Estimation of the Bimolecular Rate Constant for Exciplex Formation from the Analysis of Its Emission Spectrum

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Received: January 13, 1997; In Final Form: April 23, 1997[⊗]

The bimolecular rate constant for the quenching of 1-methylnaphthalene by triethylamine was measured in series of solvents covering a large range of solvent polarity ($\epsilon = 2-37$). The formation of a fluorescent exciplex was observed in all the solvents studied. Analyzing the emission of the exciplex, it is possible to estimate the relevant parameters associated with the radiative back electron transfer process, namely, the solvent dependent Gibbs energy change, the solvent reorganization energy, and the internal reorganization energy. These parameters are used to calculate, according to Marcus theory, the rate constant for the photoinduced forward electron transfer reaction. A good correlation between calculated and experimental quenching rate constants is observed.

Introduction

In the recent decade, many of the predictions of the electron transfer theories, such as the existence of the inverted region and the effects of varying the distance between the electron donor (D) and the electron acceptor (A), have been corroborated.[1−4] Another important achievement was the experimental verification of the predicted relationship between radiative and nonradiative electron transfer reactions.[5] The analysis of the emission spectra of exciplexes, as well the spectral fitting of CT complex absorption and fluorescence bands, was shown to provide significant information concerning the whole electron transfer process.[6−11] Hence, the information obtained from a radiative process $(A^{\bullet-}D^{\bullet+}) \rightarrow A + D + h\nu_f$ can be used, for instance, to estimate the rate constant for the corresponding nonradiative thermal reaction $(A^{\bullet-}D^{\bullet+}) \rightarrow A + D$. An excellent agreement between calculated and experimental rate constants in a diversity of media has been obtained that way.[12−14] The information obtained from fluorescent charge transfer states may also be used to investigate the forward photoinduced electron transfer process, $A^*D \rightarrow (A^{\bullet-}D^{\bullet+})$, as it was shown in the study of several D/A rigidly linked systems.[15,16] However, and despite this apparent success, a similar approach has not been intended for the estimation of second-order rate constants for typical D/A systems in fluid solution, $A^* + D \rightarrow (A^{\bullet-}D^{\bullet+})$. This is the primary aim of this report.

According to Marcus,[17,18] the overall rate constant for an outer sphere bimolecular electron transfer reaction is given by

$$k_{et} = Z \exp[-\Delta G^*_{et}/RT] \tag{1}$$

where Z is the bimolecular collision number in solution (taken to be $\sim 10^{11}$ M^{-1} s^{-1}) and ΔG^*_{et} is the Gibbs free activation energy needed to reorganize the nuclei of reactants and the surrounding solvent molecules prior to electron transfer. This activation energy is related to the overall Gibbs free energy change, ΔG^{ϵ}_{et}, and to the total reorganization energy, λ^{ϵ}, by the Marcus equation

$$\Delta G^*_{et} = \frac{\lambda^{\epsilon}}{4}\left(1 + \frac{\Delta G^{\epsilon}_{et}}{\lambda^{\epsilon}}\right)^2 \tag{2}$$

where the superscript ϵ, which represents the relative static dielectric constant of the medium, was included to denote those free energy variables that are solvent dependent. λ^{ϵ} has two contributions: $\lambda^{\epsilon} = \lambda^{\epsilon}_s + \lambda_v$. The term λ^{ϵ}_s stands for the solvent reorganization energy, and λ_v is the internal reorganization energy.

In the specific case of photoinduced electron transfer reactions, it is possible to estimate ΔG^{ϵ}_{et} from electrochemical and spectroscopic measurements:[19]

$$\Delta G^{\epsilon}_{et} = e\Delta E^{\epsilon} + w^{\epsilon} - E_{00} \tag{3}$$

where ΔE^{ϵ}, defined here as a positive magnitude, is the difference between the oxidation potential of the electron donor and the reduction potential of the electron acceptor. E_{00} represents the energy of the excited state, and w^{ϵ} is the free energy gained by bringing the formed ions from infinite to a given encounter distance.

Since Z and λ_v may be considered as nearly solvent independent,[20] the reaction medium controls the electron transfer rate modifying ΔG^{ϵ}_{et} and λ^{ϵ}_s. Hence, in order to correlate experimental values of k_{et} with the theoretical Marcus expression (eq 1), it is critical to estimate ΔG^{ϵ}_{et} and λ^{ϵ}_s with some degree of confidence. Unfortunately, this cannot be done for a number of reasons: (a) True redox potentials are measured in polar solvents such as acetonitrile or dimethylformamide. Interference caused by the supporting electrolyte[21,22] and other problems inherent to the reference electrode make the estimation of $e\Delta E^{\epsilon}$ in low-polarity solvents difficult if not impracticable. (b) Although w^{ϵ} is usually taken as a simple Coulombic correction, the basic nature of this term, and therefore, its solvent dependence, is subject to controversy,[23,24] and finally (c) the evaluation of λ^{ϵ}_s requires knowing in detail the reactant molecular radii as well the intermolecular D/A separation.[25]

However, for those systems for which the photoinduced electron transfer reaction is accompanied by fluorescent exciplex formation, there should be a way to estimate experimentally ΔG^{ϵ}_{et} and λ^{ϵ}_s from the solvent dependence of the emission of the exciplex, Scheme 1.

For an emissive exciplex that behaves as a pure contact ion pair (CRIP), the fluorescence emission process represents a nonadiabatic back electron transfer reaction that regenerates the neutral starting materials. Marcus[5] showed that the energy of

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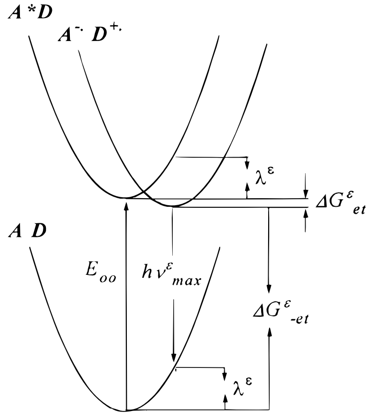
[⊗] Abstract published in *Advance ACS Abstracts,* June 1, 1997.

S1089-5639(97)00202-8 CCC: $14.00

SCHEME 1



the fluorescence maximum $h\nu^{\epsilon}_{\max}$ of the reduced emission spectrum of the exciplex[26] should be given approximately by

$$h\nu^{\epsilon}_{\max} \cong -\Delta G^{\epsilon}_{-\mathrm{et}} - \lambda^{\epsilon} \qquad (4)$$

where $-\Delta G^{\epsilon}_{-\mathrm{et}}$ represents the electronic energy difference between the exciplex ($\mathrm{A}^{\bullet-}\mathrm{D}^{\bullet+}$) and the neutral ground-state donor/acceptor pair (A/D). If the functions used to describe the Gibbs energy surfaces representing the three states in Scheme 1 are assumed to be (displaced) parabolas with identical force constants, then the total reorganization energy λ^{ϵ} for the forward and back electron transfer reactions should also be the same. It is also clear from Scheme 1 that $\Delta G^{\epsilon}_{\mathrm{et}} = -\Delta G^{\epsilon}_{-\mathrm{et}} - E_{\mathrm{oo}}$.

However, in order to estimate k_{et}, the contributions of $\Delta G^{\epsilon}_{-\mathrm{et}}$ and λ^{ϵ} to $h\nu^{\epsilon}_{\max}$ must be separated. Usually, this has been done by fitting the exciplex emission spectrum to Marcus's semiclassical expression for optical transitions.[5,7] In principle, this fitting may provide the four relevant parameters associated with the back electron transfer: $\Delta G^{\epsilon}_{-\mathrm{et}}$, $\lambda^{\epsilon}_{\mathrm{s}}$, λ_{v}, and the averaged frequency of internal vibration modes, ν_{v}. However, this procedure requires the assumption of "reasonable" values for λ_{v} and ν_{v};[6−8] otherwise it is always possible to find more than one set of four parameters that reproduce properly the observed spectrum.[9] At this point, an alternative approach can be proposed. Let us assume that the exciplex behaves as a point-dipole centered within a solvent cavity of radius ρ. As in Marcus theory, the solvent may be considered as a continuum characterized by a static dielectric constant ϵ and an optical dielectric constant taken proportional to the square of its refractive index, n. According to this model, expressions for $\lambda^{\epsilon}_{\mathrm{s}}$ and $\Delta G^{\epsilon}_{-\mathrm{et}}$ in the nonequilibrium thermodynamic Marcus approach[27] were developed by Brunschwig et al.:[28]

$$\lambda^{\epsilon}_{\mathrm{s}} = \frac{{\mu_{\mathrm{e}}}^2}{4\pi\epsilon_0\rho^3}(f_{\epsilon} - f_n) \qquad (5)$$

where $$f_{\epsilon} = \frac{\epsilon - 1}{2\epsilon + 1} \quad \text{and} \quad f_n = \frac{n^2 - 1}{2n^2 + 1}$$

In the above expression μ_{e} represents the dipole moment of the exciplex and ϵ_0 is the permittivity of the vacuum. The dependence of the driving force on the polarity of the medium may be estimated according to[28]

$$\Delta G^{\epsilon}_{-\mathrm{et}} \cong \Delta G^{37.5}_{-\mathrm{et}} - \frac{{\mu_{\mathrm{e}}}^2}{4\pi\epsilon_0\rho^3}(0.48 - f_{\epsilon}) \qquad (6)$$

where $\Delta G^{37.5}_{-\mathrm{et}} = -e\Delta E^{37.5} - w^{37.5}$, the free Gibbs energy change calculated in acetonitrile ($\epsilon = 37.5$ and $f_{37.5} = 0.48$), was chosen purposely as a reference solvent. In the above equation it is assumed that the ratio ${\mu_{\mathrm{e}}}^2/\rho^3$ is solvent independent. The magnitude $w^{37.5}$ depends on the nature of the ionic intermediate. For the formation of a solvent-separated ion pair (SSIP) in acetonitrile, a value of $w^{37.5} \approx -0.06$ eV is usually accepted.[29] However, the formation of a CRIP (the species assumed in this model) from a SSIP in a highly polar medium is predicted to be an endergonic process,[30] anticipating a less negative or even positive $w^{37.5}$. Gould et al.[7] showed that the fitting of the fluorescence spectra of several cyanoaromatic/alkylbenzene exciplexes in acetonitrile requires a $w^{37.5} \approx 0.04$ eV. In any case, the Coulombic correction is small compared to $e\Delta E^{37.5}$, which for typical exciplexes is usually larger than 2 eV.

Upon substitution of eqs 5 and 6 into eq 4, the following is obtained:

$$h\nu^{\epsilon}_{\max} \cong e\Delta E^{37.5} + w^{37.5} - \lambda_{\mathrm{v}} - \frac{2{\mu_{\mathrm{e}}}^2}{4\pi\epsilon_0\rho^3}(\Delta f - 0.24) \qquad (7)$$

where $$\Delta f = f_{\epsilon} - \frac{1}{2}f_n$$

Equation 7 establishes that a plot of the energy of emission maximum of the reduced spectrum of the exciplex *vs* Δf must be linear.[31] From the slope of the plot $2{\mu_{\mathrm{e}}}^2/4\pi\epsilon_0\rho^3$ is obtained. This value can be used to calculate $\lambda^{\epsilon}_{\mathrm{s}}$ (eq 5). From the intercept of eq 7 and provided that $e\Delta E^{37.5}$ is experimentally available, the solvent dependence on $\Delta G^{\epsilon}_{\mathrm{et}}$ (eq 6) and an approximated value of λ_{v} are also obtained. Therefore, all the parameters required to calculate the solvent dependent rate constant k_{et} are available.

In the present communication we examine this hypothesis. In order to do so, it was necessary to select an acceptor/donor system that fulfills the following conditions: (a) the sysetm must show fluorescent exciplex formation in a wide range of solvent polarity; (b) the exciplex should behave as a CRIP; it must exhibit a large and solvent independent charge transfer separation; and (c) the observed quenching rate constants must be below the difusional rate limit in all solvents. Among the possible systems, we studied the solvent effect on the quenching of the 1-methylnaphthalene (1MN) singlet excited state by triethylamine (TEA). The quenching of naphthalene and naphthalene derivatives by alkylamines has been extensively studied. The formation of fluorescent intermolecular,[32−35] intramolecular flexibly linked,[36−41] and intramolecular rigidly linked[15] naphthalene/alkylamines exciplexes has been reported. This experimental background can be profitably used to compare and contrast with our results.

Materials and Methods

Solvents of spectroscopic grade were obtained from Sintorgan and used as received. The bichromophoric compound *N*,*N*-diethyl-3-(1-naphthyl)propylamine was prepared by $\mathrm{LiAlH_4}$ reduction of the amide, which was obtained by reaction of 3-(1-naphthyl)propionic acid chloride and diethylamine. Mass (EI) (*m*/*z*): 241, 141, 115, 86, 72, 58.

Corrected fluorescence spectra were measured on a Spex Flouromax spectrometer. Fluorescence quantum yields were determined using quinine bisulfate in 0.1 N $\mathrm{SO_4H_2}$ as fluorescence standard.[42] Fluorescence lifetimes of 1-methylnaphthalene in the different solvents were measured using a Spectron SL400 Nd:YAG system generating 266 nm laser pulses (~8 ns pulse width). The experiments were performed with rectangular

TABLE 1: Difference between the Oxidation Potential of the Electron Donor (D) Measured in Acetonitrile and the Reduction Potential of the Electron Acceptor (A) in the Same Solvent, $\Delta E_{-et}^{37.5}$: Theoretically AM1 Calculated Specific Contributions of the Donors λ_D and Acceptors λ_A to the Internal Reorganization Energy and Energy of the Maximum of the Reduced Emission Spectra of the Exciplexes Measured in Ethyl Ether at 298 K, $h\nu_{max}^{4.02}$

	donor	acceptor	$e\Delta E_{-et}^{37.5}$ (eV)	λ_D (eV)	λ_A (eV)	$h\nu_{max}^{4.02}$ (eV)
1	naphthalene	9,10-dicyanoanthracene	2.58	0.17	0.10	2.38
2	pyrene	*p*-dicyanobenzene	3.00	0.15	0.10	2.86
3	naphthalene	*p*-dicyanobenzene	3.40	0.17	0.10	3.13
4	dimethylaniline	benzonitrile	3.13	0.31	0.09	2.68
5	dimethylaniline	biphenyl	3.43	0.31	0.13	3.02
6	dimethylaniline	pyrene	2.88	0.31	0.13	2.54
7	dimethylaniline	naphthalene	3.34	0.31	0.12	2.87
8	triethylamine	1-methylnaphthalene	3.55	0.61	0.11	2.77
9	triethylamine	1-cyanonaphthalene	2.98	0.61	0.13	2.18

quartz cells with right angle geometry. The detection system comprises a PTI monochromator coupled to a Hamamatsu R664 PM tube. The signal was acquired by a digitizing scope (Hewlett Packard 54504) where it was averaged and then transferred to a computer. The solutions were deoxygenated by bubbling with high-purity argon. The samples prepared in ethyl ether were degassed by three pump−thaw cycles.

Molecular orbital calculations were done using the AM1 semiempirical method developed by Dewar et al.[43] The version used was AMPAC 5.0 (Semichem: 7128 Summitt, Shawnee, KS 66216, 1994).

Results and Discussion

A Test for Eq 7: The Experimental Evaluation of λ_v. In order to test eq 7, we studied the emissive properties of a series of exciplexes formed from the electron acceptor and electron donors listed in Table 1. These exciplexes, which have been extensively studied,[44] were selected because they show a large charge transfer degree, and therefore, they may be treated as almost pure CRIP.

According to eq 7, the fourth term of this expression becomes negligible if the exciplexes are studied in a medium characterized by a $\Delta f \cong 0.24$. Hence, the energy of the maximum of the reduced fluorescence spectra was measured in ethyl ether ($\epsilon = 4.02$, $\Delta f = 0.245$), allowing the treatment of the experimental data according to the following simplified expression:

$$h\nu_{max}^{4.02} \cong e\Delta E^{37.5} + w^{37.5} - \lambda_v$$

The measured $h\nu_{max}^{4.02}$ and the values of $e\Delta E^{37.5}$ calculated from the reported redox potentials in acetonitrile[45] are shown in Table 1. As it was anticipated, this allows the calculation of λ_v (or, more correctly, $\lambda_v - w^{37.5}$) from the experimental data.

For the sake of comparison, an approximated value for λ_v can be obtained from semiempirical molecular orbital calculations.[46] The specific contribution of the donor (or acceptor) to the total internal reorganization energy for the radiative back electron transfer is calculated as the difference between the enthalpy of formation of the cation (anion) radical in the equilibrium geometry of the neutral form and the enthalpy of formation of the cation (anion) radical in its own equilibrium geometry. The calculated contributions for the acceptors (λ_A) and donors (λ_D) for the systems studied here are collected in Table 1. The total (calculated) internal reorganization energy, λ_v(calc), is obtained by addition of the acceptor and donor contributions.

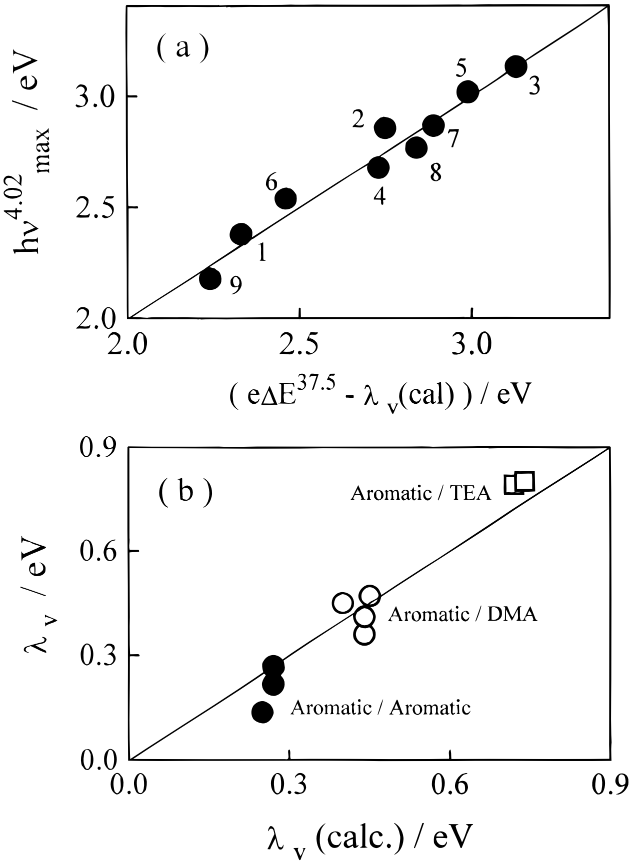


Figure 1. Linear free energy correlations: (a) Energy of the exciplex emission measured in ethyl ether *vs* the difference between the "redox energy" $e\Delta E_{-et}^{37.5}$ and the theoretically AM1 calculated internal reorganization energy, λ_v(calc). (b) experimental internal reorganization energy, λ_v, *vs* the theoretically AM1 calculated value, λ_v(calc).

Figure 1a shows a plot of $h\nu_{max}^{4.02}$ *vs* ($e\Delta E^{37.5} - \lambda_v$(calc)). The correlation between the theoretical line and the experimental data is satisfactory in spite of the multiple approximations. Note that the omission of the term $w^{37.5}$ does not seem to be significant. This suggests that the absolute magnitude of $w^{37.5}$ is smaller than the uncertainties introduced by the approximations and the experimental errors, quite probably on the order of ±0.1 eV. The importance of the internal reorganization energy in the radiative electron transfer reaction becomes apparent if the experimental evaluated internal reorganization λ_v ($\cong e\Delta E^{37.5} - h\nu_{max}^{4.02}$) is plotted against λ_v(calc), Figure 1b. The experimental data in Figure 1b are arranged in clusters; exciplexes formed by two aromatics exhibit low reorganization energies (~0.20 eV), while those exciplexes formed by aromatic and aliphatic amines show large values, ~0.40 and ~0.80 eV, respectively. The important contribution of the amine donors to λ_v may be understood in terms of the large geometrical changes that these compounds undergo on passing from their planar radical cations to their pyramidal neutral forms.[33,47]

TABLE 2: Observed Solvent Effect on the Activated Quenching Rate Constant ($k_{q'}$) in the Quenching of the Singlet Excited State of 1-Methylnaphthalene (1MN) by Triethylamine (TEA) at 298 K. Energy of the Maximum of the Reduced Fluorescence Spectrum of the Exciplex 1MN/TEA ($h\nu^{\epsilon}_{max}$) and Fluorescence Quantum Yields (ϕ_f) in the Solvents Studied

solvent	f_ϵ	Δf	$k_{q'} \times 10^{-9}$ (M^{-1} s^{-1})[a]	$h\nu^{\epsilon}_{max}$ (eV)[b]	ϕ_f
hexane	0.185	0.092	0.34	3.01	0.086
cyclohexane	0.202	0.100	0.42 (3.3)[c]	2.99	0.092 (0.055)[d]
triethylamine	0.243	0.145		2.98	
n-butyl ether	0.291	0.193	3.70	2.86	0.023
ethyl ether	0.334	0.245	3.30	2.77	0.024
chloroform	0.359	0.254		~2.72	
ethyl acetate	0.385	0.292	5.70	2.55	0.020
tetrahydrofuran	0.407	0.308	6.40	2.59	0.022
1,2-dichloroethane	0.431	0.326	5.20	2.57	
propionitrile	0.474	0.383	5.70	~2.46	
acetonitrile	0.479	0.393	8.40	~2.44	

[a] Estimated error 5%. [b] Estimated error ±0.02 eV. [c] Bimolecular rate constant for the forward electron transfer reaction. Reference 34. [d] Reference 35.

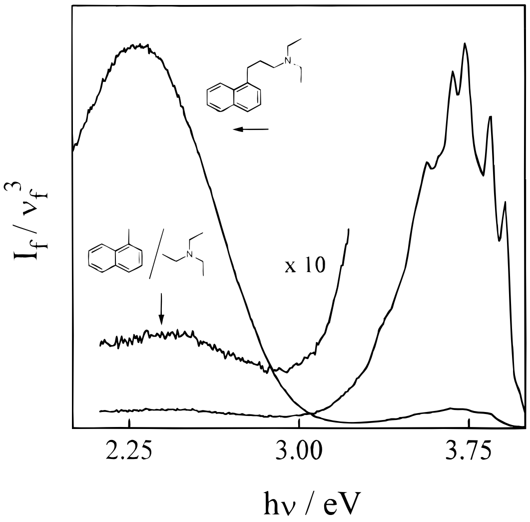


Figure 2. Reduced emission spectrum of the intermolecular 1MN/TEA exciplex in acetonitrile compared to that of the intramolecular exciplex in the same solvent.

The Solvent Effect on the Emission Spectrum of the Exciplex 1MN/TEA. The emission corresponding to the exciplex 1MN/TEA was observed in all the solvents studied. As expected, the measured $h\nu^{\epsilon}_{max}$ values and fluorescence quantum yields are highly dependent on the polarity of the medium, Table 2. In the more polar solvents of the series, propionitrile and acetonitrile, the fluorescence of the exciplex is barely detectable, Figure 2. In order to confirm that the emissions observed in these two solvents actually corresponded to the exciplex, we studied the intramolecular exciplex formed by the bichromophoric compound *N*,*N*-diethyl-3-(1-naphthyl)-propylamine. It is know that similar exciplexes emit efficiently even in strongly polar solvents.[36,38,41,48] Figure 3 compares the plots of $h\nu^{\epsilon}_{max}$ *vs* ($\Delta f - 0.24$) for both exciplexes according to eq 7. Note that the emission energy of the intramolecular exciplex follows closely that of the 1MN/TEA exciplex from hexane to propionitrile ($\Delta f = 0.383$), exhibiting the typical scatter due to specific solvent−solute interactions. The energy of the emission maximum of the intramolecular exciplex in acetonitrile seems to be lower than that expected for the linear correlation. This behavior could be explained if this emission arises from a different type of radical ion pair.

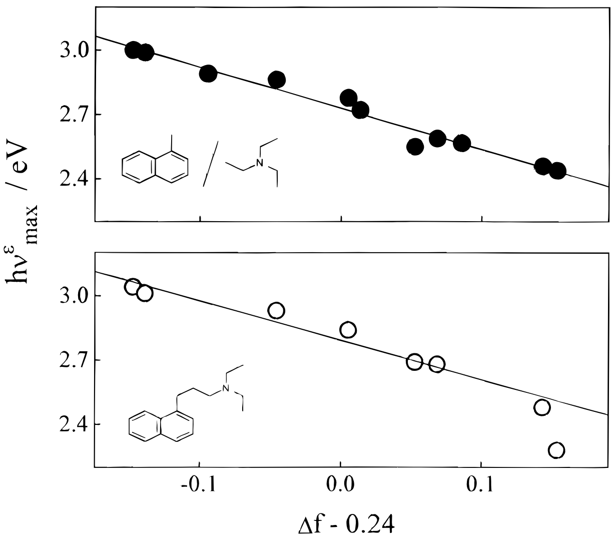


Figure 3. Dependence of the energy of the exciplex emission maximum ($h\nu^{\epsilon}_{max}$) on the solvent parameter Δf: (a, ●) intermolecular 1MN/TEA exciplex; (b, ○) intramolecular 1MN/TEA exciplex.

As demonstrated by Weller et al.,[44,49] bimolecular photoinduced electron transfer reactions may yield two different types of radical ion pairs: contact radical ion pairs (CRIP) and solvent-separated radical ion pairs (SSIP). Both species are distinguished by differences in electronic coupling and solvation,[30] and it is believed that they may be produced simultaneously from a "bifurcation" in the electron transfer mechanism. Preponderant CRIP formation occurs in low- and medium-polarity solvents, while the formation of SSIP, being more solvated species, should become important as the polarity of the solvent increases. Unfortunately, with exemption of a few particular A/D systems,[50] it is usually impossible to determine experimentally the relative importance of these parallel routes. Hence, we will correlate the experimental k_q to the parameters obtained from the fluorescence spectrum of the exciplex (CRIP), although it cannot be answered whether k_q represents mainly the rate constant for the formation of a CRIP or for the formation of a combination of both types of radical ions. This uncertainty should be particularly significant in the more polar solvents of the series: propionitrile and acetonitrile.

The plot shown in Figure 3a is fairly linear even in the nonpolar solvent range, suggesting a large, almost solvent independent, degree of charge separation in the exciplex.[44] Accordingly, theoretical studies performed on the electronic structure of the intramolecular exciplex formed by *N*,*N*-methyl-3-(1-naphthyl)propylamine also indicated that the exciplex could be treated, for most purposes, as a nearly pure ion pair state.[41]

From the plot in Figure 3a it is possible to calculate a slope of 1.91 ± 0.10 eV and an intercept of 2.75 ± 0.04 eV. These values are assigned to the terms $2\mu_e^2/4\pi\epsilon_0\rho^3$ and $(e\Delta E^{37.5} + w^{37.5} - \lambda_v)$, respectively. Since for this system $e\Delta E^{37.5}$ is 3.55 eV and the AM1 calculated value for $\lambda_v = 0.72$ eV, the difference between the experimental intercept and $(e\Delta E^{37.5} - \lambda_v(\text{calc}))$ is only 0.08 eV. One may tentatively assign this difference to $w^{37.5}$; however, this may be meaningless considering the multiple approximations included in eq 7 and the errors in $e\Delta E^{37.5}$ and $\lambda_v(\text{calc})$. Therefore we will just take for this system $\Delta G^{37.5}_{-et} = -3.55 \pm 0.04$ eV and $\lambda_v = 0.72 \pm 0.04$ eV, expecting the actual values to occur within these error margins.

The Solvent Effect on the Fluorescence Quenching of 1MN* by TEA. The quenching rate constants, k_q, for the deactivation of the singlet excited state of 1MN by TEA were obtained from typical stationary fluorescence quenching experiments. The lifetimes of the unquenched aromatic were measured in the different solvents using the time-resolved fluorescence technique (see the Materials and Methods section).

Let us assume the following kinetic scheme for the overall quenching process:

SCHEME 2

$$A^* + D \underset{k_{-d}}{\overset{k_d}{\rightleftarrows}} (A^*D) \underset{k_{bet}}{\overset{k_{et}}{\rightleftarrows}} (A^{\bullet -}D^{\bullet +}) \xrightarrow{k_g} A + D$$

where k_d represents the bimolecular rate constant for diffusion; k_{-d} the reciprocal of the duration of a collision due to Brownian motion; k_{et} the rate constant for the electron transfer process; k_{bet} the rate constant for the back electron transfer regenerating the excited aromatic; and k_g the summation of the rate constants for the processes by which the ionic intermediate disappears.

The observed rate constant k_q may be related to the theoretical expression for electron transfer by[51,52]

$$\frac{1}{k_q} = \frac{1}{k_d} + \frac{1}{k_{q'}} \quad (8)$$

where $k_{q'}$ is the "activated" quenching rate constant, the expression of which is given in terms of the rate constants in Scheme 2 by

$$k_{q'} = \frac{K_D k_{et} k_g}{k_{bet} + k_g} \quad (9)$$

In the above equation K_D represents the equilibrium constant for the formation of the cage encounter, k_d/k_{-d}; this magnitude may be taken as ~0.5−0.8.[33] Table 2 collects the values of kq', which were calculated from the experimental k_q and estimated values for k_d. The difusional rate constants were calculated using the expression derived by Smoluchowski[53] and the tabulated solvent viscosity for the different solvents at 298 K.[54] An inspection of Table 2 shows that $k_{q'}$ changes abruptly in a very narrow range of solvent polarity ($\epsilon \approx 2-4$) on going from hexane to butyl ether. As the polarity of the solvent increases, $k_{q'}$ also increases, although this change is not quite significant.

Biczóc et al.[34] showed that the quenching of 1MN by TEA in cyclohexane leads to reversible exciplex formation. A similar behavior has been also proposed for other aromatic hydrocarbons/tertiary amines exciplexes.[32,33] From time-resolved fluorescence experiments, Bistok et al. were able to estimate the rate constants k_{et}, k_{bet}, and k_g. The value of k_{et} was include in Table 2.

We studied the temperature effect on k_q in four solvents: cyclohexane, butyl ether, ethyl acetate, and acetonitrile. From these experiments it was observed that the activation enthalpy is positive in all the solvents except cyclohexane. In agreement with the interpretation given by Bistók et al., the negative activation enthalpy measured in cyclohexane is clear evidence for reversible exciplex formation.[55] An efficient redissociation of the exciplex ($k_{bet} \gg k_g$ in eq 9) explains the much lower observed $k_{q'}$ in the alkane solvents. In contrast, the positive enthalpies observed in the more polar solvents strongly suggest that $k_{q'}$ is mostly measuring the forward electron transfer reaction rate constant k_{et}. If "irreversible" exciplex formation occurs, $k_{bet} \ll k_g$ and

$$k_{q'} \approx K_D\, k_{et}$$

These results are important since we are trying to correlate the experimental $k_{q'}$ to the theoretical Marcus expression for k_{et} (eq 1).

TABLE 3: Quenching of the Singlet Excited State of 1-Methylnaphthalene (1MN) by Triethylamine (TEA): Calculated Solvent Reorganization Energy λ_s, Free Gibbs Energy Change ΔG^{ϵ}_{et}, Marcus Activation Energy ΔG^{*}_{et}, and Bimolecular Rate Constant for the Forward Electron Transfer, k_{et}; The Parameters Used for the Calculation Are $e\Delta E^{37.5}_{-et} = 3.55 \pm 0.04$ eV, $2\mu_e^2/4\pi\epsilon_0\rho^3 = 1.91 \pm 0.10$ eV, $\lambda_v = 0.72 \pm 0.04$ eV, and $Z = 1.8 \times 10^{11}$ M^{-1} s^{-1}

solvent	λ^{ϵ}_s (eV)	ΔG^{ϵ}_{et} (eV)	ΔG^{*}_{et} (eV)	$k_{et} \times 10^{-9}$ (M^{-1} s^{-1})
hexane	0.00	−0.15	0.114	2.3
cyclohexane	0.00	−0.17	0.107	2.9
n-butyl ether	0.09	−0.25	0.097	4.3
ethyl ether	0.16	−0.30	0.096	4.5
ethyl acetate	0.19	−0.34	0.090	5.7
tetrahydrofuran	0.20	−0.36	0.086	6.8
1,2-dichloroethane	0.21	−0.38	0.081	8.1
propionitrile	0.28	−0.42	0.082	7.5
acetonitrile	0.29	−0.43	0.084	7.1

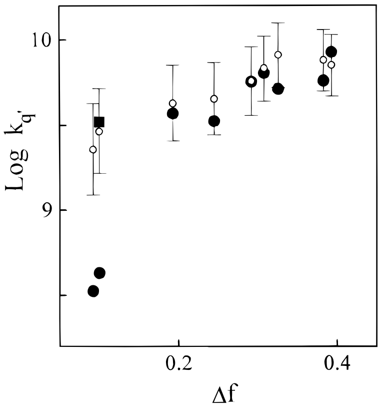


Figure 4. Linear free energy correlation plot. Plot of the activated bimolecular quenching rate constants for the quenching of 1MN by TEA *vs* the solvent parameter Δf: (●) experimental; (■) experimental rate constant for the forward electron transfer reaction in cyclohexane (ref 34); (○) rate constants for the forward electron transfer reaction calculated from eq 1 and the thermodynamic parameters givenin the text. The error bars account for the uncertainties in the calculation of ΔG^{*}_{et}.

The Correlation between Experimental and Calculated Electron Transfer Rate Constants. Table 3 shows the values of λ^{ϵ}_s, ΔG^{ϵ}_{et}, ΔG^{*}_{et}, and k_{et} calculated using the expressions 5, 6, 3, 2, 1, and taking $2\mu_e^2/4\pi\epsilon_0\rho^3 = 1.91 \pm 0.10$, $\Delta G^{37.5}_{-et} = 3.55 \pm 0.04$ eV, $\lambda_v = 0.72 \pm 0.04$ eV, and $E_{oo} = 3.98$ eV.[41] The preexponential factor Z was taken as an ajustable parameter. The averaged Z value that better fits the theoretically calculated k_{et} to the experimental $k_{q'}$ is 1.8×10^{11} M^{-1} s^{-1}.

As could be anticipated, as the polarity of the solvent increases, the photoreaction becomes more exergonic and the solvent barrier grows. Since these changes oppose, ΔG^{*}_{et} becomes almost insensitive to the properties of the medium. In Figure 4, the calculated rate constants are compared to the experimental values. We think that both the absolute value for the electron transfer rate constant and its solvent dependence are reasonably predicted. The error bars were calculated as the propagation of the errors in the experimental parameters $2\mu_e^2/4\pi\epsilon_0\rho^3$, $\Delta G^{37.5}_{-et}$, and λ_v into ΔG^{*}_{et}.

Finally, we wish to comment on some ambiguous points that are involved in this study.

(a) Nelsen et al.[46] showed for several amines that the neutral amine form is much easier to bend than the cationic form, making the functions used to describe the potential energy surfaces of these two species not identical. This results in different calculated internal reorganization energies for the oxidation of the amine $\lambda_v(\mathrm{D} \rightarrow \mathrm{D}^{\bullet+})$ and for the reduction of the cation radical $\lambda_v(\mathrm{D}^{\bullet+} \rightarrow \mathrm{D})$. However, these authors also proved that the contribution of the amine to the activation energy for electron transfer is always closely calculated by $\lambda_v(\mathrm{D}^{\bullet+} \rightarrow \mathrm{D})/4$. This justifies the use of $\lambda_v = 0.61$ eV for TEA in the calculation of the forward electron transfer rate constant, k_{et}.

(b) The reorganization energy of the solvent calculated from the dipole moment of the exciplex is small compared to the experimentally or theoretically calculated values[56] for other CRIPs. For instance, Gould et al.[6,8] showed for a series of cyanoaromatic/poly(alkylbenzene) CRIPs in acetonitrile that λ_s can be as large as 0.55 eV. This value is almost twice that estimated for the exciplex 1MN/TEA in the same solvent. Moreover, since for most exciplexes the term $2\mu_e{}^2/4\pi\epsilon_0\rho^3$ is < 2 eV,[44] the model assumed here predicts that λ_s cannot exceed ~0.4 eV under any circumstances.[57]

(c) In the more polar solvents of the series the quenching process may lead to the formation of SSIP. However, the parameters obtained from the emission of the exciplex fit acceptably the experimental rate constants in the whole range of solvent polarity. While SSIP formation in a polar solvent should be favored by a more negative ΔG^*_{et} (how more negative can it be?), a larger solvent barrier λ^ϵ_s should slow down the process. Since these changes compensate, it is likely that the rate constants for SSIP and CRIP formation are of the same order of magnitude, making the observed correlation in the more polar solvents fortuitous. Alternatively, it may be considered that the bimolecular reaction leads to exciplex formation with unit efficiency in all solvents.[58] In this case, the low efficiency for exciplex emission in the more polar solvents is explained as a consequence of a fast decrease of the exciplex radiative rate constant with decreasing $|\Delta G^\epsilon_{-et}|$. Despite that this may explain the good correlation observed in Figure 4, the hypothesis requires a significative solvent dependent degree of mixing between the locally excited (A*D) and pure charge transfer state ($\mathrm{A}^{\bullet-}\mathrm{D}^{\bullet+}$). Further studies are certainly required to understand this behavior.

Conclusions

As a conclusion for this study, we would like to emphasize the consistency found between experiments and the relationship predicted by the modern electron transfer theories for the back and forward electron transfer pathways. As the polarity of the solvent decreases, the photoreaction becomes less spontaneous and the solvent barrier is reduced. Since these changes oppose, the forward rate constant for electron transfer k_{et} is nearly solvent independent.

However, we would like to remark that the approach presented in this paper does not represent a general method in determining k_{et}. For most systems showing fluorescent exciplex formation, the main requirement of the model, namely, that the exciplex behaves as a nearly pure CRIP, is probably not fulfilled.

On the other hand, eq 7, which arises from the relatively simple dipole in the continuum model, may represent a useful tool in achieving information related to electron transfer thermodynamics. It was shown that it describes, at least qualitatively, the emissive proprieties of several highly polar exciplexes.

Acknowledgment. We thank the Consejo de Investigaciones Científicas y Tecnológicas de la Provincia de Córdoba (CONICOR) for financial support. Stimulating discussions with Professor Carlos M. Previtali and Professor Juan J. Cosa are also gratefully acknowledged.

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