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Photoinduced Electron Transfer in Hydrogen Bonded Donor−Acceptor Systems. Free Energy and Distance Dependence Studies and an Analysis of the Role of Diffusion

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Abstract: The free energy dependence of electron transfer in a few small-molecule donor−acceptor systems having hydrogen-bonding appendages was studied to evaluate the role of diffusion in masking the inverted region in bimolecular PET reactions. A small fraction of the probe molecules associate and this led to the simultaneous observation of unimolecular and diffusion-mediated quenching of the probe fluorescence. Free energy dependence studies showed that the unimolecular electron transfer obeys Marcus behavior and the diffusion-mediated electron transfer obeys Rehm−Weller behavior. The absence of an inverted region in bimolecular PET reactions is thus attributed to diffusion. The results of the free energy dependence studies suggest that distance dependence of electron transfer plays a role in masking the inverted region. To ascertain this aspect we have carried out a study of the distance dependence of electron transfer in the hydrogen-bonded donor−acceptor systems. For a system in the normal region an exponential rate decrease was observed. For a system in the inverted region it was observed that the rate depends very feebly on distance. Thus distance dependence studies did not confirm the prediction of enhanced rates at larger distances in the inverted region.

Introduction

According to the Marcus theory for nonadiabatic electron transfer, the rate of electron transfer is given by[1]

$$k_{\mathrm{et}} = (2\pi/\hbar)H_{\mathrm{el}}^{\ 2}(4\pi\lambda k_{\mathrm{B}}T)^{-1/2}\exp[-(\lambda + \Delta G^{\circ})^2/4\lambda k_{\mathrm{B}}T] \quad (1)$$

where $\hbar$ is the Planck's constant divided by 2π, λ is the reorganization energy, k_{B} is the Boltzmann constant, T is the temperature, and H_{el} is the coupling matrix element. H_{el} is given by

$$H_{\mathrm{el}}^{\ 2} = (H_{\mathrm{el}}^{\ 0})^2\exp[-\beta(d - d_0)] \quad (2)$$

H_{el}^{0} is the coupling element at distance $d = d_0$ and β is the damping factor. Equation 1 envisages three kinetic regimes for electron-transfer reactions depending on the driving force range: (1) a "normal regime" for small driving forces ($\Delta G^{\circ} > -\lambda$), where the process is thermally activated and is favored by an increase in the driving force, (2) an "activationless" regime ($\Delta G^{\circ} = -\lambda$), and (3) an "inverted regime" for strongly exergonic reactions ($\Delta G^{\circ} < -\lambda$), where the process slows down with increasing driving force. The prediction of the inverted region, although controversial for a long time, is now well-established in fixed distance electron-transfer reactions.[2] Observations of the inverted region in bimolecular photoinduced electron transfer (PET) reactions, however, are extremely rare.[3] These reactions follow the Rehm−Weller behavior, i.e., the rate increases with an increase in driving force, reaches a maximum, and stays there, no matter how exergonic the process becomes.[4] The following four reasons have been suggested to explain the nonobservance of the inverted region in bimolecular charge separation reactions:[5] (1) diffusion, (2) formation of products in the excited state, (3) lack of a true homogeneous series of donors and acceptors, and (4) the presence of extra reaction

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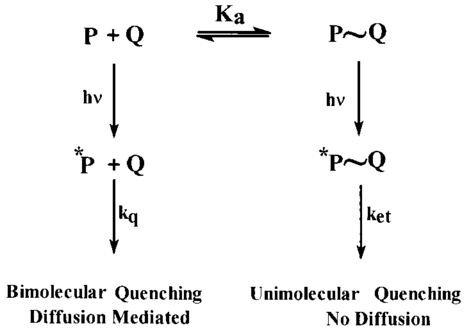
Scheme 1. Scheme Outlining the Strategy for Simultaneous Observation of the Unimolecular and Bimolecular Quenching Rate Constants



channels. It is also suggested that if these problems are circumvented by choosing appropriate reactants, it is possible to observe the inverted region in bimolecular PET reactions.[3a]

We reasoned that the role of diffusion in masking the inverted region can be proved or disproved conclusively by a study of electron transfer in noncovalently bound donor−acceptor systems. If the association constant for such systems is low, rate constants for fixed distance and diffusion-mediated electron transfers involving the same donor−acceptor systems can be obtained simultaneously from the same set of experiments. The strategy is outlined in Scheme 1, where "∼" stands for any noncovalent bond that keeps the probe (P) and quencher (Q) molecules at a fixed distance apart. If K_a is small, a small fraction of the probes and quenchers remain associated and the remaining fraction are free to diffuse in solution. Upon irradiation both the associated and unassociated probe molecules are excited. Fluorescence of the associated probes will be quenched by unimolecular, fixed-distance electron transfer involving the associated quencher, whereas fluorescence of the unassociated probes will be quenched by diffusion-mediated bimolecular electron transfer. The rate constants for both these reactions can be obtained simultaneously by fluorescence lifetime measurements (vide infra). The role of diffusion in masking the inverted region will be proved unequivocally if Marcus behavior is observed for quenching in the associated fraction and Rehm−Weller behavior is observed for quenching in the freely moving segment. If Rehm−Weller behavior is observed for both cases, it can be concluded that diffusion has no role in masking the observation of the inverted region. With this idea in mind, we have carried out a study of free energy dependence of electron transfer in weakly associated hydrogen-bonded systems and our preliminary results were published recently in this journal.[6] We have observed Rehm−Weller behavior for the bimolecular and Marcus behavior for the unimolecular electron transfer reactions and this study confirmed that diffusion is the major reason for not observing the inverted region in bimolecular PET reactions in the moderately large driving force regime.

The simplistic picture presented in Scheme 1 does not take into consideration the presence of **P**∼**P** and **Q**∼**Q** species. Since hydrogen-bonding interactions are nonspecific in nature, these species may also be present in solution. Since the concentration of **P** used is extremely small (10^{-5} M), the concentration of **P**∼**P** species will be extremely low and this does not present any problem in the analysis. Assuming a self-association constant of 100 M^{-1} for **Q**, we obtain a value of 10^{-4} M for the concentration of the **Q**∼**Q** species when the quencher concentration used is 1 mM. Thus about 10% of the quencher will be present as self-associated species and the error in the value of diffusional quenching may be about 10%. This error limit may still be smaller because of the slower diffusion coefficient of the large associated species. In one of the earlier papers in this area, Nocera and co-workers studied the quenching of excited $(bpy)_2Ru(bpy\text{-amidine})^{2+}$ by 3,5-dinitrobenzoic acid.[7n] They have shown that the diffusional bimolecular quenching rate constants in the absence and presence of the hydrogen-bonding interface are similar. This shows that the error due to self-association of the quencher is small.

In the present paper we analyze the role of diffusion in detail. Diffusion can mask the inverted region in two ways: (1) by limiting the rate constant and (2) by enhancing the rate constant at distances greater than contact distance in the inverted region (vide infra). Free energy dependence studies suggest that diffusional electron transfer in the inverted region may have higher rates at larger distances. To throw some light into this aspect, we have carried out a study of distance dependence of electron transfer in hydrogen-bonded systems. We have studied the distance dependence in systems which fall in the normal as well as in the inverted regions. The results show very different distance dependence for electron-transfer reactions in the normal and inverted regions.

Experimental Section

Methods. The absorption spectra were recorded on a Shimadzu UV 2100 or a GBC double-beam UV−vis spectrometer. Fluorescence spectra were recorded on a SPEX Fluorolog F112X spectrofluorimeter. Fluorescence lifetimes were determined with an Edinburgh Instruments FL900CD single-photon counting system and the data were analyzed by Edinburgh software. For the fluorescence measurements probe concentrations were 1×10^{-5} M and quencher concentrations were in the range of (1 to 4) $\times 10^{-3}$ M. Proton NMR binding studies were carried out with a 300 MHz Brüker Avance DPX spectrometer. Cyclic voltammograms were recorded with a BAS CV50W voltammetric analyzer. Solutions of the aromatic compounds (1×10^{-3} M) in acetonitrile containing 0.1 M tetra-*n*-butylammonium tetrafluoroborate as supporting electrolyte were thoroughly deaerated before use. A glassy carbon electrode was used as the working electrode and a platinum wire was used as the counter electrode.

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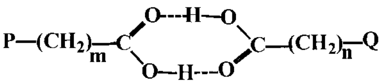
Scheme 2. Structure of the Hydrogen-Bonded Complex



Materials. All the probes and quencher molecules used for this study were prepared by known procedures. These were thoroughly purified and dried before use. $CDCl_3$ used for the NMR experiments was dried over molecular sieves. The dichloromethane, chloroform, and toluene used for fluorescence lifetime measurements were rigorously dried and deaerated before use. Spectroscopic grade acetonitrile was used for the cyclic voltammetric studies.

Results and Discussion

Study of photoinduced electron-transfer reactions in noncovalently bound donor−acceptor systems, particularly hydrogen-bonded donor−acceptor systems, is an area of active current interest.[7] For our studies we have selected donors and acceptors that can be assembled by two-point hydrogen-bonding interactions involving carboxylic acid groups as shown in Scheme 2, where P is the probe and Q is the quencher and $m = n = 1$. The length of the acetic acid dimer is 6.90 Å.[8] In our systems an additional single bond is present on either side of the hydrogen bond interface and hence the edge-to-edge distance between the probe and quencher will be ~9.40 Å. For carboxylic acid groups directly attached to aromatic rings, the association constants reported are in the 350−700 M^{-1} range.[7h,m,n,q] The CH_2 groups present in our system reduce the association constants to the 50−200 M^{-1} range in dichloromethane solution.[6] These CH_2 groups also serve to isolate the chromophores of P and Q from the carboxylic acid bridge.

The structures of the probes and quenchers used in the study are shown in Chart 1. The probe molecules used, namely pyreneacetic acid (**PA**) and anthraceneacetic acid (**AA**), can take part in photoinduced oxidation and reduction reactions and all the quencher molecules are known quenchers of the fluorescence of these molecules by an electron-transfer mechanism.[9]

Decays of the probe molecules were exponential in the absence of quenchers. When a quencher is added, a fraction of the probe is associated and the rest remains free. As mentioned earlier both unimolecular and bimolecular quenching pathways exist and this results in a biexponential decay of the probe that can be expressed by eq 3.

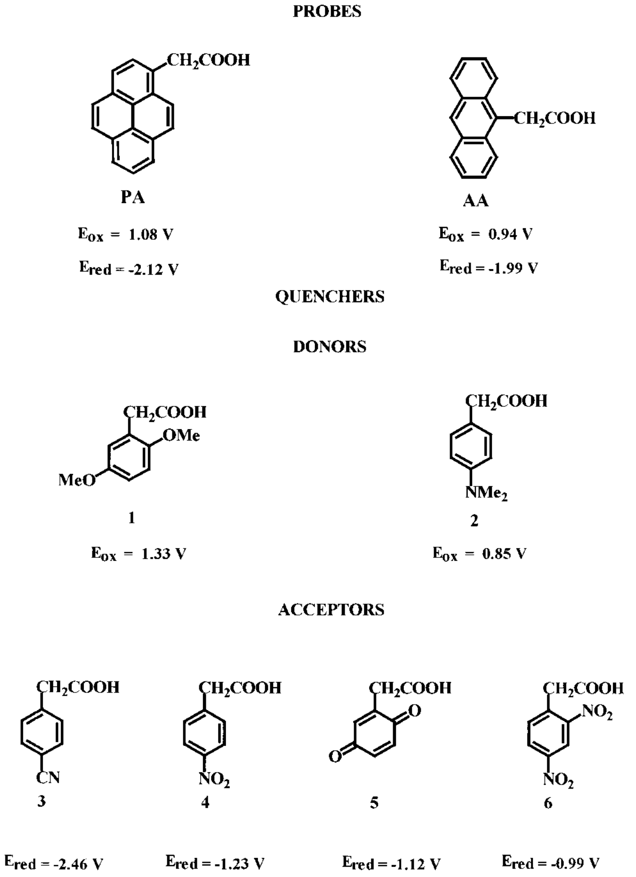
$$I_{(t)} = \chi_{(P-Q)} \exp(-t/\tau_1) + \chi_{(P)} \exp(-t/\tau_2) \qquad (3)$$

Where

$$\tau_1 = (k_0 + k_{et})^{-1} \qquad (4)$$

$$\tau_2 = (k_0 + k_q[Q])^{-1} \qquad (5)$$

Chart 1. Structures of the Probes and Quenchers Used in This Study[a]



[a] The redox potentials are all referenced to SCE.

$\chi_{(P-Q)}$ and $\chi_{(P)}$ are the mole fractions of the associated and unassociated probe molecules, respectively, k_0 ($=1/\tau_0$) is the intrinsic decay rate of the probe, k_{et} is the unimolecular rate constant of electron transfer within the associated complex, and k_q is the bimolecular quenching rate constant for the unassociated probe molecules.[10] According to eqs 3−5, the short lifetime component (τ_1) is independent of the quencher concentration and the long lifetime component (τ_2) is dependent on quencher concentration. From the short lifetime component, the rate constant for electron transfer within the hydrogen-bonded complex can be calculated by using eq 6.

$$k_{et} = 1/\tau_1 - 1/\tau_0 \qquad (6)$$

The quenching rate constant k_q for the bimolecular process can be obtained from the slope of the Stern−Volmer plot of τ_0/τ_2 vs quencher concentration.

$$\tau_0/\tau_2 = 1 + k_q\tau_0[Q] \qquad (7)$$

With the redox potentials measured in acetonitrile, the free energies of electron transfer $\Delta G°$ can be calculated by using eq 8,[11]

$$\Delta G^\circ = E_{ox} - E_{red} - E_{00} - \frac{e^2}{2}\left(\frac{1}{r_P} + \frac{1}{r_Q}\right)\left(\frac{1}{37} - \frac{1}{\epsilon_s}\right) - \frac{e^2}{\epsilon_s d} \qquad (8)$$

where E_{ox} is the oxidation potential of the donor, E_{red} is the reduction potential of the acceptor, ϵ_s is the dielectric constant of the solvent, r_P and r_Q are the radii of the probe and quencher molecules, respectively, and "d" is the distance separating these partners.

It was observed that probe−quencher association takes place only in less polar solvents such as dichloromethane, chloroform, toluene, etc. In the presence of quenchers, probe decays were biexponential. Analysis of the decay showed that (1) τ_1 is independent of quencher concentration, (2) the relative contribu-

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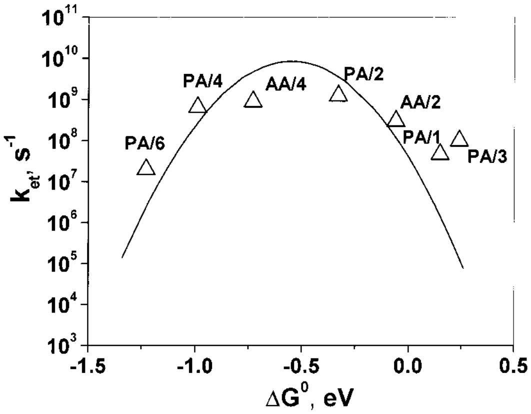

Figure 1. Dependence of electron-transfer rates (k_{et}) in the hydrogen-bonded complex on free energy in chloroform. The solid line is a computed curve with $H_{el} = 5$ cm^{-1} and $\lambda = 0.55$ eV.

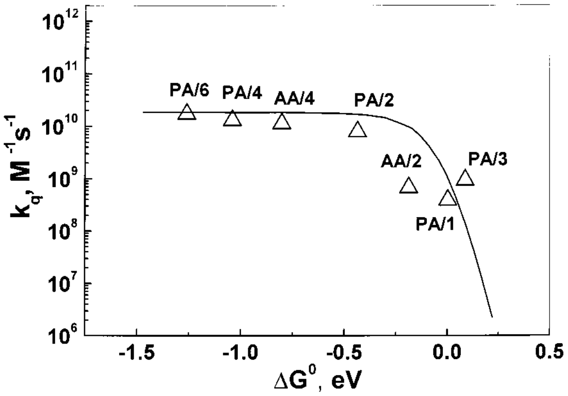

Figure 2. The plot of bimolecular quenching rate constants (k_q) vs $\Delta G°$ in chloroform. The solid line is a fit to the Rehm−Weller equation.

Table 1. Free Energies ($\Delta G°$) and Rate Constants (k_{et} and k_q) for the Donor−Acceptor Systems in Dichloromethane and Chloroform[a]

	dichloromethane			chloroform		
system	$\Delta G°$, eV	k_{et}, 10^7 s^{-1}	k_q, 10^9 M^{-1}s^{-1}	$\Delta G°$, eV	k_{et}, 10^7 s^{-1}	k_q, 10^9 M^{-1}s^{-1}
PA/1	−0.04	6.2	0.04	0.15	4.7	0.32
PA/2	−0.52	89.9	9.29	−0.33	127.0	6.80
PA/3	0.05	1.9	0.21	0.24	10.0	0.78
PA/4	−1.18	39.0	12.80	−0.99	66.0	11.3
PA/5	−1.29	8.9	22.60			
PA/6	−1.42	5.2	12.80	−1.23	2.0	15.0
AA/2	−0.24	43.0	7.36	−0.06	30.0	0.56
AA/4	−0.92	144.0	16.60	−0.73	90.0	9.80

[a] The numbers in column 1 corresponds to the number of the quencher in Chart 1.

tion of τ_1 increases with quencher concentration, and (3) τ_2 decreases with increases in quencher concentration. We have calculated k_{et} and k_q values as mentioned earlier for several of the probe−quencher systems and it is shown that k_{et} follows the Marcus theory and k_q follows Rehm−Weller behavior. An important confirmation of Marcus theory comes from the solvent dependence of the Marcus plot. According to eq 1, the maximum rate occurs when $\Delta G° = -\lambda$. The reorganization energy λ is expected to be smaller in less polar solvents and hence the maximum in the Marcus plot is expected to shift to less negative free energy values in less polar solvents.[1e] This is found to be true in the present case. In dichloromethane λ obtained was 0.7 eV, which is found to shift to 0.55 eV in chloroform. Figure 1 shows a plot of k_{et} vs $\Delta G°$ and Figure 2 shows the plot of k_q vs $\Delta G°$ in chloroform solution for the probe−quencher systems. Table 1 presents the values of k_{et} and k_q in two solvents. From Figures 1 and 2 it is clear that the unimolecular reaction obeys the Marcus equation and bimolecular reaction follows Rehm−Weller behavior.

In the case described here, the only difference between a system which obeys Marcus behavior and one which obeys Rehm−Weller behavior appears to be the free diffusion of the partners in the latter case. This prompted us to suggest that the nonobservance of the inverted region in bimolecular PET reactions is due to diffusion in the moderately large free energy regime. This aspect is analyzed in detail below.

It has been suggested in the literature that diffusion can mask the inverted region in two ways. The first of this is by limiting the rate constant to the diffusion rate. This factor was recognized very early and has been discussed by several authors. For a bimolecular electron-transfer reaction, the quenching rate constant is given by eq 9,

$$\frac{1}{k_q} = \frac{1}{k_{act}} + \frac{1}{k_{dif}} \tag{9}$$

where k_{act} is the rate constant for activated electron transfer.[12] When k_{act} is large, $1/k_{act}$ can be neglected and hence $k_q \approx k_{dif}$, which leads to limiting of the rate constants by diffusion. Using these arguments, it can be shown that the inverted region will be masked in the moderately large driving force regime because of diffusion, but should be observable in bimolecular PET reactions at $\Delta G° < -2$ eV. The original Rehm−Weller data did not, however, show any sign of the inverted region even at $\Delta G° = -2.6$ eV.[4b]

Rau and co-workers have suggested that the inverted region is not observed in bimolecular PET reactions because of the distance dependence of electron-transfer rates brought about by diffusion.[13] This can be explained as follows. In the case of freely diffusing molecules, the distance between the probe and quencher is variable. In Marcus theory, the maximum rate occurs when $\Delta G° = -\lambda$. For a probe−quencher system in the normal region, the maximum rate occurs at contact distance. For a system in the inverted region, $\Delta G° < -\lambda$ at contact distance. λ, however, is distance dependent and increases with distance (vide infra). Hence at some distance larger than contact distance ($d > d_0$), $\Delta G° = -\lambda$ can be achieved and the rate will be diffusion controlled at this distance. We examine this suggestion below.

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(10) One of the reviewers has pointed out that k_{diss}, the rate constant for the dissociation process $P^*{-}Q \rightarrow P^* + Q$, should also be taken into account. In that case eq 4 has to be modified as $\tau_1 = (k_o + k_{et} + k_{diss})^{-1}$. The importance of k_{diss} has been discussed by Gould and Farid in their analysis of contact and solvent separated ion pair decay kinetics (see refs 2i−k). For benzoic acid in chloroform solution, the association (k_{ass}) and dissociation rate constants were determined by Borucki, (Borucki, L. *Ber. Bunsen-Ges. Phys. Chem.* **1967**, *71*, 504). At 20 °C, values of $k_{ass} = 4.7 \times 10^9$ M^{-1} s^{-1}, $k_{diss} = 7.4 \times 10^6$ s^{-1}, and $K_a = 635$ M^{-1} were obtained. For the arylacetic acids used in this study, K_a values were about 6-fold smaller. Assuming the same k_{ass} values, an upper limit of 4.3×10^7 s^{-1} can be calculated for k_{diss} in these cases. Thus, for the **PA/1**, **PA/3**, and **PA/6** systems where k_{et} values are low (Table 1), contribution from k_{diss} may be significant. Hence, for these systems the actual values of k_{et} may be slightly lower than those presented in Table 1.

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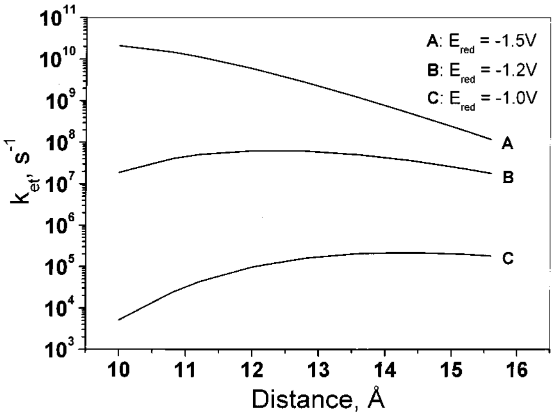

Figure 3. Calculated rate vs distance curves in toluene for (A) normal and (B and C) inverted regions. Values of $H_{el}{}^0 = 60$ cm^{-1}, $\beta = 1.1$ Å^{-1}, $\lambda_i = 0.2$ eV, $r_P = 6$ Å, $r_Q = 4$ Å, and $E_{ox} = 1.08$ V were used.

The reorganization energy λ is the sum of the inner shell (λ_{in}) and outer shell (λ_{out}) reorganization energies. λ_{in} is solvent and distance independent whereas λ_{out} is dependent on these factors and is given by eq 10,[14]

$$\lambda_{out} = \Delta e^2\left(\frac{1}{2r_P} + \frac{1}{2r_Q} - \frac{1}{d}\right)\left(\frac{1}{\epsilon_{op}} - \frac{1}{\epsilon_s}\right) \tag{10}$$

where ϵ_{op} is the optical dielectric constants of the solvent. According to this equation, λ_{out} increases with distance in polar solvents and is independent of distance in nonpolar solvents. An opposite trend is expected for $\Delta G°$, which according to eq 8 is also distance dependent. $\Delta G°$ increases with distance in nonpolar solvents and is relatively independent of distance in polar solvents. The opposing effects of separation distance "*d*" on H_{el} and λ (in polar solvents) or $\Delta G°$ (in nonpolar solvents) prompted several authors to predict that for systems in the inverted region the rate at larger separations is several orders of magnitude larger than that in the normal region and that the rate maximum in the inverted region occurs at $d > d_0$.[15] Following the treatments given by these authors, we have calculated the rate vs distance curves for our type of systems in a nonpolar solvent such as toluene and this is shown in Figure 3. Values of $H_{el}{}^0 = 60$ cm^{-1}, $\beta = 1.1$ Å^{-1}, $\lambda_{in} = 0.2$ eV, $r_P = 6$ Å, and $r_Q = 4$ Å were used in the calculation (for the above values of $H_{el}{}^0$, β, and $d_0 = 7$ Å, $H_{el} \sim 5$ cm^{-1}, which is the value obtained from the fit to Figure 1). It can be seen from Figure 3 that for a system in the normal region (curve A) the rate maximum occurs at short distance, but for systems in the inverted region (curves B and C), the rate maximum can be expected at $d > 10$ Å.

To the best of our knowledge, the prediction that for systems in the inverted region the rate maximum occurs at larger distances has not been experimentally verified. Our experiments provide some indirect evidence for the above prediction and suggest that this factor also may contribute to the masking of the inverted region in bimolecular PET reactions. The first of such evidence comes from an analysis of the data presented in Table 1 and Figures 1 and 2.

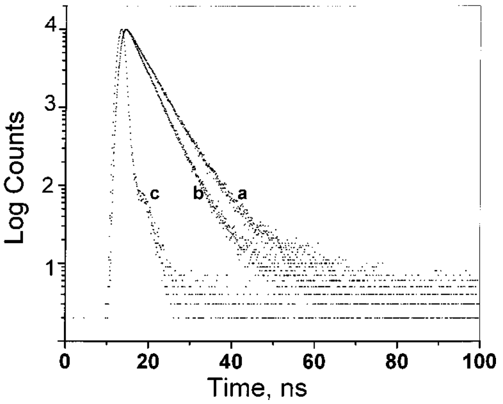

Figure 4. Fluorescence decay profiles of AA in the (a) absence and (b) presence of **6** (4×10^{-3} M); (c) is the lamp profile.

Probe/quencher systems **PA/4**, **PA/5** and **PA/6** fall in the inverted region. When these systems were allowed to undergo electron transfer at a fixed distance, the rates were low (see Figure 1 and Table 1). When the same probe quencher systems were allowed to diffuse freely, quenching occurred with diffusion controlled rates (see Figure 2 and Table 1). This result can be interpreted to mean that at an edge−edge distance of 9.4 Å quenching is slow, but at some other distance quenching occurred with a higher rate. A similar inference is obtained from a study of electron transfer in the **AA/6** system.

Electron transfer in the AA/6 system: The **AA/6** system falls in the inverted region. Figure 4 shows the fluorescence decay profiles of **AA** (1×10^{-5} M) in the absence and presence of **6** (4×10^{-3} M). Both the decays fit well into single-exponential functions. The short lifetime component which characterizes electron transfer in the hydrogen-bonded system is absent in the decay profile at all quencher concentrations studied. From a plot of τ_{0}/τ vs [**6**], k_q was calculated and the value obtained was 1.6×10^{10} M^{-1} s^{-1}. This shows that quenching in the freely diffusing molecules takes place with diffusion-controlled rates.

The fact that biexponential decay is absent in the **AA/6** system suggests two possibilities: (1) hydrogen-bonded complex is not formed in this case and (2) hydrogen-bonded complex is formed but the rate of electron transfer within the complex (k_{et}) is lower than k_0 and hence is nonobservable. NMR studies support the latter suggestion. For **AA** the carboxyl proton appeared as a broad singlet around 11 ppm in CDCl$_3$. Upon addition of small amounts of **6**, this peak shows an upfield shift. Although we could not determine the association constant due to the very poor solubility of both **AA** and **6** in this solvent, NMR studies suggest that **AA** and **6** indeed associate in solution. Thus, if biexponential decay is not observed, it must indeed be due to the inefficiency of the electron-transfer process within the hydrogen-bonded complex compared to the intrinsic decay rate of **AA**. This result can be interpreted to mean that at an edge−edge distance of 9.4 Å, the PET process is not at all efficient, but at some other distances PET occurred with diffusion-controlled rates.

Figures 1, 2, and 4 suggest that diffusional electron transfer in the inverted region occurs with higher rates at some distance other than the hydrogen-bonding distance of 9.4 Å. The data as such do not say whether this distance is lower or higher than 9.4 Å. Taking the clue from Figure 3 (B and C) we suggest that this distance may be greater than 9.4 Å. To seek some support for this, we have carried out a study of distance dependence of electron transfer in these systems.

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Distance dependence of electron transfer in hydrogen-bonded donor−acceptor systems: In this section we report some results of our studies on the distance dependence of electron-transfer reactions in hydrogen-bonded donor−acceptor systems. We are aware that the systems we are dealing with are flexible and several conformations of the systems can be present in the medium. Nevertheless, we have undertaken a distance-dependence study for three reasons: (1) distance dependence of electron transfer in hydrogen-bonded systems involving small-molecule donor−acceptor systems has not been studied, (2) these systems provide an opportunity to study the distance dependence of electron transfer in the inverted region by fluorescence methods, and (3) it may throw some light into our discussion regarding the masking of the inverted region due to distance dependence of the rate constants in this free energy regime.

Electron-transfer reactions involving donors and acceptors held together by hydrogen-bonding interactions are common in biological systems. The “pathway model” for biological electron transport is based on the assumption that covalent bonds, hydrogen bonds, ionic contacts, van der Waals contacts, etc. modulate the electronic coupling between the donor and acceptor.[16] The distance between the donor and acceptor is obviously very important. Thus a study of the distance dependence of electron transfer in such systems is also important. In the present work, we have varied the distance between the probe and quencher by changing the values of “*m*” and “*n*” for the hydrogen-bonded complex shown in Scheme 2. For every CH_2 group the distance is assumed to increase by 1.27 Å.[17] Although the methylene chain is flexible, for small values of *m* and *n*, we expect the complex to assume near-linear configurations.

There exist several outstanding studies on the distance dependence of electron-transfer reactions.[18] Most of these studies, however, pertain to the normal region. Despite its great importance and significance, especially in the design of supramolecular devices based on PET, distance dependence of electron transfer in the inverted region has not been studied in detail.[17] This, we believe, is attributed to the fact that there is a general absence of systems in the inverted region that can be studied by fluorescence quenching methods. The inverted region is observed only rarely in bimolecular reactions. Even for those intramolecular reactions where the inverted region is observed, the bell-shaped function actually consists of two distinct parts: (1) a photoinduced forward process, which is restricted to the normal region and (2) the thermal back electron transfer, which is restricted to the inverted region.[2] Thus the inverted region is generally not amenable to studies by fluorescence techniques. In the hydrogen-bonded systems at hand, **PA/4**, **PA/5**, and **PA/6** belong to the inverted region and can be studied by fluorescence lifetime methods. This is a major reason for undertaking the distance-dependence study.

Table 2. Relevant Data for the Probes and Quenchers Used in the Distance Dependence Study

chromophore	*m*/*n*	τ_f,[a] ns	E_{ox}, V	E_{red}, V
PA	1	100 ± 10 (150 ± 5)	1.08	−2.12
	2	90 ± 10 (130 ± 5)	1.10	−2.18
	3	85 ± 10 (130 ± 5)	1.12	−2.13
2	1		0.85	
	2		0.98	
4	1			−1.23
	2			−1.17
	3			−1.17

[a] τ_f values are in dichloromethane and the values in parentheses are those obtained in toluene.

We have studied the distance dependence of the **PA/2** system, which falls in the normal region, and that of the **PA/4** system, which falls in the inverted region, by fluorescence lifetime measurements discussed earlier. These studies, however, are complicated by a few experimental limitations. The CH_2 groups make the system flexible and reduce the association constant. As a result, the biexponential decay attributed to association is not observed for $(m + n) > 5$ in dichloromethane solution. Better association is observed in toluene where association is observed up to $(m + n) = 6$. In this solvent, however, the **PA/2** system exhibited excimer emission even at low concentrations of **2**, which complicated the analysis of the decay functions. Thus the **PA/2** system was studied for $(m + n) \leq 5$ in dichloromethane. For the **PA/4** system, $(m + n) \leq 5$ were studied in both solvents, but $(m + n) = 6$ could only be studied in toluene. The trend observed in both solvents, however, was the same. The redox potentials of the compounds did not show appreciable change with additional CH_2 groups. So for the sake of simplicity, the redox potentials of the parent compounds ($m = n = 1$) were used for all systems in the calculations. Relevant data for the probes and quenchers used are summarized in Table 2.

Results of the distance-dependence studies are given in Table 3 and plotted in Figure 5. For the **PA/2** system, which falls in the normal region, the rate falls from 9.0×10^8 to 8.3×10^7 s^{-1}, when $(m + n)$ changes from 2 to 5. We have tried to fit the data using eqs 1, 8, and 10 and the fit obtained with $H_{el}{}^0 = 30$ cm^{-1} and $\beta = 0.7$ $Å^{-1}$ is also shown in Figure 5. (Better fit to the data can be obtained, but this will have very low β values and hence these are not presented here.) Figure 5 shows the results of the distance-dependence study for the **PA/4** system, which falls in the inverted region. Although the data show a small initial increase followed by a decrease (Table 3) it may perhaps be more appropriate to suggest that the rate depended very feebly on distance in this system. Thus our conclusion from the distance-dependence studies is the following: (1) distance dependence of electron transfer in the normal region in hydrogen-bonded systems is similar to that in covalently linked systems, (2) systems in the normal and inverted regions exhibit

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Table 3. Kinetic Data for Electron Transfer in the PA/2 and PA/4 System[a]

chromophore	$m + n$	k_{et}, s^{-1}
PA/2	2	9.0×10^{8}
	3	5.3×10^{8}
	4	1.7×10^{8}
	5	8.3×10^{7}
PA/4	2	3.9×10^{8}
	3	4.4×10^{8}
	4	3.4×10^{8}
	5	3.2×10^{8}
	6	3.0×10^{8}

[a] **PA/2** is carried out in dichloromethane and **PA/4** is carried out in toluene.

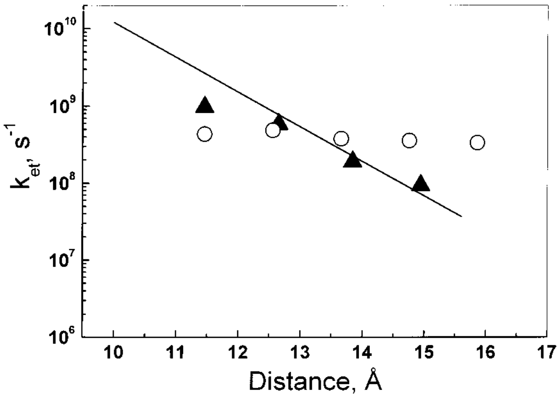

Figure 5. Distance dependence of rate constants (k_{et}) for (▲) the **PA/2** system in dichloromethane and (○) for the **PA/4** system in toluene. The solid line is a fit using $H_{el}^0 = 30$ cm^{-1}, $\beta = 0.7$ Å^{-1}, $\lambda_i = 0.2$ eV, $r_P = 6$ Å, and $r_Q = 4$ Å for the **PA/2** system.

very different behaviors, and (3) rates in the inverted region failed to show a large increase in rate at larger separations. It is to be noted here that in an earlier study in covalently linked flexible systems, Mallouk and co-workers also did not observe the predicted rate increase at larger separations in the inverted region.[17]

Figures 1, 2, and 4 suggest enhanced diffusional electron transfer rates at larger distances in the inverted region. Distance-dependence studies in the inverted region in hydrogen-bonded systems, however, did not show this increase in rates. Perhaps more rigid systems will show large enhancements. In any event this factor may not contribute significantly toward the masking of the inverted region in diffusional electron-transfer reactions in the deep inverted region. In the familiar two-sphere model on which eq 10 is based, λ_{out} becomes independent of separation distance at large d. For two identical spheres, λ_{out} changes only by a factor of 2 when distance changes from contact distance to infinite separation. Extrapolation of the curve in Figure 1 yields $k_{et} < 10^4$ s^{-1} when $\Delta G° = -1.5$ eV in chloroform solution. In this situation, the predicted enhancement in rate will be much smaller than the diffusion-controlled rates. Thus masking of the inverted region in bimolecular PET reactions in the deep inverted region is most probably due to other factors such as formation of products in the excited states or presence of other reaction channels.

Conclusions

We have studied the free energy and distance dependence of electron transfer in a few donor−acceptor systems assembled through hydrogen-bonding interactions. Our study shows that when diffusion is prevented Marcus behavior is observed and when diffusion is allowed Rehm−Weller behavior is observed. Thus the nonobservance of the inverted region in PET reactions is attributed to diffusion. Results of the free energy dependence studies suggested that the distance dependence of electron transfer plays a role in masking the inverted region. Studies on the dependence of rate on distance in hydrogen-bonded systems reveal different behaviors for the normal and inverted regions. In the normal region the rate shows an exponential decrease with distance, whereas rates are relatively distance independent in the inverted region. Thus distance-dependence studies did not confirm the prediction of enhanced rates at larger distances in the inverted region. In any case, this factor may not contribute significantly to the masking of the inverted region in bimolecular PET reactions in the large driving force regime.

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