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Mechanisms of Exciplex Formation. Roles of Superexchange, Solvent Polarity, and Driving Force for Electron Transfer

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Abstract: The efficiencies (α) with which exciplexes or excited charge-transfer (CT) complexes (collectively termed Ex's) are formed in bimolecular electron-transfer quenching reactions of excited electron acceptors (A^*) by donors (D) are determined. The acceptors are 9,10-dicyanoanthracene (DCA) and 2,6,9,10-tetracyanoanthracene (TCA). The donors are simple alkyl-substituted benzenes. The solvents vary in polarity, from cyclohexane to acetonitrile. The lifetimes of the Ex's (τ) and the efficiencies with which bimolecular quenching leads to Ex emission (Φ_f) are determined. The ratio Φ_f/τ corresponds to αk_f, where k_f is the radiative rate constant of the Ex. αk_f is found to decrease with increasing solvent polarity, as observed previously for other acceptor/donor systems. With only a few exceptions, this is the result of a decrease in k_f, rather than a decrease in α. The rate constant k_f also decreases with decreasing redox energy of the A/D pair. These changes in k_f are caused by varying contributions of locally excited and pure ion-pair states to the electronic structure of the Ex. Values for α of less than unity are found, however, for some quenching reactions in acetonitrile, as a result of direct formation of solvent-separated radical-ion pairs (SSRIP) from the A^*/D encounter pair. The competition between SSRIP and Ex formation is determined by the rate of SSRIP formation, which is driving force dependent and exhibits Marcus normal-region behavior. The Ex's are also bypassed in the quenching reactions of TCA* in *o*-dichlorobenzene. In this case, superexchange interactions in the encounter pair facilitate direct formation of the SSRIP.

I. Introduction

Exciplexes are transient charge-transfer (CT) species formed in bimolecular quenching reactions of excited states. The role of exciplexes in photoinduced electron-transfer reactions of organic molecules in homogeneous solution is very well documented,[1] and the kinetics and chemistry of these species have been extensively studied.[1,2] Exciplexes are closely related to the excited charge-transfer complexes formed upon excitation of ground-state CT complexes of acceptor/donor pairs (AD).[3] The term exciplex is used to describe such excited CT states when the acceptor and donor do not form a complex in the ground state, and excited-state charge transfer occurs only upon bimolecular encounter of an excited molecule and a quencher. An excited CT complex, however, can be formed either as a result of a bimolecular quenching reaction or directly by light absorption in the CT band of the ground-state complex. The electronic state of an exciplex or excited CT complex, which we will refer to collectively as Ex's, is usually described as a mixture of radical-ion pair ($A^{\bullet-}D^{\bullet+}$), locally excited (A^*D), and neutral (AD) states of the acceptor and donor.[1,4] When the contribution of the ion-pair state is dominant, an Ex can be regarded as equivalent to a contact radical-ion pair (CRIP).[1,3] In this case the Ex is closely related to another species, the solvent-separated radical-ion pair (SSRIP, $A^{\bullet-}(S)D^{\bullet+}$), which plays an important role in photoinduced electron-transfer reactions in polar solvents.[1,5]

Despite the large body of work related to the photophysics and chemistry of exciplexes and excited CT complexes, it is not generally known whether bimolecular electron-transfer quenching reactions always result in the formation of Ex species with unit efficiency or whether in more polar solvents the Ex might be formed with lower efficiency as a result of direct formation of a SSRIP. One of the best studied systems in this regard is the anthracene (acceptor)/*N,N*-dimethylaniline (donor) pair. The emission quantum yields and lifetimes for this exciplex have been measured in solvents with polarity varying from methylcyclohexane to acetone.[6] Both the emission quantum yield and the lifetime were observed to decrease with increasing solvent polarity. However, the emission quantum yield decreased faster than the measured lifetime. To explain these results, it was proposed that the reaction proceeds through an encounter pair (A^*/D), where direct formation of a SSRIP can occur in competition with Ex formation (eq 1).[6] It was suggested that SSRIP formation becomes more probable with increasing solvent polarity because SSRIP formation becomes more energetically favorable under these conditions.[7]

$$\begin{tikzcd} & \mathrm{Ex} \\ A^*/D \arrow[ur] \arrow[dr] & \\ & A^{\bullet-}(S)D^{\bullet+} \end{tikzcd} \qquad (1)$$

An alternative explanation has been offered for this type of behavior, however, in which the bimolecular reaction results in exciplex formation with unit efficiency in all solvents, but in which the exciplex radiative rate constant decreases with increasing solvent polarity, because of increasing contributions of the pure

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[1] (a) Beens, H.; Weller, A. In *Organic Molecular Photophysics*; Birks, J. B., Ed.; Wiley: New York, 1975; Vol. 2, Chapter 4. (b) Mataga, N.; Ottolenghi, M. In *Molecular Association*; Foster, R., Ed.; Academic: New York, 1979; Vol. 2, p 1.

[2] (a) Caldwell, R. A.; Creed, D. *Acc. Chem. Res.* **1980**, *13*, 45. (b) Mattes, S. L.; Farid, S. *Acc. Chem. Res.* **1982**, *15*, 80. (c) Mattes, S. L.; Farid, S. *Science* **1984**, *226*, 917. (d) Mattes, S. L.; Farid, S. In *Organic Photochemistry*; Padwa, A., Ed.; Dekker: New York, 1983; Vol. 6, p 233.

[3] Mulliken, R. S.; Person, W. B. *Molecular Complexes: A Lecture and Reprint Volume*; Wiley-Interscience: New York, 1969.

[4] This description is appropriate for a good donor and a good acceptor, where the energy of the lowest singlet excited state of the acceptor is lower than that of the donor, which is the case for the present systems. Henceforth, the radical-ion-pair state will be referred to simply as the ion-pair state.

[5] (a) Weller, A. *Z. Phys. Chem. (Munich)* **1982**, *130*, 129. (b) Gould, I. R.; Young, R. H.; Farid, S. In *Photochemical Processes in Organized Molecular Systems*; Honda, K., Ed.; Elsevier: Amsterdam, 1991; p 19. (c) Gould I. R.; Mueller, L. J.; Farid, S. *Z. Phys. Chem. (Munich)* **1991**, *170*, 143.

[6] Knibbe, H.; Röllig, K.; Schäfer, F. P.; Weller, A. *J. Chem. Phys.* **1967**, *47*, 1184.

[7] Weller, A. *Z. Phys. Chem. (Munich)* **1982**, *133*, 93.

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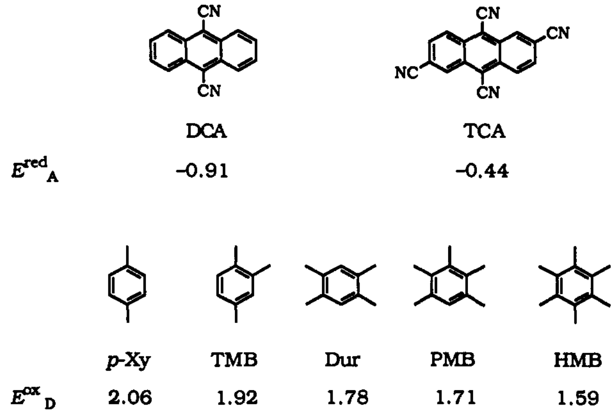
Chart 1. Structures and Redox Properties of Acceptors and Donors in Acetonitrile (V vs SCE)[10]



ion-pair state (and decreasing contributions of locally excited states) to the overall electronic structure of the exciplex.[8] The first interpretation of the data suggests that a fundamental change occurs in the mechanism of electron-transfer quenching with increasing solvent polarity, whereas the second suggests that a fundamental change occurs in the electronic structure of the exciplex with solvent polarity. In general, it is not known which of these two effects is more important, despite the fact that such information is fundamental to the understanding of bimolecular photoinduced electron-transfer reactions.

In this work we describe a detailed study of the emission quantum yields and radiative rates for the Ex formed between cyanoanthracene acceptors and alkyl-substituted benzene donors in solvents with widely varying polarities. The factors that control the emission efficiencies for these Ex's are determined by varying the donor, the acceptor, and the solvent polarity and by comparing the emission efficiencies of exciplexes formed in bimolecular quenching reactions with those for closely related excited CT complexes formed by excitation in their ground-state CT absorption bands. From these experiments, the effiency with which Ex formation occurs in the bimolecular quenching reactions can be determined.[9]

II. Results and Discussion

A. Fluorescence Properties of Exciplexes/Excited CT Complexes. The electron acceptors used in this work are 9,10-dicyanoanthracene (DCA) and 2,6,9,10-tetracyanoanthracene (TCA). The lowest singlet excited states of the acceptors have similar energies (2.90 and 2.87 eV, respectively),[10] although their reduction potentials ($E^{\mathrm{red}}_{\mathrm{A}}$) are quite different (Chart 1).[10] The donors are the simple methyl-substituted benzenes *p*-xylene (*p*-Xy), 1,2,4-trimethylbenzene (TMB), durene (Dur), pentamethylbenzene (PMB), and hexamethylbenzene (HMB) (Chart 1). The oxidation potentials of the donors ($E^{\mathrm{ox}}_{\mathrm{D}}$) decrease with increasing methyl substitution on the benzene ring.

Excitation of the cyanoanthracene acceptors in the presence of the donors in argon-purged solution in solvents with varying polarity (Table 1) gives typical Ex emission spectra, as indicated in Figure 1 and as reported previously by others.[11] Excitation was performed at wavelengths greater than 370 nm, where the alkylbenzenes do not absorb and only the cyanoanthracenes are excited. For DCA as the acceptor, ground-state CT complex formation does not occur to any appreciable extent with most of the donors used here (an exception is with the strongest donor HMB in the least polar solvent cyclohexane) and exciplexes are formed as a result of bimolecular quenching of the DCA*. For TCA as the acceptor, ground-state CT complex formation occurs to varying extents, depending upon the donor, its concentration, and the solvent (see further below). Irradition at wavelengths shorter than ca. 430 nm results in excitation of both the uncomplexed TCA and the CT complex. Irradiation at wavelengths greater than 450 nm results in exclusive excitation of the CT complexes.

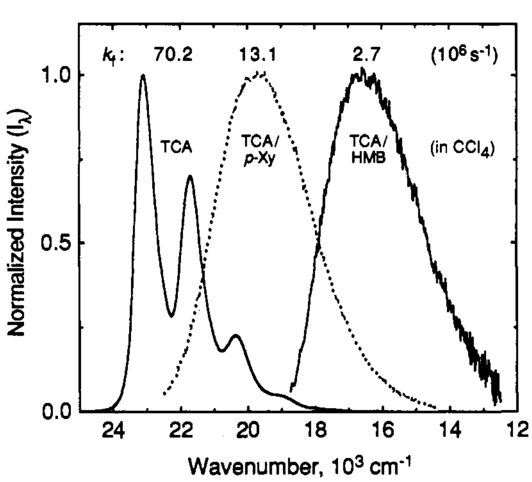


Figure 1. Emission spectra and radiative rate constants (k_f) of 2,6,9,10-tetracyanoanthracene (TCA) and the excited CT complexes of TCA with *p*-xylene (0.2 M) and with hexamethylbenzene (0.2 M), in carbon tetrachloride at room temperature. Residual TCA* emission has been subtracted from the total emission spectra obtained in the presence of the donors.

An important issue relevant to the present study is whether the emitting excited CT complexes formed via excitation in the CT absorption bands of the ground-state AD complexes are the same as those formed via bimolecular reaction of the uncomplexed excited acceptor and donor (A* + D). It has been reported in some cases that the emitting species formed via these two excitation routes are, in fact, not the same.[12,13] Usually, differences in emission spectra, or in efficiencies of product formation for excitation under different conditions, are cited as evidence in support of this suggestion.[12,13] The two excitation processes could certainly result in the formation of excited CT species in different initial geometries. The important question for the present purposes, however, is whether relaxation to a common species occurs prior to emission. This question can be answered by comparing the emission spectra obtained via the two excitation modes. At donor concentrations less than ca. 0.01 M, TCA is largely uncomplexed and excitation at wavelengths corresponding to the 0–0 absorption band ($\lambda_{\max}$ = 427–435 nm, depending on the solvent) results mainly in the formation of TCA*, which can then be quenched upon diffusive encounter with the donor. At higher donor concentrations, and with excitation at wavelengths longer than 450 nm, excitation of the CT complex occurs exclusively. The emission spectra obtained via these two excitation modes in a variety of solvents are found to be identical for the donors of Chart 1 (see further below). Therefore, for these acceptor/donor systems in these solvents at room temperature, both excitation modes lead to the same Ex species.[14]

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[8] (a) Mataga, N.; Okada, T.; Yamamoto, N. *Chem. Phys. Lett.* **1967**, *1*, 119. (b) Mataga, N.; Murata, Y. *J. Am. Chem. Soc.* **1969**, *91*, 3144.

[9] Some of these results have been presented previously in preliminary form.[5c]

[10] Gould, I. R.; Ege, D.; Moser, J. E.; Farid, S. *J. Am. Chem. Soc.* **1990**, *112*, 4290.

[11] (a) Chandross, E. A.; Ferguson, J. *J. Chem. Phys.* **1967**, *47*, 2557. (b) Itoh, M.; Kumano, Y.; Okamoto, T. *Bull. Chem. Soc. Jpn.* **1976**, *49*, 42.

[12] See, for example: Jones, G., II. In *Photoinduced Electron Transfer, Part A. Conceptual Basis*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; p 245.

[13] Gould, I. R.; Noukakis, D.; Gomez-Jahn, L.; Young, R. H.; Goodman, J. L.; Farid, S. *Chem. Phys.* **1993**, *176*, 439.

[14] (a) The same conclusion was reached for some of these and other DCA/donor systems at low temperature.[11b,14b] (b) Itoh, M.; Mimura, T. *Chem. Phys. Lett.* **1974**, *24*, 551.

Table 1. Average Fluorescence Wavenumbers, Quantum Yields, Lifetimes, and Radiative Rate Constants for Cyanoanthracene/Alkylbenzene Exciplexes/Excited CT Complexes in Different Solvents

A[a]	D[b]	solvent[c]	$\bar{\nu}_{av}$[d] (10^3 cm^{-1})	Φ_f[e]	τ[f] (ns)	k_f[g] (10^6 s^{-1})	k'_f[h] (10^6 s^{-1})
DCA	Dur	CHX	20.33	0.84	(37.5)	22.40	8.69
DCA	PMB	CHX	19.80	0.80	49.5	16.16	6.27
DCA	HMB	CHX	18.97	0.66	70.4	9.38	3.64
TCA	*p*-Xy	CHX	19.69	0.79	44.0	17.95	6.96
TCA	TMB	CHX	18.89	0.70	73.9	9.47	3.67
TCA	Dur	CHX	17.82	0.51	104.5	4.88	1.89
TCA	PMB	CHX	17.41	0.41	93.6	4.38	1.70
TCA	HMB	CHX	16.56	0.196	62.5	3.14	1.22
TCA	*p*-Xy	CTC	18.98	0.65	49.8	13.05	4.72
TCA	TMB	CTC	18.09	0.52	72.0	7.22	2.61
TCA	Dur	CTC	16.89	0.39	88.9	4.39	1.59
TCA	PMB	CTC	16.45	0.23	66.1	3.48	1.26
TCA	HMB	CTC	15.63	0.091	33.6	2.71	0.98
DCA	Dur	TCE	19.42	0.70	(39.7)	17.6	6.15
DCA	PMB	TCE	18.82	0.55	48.1	11.4	3.99
DCA	HMB	TCE	18.02	0.26	41.0	6.34	2.22
TCA	*p*-Xy	TCE	18.41	0.41	51.8	7.92	2.77
TCA	TMB	TCE	17.53	0.29	54.8	5.29	1.85
TCA	Dur	TCE	16.27	0.15	46.6	3.22	1.13
TCA	HMB	TCE	14.75	0.026	12.2	2.13	0.75
DCA	PMB	Diox	18.25	0.54	78.5	6.88	2.69
DCA	HMB	Diox	17.35	0.31	69.9	4.43	1.73
TCA	Dur	Diox	14.91	0.017	8.7	1.95	0.76
TCA	HMB	Diox	13.74	0.0036	2.6	1.38	0.54
DCA	PMB	*p*-Xy	18.67	0.72	70.0	10.3	3.48
DCA	HMB	*p*-Xy	17.89	0.50	82.9	6.03	2.04
TCA	PMB	Tol	14.98	0.049	20.9	2.34	0.78
TCA	HMB	Tol	14.15	0.019	9.2	2.07	0.69
DCA	Dur	FB	18.71	0.71	(69.4)	10.2	3.65
DCA	PMB	FB	18.04	0.53	78.3	6.77	2.42
DCA	HMB	FB	17.08	0.31	68.5	4.53	1.62
TCA	*p*-Xy	FB	17.20	0.087	22.5	3.87	1.38
TCA	TMB	FB	16.21	0.041	14.7	2.79	1.00
TCA	Dur	FB	14.91	0.016	7.2	2.22	0.79
TCA	PMB	FB	14.45	0.0082	4.6	1.78	0.64
TCA	HMB	FB	13.52	0.0035	2.1	1.67	0.60
DCA	PMB	DCM	17.32	0.25	51.2	4.88	1.90
DCA	HMB	DCM	16.35	0.093	28.1	3.31	1.29
TCA	*p*-Xy	DCM	16.68	0.015	5.3	2.83	1.10
TCA	Dur	DCM	14.45	0.0028	1.61	1.74	0.68
TCA	PMB	DCM	13.93	0.0016	1.05	1.52	0.59
TCA	HMB	DCM	13.11	0.00056	0.50	1.12	0.44
DCA	PMB	*o*-DCB	17.82	0.35	52.2	6.71	2.01
DCA	HMB	*o*-DCB	16.90	0.17	36.1	4.71	1.41
TCA	*p*-Xy	*o*-DCB	16.98	0.028	11.3	2.48/α[i]	0.74/α[i]
TCA	TMB	*o*-DCB	16.00	0.015	7.4	2.03/α[i]	0.61/α[i]
TCA	Dur	*o*-DCB	14.85	0.0068	4.3	1.58/α[i]	0.47/α[i]
TCA	PMB	*o*-DCB	14.25	0.0043	3.1	1.39/α[i]	0.42/α[i]
DCA	Dur	BN	16.76	0.019	5.1	3.72	1.58
DCA	PMB	BN	16.20	0.017	5.6	3.04	1.29
DCA	HMB	BN	15.40	0.0091	4.4	2.07	0.88
DCA	Dur	AN	16.12	0.0045	1.6	2.81	1.30
DCA	PMB	AN	15.52	0.0044	1.9	2.32	1.07
DCA	HMB	AN	14.86	0.0023	1.8	1.28/α[i]	0.59/α[i]

[a] The acceptors are DCA (9,10-dicyanoanthracene) and TCA (2,6,9,10-tetracyanoanthracene). [b] The structures of the donors are given in Chart 1. [c] The solvents and their refractive indices are cyclohexane (CHX, 1.426), carbon tetrachloride (CTC, 1.4595), trichloroethylene (TCE, 1.4755), *p*-dioxane (Diox, 1.422), *p*-xylene (*p*-Xy, 1.495), toluene (Tol, 1.496), fluorobenzene (FB, 1.465), dichloromethane (DCM, 1.424), *o*-dichlorobenzene (*o*-DCB, 1.551), butyronitrile (BN, 1.384), and acetonitrile (AN, 1.344). [d] The average emission frequency of the exciplex/excited CT complex (eq 2).[15b] [e] Emission quantum yield for bimolecular reaction of A* and D. [f] Ex emission lifetimes obtained from single photon counting experiments.The numbers in parentheses indicate that an equilibrium was observed between the Ex and A* and the Ex lifetime was extrapolated to infinite [D]. [g] Ex radiative rate constant. [h] Calculated from k_f and the solvent refractive index (n) according to eq 10. [i] In this case the Ex was formed with an efficiency (α) that is less than unity (see text).

As expected,[1,11] the Ex emissions occur at longer wavelength with increasing solvent polarity, with increasing ability of the donor to donate an electron (i.e., with lower donor oxidation potential, E^{ox}_D, Chart 1), and with increasing ability of the acceptor to accept an electron (i.e., with less negative acceptor reduction potential, E^{red}_A, Chart 1). An average emission frequency that is appropriate for excited CT states can be defined as shown in eq 2, in which I_λ is the intensity of the emission at frequency ν, measured per unit wavelength.[13,15] For the Ex studied here, the $\bar{\nu}_{av}$ are smaller than the emission maxima ($\bar{\nu}_{max}$) by 800–1100 cm^{-1}, depending upon the width of the emission spectrum. The $\bar{\nu}_{av}$ for the various Ex species are summarized in Table 1.

$$\nu_{av} = \int \nu^{-2} I_\lambda \, d\nu \Big/ \int \nu^{-3} I_\lambda \, d\nu \qquad (2)$$

B. Efficiencies and Mechanisms of Formation of Ex. For each system included in the present study, the lifetime (τ) of the Ex and the quantum yield of Ex emission (Φ_f) were measured for the bimolecular reactions of the excited acceptors (A*) with the donors

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(15) (a) The applicability of this average frequency is discussed in the accompanying paper.[15b] (b) Gould, I. R.; Young, R. H.; Mueller, L. J.; Albrecht, A. C.; Farid, S. *J. Am. Chem. Soc.*, following article in this issue.

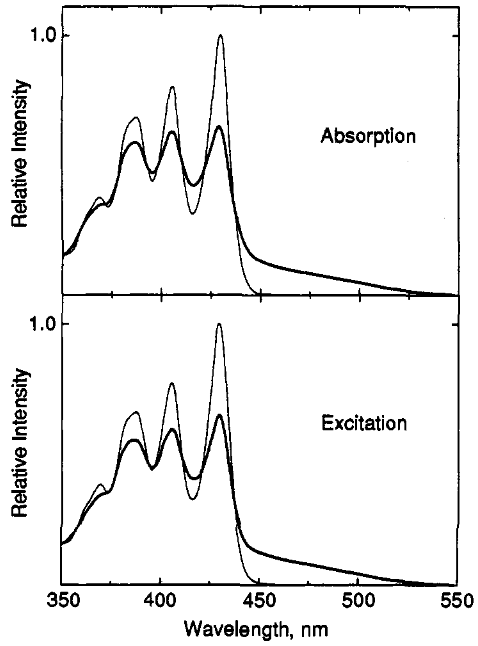


Figure 2. Absorption and excitation spectra for 2,6,9,10-tetracyanoanthracene (TCA) in the presence (heavy curves) and absence (light curves) of 0.56 M pentamethylbenzene in trichloroethylene. The excitation spectra are normalized to match the absorption spectra at the respective absorption maxima.

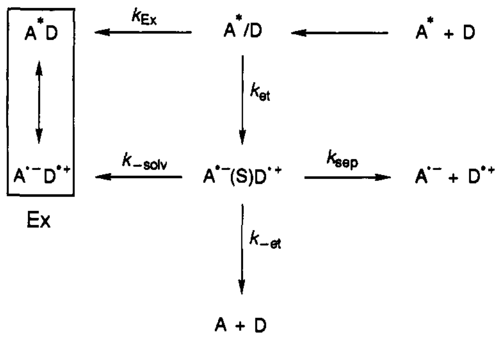
(D). As used in this work, Φ_f is the number of photons emitted from the Ex per A* quenched, i.e. the measured values were corrected for incomplete interception of A*. The τ and Φ_f data are summarized in Table 1. For the bimolecular quenching process (A* + D), Φ_f and τ are related as shown in eq 3. Here, k_f is the radiative rate constant for the Ex and α is the efficiency with which the Ex is formed *in the bimolecular reaction.*

$$\Phi_f/\tau = \alpha k_f \qquad (3)$$

For any acceptor/donor pair, Φ_f/τ decreases with increasing solvent polarity (Table 1), in a manner that is qualitatively similar to that observed previously for related systems.[6,8] In order to determine whether this is because of a decrease in α, k_f, or both, advantage is taken of the fact that TCA forms ground-state complexes with the alkylbenzenes. In the presence of increasing concentrations of donor, the TCA absorptions in the 350–450-nm region become less structured and a broad CT absorption appears at longer wavelength (Figure 2). If excitation of the CT complex is performed (rather than excitation of the uncomplexed acceptor), then the excited CT complex is formed with unit efficiency. In these cases, the quantity α for formation of the excited CT complex in the corresponding bimolecular reaction can be determined directly by comparing the relative Ex emission efficiencies for the A* + D reaction and for CT excitation. If the emission efficiencies are the same, then α is unity. A value for α of less than unity would indicate that (1) the emitting excited CT complex must be formed from the encounter pair with less than unit efficiency, i.e. the SSRIP must be formed directly at least part of the time from the encounter pair A*/D (eq 1), *and* (2) once formed, other processes within the SSRIP (e.g., nonradiative decay and/or further separation to give the free radical ions) must compete with "collapse" of the SSRIP to form the contact Ex.

A general mechanism for formation of an Ex in a bimolecular electron-transfer reaction is shown in Scheme 1.[5b] The formation efficiencies of the Ex in the various acceptor/donor/solvent systems can be understood in terms of the competitive processes included in the scheme. Here, the Ex is shown as $A^*D \leftrightarrow A^{\bullet-}D^{\bullet+}$ to illustrate the possibility of mixing of pure ion-pair and locally excited states. The mechanism illustrates the ways in which the Ex can be formed but, for the sake of clarity, does not include the Ex deactivation processes. The mechanism is appropriate for the case where Ex formation from A* + D is exothermic and the rate constant for the A* + D reaction is essentially diffusion controlled.

Scheme 1. Mechanisms of Formation of Exciplexes and Excited CT Complexes (Ex) in Bimolecular Electron-Transfer Reactions[a,5b]



[a] Not included are the deactivation processes of the Ex.

Three of the processes included in Scheme 1 (k_{Ex}, k_{-solv}, and k_{sep}) involve diffusive motions of the acceptor and the donor. Formation of the Ex from the encounter pair A*/D (k_{Ex}) involves diffusion of the acceptor and donor so that these species come into contact. A reasonable assumption is that, once A* and D are in contact, formation of the Ex is very fast and the rate-determining step is the diffusive process. The rate of this process is thus expected to vary somewhat with solvent viscosity, but not necessarily with solvent polarity. The relative energies of the Ex, SSRIP, and separated radical ions will, however, vary strongly with solvent polarity.[7] Except in highly polar solvents, the separated radical ions ($A^{\bullet-} + D^{\bullet+}$) are higher in energy than the SSRIP, which are higher in energy than the Ex. With decreasing solvent polarity, these energy differences increase. Hence, the rate constant for separation of the SSRIP (k_{sep}) is expected to rapidly decrease, and the rate constant for formation of the Ex from the SSRIP (k_{-solv}) is expected to increase, with decreasing solvent polarity.

The two remaining processes are electron transfer in the encounter pair to form a SSRIP (k_{et}) and return electron transfer in the SSRIP (k_{-et}). Quite different dependencies on solvent polarity are expected for k_{et} and k_{-et}. For electron-transfer reactions in which the driving force ($-\Delta G$) is less than the total electron-transfer reorganization energy (λ), an increase in rate constant with increasing $-\Delta G$ is expected, i.e. Marcus "normal-region" behavior. When $-\Delta G$ is greater than λ, then a decrease in rate with increasing driving force is expected, i.e. Marcus "inverted-region" behavior.[16] The k_{et}'s for the SSRIP-forming reactions' are expected to exhibit normal-region behavior whereas the k_{et}'s for the return electron transfer reactions' are expected to exhibit inverted-region behavior.

In the most polar solvent, acetonitrile, the energy of the SSRIP is given approximately by the difference in the electrochemical redox potentials of the acceptor and donor (E_{redox})[10] (eq 4). Thus, the driving force ($-\Delta G_{et}$) for the SSRIP-forming reaction (k_{et}) is the difference between this energy and the energy of the cyanoanthracene excited state (E_{A^*}), as shown in eq 5 and

$$E_{redox} = E^{ox}{}_{D} - E^{red}{}_{A} \qquad (4)$$

$$-\Delta G_{et} = E_{A^*} - E_{redox} \qquad (5)$$

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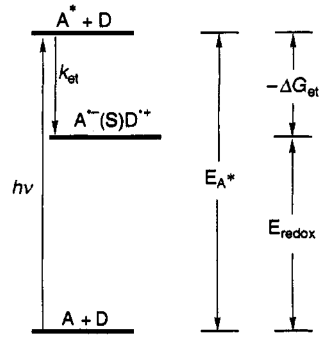
(16) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265.

Scheme 2. Relationship between the Excitation Energy (E_{A^*}), Redox Energy ($E_{redox} = E^{ox}{}_D - E^{red}{}_A$), and Driving Force ($-\Delta G_{et}$) for the Formation of SSRIP ($A^{\bullet-}(S)D^{\bullet+}$) in Acetonitrile



$$-\Delta G_{et} = E_{A^*} - E_{redox}$$

Table 2. Driving Force for the Formation of Solvent-Separated Radical-Ion Pairs from Encounter Pairs ($-\Delta G_{et}$) and the Efficiency of Ex Formation (α) in the Bimolecular Electron-Transfer Reactions of Cyanoanthracene Excited Acceptors (A*) with Alkylbenzene Donors (D) in Acetonitrile

A[a]	D[b]	$-\Delta G_{et}$[c] (eV)	α	k_{et}/k_{Ex}[d]
TCA	*p*-Xy	0.37	0.8 ± 0.07	0.2–0.4
DCA	HMB	0.40	0.7 ± 0.05	0.3–0.5
TCA	TMB	0.51	0.3 ± 0.05	1.9–3.0
TCA	Dur	0.65	0.1 ± 0.02	7.3–11.5

[a] The acceptors are DCA (9,10-dicyanoanthracene) and TCA (2,6,9,10-tetracyanoanthracene). [b] The structures of the donors are given in Chart 1. [c] Determined using eqs 4 and 5, with E_{A^*} values for DCA and TCA (in acetonitrile) being 2.90 and 2.87 eV, respectively.[10] [d] Determined using eq 7.

illustrated in Scheme 2.[17] For radical-ion pairs of TCA in this solvent, return electron transfer in the SSRIP is characterized by a total λ of 1.9 eV.[17] The appropriate value for the SSRIP-forming forward electron transfer reaction may be somewhat different, but it is surely much larger than that for return electron transfer in the CRIP (0.75 eV).[17] The $-\Delta G_{et}$ values for the SSRIP-forming reactions of DCA* and TCA* with the alkylbenzenes are estimated according to eq 5 to be between 0.2 and 0.8 eV (Table 2, see further below), and therefore, Marcus normal-region behavior is expected for k_{et} in acetonitrile.

In the SSRIP-forming reactions, k_{et}, a charge-separated state is formed from a neutral species. For reactions of this type, both the electron-transfer driving force ($-\Delta G_{et}$) and the reorganization energy (λ) decrease with decreasing solvent polarity, as a result of decreased stabilization of the charge-separated state. To the extent that variations in the solvent refractive index can be neglected, these two effects should be of approximately equal magnitude and $\Delta G_{et} + \lambda$ should be approximately independent of solvent.[18a] Thus, if the reactions exhibit Marcus normal behavior in acetonitrile (see above), they should exhibit Marcus normal behavior also in solvents of lower polarity. In addition, although k_{et} might be expected to decrease with decreasing solvent polarity,[18b] for charge separation reactions in the normal region, the decrease may be quite gradual until the reaction becomes significantly endothermic.[18c] Thus, if direct SSRIP formation from the encounter pair is fast enough (k_{et} is large enough) to compete with Ex formation (k_{Ex}) in polar solvents such as acetonitrile, it may also be fast enough to be competitive in less polar solvents.

In contrast, the return electron transfer reactions in the SSRIP (k_{-et}) are clearly in the inverted region.[10,13,17] In these reactions, a neutral species is formed from a charge-separated state. With decreasing solvent polarity, the reorganization energy again decreases but the driving force ($-\Delta G_{-et}$) increases, so $\Delta G_{-et} + \lambda$ decreases (becomes more negative) and the electron-transfer process is pushed further into the inverted region. Consequently, the rate constant (k_{-et}) decreases rapidly with decreasing solvent polarity.[19] As a result, if SSRIP formation does actually occur in low polarity solvents, k_{-et} will probably be so small that it may not compete with k_{-solv}. Therefore, Ex formation efficiency could still be high even if the Ex is not the primary product.

1. Formation of Ex in Bimolecular Electron-Transfer Reactions with Unit Efficiency. Determination of the relative emission efficiencies for the CT excitation and the bimolecular quenching pathways is most easily performed by comparing excitation and absorption spectra for systems in which the donor concentration is sufficient both to complex a significant portion of the TCA and to efficiently quench the uncomplexed TCA*. A typical experiment is illustrated in Figure 2 in which the absorption spectra and excitation spectra are shown for TCA with PMB as the donor in trichloroethylene. The excitation spectrum was measured for the Ex emission monitored at 650 nm. The absorption and excitation spectra are very similar both in the presence and also in the absence of the donor. In particular, the ratio of the intensities at 460 nm (absorption in the CT band) and 429 nm (the absorption maximum of TCA) in the excitation spectrum in the presence of the donor is the same as that in the corresponding absorption spectrum. This experiment demonstrates that the emission efficiency is the same whether the uncomplexed TCA or the CT complex is excited, i.e. the Ex is formed with equal efficiency for both excitation pathways. Thus, for this system, α is equal to unity. In fact, such experiments for TCA with the donors discussed here clearly show that α is unity in most of the solvents studied with only a few exceptions, which are discussed in more detail below.[20]

The radiative rate constants for the TCA systems in which α is confirmed to be unity are plotted as the open squares in Figure 3 vs the average emission frequency of the Ex (ν_{av}). In order to compare solvents of different polarity, the radiative rates are corrected for the solvent refractive index (see below). The corrected radiative rate constants are denoted k'_f. The data exhibit a smooth decrease in k'_f with decreasing emission frequency. Also included in Figure 3 are the $\alpha k'_f$ data for the DCA exciplexes (open circles). Remarkably, these data exhibit the same smooth

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(17) Gould, I. R.; Young, R. H.; Moody, R. E.; Farid, S. *J. Phys. Chem.* **1991**, *95*, 2068.

(18) (a) $\Delta G_{et} + \lambda$ is the vertical energy difference between the neutral reactants and ionic products. Since the reactants do not polarize the solvents, this quantity does not depend on the static dielectric constant of the solvent. This situation is illustrated by the standard dielectric-continuum expressions for ΔG_{et} and λ given, for instance, in ref 18c. The situation is complicated somewhat by the fact that the refractive index of acetonitrile is considerably smaller than that of most other solvents used here. (b) Let λ_s denote the reorganization energy associated with low-frequency (mostly solvent) motions, and neglect, for a moment, the involvement of high-frequency intramolecular vibrations. The activation free energy for forward electron transfer, then, is $(\Delta G_{et} + \lambda_s)^2/4\lambda_s$. This quantity will increase with decreasing solvent polarity (smaller λ_s in the denominator). The decrease will be greater, the larger the numerator, i.e. the less exothermic the reaction. When high-frequency (intramolecular) vibrational modes are involved, the rate expression consists of a sum of terms with individual activation free energies of the same form (see eq 8), each of which increases with decreasing solvent polarity. (Deep in the Marcus normal region, nevertheless, the dominant contribution is the vibrationless term, $j = 0$.) When the reaction approaches adiabaticity, additional solvent-response factors also tend to make the reaction slower in less polar solvents (see eq 8). (c) For a clear example, see: Kroon, J.; Verhoeven, J. W.; Paddon-Row, M. N.; Oliver, A. M. *Angew. Chem., Int. Ed. Engl.* **1991**, *30*, 1358. (d) It is difficult to estimate λ_s and ΔG_{-et} for SSRIP formation in low-polarity solvents accurately enough to determine at what endothermicity k_{et} becomes small compared to k_{Ex}. When SSRIP formation is highly endothermic, however, a large k_{et} implies a yet much larger rate constant for the reverse process SSRIP → A*/D (not included in Scheme 1) and net production of SSRIP would be suppressed for this reason if no other.

(19) For a clear example, see ref 13.

(20) These experiments are also consistent with the conclusion reached earlier, that the emitting excited CT complex formed by the two excitation routes is the same.

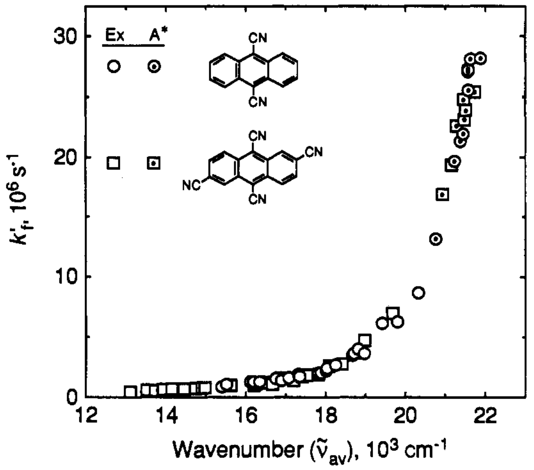

Figure 3. Plot of radiative rate constants, corrected for solvent refractive index (k'_f, eq 10), for exciplexes and excited CT complexes of 9,10-dicyanoanthracene (circles) and of 2,6,9,10-tetracyanoanthracene (squares) as acceptors with methyl-substituted benzenes as donors in various solvents as a function of average emission frequency. Only data points for which the Ex formation efficiency α is unity are included (see text). The dotted circles and squares are the corresponding data for the same acceptors in various solvents in the absence of added donors.

decrease with decreasing emission frequency, and in fact, the DCA and TCA data are essentially indistinguishable. Furthermore, no specific solvent effects are observed. The k_f's appear to depend simply upon the emission frequency (ν_{av}) rather than upon any specific structural feature or whether a ground-state CT complex is formed. The decrease in the radiative rates of the TCA systems must be caused by a decrease in k'_f because α is unity for these species as described above. The close similarity between the data for the two acceptors strongly suggests that the decrease in $\alpha k'_f$ with emission frequency for the DCA systems is also caused by a decrease in k'_f rather than in α. In addition, for the DCA/HMB pair in cyclohexane, where appreciable CT complex formation can actually be observed, the absorption and excitation spectra are identical, as observed for the TCA cases discussed above, which confirms that α for this system is indeed unity.

In support of the conclusion that α is unity for the DCA systems is the observation that the radiative rates for both acceptor systems show the same smooth decrease in radiative rate constant with decreasing ν_{av}, whether ν_{av} decreases because of increasing solvent polarity or decreasing E_{redox} (eq 4) of the acceptor/donor pair. E_{redox} decreases with decreasing donor oxidation potential and/or increasing (less negative) acceptor reduction potential. Increasing solvent polarity and decreasing E_{redox} both decrease the energy of the Ex species, which results in a corresponding decrease in ν_{av} and the radiative rate constant. Thus, the decrease in ν_{av} and radiative rate constant for any particular A/D pair with increasing solvent polarity can be reproduced in any particular nonpolar solvent by decreasing E_{redox}, i.e. by using different A/D pairs. Evidently the effects of increasing solvent polarity and decreasing E_{redox} are the same. The fact that the Ex formation efficiency is unity in the nonpolar solvent cyclohexane supports the suggestion that, also for the DCA systems, it is k'_f that decreases, rather than α, with increasing solvent polarity. As discussed in detail below, the decrease in k'_f with decreasing emission frequency is caused by a corresponding increase in the ion-pair character of the Ex.

The driving force for k_{et} can be estimated in nonpolar solvents using an approach described by Weller,[7] according to which the energy of a radical-ion pair separated by ca. 7 Å in an aliphatic hydrocarbon solvent is higher than E_{redox} (in acetonitrile) by roughly 1.2 eV. For the best acceptor (TCA) and the best donor (HMB), E_{redox} is 2.03 eV. Thus the energy of the SSRIP of this acceptor/donor pair in cyclohexane is ca. 3.23 eV, which is higher than the energy of TCA* (ca. 2.9 eV). The energies of the SSRIP of the other acceptor/donor pairs will be even higher than the TCA/HMB pair, and thus for all pairs, SSRIP formation from the encounter pair (k_{et}) should be endothermic and probably slow.[18c,d] Direct SSRIP formation in the encounter pair is therefore unlikely to compete with Ex formation, which explains the fact that α is observed to be unity for these reactions. In fact, α will almost certainly be unity in nonpolar solvents even if there are reactions in which SSRIP formation is exothermic because, as indicated above, k_{-et} and k_{sep} are unlikely to compete with k_{-solv} in the SSRIP. In nonpolar solvents, k_{-solv} is likely to be large because formation of the Ex from the SSRIP is exothermic.[18d]

With increasing solvent polarity, SSRIP formation from the encounter pair becomes more energetically feasible, to the extent that all of the reactions included in the present work are exothermic in acetonitrile (see above). In fact, some of the reactions in this solvent are characterized by α values that are less than unity, as discussed in detail in the next section. This means that at least *some* of the encounter pairs lead to the formation of SSRIP. Because the rate constants for this process, k_{et}, do not necessarily depend strongly on solvent polarity (see above), it is likely that direct formation of SSRIP may also occur in some of the encounter pairs in medium polarity solvents. Nevertheless, α values of unity are obtained in solvents with polarities up to dichloromethane. Therefore, in the cases in which SSRIP formation may be occuring from the encounter pair, k_{-solv} must be significantly greater than $k_{-et} + k_{sep}$. As discussed above, both k_{-et} and k_{sep} are expected to decrease very rapidly with decreasing solvent polarity and k_{-solv} presumably increases.

In summary, the data presented here suggest that, with a few exceptions detailed below, Ex formation occurs with near unit efficiency for most of the acceptor/donor/solvent systems. The high Ex formation efficiency even extends to most of the reactions of DCA* in solvents as polar as butyronitrile and acetonitrile (see further below, however). This means that any mechanism that describes the dynamics of the bimolecular electron-transfer reactions must take into account the intermediacy of Ex species even, sometimes, in solvents as polar as acetonitrile and even if they might not be the *primary* intermediates in the bimolecular electron-transfer reaction. Ex formation efficiencies of less than 100% are observed for some of the reactions of DCA* and TCA* in acetonitrile and butyronitrile and for the reactions of TCA* in *o*-dichlorobenzene. The reactions in these solvents can be understood as a consequence of two different medium effects on the bimolecular quenching reaction.

2. Driving-Force-Dependent Formation of Solvent-Separated Radical-Ion Pairs.

In the case of acetonitrile as the solvent, values of α are encountered that are less than unity for some of the A/D pairs. In acetonitrile, the SSRIP's are highly stabilized, and for the present A/D pairs, their formation from the encounter pair A*/D is exothermic. The $-\Delta G_{et}$ values for formation of the SSRIP from the A*/D, determined using eqs 4 and 5, are summarized in Table 2.

The emissions from the Ex when TCA is used as the acceptor in acetonitrile are very weak, and therefore, α was estimated using a more sensitive method than the comparison of absorption and excitation spectra.[21] The fluorescence intensities of the Ex were measured at different donor concentrations for excitation at a wavelength where both the AD complex and the uncomplexed A absorb. Under these conditions, the ratios of the Ex emission quantum yields $(\Phi_f)_{[D]}$ and $(\Phi_f)_{[D']}$ at two donor concentrations [D] and [D'] and the respective Ex lifetimes $\tau_{[D]}$ and $\tau_{[D']}$ are

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(21) (a) The data for these acceptor/donor pairs are not included in Table 1 because the emission spectra occur at too long wavelength and are too weak for accurate determination of their maxima and quantum yields.[21b] (b) Gould, I. R.; Farid, S. *J. Phys. Chem.* **1992**, *96*, 7635.

related by eq 6. In eq 6, K_{CT} is the equilibrium constant for

$$\frac{(\Phi_f)_{[D]}}{(\Phi_f)_{[D']}}\frac{\tau_{[D']}}{\tau_{[D]}} = \left(\frac{\alpha + rK_{CT}[D]}{\alpha + rK_{CT}[D']}\right)\left(\frac{1 + rK_{CT}[D']}{1 + rK_{CT}[D]}\right) \quad (6)$$

formation of the charge-transfer complex and r is the ratio of the extinction coefficients of the AD complex and the uncomplexed acceptor (ϵ_{AD}/ϵ_A) at the excitation wavelength. The experiments were actually performed with excitation at an isosbestic point so that $r = 1.0$. Values for α were obtained directly using eq 6 after values for K_{CT} were estimated. The details of these experiments are given in the Experimental Section.

The results are summarized in Table 2. The clear conclusion is that α decreases sharply with increasing driving force for SSRIP formation, from ca. 0.8 for TCA/p-Xy ($-\Delta G_{et} = 0.37$ eV) to ca. 0.1 for TCA/Dur ($-\Delta G_{et} = 0.65$ eV). With a further increase in driving force, i.e. for TCA/PMB and TCA/HMB ($-\Delta G_{et} > 0.72$ eV), the Ex emissions are too weak for α to be accurately determined. For these systems, however, previous studies have shown that the yields of formation of separated radical ions are significantly smaller for CT excitation compared to the A* + D bimolecular quenching route, clearly indicating that α is small in these cases also.[17] In addition, we have previously studied the TCA/mesitylene pair in acetonitrile, which has a small driving force for SSRIP formation ($-\Delta G_{et} = 0.32$ eV), and indeed, a value close to unity was determined for this system.[21b] Taken together, these results provide strong support for a steep dependence of α on driving force.

For DCA* as the acceptor, α cannot be determined from excitation spectra because of the absence of ground-state CT complex formation. Information concerning the magnitude of α, however, can still be obtained. Shown in Figure 4B is a plot of $\alpha k'_f$ for the DCA Ex in all solvents, plotted in semilogarithmic form to expand the lower region.[22] The data points for the DCA/Dur ($\tilde{\nu}_{av} = 16.08 \times 10^3$ cm^{-1}, $\alpha k'_f = 1.30 \times 10^7$ s^{-1}) and DCA/PMB ($\tilde{\nu}_{av} = 15.48 \times 10^3$ cm^{-1}, $\alpha k'_f = 1.07 \times 10^7$ s^{-1}) pairs in acetonitrile fit very well with the rest of the data points, which indicates that α in these systems is near unity (see above). However, the point for the DCA/HMB pair in this solvent ($\tilde{\nu}_{av} = 14.82 \times 10^3$ cm^{-1}, $\alpha k'_f = 0.59 \times 10^7$ s^{-1}, triangle in Figure 4B) is low compared to those for the rest of the radiative rate data, which indicates that α is low. From the extent to which this point is lower than the rest of the data, a value of ca. 0.7[5c] can be estimated for α. The driving force for SSRIP formation for the DCA/HMB pair ($-\Delta G_{et}$) is 0.40 eV. The α value for this A/D pair is thus consistent with those of the TCA systems (Table 2), providing further support for a steep dependence for the efficiency of SSRIP formation on driving force.

Direct formation of the SSRIP in the encounter pair also appears to occur in the reactions of TCA* in butyronitrile (a less polar solvent than acetonitrile), although we have not made an extensive study in this solvent. For example, for the reaction TCA* + Dur, an α value of ca. 0.15 is determined by use of eq 6, which is similar to the value for the same pair in acetonitrile.

The dependence of α on $-\Delta G_{et}$ can be understood by consideration of the mechanisms for Ex formation discussed above (Scheme 1). The fact that α is less than unity *requires* that at least some of the encounter pairs form the SSRIP directly (k_{et}). It is most likely that the variable α occurs as a result of the competition between k_{et} and k_{Ex}. An alternative situation, where all of the encounter pairs result in SSRIP formation and the variable α is the result of changes in the ratio of k_{-solv} to (k_{-et} + k_{sep}), is considered to be less likely for the following reason. With increasing oxidation potential of the donor, the driving force for the return electron transfer reaction in the SSRIP increases and therefore k_{-et} decreases.[21b] For example, when p-Xy and Dur are used as the donors, (k_{-et} + k_{sep}) values have been estimated to be ca. 1×10^{10} and 2×10^{10} s^{-1}, respectively.[10,21b] If all of the reactions were to proceed through the SSRIP, in order to account for an α of 0.1 for the TCA/Dur system, k_{-solv} would have to be 2.2×10^9 s^{-1}. Similarly, to account for an α value of 0.8 for the TCA/p-Xy system, k_{-solv} would have to be 4×10^{10} s^{-1}. It does not seem reasonable that k_{-solv} would vary in this manner, and it seems more likely, therefore, that it is predominantly the competition in the encounter pair that determines α.

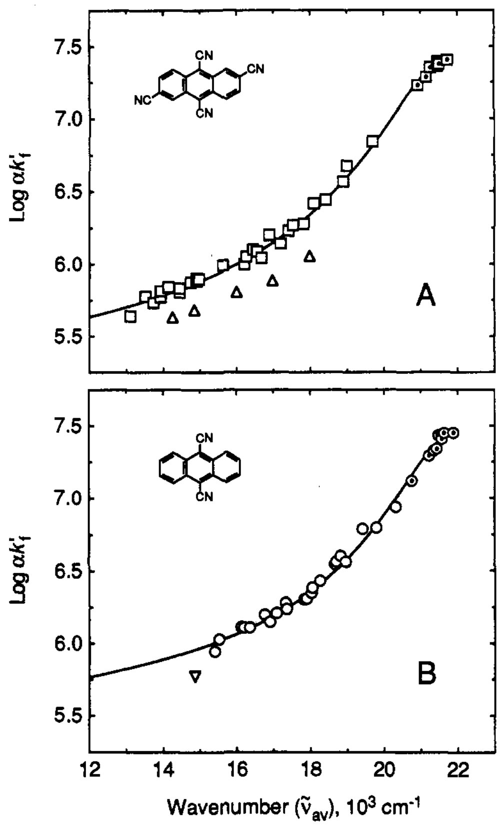

Figure 4. Log of the Ex formation efficiency (α) times the radiative rate constant corrected for the solvent refractive index (k'_f) for exciplexes and excited CT complexes of (A) 2,6,9,10-tetracyanoanthracene and (B) 9,10-dicyanoanthracene as acceptors with methyl-substituted benzenes as donors in various solvents at room temperature, plotted versus the average emission wavenumber. The curves drawn through the data points represent a theoretical dependence of k'_f on ν_{av}, as described in detail in the accompanying paper.[15b] The data points indicated by triangles refer to (A) various donors in o-dichlorobenzene and (B) hexamethylbenzene as the donor in acetonitrile. The Ex formation efficiency α is less than unity for these points (see text).

When $k_{et} \ll k_{Ex}$, Ex formation is efficient and α is essentially unity. When k_{et} becomes competitive with k_{Ex}, then SSRIP formation in the encounter pair can occur and α becomes less than unity. When k_{et} is significantly larger than k_{Ex}, then the Ex is bypassed. This is the case where $-\Delta G_{et}$ is largest because the reactions are in the Marcus normal region. According to this mechanism, α is related to k_{et} and k_{Ex}, as indicated in eq 7. The dependence of the ratio k_{et}/k_{Ex} on $-\Delta G_{et}$, determined in this way (Table 2), is shown in Figure 5.

$$\alpha = k_{Ex}/(k_{et} + k_{Ex}) \quad (7a)$$

$$k_{et}/k_{Ex} = \alpha^{-1} - 1 \quad (7b)$$

Estimates for k_{et} can be obtained from the values of α by assuming a value for k_{Ex}. As indicated above, this is presumably determined by the rate of the diffusive motions of A* and D in the encounter pair. Taking an approximate value for k_{Ex} of

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[22] The curve drawn through the data points represents a theoretical dependence of k'_f on ν_{av}. The evaluation of this curve and the fitting procedure are described in detail in the accompanying paper.[15b]

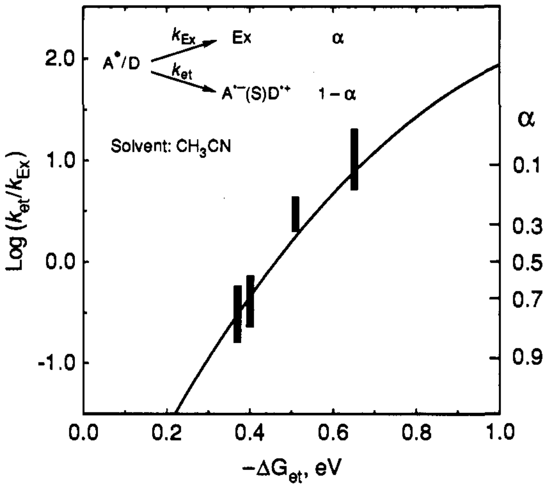

Figure 5. (left axis) Log of the ratio of the rates of SSRIP formation (k_{et}) and Ex formation (k_{Ex}) from the encounter pair (A^{*}/D) in acetonitrile and (right axis) Ex formation efficiencies (α) plotted as a function of the driving force for the SSRIP-forming electron-transfer reaction ($-\Delta G_{et}$). (k_{et}/k_{Ex}) and α are related as shown in eq 7. The SSRIP and Ex are formed with equal efficiency, $\log(k_{et}/k_{Ex}) = 0$, at $-\Delta G_{et} \approx 0.45$ eV. The curve is a prediction of the dependence of k_{et} on ΔG_{et}, as discussed in the text.

10^{10} s^{-1},[23] the k_{et} values range from ca. $3 \pm 1 \times 10^{9}$ s^{-1} for TCA/*p*-Xy to ca. $9 \pm 2 \times 10^{10}$ s^{-1} for TCA/Dur. The curve drawn through the data points corresponds to a theoretical prediction of the driving force dependence of $\log(k_{et}/k_{Ex})$. The dependence of k_{et} on $-\Delta G_{et}$ is calculated using eq 8.[24a,b] This equation expresses

$$k_{et} = \sum_{j=0}^{\infty} F_j V^2 \left(\frac{4\pi^3}{h^2 \lambda_s k_B T} \right)^{1/2} (1 + H_j)^{-1} \times \exp\left[-\frac{(\Delta G_{et} + jh\nu_v + \lambda_s)^2}{4\lambda_s k_B T} \right] \quad (8a)$$

$$H_j = \frac{8\pi^2 F_j V^2 \tau_L}{h\lambda_s} \quad (8b)$$

the electron-transfer rate constant in a solvent with a Debye frequency spectrum. The longitudinal relaxation time is τ_L, the low-frequency part (e.g., solvent) of the reorganization energy is λ_s, and the electronic coupling matrix element is V. High-frequency (intramolecular) vibrations are represented by a single mode with frequency ν_v and reorganization energy λ_v. This mode is initially in its ground state but may acquire one or more quanta of energy ($jh\nu_v$) in the electron-transfer event.[24c] The F_j are Franck–Condon factors for excitation of this mode. Taking τ_L to be 0.7 ps for acetonitrile[17,24d,e] and values for λ_v and ν_v of 0.2 eV and 1400 cm^{-1}, that are typical for the current systems, we can fit the data with a λ_s of 1.2 eV and a V of 150 cm^{-1}.

The value of 1.2 eV for λ_s is intermediate between those determined previously for return electron transfer reactions in contact (0.55 eV) and solvent-separated radical-ion pairs (1.72 eV).[17] The value of V of 150 cm^{-1} is also approximately intermediate between values established previously for these reactions,[17] suggesting that formation of the SSRIP is occurring, perhaps not surprisingly, at A/D separation distances that are smaller than those typical for thermalized SSRIP.

Although the data are consistent with these values for λ_s and V, there are clearly not enough data points to define these parameters accurately. There is also considerable uncertainty in estimating k_{Ex} and τ_L. The analysis of the data in terms of eq 8 as illustrated in Figure 5 also depends upon several other assumptions. As mentioned above, it is assumed that the efficiency of formation of the Ex is determined only by the competitive processes within the encounter pair. The analysis also assumes that the encounter pair is the same for all of the SSRIP-forming reactions. The encounter pair presumably does not have a well-defined structure. For example, there are no Coulombic forces to hold the acceptor and donor together as in the Ex and the SSRIP. As a consequence, the SSRIP-forming reaction may occur with the A* and D in different relative orientations or at different distances, which will decrease the reliability of the parameters λ_s and V estimated above. Therefore, the curve in Figure 5 should be viewed only as a *guide* to estimate the driving-force dependence for the partition between SSRIP and Ex formation in the encounter pair.

It is important to note that the dependence of α on the driving force indicated in Figure 5 may be different for other A/D systems, even in the same solvent, because the reorganization energies may be different. For example, an increase in λ_s would shift the curve in Figure 5 to the right and down, decreasing k_{et}/k_{Ex} for a given value of $-\Delta G_{et}$,[25] leading to a higher value of α. Indeed, preliminary results obtained with 1,4-dicyanobenzene as the excited acceptor in acetonitrile with the alkylbenzenes (Chart 1) as donors suggest that α is, in fact, approximately unity for all of these A/D pairs over a range of $-\Delta G_{et}$ from 0.5 to 1.0 eV.[26] In the same $-\Delta G_{et}$ range, the α values for the TCA systems change from ca. 0.5 to near zero. This difference is probably a consequence of the smaller size of the radical anion of dicyanobenzene compared to those of the cyanoanthracenes, which results in a larger reorganization energy.[10,13]

3. Through-Solvent Electron Transfer Mediated by Superexchange Interactions. Values of α that are less than unity were also obtained for the bimolecular reactions of TCA* with the alkylbenzene donors when *o*-dichlorobenzene (*o*-DCB) was used as the solvent. Comparisons of the absorption and CT emission excitation spectra for PMB as the donor indicate that α is ca. 0.6.[5c] This result is confirmed by the observation that the $\alpha k'_f$ values obtained with TCA* in *o*-DCB are lower than would be predicted for an α of unity, as indicated in Figure 4. The triangles in Figure 4A correspond to the donors *m*-xylene, *p*-Xy, TMB, Dur, and PMB in *o*-DCB. These points are lower than the rest of the data, which indicates that α is smaller than unity for all of these donors. The radiative rate constant data indicate that the α values for these different donors are, in fact, essentially the same, i.e. ca. 0.6.

This behavior can be explained as a consequence of partial charge-transfer interactions between TCA* and the solvent *o*-DCB (i.e., $TCA^{*\delta-}$-*o*-$DCB^{\delta+}$. Such CT interactions in an encounter pair A*/S/D will tend to "extend" the wave function of the excited acceptor by delocalizing the HOMO of the TCA into the *o*-DCB. As a result, the electronic coupling matrix element for electron transfer from the donor to the excited acceptor in a solvent-separated configuration should be increased. In effect, the CT interactions of the TCA* with the solvent represent an extreme example of a superexchange-enhanced rate of electron

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(23) North, A. M. *Q. Rev., Chem. Soc.* **1966**, *20*, 421.

(24) (a) Jortner, J.; Bixon, M. *J. Chem. Phys.* **1988**, *88*, 167. (b) The F_j are given by $\exp(-S)S^j/j!$, where S is given by $\lambda_v/h\nu_v$. (c) The main contribution to eq 8 comes from the $j = 0$ term, but the $j = 1$ term is not negligible. The "adiabaticity corrections" $(1 + H_j)^{-1}$ decrease k_{et} by roughly a factor of two relative to the "nonadiabatic" value. (d) Maroncelli, M.; MacInnes, J.; Fleming, G. R. *Science* **1989**, *243*, 1674. (e) Kahlow, M. A.; Kang, T. J.; Barbara, P. F. *J. Chem. Phys.* **1988**, *88*, 2372.

(25) An increase in the reorganization energy associated with the rearranged high-frequency modes (λ_v) will also result in a decrease in k_{et} for a fixed value of $-\Delta G_{et}$. In this case the curve shown in Figure 5 will be displaced vertically downward.

(26) Gould, I. R.; Farid, S. Unpublished work.

(27) (a) McConnell, H. M. *J. Chem. Phys.* **1961**, *35*, 508. (b) Miller, J. R.; Beitz, J. V. *J. Chem. Phys.* **1981**, *74*, 6746. (c) Exchange interactions between the HOMO of *o*-DCB and the HOMO of TCA (singly occupied in TCA*) are presumably the most important. The energy of the HOMO of *o*-DCB is lower than that of TCA. This must be the case since the pure ion-pair state $TCA^{\cdot-}$ *o*-$DCB^{\cdot+}$ is higher in energy than the TCA* *o*-DCB state (the TCA*/*o*-DCB system has only ca. 20% charge transfer[15b]).

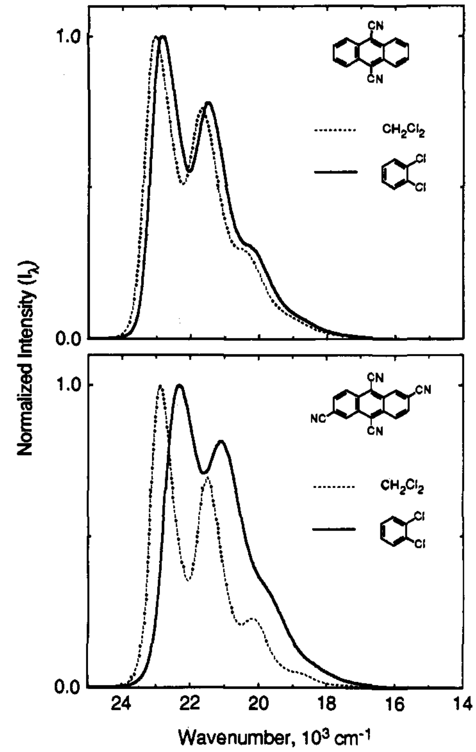


Figure 6. Emission spectra of (top) 9,10-dicyanoanthracene and (bottom) 2,6,9,10-tetracyanoanthracene in dichloromethane (dashed curves) and *o*-dichlorobenzene (solid curves) at room temperature.

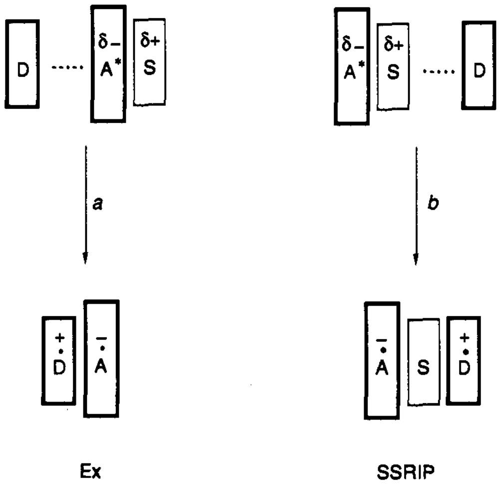
transfer.[27] The values for α of less than unity are then explained as a result of the enhanced rates of formation of the SSRIP in the encounter pair (k_{et}) which thus effectively compete with Ex formation (k_{Ex}). Once the SSRIP is formed, other processes within the SSRIP must compete effectively with collapse to form the Ex, so that the overall Ex formation efficiency is reduced from unity.

In order for this behavior to be observed, two properties of the *o*-DCB appear to be important: (1) the solvent has a fairly high polarity and (2) the solvent has occupied molecular orbitals that are sufficiently high in energy to allow strong CT interactions with the TCA*. In support of this idea is the observation that α is essentially unity for the reactions of DCA* in *o*-DCB, for TCA* in dichloromethane, and for TCA* in toluene. Compared to TCA*, DCA* is a weaker acceptor (the HOMO of DCA is more than 0.4 eV higher in energy than that of TCA) and thus superexchange interactions involving the HOMOs of DCA and *o*-DCB are correspondingly weaker. Analogously, the energy of the HOMO of dichloromethane is much lower than that of *o*-DCB, thus effectively precluding superexchange interactions, even with TCA*. Toluene is a better donor than *o*-DCB, and therefore, superexchange-mediated SSRIP formation may occur in this solvent also. However, if a SSRIP is formed in this solvent, the low polarity should result in a negligible rate of separation (k_{sep}) and a high rate of collapse to the Ex ($k_{-\mathrm{solv}}$).

The different accepting abilities of DCA* and TCA* are reflected in their fluorescence spectra in different solvents. Shown in Figure 6 are the emission spectra of DCA and TCA in *o*-DCB and also in dichloromethane. The vibrational structure of DCA is similar in both solvents, whereas the spectrum of TCA in *o*-DCB is considerably broader and somewhat red shifted compared to that in dichloromethane. This is readily explained as arising from the CT interactions of TCA* with *o*-DCB, which result in an increased solvent reorganization energy, which in turn results in spectral broadening, loss of vibrational structure, and red shifting (see also below).

The fact that α is ca. 0.6 for TCA with each of the donors indicates that the efficiency of direct SSRIP formation is independent of the driving force for electron transfer, in contrast to the behavior observed in acetonitrile. An interesting, though speculative, explanation for this behavior is that the superexchange interactions enhance the rate of SSRIP formation to the extent that the course of the reaction is simply determined by the approach of the donor molecule in the encounter pair, rather than the rate of electron transfer (as for Ex formation), as indicated in Scheme 3. The approach indicated in path *a* of Scheme 3 would lead to the Ex through direct interaction of A* with D, whereas the approach indicated in path *b* would lead, via superexchange mediation, to the SSRIP. If formation of both the SSRIP and the Ex is determined simply by the rate of diffusive encounter and the partition simply by the direction of the diffusive encounter, α would not depend upon the driving force of either electron-transfer reaction. For this simple scheme to operate, the excited-state CT interactions must occur between A* and a specific solvent molecule and the rate of exchange of this solvent molecule (eq 9) must be slow compared to the rates of reaction within the encounter pair.

Scheme 3. Schematic Representation of the Formation of Ex and SSRIP in the Reactions of Excited TCA (A*) with Donors (D) in *o*-Dichlorobenzene as the Solvent (S)



$$\mathrm{S} + \overset{\delta-\,\delta+}{\mathrm{A^{*}\,S}} \rightleftharpoons \overset{\delta+\,\delta-}{\mathrm{S\,A^{*}}} + \mathrm{S} \qquad (9)$$

As indicated above, for α to be less than unity, SSRIP formation must occur from the encounter pair *and* other processes within the SSRIP must compete with conversion to the Ex. For the SSRIP in *o*-DCB, it is possible that return electron transfer $k_{-\mathrm{et}}$ will be more rapid than for another solvent of similar polarity, again as a result of superexchange interactions.

Although superexchange interactions are often invoked to explain long-distance electron-transfer reactions in covalently linked acceptor/donor species,[28] the reactions of TCA in *o*-DCB described here are examples of the less frequently observed phenomenon of superexchange-enhanced electron transfer in nonlinked systems.[27b,29]

Finally, the interactions between the TCA* and the *o*-DCB solvent are so strong that the excited TCA/solvent in this case could be considered to be an exciplex. Considered in this way,

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(28) See, for example: Wasielewski, M. R. In *Photoinduced Electron Transfer, Part A. Conceptual Basis*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; p 161.

(29) See, for example: (a) Jortner, J.; Bixon, M. In *Dynamics and Mechanisms of Photoinduced Electron Transfer and Related Phenomena*; Mataga, N., Okada, T., Masuhara, H., Eds.; North-Holland: Amsterdam, 1992; p 513. (b) McLendon, G. *Acc. Chem. Res.* **1988**, *21*, 160. (c) Beratan, D. N.; Onuchic, J. N.; Winkler, J. R.; Gray, H. B. *Science* **1992**, *258*, 1740. (d) Liu, J. Y.; Schmidt, J. A.; Bolton, J. R. *J. Phys. Chem.* **1991**, *95*, 6924.

the formation of a TCA/alkylbenzene Ex in this solvent represents an example of the well-known exciplex exchange phenomenon.[30]

4. Summary of the Mechanisms of Ex Formation in Bimolecular Electron-Transfer Reactions. An important result from the present work is that the formation efficiency of Ex species in the bimolecular electron-transfer reactions studied here is essentially unity in most cases. In nonpolar solvents this is easily understood because SSRIP formation (k_{et}, Scheme 1) may not occur in the first place for energetic reasons. Even if a SSRIP is formed in a nonpolar solvent, Ex formation from this species (k_{-solv}, Scheme 1) is likely to be much faster than radical-ion separation or return electron transfer, so that the overall Ex formation efficiency will be high.

The results in acetonitrile indicate that SSRIP formation from the encounter pair *must* occur under some circumstances because α values less than unity are obtained. Radical-ion separation and return electron transfer in this case will occur at much higher rates than in less polar solvents, and k_{-solv} may well occur with a lower rate. Thus the Ex can be effectively bypassed under these circumstances. The fact that the bimolecular quenching mechanism in acetonitrile changes from Ex formation to SSRIP formation as the driving force varies suggests that the reorganization energies and electronic matrix elements for electron transfer might change as a function of the driving force, from those characteristic for Ex formation to those for SSRIP formation. This idea has been discussed previously by several authors.[6,31] In particular, it has been suggested that this is the reason that no inverted region effect is observed for the A* + D reaction. To the best of our knowledge, the current results provide one of the few direct experimental verifications for the suggestion of a change in quenching mechanism with changes in driving force.

The fact that SSRIP formation can occur in acetonitrile suggests that this process is also likely in moderate polarity solvents such as methylene chloride because k_{et} may decrease only slowly with decreasing polarity, for the reasons discussed above. In the moderate polarity solvents, however, α values of unity are obtained. Thus, either SSRIP formation does not occur or, more likely, return electron transfer and separation in the SSRIP cannot compete with collapse to Ex, as is most certainly the case in nonpolar solvents. The reactions of TCA* in *o*-dichlorobenzene are clearly exceptional, as indicated by the spectroscopy of the TCA* in this solvent.

C. Dependence of the Ex Radiative Rate Constant on Charge-Transfer Character. For the Ex studied here, the decreases in $\alpha k'_f$ with increasing solvent polarity or decreasing E_{redox} are due to decreases in k'_f rather than decreases in α, with the exception of the few cases discussed above. In order to understand the reason for the variations in the radiative rate constants for the various acceptor/donor/solvent systems, the factors that control this quantity must be considered. As discussed in detail in the accompanying paper,[15b] the radiative rate constant (k_f) can be expressed as shown in eq 10,as a function of the solvent refractive

$$k'_f = \frac{k_f}{n\left(\dfrac{n^2+2}{3}\right)^2} = 313.7\tilde{\nu}_{av}^{\,3}M^2 \qquad (10)$$

index (n), the average emission wavenumber ($\tilde{\nu}_{av}$, expressed in 10^3 cm^{-1}), and the electronic transition moment for the emission process (M, in debye). To compare measurements in different solvents, it is convenient to refer to the radiative rate constant corrected for refractive index (k'_f).

The present Ex states are predominantly mixtures of pure ion-pair ($A^{\bullet-}D^{\bullet+}$) and locally excited (A*D) states. In the limiting case of an Ex that is essentially a pure ion-pair, M should be small because the emission corresponds to an intermolecular electron-transfer process. In the limiting case of an Ex that is essentially a pure locally excited species, M should be relatively large because it represents an allowed intramolecular transition. As the energy of the pure ion-pair state increases, the energy difference between this state and the locally excited state decreases, mixing of the states increases, the actual Ex state acquires more locally excited and less charge-transfer character, and M and k'_f become larger.[8,32] For an Ex that is essentially a pure ion pair, eq 11 relates M to $\Delta\mu$, the magnitude of the difference between

$$M = \frac{\tilde{H}_{01}\Delta\mu}{\tilde{\nu}_{av}} \qquad (11)$$

the static dipole moments of the neutral (AD) and the ion-pair states and $\tilde{H}_{01}$, the value (in wavenumbers) of the electronic matrix element coupling the $A^{\bullet-}D^{\bullet+}$ and the AD states.[33] In this limiting case, k'_f should increase linearly with $\tilde{\nu}_{av}$. A plot of k'_f vs $\tilde{\nu}_{av}$ for the present Ex (Figure 3, open symbols) curves strongly upward, indicating that M increases with increasing $\tilde{\nu}_{av}$ and increasing A*D character.

If the variations of k'_f with solvent polarity and redox energy are caused by variations in the extent of mixing of the ion-pair and locally excited states, it would clearly be of interest to compare the radiative rate constants of the Ex with those for the "pure" locally excited state species. Good estimates for the latter can be obtained from the radiative rate constants of the excited cyanoanthracene acceptors in the absence of added donors. Summarized in Table 3 are the average emission frequencies, emission quantum yields, lifetimes, and radiative rate constants for DCA and TCA, in the absence of added donor, in a variety of solvents.[34] It is clear that both k'_f and $\tilde{\nu}_{av}$ are not constants for the acceptors in these solvents. The k'_f and $\tilde{\nu}_{av}$ are smallest in the aromatic hydrocarbon solvents, which have the largest electron-donor ability. This suggests that, in addition to other effects, charge-transfer interactions should be considered even between the solvent and the excited singlet states of the cyanoanthracenes, as discussed above for TCA* in *o*-DCB. Support for this idea is provided by the emission spectra observed for DCA* in neat toluene, *p*-xylene, and 1,2,4-trimethylbenzene (Figure 7). As the electron-donating ability of the solvent increases, the DCA* emission shifts progressively to longer wavelengths and the emission spectrum broadens and loses vibrational structure, in a manner similar to that discussed above for TCA* in *o*-DCB. Indeed, for DCA in 1,2,4-trimethylbenzene, this effect is so pronounced that the spectrum in this case starts to resemble those of the conventional exciplexes (Figure 1). This resemblance extends to the k'_f data shown in Figure 3, where the radiative rate constants for the excited acceptor/solvent systems are shown as the dotted circles and squares. The k'_f values for DCA* are highest in the least donating solvents ((2.7–2.8) × 10^7 s^{-1}, Table 3). The corresponding values in the aromatic hydrocarbon solvents are significantly lower, so that k'_f values for DCA in toluene, *p*-xylene, and 1,2,4-trimethylbenzene (2.19 × 10^7, 1.97 × 10^7, and 1.32 × 10^7 s^{-1}) effectively merge with the corresponding data for the conventional Ex species.

The radiative rate data for acceptor/solvent systems and the conventional Ex exhibit a continuous dependence on $\tilde{\nu}_{av}$. In addition, the extent of vibrational structure in the emitting species

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(30) Ohta, H.; Creed, D.; Wine, P. H.; Caldwell, R. A.; Melton, L. A. *J. Am. Chem. Soc.* **1976**, *98*, 2002.

(31) See, for example: (a) Rau, H.; Frank, R.; Greiner, G. *J. Phys. Chem.* **1986**, *90*, 2476. (b) Stevens, B.; Biver, C. J.; McKeithan, D. N. *Chem. Phys. Lett.* **1991**, *187*, 590. (c) Kikuchi, K.; Takahashi, Y.; Katagiri, T.; Niwa, T.; Hoshi, M.; Miyashi, T. *Chem. Phys. Lett.* **1991**, *180*, 403. (d) Kakitani, T.; Yoshimori, A.; Mataga, N. *J. Phys. Chem.* **1992**, *96*, 5385.

(32) Oevering, H.; Verhoeven, J. W.; Paddon-Row, M. N.; Warman, J. M. *Tetrahedron* **1989**, *45*, 4751.

(33) Cannon, R. D. *Electron Transfer Reactions*; Butterworths: Boston, MA, 1980; Section 8.3.

(34) (a) The average emission frequencies for the excited acceptors in the absence of added donor given in Table 3 are evaluated using the method of Strickler and Berg.[34b] For further discussion, see the accompanying paper.[15b] (b) Strickler, S. J.; Berg, R. A. *J. Chem. Phys.* **1962**, *37*, 814.

Table 3. Fluorescence Data and Singlet Excited-State Parameters for 9,10-Dicyanoanthracene (DCA) and 2,6,9,10-Tetracyanoanthracene (TCA) in Different Solvents

A	solvent	$\tilde{\nu}_{av}{}^{a}$ (10^3 cm^{-1})	$\Phi_f{}^{b}$	τ^c (ns)	$k_f{}^{d}$ (10^6 s^{-1})	$k'_f{}^{e}$ (10^6 s^{-1})
DCA	carbon tetrachloride	21.88	0.88	11.3	77.9	28.2
DCA	trichloroethylene	21.63	0.90	11.2	80.4	28.1
DCA	acetonitrile	21.56	0.88	14.9	59.1	27.3
DCA	dioxane	21.57	0.89	12.8	69.5	27.2
DCA	dichloromethane	21.56	0.89	12.8	69.5	27.1
DCA	fluorobenzene	21.57	0.88	12.3	71.5	25.6
DCA	toluene	21.44	0.87	13.3	65.4	21.9
DCA	*o*-dichlorobenzene	21.37	0.87	12.2	71.3	21.3
DCA	*p*-xylene	21.23	0.89	15.3	58.2	19.7
DCA	1,2,4-trimethylbenzene	20.76	0.82	20.5	40.0	13.2
TCA	carbon tetrachloride	21.73	0.87	12.4	70.2	25.4
TCA	acetonitrile	21.46	0.90	16.8	53.6	24.8
TCA	dichloromethane	21.51	0.84	13.7	61.3	23.9
TCA	trichloroethylene	21.47	0.78	11.8	66.1	23.1
TCA	dioxane	21.27	0.40	6.9_3	57.7	22.6
TCA	fluorobenzene	21.16	0.85	15.7	54.1	19.3
TCA	*o*-dichlorobenzene	20.93	0.55	9.7_4	56.5	16.9

[a] Average emission frequency determined according to the method of Strickler and Berg (ref 34b).[15b] [b] Emission quantum yield. [c] Singlet excited-state lifetime from single photon counting measurements. [d] The radiative rate constant k_f is determined as Φ_f/τ. [e] Calculated from k_f and the solvent refractive index (n) according to eq 10.

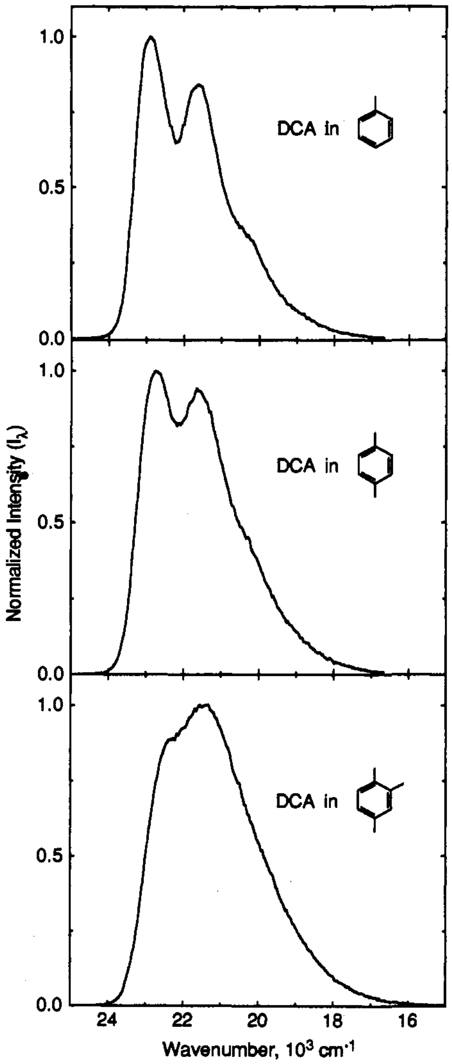

Figure 7. Emission spectra of 9,10-dicyanoanthracene in (top) toluene, (middle) *p*-xylene, and (bottom) 1,2,4-trimethylbenzene as solvents at room temperature.

changes smoothly from highly structured to structureless with decreasing $\tilde{\nu}_{av}$. These observations provide convincing support for the suggestion that the dependence of k'_f on $\tilde{\nu}_{av}$ is mainly a consequence of variable mixing of the ion-pair and locally excited states. The species with mostly locally excited character exhibit structured emission spectra, and those with moderate-to-high ion-pair character exhibit broad structureless spectra. The species that are intermediate between these extremes, for example, DCA in neat, 1,2,4-trimethylbenzene (Figure 7), represent interesting cases of excited CT states with sufficient locally excited character that a degree of structure can still be detected in their spectra. Taken together, the acceptor/solvent and Ex systems provide a comprehensive set of data for quantitatively studying the consequences of varying degrees of ion-pair and locally excited character in the Ex states. A detailed quantitative analysis of the radiative rate data, which allows the extent of charge transfer in the emitting species to be determined, is given in the accompanying paper.[15b]

III. Conclusions

An exciplex or excited CT complex intermediate is formed with essentially unit efficiency in most of the bimolecular electron-transfer reactions studied here. A complete mechanism for these reactions *must*, therefore, take these species into account, even in, in some cases, polar solvents. Although the present study is limited to a specific set of donors and acceptors, it is likely that Ex formation will occur in other reactions in solvents as polar as acetonitrile, and in fact, we have shown that this is the case when 1,4-dicyanobenzene is used as the acceptor with the same donors.[26] The Ex is bypassed for some of the reactions of acetonitrile, however, and in fact, the data for these systems are most reasonably interpreted in terms of a progressive change from Ex formation to SSRIP formation within the encounter pair, as a function of electron-transfer driving force. The fact that direct SSRIP formation occurs in acetonitrile suggests that it may also occur in less polar solvents. Because the yield of Ex is unity in the less polar solvents, the collapse of the SSRIP to the Ex would have to be much faster than the other processes within the SSRIP in such cases. The exceptional situation involves *o*-dichlorobenzene as the solvent. In this case, high-energy occupied orbitals in the solvent enable superexchange interactions to enhance the rate of the SSRIP-forming reaction. The overall result is that the Ex can be partially bypassed in this case also.

These results clearly demonstrate that, for the exciplexes/excited CT complexes (Ex) studied here, the primary reason that the emission quantum yield (Φ) decreases with increasing solvent polarity faster than the lifetime (τ) is that the Ex radiative rate constants decrease, rather than the efficiencies with which the Ex's are formed in the bimolecular electron-transfer reactions. By comparing the radiative rate constants of a wide range of Ex's with those of "pure" locally excited cyanoanthracene species and intermediate solvent-perturbed cases, it is concluded that the radiative rate constants reflect varying degrees of mixing of ion-pair and locally excited states. Such mixing is particularly important for the present systems because of the low-lying, strongly coupled[15b] excited states of the cyanoanthracenes. Although we have no direct experimental evidence regarding previously studied systems, such as the anthracene/dimethylaniline pair,[6] it seems reasonable that such solvent-dependent mixing may be a general phenomenon whenever the donor or the acceptor has low-lying excited states.

IV. Experimental Section

The donors and acceptors were available from previous work.[10] The solvents acetonitrile (Baker HPLC grade), *o*-dichlorobenzene (Aldrich HPLC grade), cyclohexane (Aldrich HPLC grade), trichloroethylene (Aldrich HPLC grade), fluorobenzene (Aldrich), chloroform (Aldrich HPLC grade), carbon tetrachloride (Aldrich HPLC grade), *p*-dioxane (Aldrich HPLC grade), dichloromethane (Baker HPLC grade), and butyronitrile (Aldrich) were distilled prior to use.

All experiments were performed in 1-cm^2 cuvettes equipped with arms for argon purging. All solutions were argon purged for at least 10 min, unless specified.

Absorption spectra were recorded using a Perkin-Elmer Lambda 9 spectrometer. Steady-state emission spectra were recorded using a Spex 2-1-2 Fluorolog spectrometer. Corrected emission spectra were obtained using a calibrated quartz lamp and the method recommended by the manufacturer. Emission spectra were recorded for solutions of the acceptors (ca. 10^{-5} M) with and without donor (0.005–0.2 M). The Ex emission quantum yields were determined relative to those of the unquenched acceptors in the same solvent. The exciplex emission intensities were obtained by subtracting the residual excited-state acceptor emission from the total emission spectrum. To correct for incomplete interception of A* by the donor, the remaining emission was divided by $(1 - \Phi^{A*}/\Phi^{A*}{}_0)$, where Φ^{A*} represents the quantum yield of the residual acceptor emission and $\Phi^{A*}{}_0$ represents the quantum yield of the unquenched excited acceptor. For the quantum yield determinations, the solutions had identical optical densities (up to ca. 0.2, depending on the solubility of the acceptors) at the excitation wavelength. The emission quantum yields for the unquenched acceptors in the various solvents were determined relative to that of DCA in air-saturated acetonitrile, which was taken to be 0.80.[13] Accurately corrected emission spectra can be obtained for wavelengths as high as 800 nm using our spectrometer. In some cases, the Ex emissions extended beyond 800 nm and the spectra in this region were estimated by simulating the spectra using a procedure described elsewhere.[13]

Emission lifetimes were obtained using the technique of single photon counting, using an apparatus that has been described elsewhere.[21b] The excitation wavelength was typically 378 nm, and the analyzing wavelengths varied from ca. 450 to 700 nm, depending upon the system. The radiative rate constants were obtained from measurements of Φ_f and τ at the same donor concentration. In some instances, a weak dependence of τ on [D] was observed that can be attributed to interception of the Ex by another donor molecule.[35] As reported previously, this interception rate increases with increasing Ex charge-transfer character and also with increasing solvent polarity.[35] For example, from measurements of the Ex lifetime as a function of donor concentration, the Ex interception rate constant is determined to be ca. 3.4×10^7 M^{-1} s^{-1} for the TCA/HMB pair in cyclohexane. For the Ex of TCA in dichloromethane, however, the interception rate constants with the different donors were all ca. 2–5 $\times$ 10^8 M^{-1} s^{-1}. In contrast, for the DCA/Durene/cyclohexane system, which has the smallest charge-transfer character of all the Ex's studied here, no change in the Ex lifetime, fluorescence quantum yield, or spectral distribution could be detected for donor concentrations ranging from 0.007 to 0.14 M.

In most cases, the Ex lifetimes were determined as the decay component in a two-exponential analysis of the single photon counting data, in which the rate of Ex formation is given by the rise component. In a few cases where the Ex lifetime was short, however, it was more reliable to use low donor concentrations so that this order was reversed, i.e. the Ex lifetime was given by the rise component, as discussed elsewhere.[35,36] The latter approach was used in the case of DCA/donors in acetonitrile and for several TCA/donors when the Ex lifetime was ca. 1–2 ns. In a number of cases (for example, TCA/PMB in dichloromethane, τ = 1.05 ns), experiments were performed at both high and low donor concentrations and analyses were performed under both "normal" and "reversed" conditions. When the energy of the Ex is close to that of A*, an equilibrium can be established between the Ex and the A* + D. Such equilibria were observed for the DCA/durene pair (cf. Table 1). In these cases, the Ex decay rates were obtained from studies at different donor concentrations with conventional data analysis.[37]

The values of α for the reactions of TCA* in acetonitrile were estimated using eq 6. The equilibrium constants K_{CT} were estimated from conventional Benesi–Hildebrand plots.[38] Measurements for the α determinations were performed using two different concentrations of the donor [D] and [D′]. For TCA/*p*-Xy ($-\Delta G_{et}$ = 0.37 eV), with [D] = 1.0 M and [D′] = 0.15 M, the ratio $(\Phi_f)_{[D]}/(\Phi_f)_{[D']}$ was near unity, with an experimental error of ca. 3–5%. As a result of interception of Ex by the donor, the ratio of the lifetimes $(\tau_{[D']}/\tau_{[D]})$ was 1.07 ± 0.02. The equilibrium constant (K_{CT}) in this case is ca. 0.5 ± 0.1 M^{-1}, and thus α can be estimated from eq 6 to be ca. 0.8 ± 0.07. For TCA/TMB ($-\Delta G_{et}$ = 0.51 eV), with [D] = 0.46 M and [D′] = 0.14 M, the ratio $(\Phi_f)_{[D]}/(\Phi_f)_{[D']}$ is 1.35. Because of the small difference in the concentrations, the lifetimes in this case are very similar. At 18 °C, K_{CT} = ca. 1 M^{-1}, which corresponds to an α of 0.3 ± 0.05. For TCA/Dur ($-\Delta G_{et}$ = 0.65 eV), with [D] = 0.30 M and [D′] = 0.11 M, the ratio $(\Phi_f)_{[D]}/(\Phi_f)_{[D']}$ is 1.65. At 18 °C, K_{CT} = ca. 2.6 M^{-1}, which corresponds to an α of 0.1 ± 0.02.

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(35) Gould, I. R.; Farid, S. *J. Am. Chem. Soc.* **1993**, *115*, 4814.

(36) Moore, J. W.; Pearson, R. G. *Kinetics and Mechanisms*, 3rd ed.; Wiley: New York, 1981.

(37) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley: New York, 1970; p 304.

(38) Benesi, H. A.; Hildebrand, J. H. *J. Am. Chem. Soc.* **1949**, *71*, 2703.