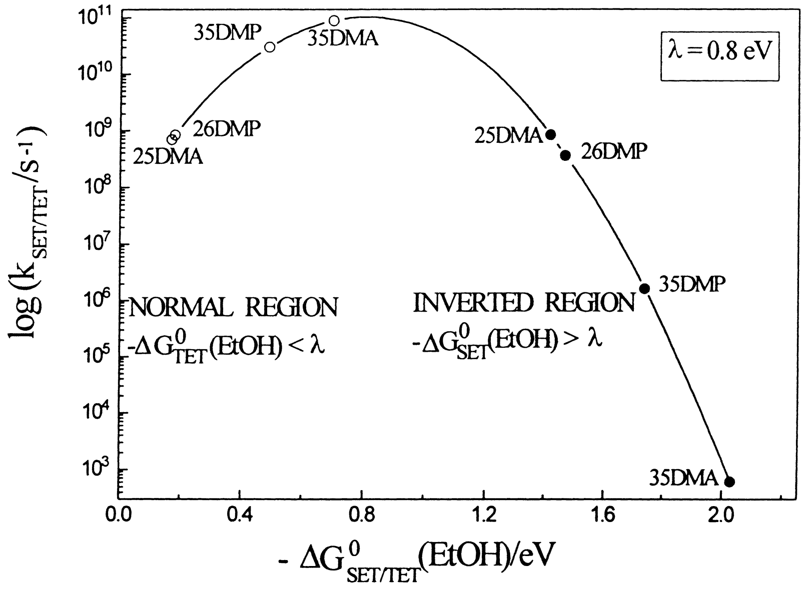


Fig. 3. A plot of log(k_{ET}) as a function of Gibbs free energy change ($-\Delta G^0_{ET}$) for the present systems of the donors (shown in the curve) – acceptor 2NF in an EtOH rigid glassy matrix at 77 K. k_{ET} values were computed by using Eq. (7) assuming the value of $A=1\times10^{11}$ s^{-1} as proposed by Rehm and Weller ([1]). SET: ET reactions between excited singlet (S_1) donor and ground state acceptor (represented by ● symbol). TET: ET reactions between excited triplet (T_1) donor and ground state acceptor (represented by ○ symbol).

these reactions occur in MIR region whereas its involvement with excited triplet donors in ET results in less exothermic reactions which occur in the normal/intermediate region (Fig. 3).

The general scheme of the various photoprocesses which seem to be involved, from the present investigations, within the present D–A systems at 77 K in EtOH rigid glassy matrix is presented in the Scheme 1.

4. Conclusions

In the present paper we have argued that in EtOH rigid glassy matrix at 77 K highly exothermic photoinduced ET reactions occur not only in the excited singlet (S_1) states of the present donors, but their triplets (T_1) are also involved in such reactions with the unexcited (ground state) acceptor 2NF. Nevertheless, in the former case, ET reactions occur in the MIR and such reactions proceed concurrently with the Förster's type energy transfer. These two concurrent processes seem to be responsible for the quenching observed in the donor fluorescence. It was proposed, from the thermodynamic consideration, that the occurrence of ET reactions between the excited triplet (T_1) donors and the ground state electron acceptor 2NF is also possible though in this case the reactions seem to be occurring in the normal/intermediate region. It has been suggested from the investigations made by steady state and time-resolved techniques that the combined effect of the triplet–triplet ($T_1^D \rightarrow T_1^A$) energy transfer process and triplet (T_1) state ET reactions might be primarily responsible for the observed triplet quenching phenomena of the donor molecules.

Following the Weller equation (Eq. (4)), the destabilization energy (ΔG^0_d) has been computed (to estimate the driving energy for ET reactions in solid solution) for the ion pair states of the present donor–acceptor molecules. However, ΔG^0_d is found not to affect the free energy change to a large extent. This indicates that in EtOH solid solution at 77 K dipole rotations of the solvent may not be fully eliminated unlike the situation observed by Wasielewski et al. in the case of less polar methyltetrahydrofuran glass environment.

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