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Photoinduced Electron Transfer in Hydrogen Bonded Donor−Acceptor Systems. Study of the Dependence of Rate on Free Energy and Simultaneous Observation of the Marcus and Rehm−Weller Behaviors†

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Abstract: Hydrogen bonding networks play a very important role in biological electron-transfer processes. The free energy dependence of electron transfer in a few small-molecule donor−acceptor systems, having hydrogen bonding appendages, were studied by fluorescence lifetime quenching measurements. Two types of electron transfers take place in these systems. A fraction of the molecules associates and exists as hydrogen bonded species and electron transfer in this segment is unimolecular. A major fraction of the donors and acceptors freely diffuse in the medium and electron transfer is bimolecular in this segment. Free energy dependence studies showed that the former obeys the Marcus equation and the latter follows the Rehm−Weller behavior. The absence of the inverted region in bimolecular charge separation reactions is thus attributed to diffusion in the moderately large driving force regime.

Introduction

Study of photoinduced electron-transfer reactions (PET), wherein the donor (D) and acceptor (A) are assembled by hydrogen bonding interactions, has attracted considerable interest in recent years.[1] These investigations have clearly established that hydrogen bonds can act as an effective conduit for the transfer of electrons from D to A. These studies are extremely important because of their direct relevance to the study of electron transfer in biological systems.[2] For example, in the case of protein electron transfer, electronic coupling through hydrogen bonds is extremely important due to the prevalence of hydrogen bond networks in proteins. Because of the directionality of hydrogen bonds it is possible to know the separation and relative orientation of the components in hydrogen bonded systems.[3] Hence hydrogen bonded D···A systems provide an attractive alternative to covalently linked D−A systems for the study of electron-transfer reactions. Although a large number of reports dealing with studies of electron-transfer reactions in hydrogen bonded systems are available, systematic studies dealing with the effect of factors such as driving force, distance, etc. on the rate of electron transfer in such systems are absent in the literature. In this paper we report the first systematic study of the dependence of the rate of electron transfer (k_{et}) on free energy ($\Delta G°$) in hydrogen bonded donor−acceptor systems.

According to Marcus theory for nonadiabatic electron transfer for weakly interacting donor−acceptor systems, the rate constant for electron transfer is given by eq 1,[4] where $\hbar$ is the Planck's

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

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. Equation 1 envisages three typical kinetic regimes for electron-transfer reactions depending on the driving force range: (i) a "normal" regime for small driving forces ($\Delta G° > -\lambda$) where the process is thermally activated

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[1] (a) Piotrowiak, P. *Chem. Soc. Rev.* **1999**, *28*, 143. (b) Ward, M. D. *Chem. Soc. Rev.* **1997**, *26*, 365. (c) Sessler, J. L.; Wang, B.; Springs, S. L.; Brown, C. T. In *Comprehensive Supramolecular Chemistry*; Atwood, J. L., Davies, J. E. D., MacNicol, D. D., Vogtle, F., Murakami, Y., Eds.; Pergamon: Oxford, 1996; Vol. 4, p 311. (d) Williamson, D. A.; Bowler, B. E. *J. Am. Chem. Soc.* **1998**, *120*, 10902. (e) Sessler, J. L.; Brown, C. T.; O'Connor, D.; Springs, S. L.; Wang, R.; Sathiosatham, M.; Hirose, T. *J. Org. Chem.* **1998**, *63*, 7370. (f) Osuka, A.; Yoneshima, R.; Shiratori, H.; Okada, H.; Taniguchi, S.; Mataga, N. *Chem. Commun.* **1998**, 1567. (g) Deng, Y.; Roberts, J. A.; Peng, S.-M.; Chang, C. K.; Nocera, D. G. *Angew. Chem., Int. Ed. Engl.* **1997**, *36*, 2124. (h) Kirby, J. P.; Roberts, J. A.; Nocera, D. G. *J. Am. Chem. Soc.* **1997**, *119*, 9230. (i) Hayashi, T.; Miyahara, T.; Kumazaki, S.; Ogoshi, H.; Yoshihara, K. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1964. (j) Cukier, R. I.; *J. Phys. Chem.* **1996**, *100*, 15428. (k) Arimura, T.; Brown, C. T.; Springs, S. L.; Sessler, J. L. *Chem. Commun.* **1996**, 2293. (l) Kirby, J. P.; van Dantzig, N. A.; Chang, C. K.; Nocera, D. G. *Tetrahedron Lett.* **1995**, *36*, 3477. (m) de Rege P. J. F.; Williams, S. A.; Therien, M. J. *Science* **1995**, *269*, 1409. (n) Roberts, J. A.; Kirby, J. P.; Nocera, D. G. *J. Am. Chem. Soc.* **1995**, *117*, 8051. (o) Osuka, A.; Shiratori, H.; Yoneshima, R.; Okada, T.; Taniguchi, S.; Mataga, N. *Chem. Lett.* **1995**, 913. (p) Sessler, J. L.; Wang, B.; Harriman, A. *J. Am. Chem. Soc.* **1993**, *115*, 10418. (q) Turro, C.; Chang, C. K.; Leroi, G. E.; Cukier, R. I.; Nocera, D. G. *J. Am. Chem. Soc.* **1992**, *114*, 4013. (r) Harriman, A.; Kubo, Y.; Sessler, J. L. *J. Am. Chem. Soc.* **1992**, *114*, 388.

[2] (a) Bowler, B. E.; Meade, T. J.; Mayo, S. L.; Richards, J. H.; Gray, H. B. *J. Am. Chem. Soc.* **1989**, *111*, 8757. (b) Meade, T. J.; Gray, H. B.; Winkler, J. R. *J. Am. Chem. Soc.* **1989**, *111*, 4353. (c) Therien, M. J.; Selman, M.; Gray, H. B.; Chang, I.-J.; Winkler, J. R. *J. Am. Chem. Soc.* **1990**, *112*, 2420. (d) Winkler, J. R.; Gray, H. B. *Chem. Rev.* **1992**, *92*, 369. (e) Onuchic, J. N.; Beratan, D. N. *J. Chem. Phys.* **1990**, *92*, 722. (f) Beratan, D. N.; Onuchic, J. N. *Adv. Chem. Ser.* **1991**, *228*, 71. (g) Beratan, D. N.; Betts, J. N.; Onuchic, J. N. *Science*, **1991**, *252*, 1285. (h) Betts, J. N.; Beratan, D. N.; Onuchic, J. N. *J. Am. Chem. Soc.* **1992**, *114*, 4043. (i) Beratan, D. N.; Betts, J. N.; Onuchic, J. N. *J. Phys. Chem.* **1992**, *96*, 2852.

[3] Philip, D.; Stoddart, J. F. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1154.

[4] Marcus, R. A.; Sutin, M. *Biochim. Biophys. Acta* **1985**, *811*, 266.

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and is favored by an increase in the driving force; (ii) an "activationless" regime ($\Delta G^\circ = -\lambda$); and (iii) an "inverted" regime for strongly exergonic reactions ($\Delta G^\circ < -\lambda$) where the process slows down with increasing driving force. Although the inverted region is well established in thermal charge shift and charge recombination reactions,[5] it is almost nonexistent for bimolecular photoinduced charge separation reactions except for a couple of recent reports.[6] Bimolecular charge separation reactions normally obey the Rehm–Weller behavior, i.e., the plot of the rate constant versus free energy rises rapidly in the normal region and then reaches the diffusion limit and stays there no matter how exergonic the process becomes.[7] Several reasons have been suggested for not observing the inverted region in charge separation reactions.[8] These include the following: (1) limiting of the rate constant by diffusion, (2) formation of products in the excited state, (3) presence of extra reaction channels other than electron transfer, and (4) lack of a true homogeneous series of donors and acceptors. In a recent report, Tachiya and Murata made a distinction between Marcus and Rehm–Weller type electron transfers.[9] The Marcus equation gives the first-order rate constant for a donor–acceptor pair at a fixed separation, while the Rehm–Weller behavior is concerned with a second-order rate constant. They have calculated the second-order diffusion mediated rate constant by using a recently developed theory for diffusion mediated reactions which takes into account the donor–acceptor distance dependence of the first-order rate constant. The theory they developed also predicted the inverted region, but at very large driving forces ($\Delta G^\circ < -2$ eV).

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 hydrogen bonded D···A systems for the following reason. The association constant in hydrogen bonded systems is usually low. This means that only a small fraction of the donors and acceptors remains associated while the remaining molecules are free to diffuse in solution. Upon excitation, electron transfer takes place in the associated as well as free forms, and the rate constants of these reactions can be determined by fluorescence lifetime quenching studies. Thus, a direct comparison of electron-transfer rates in associated (fixed distance) and unassociated (diffusion mediated) forms of the same donor–acceptor pair is possible in these systems. In the work described here, we have assembled donors and acceptors through two-point hydrogen bonding interactions involving carboxylic acid groups. Study of electron transfer in a few systems associated through carboxylic acid groups is already available in the literature.[1h,m,n,q] The association constants were determined by ^{1}H NMR or fluorescence studies. Electron transfers in these donor–acceptor systems were studied by fluorescence lifetime quenching measurements. By systematically varying the redox potentials of the quencher molecules we have studied the dependence of the rate of electron transfer on driving force in these systems.

Experimental Section

Methods. Proton NMR binding studies were carried out using a 300 MHz Bruker Avance DPX spectrometer. 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 F 112X spectrofluorimeter. Fluorescence lifetimes were determined using 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 $(1-4) \times 10^{-3}$ M. Cyclic voltammetric studies were carried out by using 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.

Materials. All the probes and quencher molecules used for the 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 used for the fluorescence lifetime measurements was rigorously dried and deaerated before use. Spectroscopic grade acetonitrile was used for the cyclic voltammetric studies.

Results and Discussion

In our study the probes and quenchers are aromatic molecules with acetic acid moieties attached to them. Although the CH_2 group of the acetic acid moiety imparts some flexibility to the system, it serves to isolate the carboxylic acid moiety from the chromophore unit. Thus the carboxylic acid group is not part of the chromophore and it serves only to assemble the donor and acceptor through a hydrogen bonding interface. Pyreneacetic acid (**PA**) and anthraceneacetic acid (**AA**) were used as fluorescing probe molecules in this study (see Chart 1). Pyrene and anthracene derivatives were selected for this purpose because these polycyclic hydrocarbons are known to undergo oxidative as well as reductive photoelectron-transfer reactions.[10] Thus they can act as excited-state electron acceptors in the presence of donors such as amines and alkoxyaromatics. They can also function as electron donors in the presence of acceptors such as cyanoaromatics, nitroaromatics, or quinones. Thus by

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(5) (a) Miller, J. R.; Beitz, J. V. *J. Chem. Phys.* **1981**, *74*, 6476. (b) Miller, J. R.; Calcaterra, L. T.; Closs, G. L. *J. Am. Chem. Soc.* **1984**, *106*, 3047. (c) Closs, G. L.; Miller, J. R. *Science* **1988**, *240*, 440. (d) Wasielewski, M. R.; Niemczyk, M. P.; Svec, W. A.; Pewitt, E. B. *J. Am. Chem. Soc.* **1985**, *107*, 1080. (e) Wasielewski, M. R.; Johnson, D. G.; Svec, W. A. In *Supramolecular Photochemistry*; Balzani, V., Ed.; D. Riedel: Amsterdam, 1987; p 255. (f) Harrison, R. J.; Pearce, B.; Beddard, G. S.; Cowan, J. A.; Sanders, J. K. M. *Chem. Phys.* **1987**, *116*, 429. (g) Mataga, N.; Ashai, T.; Kanda, Y.; Okada, T.; Kakitani, T. *Chem. Phys.* **1988**, *127*, 249. (h) Segawa, H.; Takehara, C.; Honda, K.; Schimidzu, T.; Ashai, T.; Mataga, N. *J. Phys. Chem.* **1992**, *96*, 503. (i) Gould, I. R.; Farid, S. *J. Am. Chem. Soc.* **1988**, *110*, 7883. (j) Gould, I. R.; Ege, D.; Moser, J. E.; Farid, S. *J. Am. Chem. Soc.* **1990**, *112*, 4290. (k) Gould, I. R.; Farid, S. *Acc. Chem. Res.* **1996**, *29*, 522. (l) Fox, L. S.; Kozik, M.; Winkler, J. R.; Gray, H. B. *Science* **1990**, *247*, 1069. (m) McCleskey, T. M.; Winkler, J. R.; Gray, H. B. *J. Am. Chem. Soc.* **1992**, *114*, 6935. (n) Zou, C.; Miers, J. B.; Ballew, R. M.; Dlott, D. D.; Schuster, G. B. *J. Am. Chem. Soc.* **1991**, *113*, 7823.

(6) (a) Turro, C.; Zaleski, J. M.; Karabatsos, Y. M.; Nocera, D. G. *J. Am. Chem. Soc.* **1996**, *118*, 6060. (b) Thanasekaran, P.; Rajendran, T.; Rajagopal, S.; Srinivasan, C.; Ramaraj, R.; Ramamurthy, P.; Venkatachalapathy, B. *J. Phys. Chem. A* **1997**, *101*, 8195.

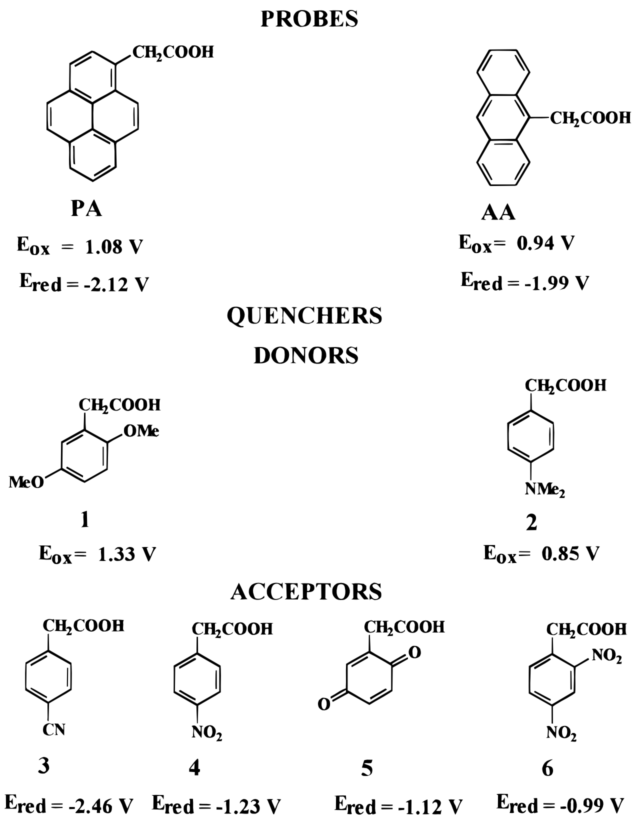
(7) (a) Rehm, D.; Weller, A. *Ber. Bunsen-Ges. Phys. Chem.* **1969**, *73*, 834. (b) Rehm, D.; Weller, A. *Isr. J. Chem.* **1970**, *8*, 259. (c) Bock, C. R.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1975**, *97*, 2909. (d) Ballardini, R.; Varani, G.; Indelli, M. T.; Scandola, F.; Balzani, V. *J. Am. Chem. Soc.* **1978**, *100*, 7219. (e) Scheerer, R.; Grätzel, M. *J. Am. Chem. Soc.* **1977**, *99*, 867. (f) Nagle, J. K.; Dressick, W. J.; Meyer, T. J. *J. Am. Chem. Soc.* **1979**, *101*, 3993. (g) Indelli, M. T.; Ballardini, R.; Scandola, F. *J. Phys. Chem.* **1984**, *88*, 2547.

(8) (a) Suppan, P. *Top. Curr. Chem.* **1992**, *163*, 95. (b) Hug, G. L.; Marciniak, B. *J. Phys. Chem.* **1995**, *99*, 1478. (c) Efrima, S.; Bixon, M. *Chem. Phys. Lett.* **1974**, *25*, 34. (d) Weller, A.; Zachariasse, K. *Chem. Phys. Lett.* **1971**, *10*, 590. (e) Joussot-Dubien, J.; Albrecht, A. C.; Gerischer, H.; Knox, R. S.; Marcus, R. A.; Schott, M.; Weller, A.; Willig, F. In *Light Induced Charge Separation in Biology and Chemistry*; Gerischer, H., Katz, J. J., Eds.; Verlag Chemie: New York, 1979; p 129.

(9) Tachiya, M.; Murata, S. *J. Phys. Chem.* **1992**, *96*, 8441.

(10) (a) Julliard, M. In *Photoinduced Electron Transfer, Part B*; Fox, M. A., Channon, M., Eds.; Elsevier: New York, 1998; p 216 and references therein. (b) Murakami, H.; Hohsaka, T.; Ashizuka, Y.; Sisido, M. *J. Am. Chem. Soc.* **1998**, *120*, 7520. (c) Zanini, G. P.; Montejano, H. A.; Previtall, C. M. *J. Chem. Soc., Faraday Trans.* **1995**, *91*, 1197. (d) Mataga, N. *Pure Appl. Chem.* **1984**, *56*, 1255. (e) Aoki, I.; Sakaki, S.; Shinkai, S. *J. Chem. Soc., Chem. Commun.* **1992**, 730.

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



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

using these probe molecules it was possible to study electron transfer over a wide range of $\Delta G°$ values.

Figure 1 shows the absorption and emission spectra of **PA** in dichloromethane solution. The absorption maximum was 344 nm and the emission maximum was 375 nm. The singlet state energy ($E_{0,0}$) calculated from the absorption spectrum was 3.6 eV. The fluorescence decay of **PA** was exponential with a lifetime (τ_0) of 100 ± 10 ns. For **AA**, the absorption maximum was 387 nm and the emission maximum was 412 nm. The $E_{0,0}$ and τ_0 values were 3.2 eV and 5.0 ± 0.2 ns, respectively. It is clear from these data that the presence of the carboxyl group affects the photophysical parameters of pyrene or anthracene chromophore only marginally.

The quencher molecules we have used are also shown in Chart 1. The absorption spectra and redox potentials of the parent aromatics are relatively unaffected by the presence of the acetic acid moieties in these cases also. All these aromatics are known quenchers of pyrene or anthracene fluorescence by the electron-transfer mechanism.[10] All these molecules, except for the quinone derivative, have their singlet energies higher than those of the probe molecules and hence energy transfer as a possible pathway for fluorescence quenching is ruled out. In the case of the quinone derivative, even though energy transfer quenching is a possibility, we rule out this possibility because of the following. In hydrogen bonded assemblies singlet−singlet energy transfer is known to take place by the Föster mechanism and the Dexter mechanism is not expected to contribute significantly.[11] The rate constant for energy transfer by the Förster mechanism will be proportional to the extinction coefficient of the quinone. Since the quinone derivative has a very low extinction coefficient ($\epsilon_{\max}$= 25 M^{-1} cm^{-1} at 430 nm) for its long wavelength absorption, energy transfer quenching by the Förster mechanism can be ruled out. Since the quinone is nonfluorescent, it is not expected to interfere in the fluorescence lifetime determinations.

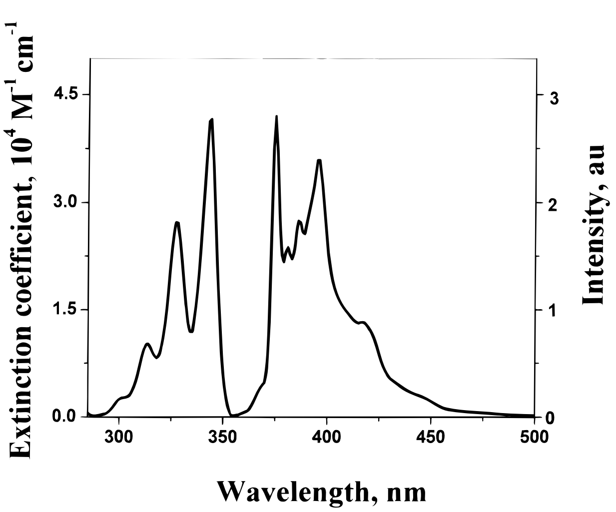


Figure 1. Absorption and emission spectra of pyrene-1-acetic acid in dichloromethane. For the emission spectrum, the excitation wavelength was 345 nm.

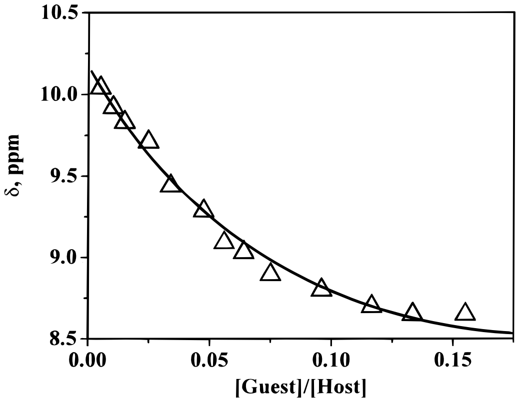


Figure 2. ^{1}H NMR binding isotherm for **2** with **PA** in $CDCl_3$ at 25 °C.

The association of the probe and quencher molecules was studied in some of these cases by ^{1}H NMR in $CDCl_3$ solution. The chemical shift of the carboxylic acid proton undergoes an upfield shift upon complexation. Figure 2 shows the change in the chemical shift of the carboxyl proton of **2** in the presence of **PA**. The data were analyzed according to a literature method[12] to obtain a value of 207 M^{-1} for K_a in this case.

Assuming a two-point hydrogen bonding interaction of the probe and quencher acetic acids, the association complex will have the structure shown in Scheme 1. The length of acetic acid dimer (determined by electron diffraction patterns and also from calculations)[13] is 6.90 Å. 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. This is indicated in Scheme 1. This distance remains constant in all our probe/quencher systems.

The decays of the probe molecules were exponential in dichloromethane solution. When a quencher molecule is added,

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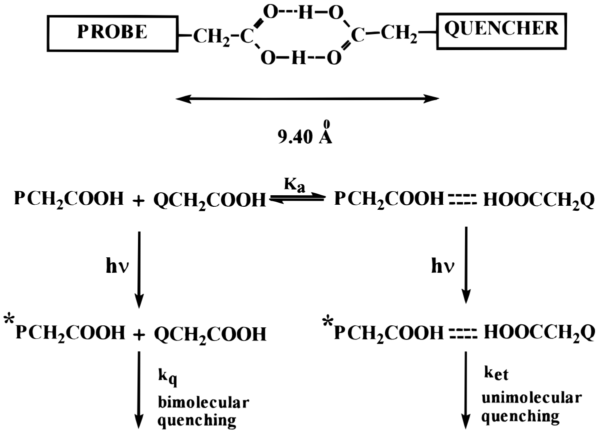
(11) Sessler, J. L.; Wang, B.; Harriman, A. *J. Am. Chem. Soc.* **1995**, *117*, 704.

(12) Kelly, T. R.; Kim, M. H. *J. Am. Chem. Soc.* **1994**, *116*, 7072.

(13) (a) Derissen, J. L. *J. Mol. Struct.* **1971**, *7*, 67. (b) Doan, V.; Köppe, R.; Kasai, P. H. *J. Am. Chem. Soc.* **1997**, *119*, 9810.

Scheme 1. Structure of the Hydrogen Bonded Complex and Scheme Showing the Excitation and Quenching of the Associated and Unassociated Forms



a fraction of the probe becomes associated and the rest remains unassociated. Upon photoexcitation, the fluorescence of the associated molecules will be quenched by electron transfer with the associated quencher, whereas the unassociated probe molecules will be quenched by free quencher molecules in solution (Scheme 1). This leads to a biphasic decay of the probe fluorescence that can be expressed by

$$I_{(t)} = \chi_{(P-Q)} \exp(-t/\tau_1) + \chi_{(P)} \exp(-t/\tau_2) \quad (2)$$

where,

$$\tau_1 = (k_0 + k_{et})^{-1} \quad (3)$$

$$\tau_2 = (k_0 + k_q[Q])^{-1} \quad (4)$$

$\chi_{(P-Q)}$ 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 of the unassociated probe molecules. According to eqs 2−4, the short lifetime component (τ_1) is independent of the quencher concentration and the long lifetime component (τ_2) is dependent on the quencher concentration. From the short lifetime component, the rate constant of electron transfer within the hydrogen bonded complex can be calculated by using eq 5. As mentioned previously, a major portion of the probe molecules are quenched by unassociated quencher molecules. The quenching rate constant k_q for this process can be obtained by the usual Stern−Volmer method.

$$k_{et} = 1/\tau_1 - 1/\tau_0 \quad (5)$$

$$\tau_0/\tau_2 = 1 + k_q\tau_0[Q] \quad (6)$$

According to this equation, a plot of τ_0/τ_2 vs quencher concentration will give $k_q\tau_0$ as the slope. The rate constant for electron transfer for the associated and unassociated forms can thus be obtained from the same experiment.

The association constants can also be determined from the fractional contributions $\chi_{(P-Q)}$ and $\chi_{(P)}$.[1m] These values are proportional to the concentration of the associated and unassociated forms of the probe, respectively. Since the quencher concentration is very large compared to the probe concentration, we can write

Table 1. Association Constants (K_a), Free Energies ($\Delta G°$ and $\Delta G°_{diff}$), and Rate Constants (k_{Et} and k_q) for the Donor−Acceptor Systems[a]

donor−acceptor system	K_a[b]	$\Delta G°$, eV	k_{et}, 10^7 s^{-1}	$\Delta G°_{diff}$, eV	k_q, 10^9 M^{-1} s^{-1}
PA/1	15	−0.04	6.2 ± 0.62	−0.07	--
PA/2	195 (207)	−0.52	89.9 ± 1.8	−0.56	9.29
PA/3	16 (59)	0.05	1.9 ± 0.19	0.02	0.21
PA/4	20 (59)	−1.18	39.0 ± 7.8	−1.21	12.8
PA/5	50	−1.29	8.9 ± 0.18	−1.32	22.6
PA/6	53	−1.42	5.2 ± 0.25	−1.45	12.8
AA/2	40	−0.24	43.0 ± 4.3	−0.28	7.36
AA/4	22	−0.92	144.0 ± 14	−0.95	16.6

[a] The numbers in column 1 corresponds to the number of the quenchers in Chart 1. [b] Values in parentheses are those obtained by NMR.

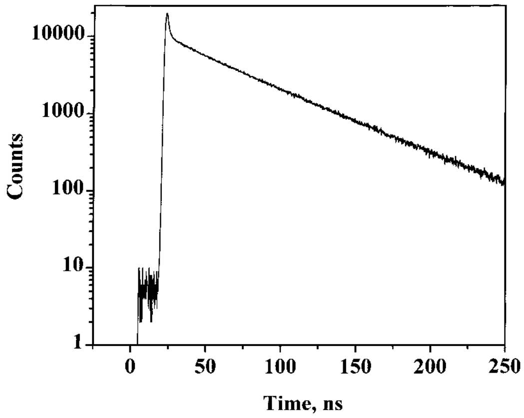


Figure 3. Fluorescence decay profile for the **PA/2** system. Excitation was at 345 nm and emission monitored at 375 nm.

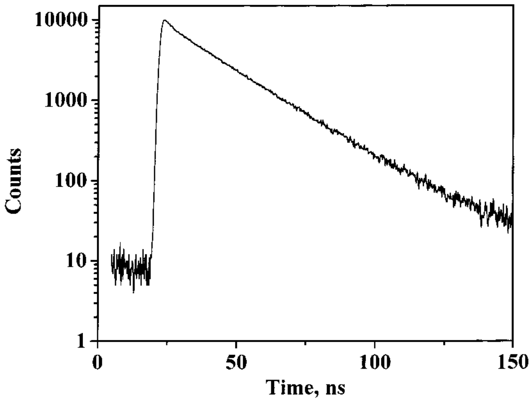


Figure 4. Fluorescence decay profile for the **PA/4** system. Excitation was at 345 nm and emission was monitored at 375 nm.

$$K_a = \frac{\chi_{(P-Q)}}{\chi_{(P)}[Q]} \quad (7)$$

Thus a plot of $\chi_{(P-Q)}/\chi_{(P)}$ vs [Q] will be linear and gives K_a as the slope. The K_a values thus determined in dichloromethane were slightly lower than those obtained by the NMR titration method in $CDCl_3$ solution (see Table 1).

The fluorescence decay profiles of **PA** in the presence of 4-(*N*,*N*-dimethylamino)phenylacetic acid (**2**) and 4-nitrophenylacetic acid (**4**) are shown in Figures 3 and 4, respectively. Figures 5 and 6 show plots of τ_1 and τ_2 vs quencher concentration in these cases.

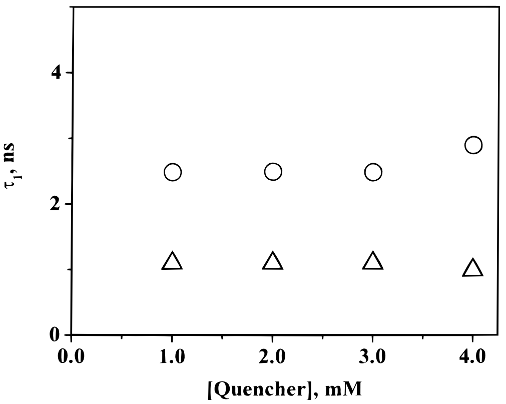


Figure 5. A plot showing the invariance of τ_1 in the case of **PA/2** (△) and **PA/4** (○) systems.

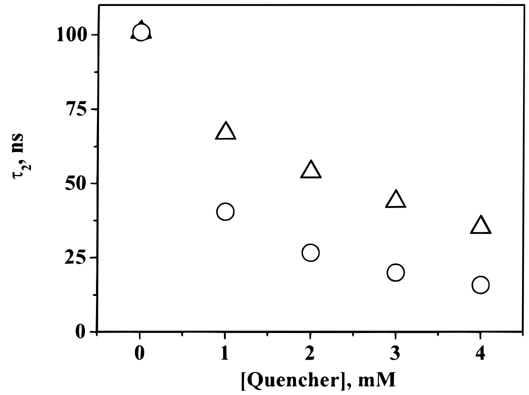


Figure 6. A plot showing the decrease of τ_2 with quencher concentration in the case of **PA/2** (△) and **PA/4** (○) systems.

The invariance of τ_1 with quencher concentration and the decrease of τ_2 with quencher concentration are evident from Figures 5 and 6. Consistent with the criteria used in other model systems involving hydrogen bonded interfaces, our experimental systems display the following properties. (1) No strong electronic interaction occurs between the probe and the quencher in the concentration range studied, because the electronic absorption of the probe−quencher mixture appears as a superposition of the spectra of the individual components. (2) The emission spectra of the probes in the presence of the quenchers did not show any additional bands that can be attributed to exciplexes even at the highest quencher concentrations used. (3) The short lifetime component in the decay profile disappears by addition of hydrogen bonding solvents such as methanol. (4) The short lifetime component was absent when quenchers without carboxylic acid functionality were used. All these factors suggest that the short component of the fluorescence decay is due to electron transfer within the associated complex. We have determined k_{et} for all quenchers with **PA** as the probe. When **AA** was used as the probe, biexponential decays could be obtained only in the cases of **2** and **4** as quenchers. This is attributed to the short lifetime of the probe. For all probe quencher systems studied (except for the **PA/1** system), k_q values were also determined by the Stern−Volmer method. In the case of the **PA/1** system, the long lifetime component did not exhibit any quenching and hence k_q could not be determined in this case.

To calculate the free energies of the electron-transfer reactions, the redox potentials in dichloromethane were required. The reduction potentials of **PA**, **AA**, and **3** could not be determined in dichloromethane because the values are outside the useful range of this solvent.[14] Hence we have determined the redox potentials of all the probes and quenchers in acetonitrile. The free energies for electron transfer in dichloromethane were then calculated by using eq 8,[15] where E_{ox} is the

$$\Delta G^\circ = E_{ox} - E_{red} - E_{0,0} - \frac{e^2}{2}\left(\frac{1}{r_P}+\frac{1}{r_Q}\right)\left(\frac{1}{37}-\frac{1}{\epsilon}\right) - \frac{e^2}{\epsilon d} \qquad (8)$$

oxidation potential of the donor, E_{red} is the reduction potential of the acceptor, ϵ is the dielectric constant of dichloromethane, r_P and r_Q are the radii of the probe and quencher molecules, and d is the distance separating these partners. r_P and r_Q were taken as 6 and 4 Å, respectively, and the center-to-center distance, d, is assumed to be 12.0 Å for the hydrogen bonded complex. For calculation of ΔG°_{diff} for the diffusive quenching, d is taken as 10 Å. The redox potentials of the probes and quenchers are given along with their structures in Chart 1 and the calculated ΔG° values are presented in Table 1. The K_a, k_{et}, and k_q values determined are also presented in Table 1.

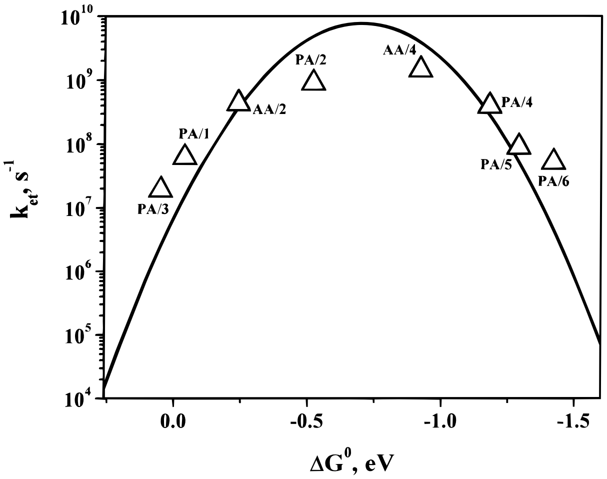


Figure 7. Dependence of electron-transfer rates (k_{et}) in the hydrogen bonded complex on free energy. The solid curve is a computed curve of eq 1 with $H_{el} = 5$ cm^{-1} and $\lambda = 0.70$ eV.

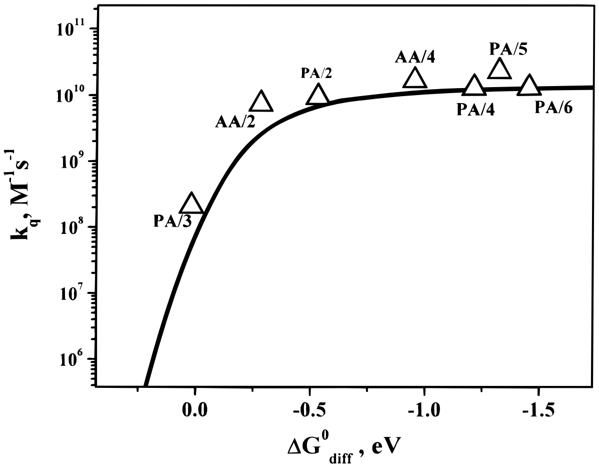


Figure 8. The plot of bimolecular quenching rate constants (k_q) vs ΔG°_{diff}. The solid line is a fit using eq 9.

Figure 7 shows a plot of k_{et} vs ΔG°. It can be seen from Figure 7 that as the driving force increases k_{et} increases initially, reaches a maximum, and then decreases. This clearly is an

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(14) Lund, H.; Baizer, M. M. *Organic Electrochemistry*; Marcell Dekker: New York, 1991.

(15) Kavarnos, G. J. *Fundamentals of Photoinduced Electron Transfer*; VCH: New York, 1993.

example of a Marcus type electron transfer and demonstrates the presence of the inverted region in these systems. The solid line in Figure 7 is a fit to the Marcus equation with $H_{el} = 5$ cm^{-1} and $\lambda = 0.70$ eV. The Marcus inverted region was demonstrated only in a very few cases of charge separation reactions and this constitutes one such case.

Figure 8 shows the plot of k_q *vs* $\Delta G°_{diff}$. It can be seen from Figure 8 that as the driving force increases, k_q first increases, reaches a maximum, and then stays there. This clearly is an example of the Rehm−Weller behavior. In the Rehm−Weller formalism, the overall quenching rate constant k_q in a bimolecular electron-transfer reaction can be expressed by eq 9,[7b,10a]

$$k_q = \frac{20 \times 10^9}{1 + 0.25[\exp(\Delta G^{\#}/RT) + \exp(\Delta G°/RT)]} \qquad (9)$$

where $\Delta G^{\#}$ is the free energy of activation for electron transfer and is given by the expression

$$\Delta G^{\#} = \frac{\Delta G°}{2} + \left[\left(\frac{\Delta G°}{2}\right)^2 + (\Delta G_0^{\#})^2\right]^{1/2} \qquad (10)$$

$\Delta G_0^{\#}$ in the above expression is the free energy of activation when there is no driving force for the reaction. For the present calculation, a value of 0.175 eV was assumed for $\Delta G_0^{\#}$. The theoretical fit calculated using eqs 9 and 10 is also shown in Figure 8. Notice that there is a reasonably good agreement between calculated and experimental values of k_q.

Our experimental design thus allows for the simultaneous observation of the Marcus and Rehm−Weller behaviors of electron transfer using the same donor−acceptor systems. Where the partners are held at fixed distance and allowed to react under unimolecular conditions, the electron transfer obeys the Marcus equation, and where they are allowed to diffuse freely, the Rehm−Weller behavior is observed. This study thus confirms that diffusion is the major reason for not observing the inverted region in charge separation reactions. However, we do realize that this contention is applicable only in the region of moderately large driving forces ($\Delta G° \geq -1.5$ eV) studied here. At very large driving forces, other factors such as formation of products in the excited state or presence of other reaction channels may become important.

Conclusions

We have studied the free energy dependence of electron transfer in a few donor−acceptor systems assembled through hydrogen bonding interactions. Our study shows that when diffusion is prevented, the Marcus inverted region can be observed, and when diffusion of the partners is allowed, Rehm−Weller behavior is observed. The nonobservance of the inverted region in charge separation reactions is thus attributed to diffusion in the region of moderately large driving forces.

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