Concentration-Dependent Photoinduced Electron-Transfer Reactions. 1:1 and 1:2 Radical-Ion Complexes

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Abstract: For some exciplexes of 9,10-dicyanoanthracene (DCA) with naphthalenes and phenanthrenes as donors, the fluorescence quantum yields and lifetimes decrease with increasing donor concentration. The rate constants for these self-quenching reactions increase with decreasing redox energy of the pair and with increasing solvent polarity. Both parameters increase the charge-transfer (CT) character of the exciplex. When the CT character is low, the quenching rate constants are too small to measure ($<10^7$ M^{-1} s^{-1}), but with increasing CT character, to the limit that the exciplex becomes essentially a contact radical-ion pair, the interception rate constant approaches the diffusion-controlled limit. The product of the self-quenching reactions is a 1:2 radical-ion complex. In addition to exciplex self-quenching, the quantum yields for formation of separated radical ions decrease with increasing donor concentration when experiments are performed in the polar solvent acetonitrile. From these data and from an analysis of the spectral distribution of the exciplex fluorescence, information is obtained concerning the driving force dependence of the rates of return electron transfer in the 1:1 and 1:2 contact and the 1:1 solvent-separated radical ion complexes. The 1:1 solvent-separated pair has the highest solvent reorganization energy, λ_s (ca. 1.6 eV), and the 1:1 contact pair the lowest (ca. 0.35 eV). The 1:2 contact complex has an intermediate λ_s of ca. 0.9 eV. The electronic coupling matrix element for return electron transfer in the contact pairs is larger than that for the solvent-separated pairs by ca. 2 orders of magnitude. The corresponding matrix element for the 1:2 contact complex is closer to that for the contact pair than that for the solvent-separated pair. Due to the relatively high matrix element and λ_s, the rates of return electron transfer in the 1:2 contact pairs are high compared to the rates of solvation, which results in the smaller yields of separated radical ions at high donor concentrations.

I. Introduction

For a number of years we have been investigating the factors that control the efficiencies with which separated radical ions are produced from the primary radical-ion pairs in photoinduced bimolecular electron-transfer reactions in polar solvents.[1] We have used cyanoanthracenes as the light-absorbing electron acceptors and alkyl-substituted benzenes, naphthalenes, and phenanthrenes as the donors. The efficiencies with which separated radical ions are formed are determined by the competition between return electron transfer and solvation/separation within the primary contact radical-ion pairs (CRIP, $A^{\bullet-}D^{\bullet+}$) and the solvent-separated radical-ion pairs (SSRIP, $A^{\bullet-}(S)D^{\bullet+}$). In the course of these studies we frequently observed that the quantum yields for formation of separated radical ions, corrected for incomplete interception of the excited acceptor, Φ_i, were dependent upon the concentration of the donor. Whenever concentration-dependent reactions were encountered, Φ_i decreased with increasing donor concentration. Two different mechanisms can give rise to such concentration-dependent radical-ion yields.

We have previously described the first mechanism in detail for the reactions between 2,6,9,10-tetracyanoanthracene (TCA) as the acceptor and alkyl-substituted benzenes as donors.[2] These acceptor/donor systems form ground-state charge-transfer (CT) complexes. Under these conditions the SSRIP and the CRIP can be formed via two pathways: (a) excitation of the uncomplexed acceptor A, followed by diffusive encounter of $^1A^*$ with a donor D, which can result in direct formation of the SSRIP, bypassing the CRIP,[3] and (b) excitation of the ground-state complex AD which results in direct formation of the CRIP.[4] Under these conditions, Φ_i can be smaller for excitation of the AD complex compared to the diffusive quenching process, due to the additional energy-wasting step (return electron transfer within the CRIP) associated with this method of excitation.[2] With increasing concentration of the donor, more of the excitation light is absorbed by the complex, and therefore the efficiency of radical-ion formation is further reduced. In this mechanism, Φ_i should also depend upon the relative extinction coefficients of the uncomplexed acceptor and the complex at the excitation wavelength, and as a result, the reactions should exhibit different concentration dependencies at different excitation wavelengths, as confirmed experimentally.[2]

In the second mechanism the donor concentration plays a role not because of ground state complex formation but as a result of interception of the initially formed radical-ion pairs by a second donor molecule. 9,10-Dicyanoanthracene (DCA) is a considerably poorer acceptor than TCA.[1a] As a result, it does not form ground-state complexes with simple alkyl-substituted aromatic hydrocarbon donors in acetonitrile. Furthermore, in the case of DCA, the diffusional quenching process does not lead directly to formation of a SSRIP (the CRIP is not bypassed) as a consequence of the smaller driving force for the charge-separation reaction.[3,5] As a result, we have not observed any dependence of Φ_i on concentration when using alkylbenzenes as donors with DCA as the acceptor. With naphthalene and phenanthrene derivatives, however, Φ_i decreases with increasing donor concentration using

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[2] Gould, I. R.; Young, R. H.; Moody, R. E.; Farid, S. *J. Phys. Chem.* **1991**, *95*, 2068.

[3] (a) The rate of direct formation of the SSRIP in the bimolecular quenching reaction, bypassing the CRIP, appears to depend upon the driving force for the charge separation reaction, increasing with increasing driving force for charge separation.[3b] (b) Gould, I. R.; Mueller, L. J.; Farid, S. *Z. Phys. Chem* (*Munich*) **1991**, *170*, 143.

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both DCA and TCA as acceptors. For TCA, ground state complex formation occurs, and at least part of the concentration dependence is due to the first mechanism described above. When using DCA, however, we attribute the decrease in radical-ion yields to the formation of radical-ion pair intermediates consisting of one acceptor and two donors (1:2 complexes). As discussed in more detail below, the CRIP are limiting examples of the well-known exciplexes, in which charge transfer from the acceptor to the donor is essentially complete.[6] There is ample precedent for the formation of such 1:2 complexes in the exciplex literature.[7] The formation of such 1:2 complexes is also closely related to the well-known phenomenon of association of radical cations with their neutral counterpart to form dimeric radical cations.[8] The binding energies and rate constants for the formation of several dimeric radical cations have been determined by time-resolved and electrochemical techniques.[9] Naphthalene and its derivatives have particularly strong tendencies to form such dimeric radical cations.[9b,e] In order for this mechanism to operate for DCA with the naphthalene and phenanthrene donors, the primary CRIP, $A^{\bullet-}D^{\bullet+}$, should be intercepted by another donor molecule to form a 1:2 radical ion complex, $A^{\bullet-}D^{\bullet+}D$, and the rate of energy-wasting return electron transfer in this species should compete with solvation to form the 1:2 SSRIP, $A^{\bullet-}(S)D^{\bullet+}D$. Under these conditions Φ_i will be reduced as a result of the additional energy-wasting return electron-transfer reaction in $A^{\bullet-}D^{\bullet+}D$.

In this work we describe in detail the requirements for observing this second mechanism for concentration-dependent radical-ion yields for the example of the reactions between DCA and the alkyl-substituted naphthalenes. In addition to the dependence of Φ_i on donor concentration, we have studied the self-quenching of the CRIP (exciplex) fluorescence by D to provide additional quantitative information concerning the concentration-dependent processes. We also discuss the factors controlling the rates of electron transfer in the different types of radical-ion pair intermediates (CRIP and SSRIP) and the way in which these parameters vary with the radical-ion pair stoichiometry (1:1 and 1:2).

Scheme I. Acceptors and Donors Used in This Study with Redox Data from Reference 1a

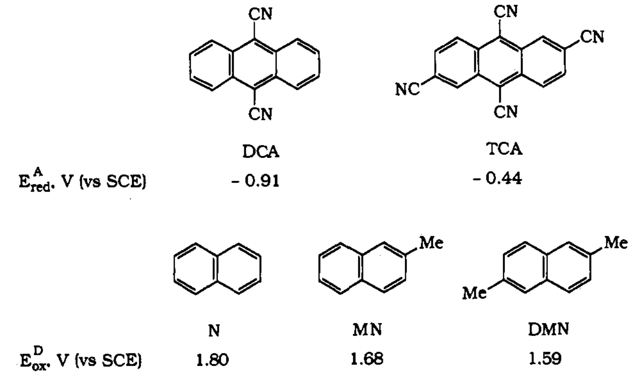

Table I. Emission Maxima for the Exciplexes of 9,10-Dicyanoanthracene (DCA) and 2,6,9,10-Tetracyanoanthracene (TCA) as Acceptors (A) and Substituted Naphthalenes as Donors in Different Solvents[a]

		ν_{max}, 10^3 cm^{-1}		
A	solvent	N[b]	MN[b]	DMN[b]
DCA	cyclohexane	20.44[c]	19.87[c]	19.26[c]
DCA	trichloroethylene		18.90[c]	18.18[c]
DCA	ethyl acetate	18.76 (0.025)	18.12	17.48 (0.31)
DCA	acetonitrile	17.54 (7.3)	16.86 (7.9)	16.18 (8.9)
TCA	trichloroethylene	17.51 (1.1)	16.88	16.07 (3.2)

[a] The numbers in parentheses are rate constants (10^9 M^{-1} s^{-1}) for exciplex interception by a second donor molecule. [b] N, MN, and DMN refer to naphthalene, 2-methylnaphthalene, and 2,6-dimethylnaphthalene as donors, respectively. [c] The lifetimes of these exciplexes are not donor-concentration dependent. The interception rate constants are estimated to be less than 10^7 M^{-1} s^{-1}.

II. Results and Discussion

The excited state acceptors used in the present work are 9,10-dicyanoanthracene (DCA) and 2,6,9,10-tetracyanoanthracene (TCA). The donors are naphthalene (N), 2-methylnaphthalene (MN), and 2,6-dimethylnaphthalene (DMN). The relevant redox data for these compounds are given in Scheme I.

(a) Self-Quenching of Exciplexes as a Function of CT Character. As reported previously, fluorescing exciplexes can be observed for DCA with the donors used in this study, not only in low-polarity solvents but also in polar solvents such as acetonitrile (Table I).[2,10] As expected, the exciplex emission maxima and emission efficiencies decrease with both solvent polarity and the ability of the hydrocarbon donor to donote an electron (decreasing oxidation potential). With TCA as the acceptor, ground state CT complex formation occurs, and fluorescing excited CT complexes can be observed in several solvents of low and moderate polarity. Using alkylbenzenes as donors, D, the intensity of the fluorescence of the DCA exciplexes and the excited CT complexes of TCA does not depend upon the concentration of the donor in any of the solvents studied. However, with the naphthalenes and phenanthrenes, in many (but not all) cases, the exciplex fluorescence intensity decreases with increasing donor concentration. The efficiencies of these self-quenching processes were estimated using a combination of steady-state and time-resolved spectroscopies. In the less polar solvents, the rate constants for exciplex interception were obtained in a conventional manner from time-resolved fluorescence measurements. The exciplex kinetics are described by growth and decay components. When the rate constant for exciplex interception by another donor is much slower than that for diffusion control, the rate of exciplex formation is faster than the rate of decay, which is then equal to $1/\tau$, in which τ is the exciplex lifetime. The slopes of plots of $1/\tau$ vs [D] yield exciplex interception rate

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constants, k_q (Table I), and the intercepts, k_E, the exciplex decay rates extrapolated to zero donor concentration. In the polar solvent acetonitrile, however, rate constants for exciplex interception could not easily be determined directly from such time-resolved measurements because the rates of exciplex decay were similar to their rates of formation for many concentrations of donor. From plots of the reciprocals of the exciplex fluorescence quantum yields, corrected for incomplete interception of $^1A^*$, $1/\Phi_f$, vs donor concentration [D], values for k_q/k_E were obtained using a conventional Stern–Volmer type analysis. Exciplex lifetimes were measured at one or more donor concentrations giving values for $(k_q[D] + k_E)$ at the different concentrations.[11] Values for k_q were thus obtained by combining the results of the steady-state and time-resolved measurements (Table I).

The interception rate constant k_q varies with solvent polarity, approaching the diffusion-controlled limit in some cases. In the less polar solvents, k_q depends upon the particular acceptor/donor combination. The different quenching rate constants can be explained partially in terms of the differing degrees of charge-transfer (CT) character within the different exciplexes in the various solvents.

Exciplexes and excited CT complexes (Ψ_{ex}) are generally described as mixtures of locally excited (LE, A*D) and ion pair ($A^{\bullet-}D^{\bullet+}$) states.[6] For the present acceptor/donor systems, the most important states are those indicated in eq 1. The CT character (ionic nature) of an exciplex increases (c_2 increases)

$$\Psi_{ex} = c_1\Psi_{A^*D} + c_2\Psi_{A^{\bullet-}D^{\bullet+}} \qquad (1)$$

with decreasing energy of the "pure" contact ion pair *relative* to that of the locally excited state, since this reduces the mixing with the LE state. When this gap is large enough, the mixing will be so weak that the exciplex is essentially a contact radical-ion pair ($c_2 \approx 1$). The energy of the pure ion pair decreases with decreasing oxidation potential of the donor (E_{ox}^{D}) and with increasing (less negative) reduction potential of the acceptor (E_{red}^{A}), i.e., with decreasing redox energy of the acceptor/donor pair, E_{redox} (eq 2). The energy of the pure ion pair will also

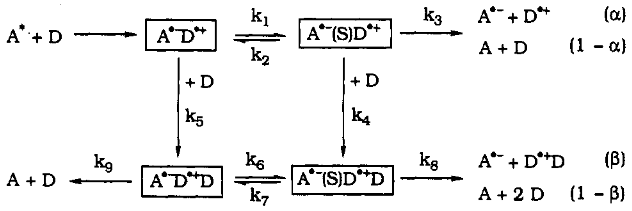
$$E_{redox} = E_{ox}^{D} - E_{red}^{A} \qquad (2)$$

decrease with increasing solvent polarity. Thus, the CT or ionic character of the exciplexes will increase with the specified changes in these parameters. We have studied this issue in detail for the case of DCA and TCA with the alkylbenzenes as donors.[12] For the alkylbenzene systems the exciplexes/excited CT complexes can be considered to be essentially pure ion pairs (≥90% CT character) when the emission maxima occur at energies that are lower than that of the 0–0 transition of the LE state of the cyanoanthracene acceptor by ca. 6×10^3 cm^{-1}.[12] The average energy of the 0–0 fluorescence band of DCA and TCA in several solvents is ca. 23×10^3 cm^{-1}.[1a] Thus, the exciplexes with emission maxima $\lesssim 17 \times 10^3$ cm^{-1} can be regarded as essentially "pure" radical-ion pairs with only minor admixture of the LE state. With increasing emission energy (increasing ion pair energy) the extent of charge transfer decreases. We assume that the dependence of the emission energy on the CT character is similar for the alkyl-substituted benzene and naphthalene systems.

If the reaction of the exciplex with a neutral donor is driven by the stabilization gained by the formation of a dimeric radical cation type species (eq 3), then the rate constant for the exciplex interception should increase with increasing ionic character of the exciplex. In support of this idea, the lifetimes of the exciplexes of DCA with N, MN, and DMN in the low-polarity solvents, cyclohexane and trichloroethylene, are essentially independent of donor concentration, i.e., the interception rate constants in all these cases are less than 10^7 M^{-1} s^{-1} (Table I). The low polarity of these solvents and the high E_{redox} of the A/D pairs *relative* to the energy of the first excited singlet state of DCA result in low CT character for these exciplexes due to significant mixing with the LE state. With the better acceptor TCA, however, interception rate constants in the range 1–3 × 10^9 M^{-1} s^{-1} are observed (Table I). In the slightly more polar solvent ethyl acetate, exciplex interception can be observed even for the exciplex formed from the pair with the highest redox energy, DCA/N, although with a modest rate constant of 2.5×10^7 M^{-1} s^{-1}. As the redox energy decreases, the interception rate constant increases rapidly so that the value for the DCA/DMN exciplex in ethyl acetate is 3.1×10^8 M^{-1} s^{-1}. Finally, in acetonitrile, the interception rate constants for the exciplexes of DCA with all three naphthalenes reach values of 7–9 × 10^9 M^{-1} s^{-1}.[13]

$$A^{\bullet-}D^{\bullet+} + D \rightarrow A^{\bullet-}D^{\bullet+}D \leftrightarrow A^{\bullet-}DD^{\bullet+} \qquad (3)$$

Scheme II. Intermediates in Photoinduced Electron-Transfer Reactions in Acetonitrile Involving Dimeric Radical-Ion Species



In addition to the extent of charge transfer reflected in the exciplex emission maxima, the polarity of the solvent also appears to play a role in determining the interception efficiency. For example, although the DCA/DMN exciplex in trichloroethylene has an emission maximum that is similar to that of DCA/MN in ethyl acetate (which suggests similar CT character), the interception rate constant for the latter is higher. Similarly, DCA/DMN in ethyl acetate and DCA/N in acetonitrile have similar emission maxima, but the latter has a much higher interception rate constant. The larger interception rate constants in the more polar solvents (with similar CT character) are perhaps the result of further lowering of the energy of the 1:2 complex relative to the 1:1 pair, due to an increased stabilization of the more highly charge-separated 1:2 species.

(b) Dynamics of the 1:1 and 1:2 Radical-Ion Complexes in Acetonitrile. In common with many other acceptor/donor systems, the DCA/substituted naphthalene systems form separated radical ions in acetonitrile solution. The quantum yields for formation of separated radical ions (Φ_i) depend upon the donor concentration. Exciplex fluorescence, however, is rarely observed in acetonitrile either because exciplexes are not formed in the bimolecular quenching event or the exciplexes are very short-lived due to rapid solvation and return electron-transfer processes. For the DCA/substituted naphthalene systems, however, exciplex emissions can be observed. Furthermore, the emission efficiencies of these exciplexes (Φ_f) also depend upon the donor concentration, as discussed above. These observations for the DCA/naphthalene systems in acetonitrile can be discussed in terms of the intermediates and steps outlined in Scheme II. The scheme contains the four possible intermediates that determine the overall efficiency for formation of separated radical ions.

The primary intermediates are the exciplexes, which are essentially 1:1 contact radical ion pairs for the DCA/substituted naphthalene systems in acetonitrile (see above). The CRIP

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[11] Details are given in the Experimental Section. The self-quenching kinetics in the polar solvent acetonitrile are discussed further in Section IIb.

[12] Gould, I. R.; Mueller, L. J.; Young, R. H.; Farid, S.; Albrecht, A. C., manuscript in preparation.

[13] Similar results are obtained using phenanthrene and alkyl-substituted phenanthrenes.

$(A^{\bullet -}D^{\bullet +})$ can undergo solvation (k_1) to the SSRIP $(A^{\bullet -}(S)D^{\bullet +})$. In competition with solvation, when naphthalenes and phenanthrenes are used as electron donors, the 1:1 contact pairs can be intercepted (k_5) by another donor molecule to yield a 1:2 contact radical-ion complex $(A^{\bullet -}D^{\bullet +}D)$. As for the 1:1 contact pair, the 1:2 contact complex can also solvate (k_6) to form the corresponding solvent-separated complex $(A^{\bullet -}(S)D^{\bullet +}D)$. In principle, both solvation reactions could be reversible processes (k_2 and k_7). Further separation within either of the solvated radical-ion species to form "free" radical ions competes with return electron transfer to form neutral products. In Scheme II, k_3 and k_8 represent the sum of the rate constants for separation and for return electron transfer within the two solvent-separated species. The efficiencies of free radical-ion formation from each of these intermediates are α and β, respectively.

The rate constants for return electron transfer within the contact 1:1 pairs are estimated to be very small compared to k_1 and are, therefore, not included in Scheme II. The relatively small rates of return electron transfer within the 1:1 contact pairs are inferred from analyses of the fluorescence spectra of these species, as discussed in detail below, and also from the relatively small variations in the rates of decay of the exciplexes in the absence of self-quenching (k_E), which are 2.1, 2.9, and 3.7 × 10^8 s^{-1} for N, MN, and DMN, respectively. If return electron transfer were contributing significantly to the decay of the 1:1 CRIP, then the k_E values would be expected to increase significantly in the order N, MN, and DMN, due to the Marcus inverted region effect.[2,14] The fact that the lifetimes of the pairs vary only slightly with driving force suggests that return electron transfer is not an important process for these species. On the basis of the kinetic data described here, however, it is evident that return electron transfer does occur within the other intermediates of Scheme II.

On the basis of Scheme II, the efficiencies of exciplex fluorescence (Φ_f) and separated radical-ion formation (Φ_i), both corrected for incomplete interception of $^1A^*$, are given by eqs 4 and 5, respectively. In these equations the subscripts 0 and ∞ denote the efficiencies as [D] → 0 and [D] → ∞. When the reciprocal of the fluorescence quantum yield, $1/\Phi_f$, is plotted vs [D], the intercept, $1/(\Phi_f)_0$, corresponds to the reciprocal of the quantum yield in the absence of exciplex interception. From such data a plot of the ratio $(\Phi_f)_0/\Phi_f$ as a function of [D] can be made (eq 4).

$$\frac{(\Phi_f)_0}{\Phi_f} = \frac{1 + \left(\frac{x}{m} + y\right)[D] + xy[D]^2}{1 + my[D]} \tag{4}$$

$$\Phi_i = \frac{(\Phi_i)_0 + (\Phi_i)_\infty\left\{\left(\frac{x}{m} + \frac{y}{n}\right)[D] + xy[D]^2\right\}}{1 + \left(\frac{x}{m} + y\right)[D] + xy[D]^2} \tag{5}$$

where

$$x = k_5/k_1 \qquad y = k_4/k_3$$

$$m = \frac{k_3}{k_2 + k_3} \qquad n = \frac{k_6}{k_6 + k_9}$$

$$(\Phi_i)_\infty = \beta\frac{pk_6}{pk_6 + k_9} \quad \text{and} \quad p = \frac{k_8}{k_7 + k_8}$$

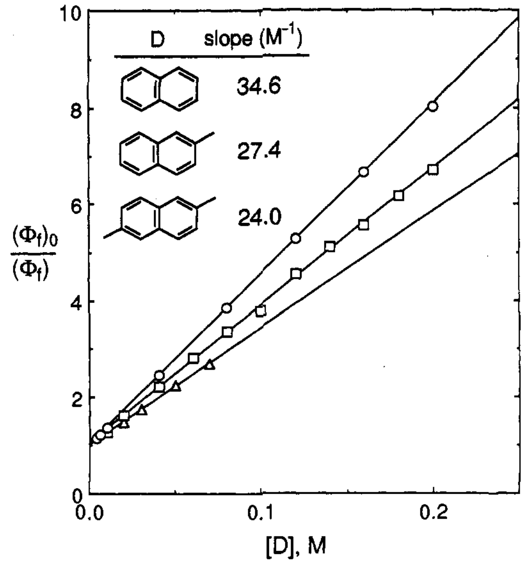

Figure 1. Plots of the ratio of the 1:1 contact radical-ion pair (exciplex) emission yield (Φ_f), corrected for incomplete interception of the excited state acceptor, relative to that extrapolated to zero donor concentration ($(\Phi_f)_0$), as a function of donor concentration, for 9,10-dicyanoanthracene with three naphthalene donors in acetonitrile. The slopes of the plots are given in the figure.

Because the energy differences between the contact and solvent-separated species in acetonitrile are likely to be small,[2] reversibility between these intermediates should be considered. In principle, the dependence of the exciplex fluorescence intensity on [D] could be used to determine the extent of reversibility for the 1:1 pairs (i.e., the value of m). If the SSRIP is formed irreversibly (m = 1), a plot of $(\Phi_f)_0/\Phi_f$ vs [D] should be linear, since under this assumption eq 4 simplifies to a standard Stern–Volmer type relation (eq 6).

$$(\Phi_f)_0/\Phi_f = 1 + (k_5/k_1)[D] \tag{6}$$

Such a plot should be nonlinear if $m < 1$. However, using reasonable estimates for the appropriate rate constants, the predicted deviation from linearity is very slight, even for $m = 0.5$. It is, therefore, not possible to reliably determine the extent of reversibility in this way.

Plots of $(\Phi_f)_0/\Phi_f$ vs [D] for DCA with N, MN, and DMN in acetonitrile are shown in Figure 1. When assumed to be linear, the slopes of these plots are 34.6, 27.4, and 24.0 M^{-1}, respectively. If $k_2 \ll k_3$ (i.e., $m \sim 1$, no reversibility), then these values correspond to k_5/k_1. As discussed above, these estimates for k_5/k_1, together with emission lifetimes τ determined at one or more donor concentration, allow k_5 and k_1 to be determined individually. The k_1 (2.1, 2.9, and 3.7 × 10^8 s^{-1}) correspond to the rates of solvation and are the CRIP decay rates in the absence of self-quenching.[15] The interception rate constants, k_5, are obtained by multiplying the slopes of the $(\Phi_f)_0/\Phi_f$ plots by k_1 to give 7.3, 7.9, and 8.9 × 10^9 M^{-1} s^{-1} for N, MN, and DMN, respectively.[15] However, consider, for example, the case in which k_2 is comparable to k_3 (i.e., m is ca. 0.5). Under these circumstances the CRIP are reformed from the SSRIP, and the CRIP kinetics become more complex, consisting of one growth and two decay components. For the present systems, however, $k_3 + k_2 > k_1$ (see further below), hence one of the decay components is much larger than the other (>90%).[16] The corresponding rate for this component in the absence of self-quenching is approximately equal to $k_1 m$ and the slopes of the essentially linear plots of $(\Phi_f)_0/\Phi_f$ vs [D] correspond to $k_5/(k_1 m)$. Thus, the multiples of the slopes of the $(\Phi_f)_0/\Phi_f$ plots and the exciplex decay rates give good estimates for k_5, whether there is reversibility or not, although the meaning of the decay rate

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(14) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.

(15) The rate constants k_1 and k_5, which refer to the specific case of reactions in acetonitrile, are equivalent to k_E and k_q, discussed in Section IIa, for the general case of exciplex self-quenching in solvents of varying polarity.

(16) For the DCA/substituted naphthalene systems in which the formation rates are close to the decay rates, a small and fast additional component (<10%) to the exciplex kinetics would not be clearly observed.

Table II. Quantum Yields for Formation of Separated Radical Ions, Extrapolated to Zero $(\Phi_i)_0$ and Infinite $(\Phi_i)_\infty$ Donor Concentrations, for Excitation of 9,10-Dicyanoanthracene in the Presence of Naphthalene Donors in Acetonitrile and Rate Constants for Return Electron Transfer (k_{-et}) within the 1:1 Solvent-Separated ($(k_{-et})^{ss}_{1:1}$) and 1:2 Contact ($(k_{-et})^{c}_{1:2}$) Radical-Ion Complexes[a]

d[b]	E_{redox}[c]	$(\Phi_i)_0$	$(\Phi_i)_\infty$	k_9/k_6	$(k_{-et})^{ss}_{1:1}$[d] (10^9 s^{-1})	$(k_{-et})^{c}_{1:2}$[e] (10^9 s^{-1})
N	2.71	0.58 ± 0.01	0.145 ± 0.005	3 ± 0.6	0.36	1.5 ± 0.3
MN	2.59	0.42 ± 0.02	0.055 ± 0.005	11 ± 1	0.69	5.5 ± 0.5
DMN	2.50	0.33 ± 0.01	0.022 ± 0.004	25 ± 5	1.02	12.5 ± 2.5

[a] The numbers are determined for values of *m* from 0.5 to 1.0 (see text). The numbers in the table represent the mean and the errors the ranges in the values corresponding to this range for *m*. [b] N, MN, and DMN refer to naphthalene, 2-methylnaphthalene, and 2,6-dimethylnaphthalene, respectively. [c] $E_{redox} = E^D_{ox} - E^A_{red}$, from ref 1a. [d] Calculated as $\{5 \times 10^8((\Phi_i)_0^{-1} - 1)\}$. [e] Calculated as $\{5 \times 10^8(k_9/k_6)\}$.

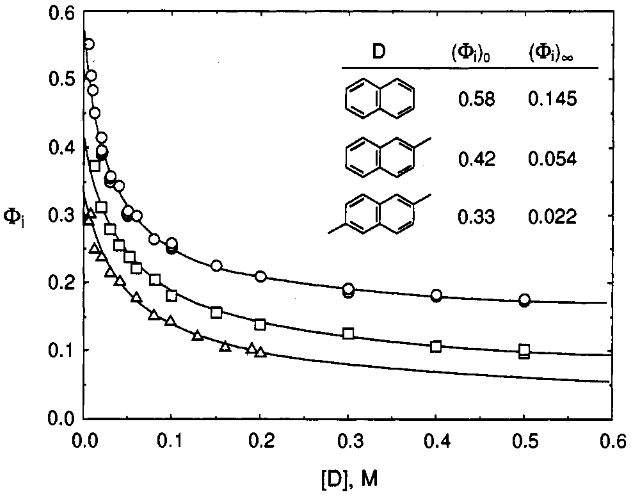

Figure 2. Plots of the quantum yields for formation of separated radical ions (Φ_i), corrected for incomplete interception of the excited state acceptor, as a function of donor concentration, for 9,10-dicyanoanthracene with three naphthalene donors in acetonitrile. The quantum yields extrapolated to zero ($(\Phi_i)_0$) and infinite ($(\Phi_i)_\infty$) donor concentrations are given in the figure. The curves are calculated according to eq 5.

extrapolated to zero donor concentration is not the same. Since the CRIP are intercepted by the neutral donors with rate constants that approach the diffusion-controlled limit, it is reasonable to assume that the $A^{\bullet-}(S)D^{\bullet+}$ are intercepted with similarly high rate constants. In these cases, the interactions between the radical ions in the pair are weaker and the dimerization rate k_4 might reach the diffusion-controlled limit (1–1.5 × 10^{10} M^{-1} s^{-1}).

Information concerning the competition between return electron transfer and formation of free radical ions from the solvent-separated 1:1 pairs, $A^{\bullet-}(S)D^{\bullet+}$, is obtained from a plot of Φ_i vs [D]. The value of Φ_i extrapolated to zero donor concentration, $(\Phi_i)_0$ (Table II), is equal to α, the fraction of the SSRIP that give separated radical ions.[17] Such plots are shown in Figure 2 for the DCA/substituted naphthalene systems. The magnitude of α is determined by the relative rates of return electron transfer and separation within the SSRIP. The rate constants for return electron transfer for each donor can be determined from α by using a value for the rate for separation within the SSRIP of 5 × 10^8 s^{-1}, as discussed in more detail below. The sum of the rate constants for these two processes corresponds to k_3, Scheme II.

Using these values of k_3 and assuming that k_4 is ca. 10^{10} M^{-1} s^{-1}, estimates can be made for k_4/k_3, i.e., *y*. On the basis of these values of *y*, and assuming *m* to be between 0.5 and 1.0, a corresponding range for the parameter *x* can be established by fitting the fluorescence self-quenching data using eq 4.

From any combination of the parameters *m*, *y*, and *x*, the denominator in eq 5 (which is equal to the numerator of eq 4) can be evaluated. Multiplying Φ_i by the corresponding value of the denominator of eq 5 and plotting the result vs [D] yields a quadratic function, and thus the remaining parameters can be determined. The intercept of this plot yields $(\Phi_i)_0$, which is equal to α, as mentioned above. The quantum yield as [D] → ∞, $(\Phi_i)_\infty$ (Table II), and also values for *n* are determined from the other coefficients of the quadratic function. The ratio of the rates of return electron transfer within the 1:2 contact complex, k_9, to the rates of solvation, k_6, is thus obtained from $\{(1/n) - 1\}$. The ranges of k_9/k_6 for $m = 0.5$ to 1.0 for the different donors are given in Table II.

Although values are obtained for k_9/k_6 and $(\Phi_i)_\infty$, absolute values cannot be obtained for β, since according to eq 5, the ratio k_7/k_8 must also be known. Therefore, only a lower limit can be set for β (β_{low}) by assuming that $k_7 \ll k_8$ (eq 7). From the data for N, MN, and DMN (Table II), the values of β_{low} are ca. 0.6

$$\beta_{low} = (\Phi_i)_\infty \left(1 + \frac{k_9}{k_6}\right) \tag{7}$$

± 0.1 for all three donors. The fact that these values are essentially constant as a function of the donor oxidation potential suggests that the actual values for β are probably higher and may be close to unity. In this case, the rates of return electron transfer would be much smaller than the separation rate, and so cannot be reliably determined. As a result, the dependence of the rates of return electron transfer on driving force cannot be determined from the current data for the 1:2 solvent-separated radical-ion pairs.

In order to fully delineate the self-quenching effect on Φ_i, relatively high concentrations of the donors were used (up to 0.5 M, Figure 2). The effects of such donor concentrations on, for example, the medium polarity are obviously difficult to assess. However, no deviations from expected behavior can be detected at concentrations higher than 0.1 M (Figure 2). Whether the initial quenching of the A* is fully diffusional or contains a contribution from static quenching is of no consequence for the data analysis presented here.

(c) Electron-Transfer Parameters for the Radical-Ion Pair Intermediates. As discussed above there are four radical ion intermediates within which return electron transfer could, in principle, occur. The present data provide quantitative information concerning the competition between return electron transfer and solvation or separation within the different intermediates. It is of interest to compare the return electron transfer processes within these different, but related, intermediates. The rates of such electron-transfer reactions have been successfully described previously using the semiclassical relationship shown in eq 8.[1,2,18] The electron-transfer rate constant is given as the

$$k_{-et} = \frac{4\pi^2}{h} V^2 \mathrm{FC}(g)$$

$$g = \Delta G_{-et}$$

$$\mathrm{FC}(g) = \sum_{j=0}^{\infty} F_j (4\pi\lambda_s k_B T)^{1/2} \exp\left[-\frac{(jh\nu_v + g + \lambda_s)^2}{4\lambda_s k_B T}\right]$$

$$F_j = \frac{e^{-S} S^j}{j!} \qquad S = \frac{\lambda_v}{h\nu_v} \tag{8}$$

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[17] We have previously reported these data for DCA and TCA with the naphthalenes and related donors.[1a]

[18] (a) Vauthey, E.; Suppan, P.; Haselbach, E. *Helv. Chim. Acta* **1988**, *71*, 93. (b) Kikuchi, K.; Takahashi, Y.; Koike, K.; Wakamatsu, K.; Ikeda, H.; Miyashi, T. *Z. Phys. Chem.* (*Munich*) **1990**, *167*, 27. (c) Ohno, T.; Yoshimura, A.; Mataga, N.; Tazuke, S.; Kawanishi, Y.; Kitamura, N. *J. Phys. Chem.* **1989**, *93*, 3546. (d) Lewitzka, F.; Lӧhmannsrӧben, H.-G. *Z. Phys. Chem.* (*Munich*) **1990**, *169*, 203.

product of an electronic coupling matrix element squared, V^2, and a Franck–Condon weighted density of states, FC(g).[19] The Franck–Condon factors are determined by the driving force for the reaction, $\Delta G_{-\mathrm{et}}$, a reorganization energy associated with rearranged solvent and other low frequency modes, λ_s, and a reorganization energy, λ_v, associated with a single averaged rearranged high-frequency mode of frequency ν_v. In principle, information concerning the reorganization parameters associated with electron transfer for a related series of acceptor/donor systems can be obtained from the dependence of the rates of return electron transfer on the reaction free energy (driving force). A value for V can also be obtained if, in addition to their driving force dependence, absolute values for the rate constants are known. If CT emission can be detected from the radical-ion pair, then information concerning the reorganization parameters can be obtained from the spectral distribution of this radiative electron-transfer process,[20,21] as indicated in eq 9.[21b] Here, I_λ is the emission intensity per unit wavelength, ν_f, the emission frequency, n the solvent refractive index, and $\Delta\mu$ the dipole moment of the excited CT state. The Franck–Condon factors for the radiative electron-transfer process are the same as for the nonradiative return electron transfer, except that in this case the energy term g takes into account that part of the radical-ion pair energy which is lost to the emitted photon.

$$I_\lambda = \nu_f^{\,3} n^3 \frac{64\pi^4}{3h^3c^3}\Delta\mu^2 V^2 FC(g)$$

$$g = \Delta G_{-\mathrm{et}} + h\nu_f \tag{9}$$

i. 1:1 Contact Radical-Ion Pairs.

$$\boxed{A^{\bullet-}D^{\bullet+}}\;\begin{array}{l}\xrightarrow{(k_{\mathrm{solv}})^{c}_{1:1}} A^{\bullet-}(S)D^{\bullet+} \\ \xrightarrow[(k_{-et})^{c}_{1:1}]{} A + D\end{array} \tag{10}$$

Although the rates of return electron transfer within the DCA/alkyl-substituted naphthalene 1:1 contact pairs ($A^{\bullet-}D^{\bullet+}$) are too small to be determined for the present systems, for the reasons given above, information concerning the reorganization parameters in these species can be obtained from an analysis of their emission spectra. The emission spectrum of the DCA/DMN CRIP in acetonitrile is shown in Figure 3. Also shown is a fit to the spectrum using eq 9. The reorganization parameters used to calculate the fitted curve are 0.35 eV for λ_s, 0.20 eV for λ_v, and 1400 cm^{-1} for ν_v.[22] Two important conclusions can be drawn from these parameters. First, estimates can be made for the rate constants for return electron transfer within the emitting CRIP using eq 8. The driving forces, $-\Delta G_{-\mathrm{et}}$, for the return electron transfer reactions of ca. 2.5 to 2.7 eV are given approximately by the difference between the donor naphthalene oxidation potentials and the reduction potential of the DCA acceptor.[1a,2] Values of ca. 700–1000 cm^{-1} have been estimated previously for the electronic-coupling matrix elements for electron transfer in CRIP which are related to the present systems.[2,12,23] Furthermore, a value within this range can be estimated for the DCA/DMN system.[24] The values of $(k_{-\mathrm{et}})^{\mathrm{c}}_{1:1}$ calculated for the naphthalene/DCA systems using these parameters are all less than 10^7 s^{-1}. This supports the assumption that the rates of return electron transfer in the DCA/substituted naphthalene CRIP in acetonitrile are very small compared to the rates of solvation, k_1 in Scheme II, of 2–4 × 10^8 s^{-1}. Second, the rates of return electron transfer within these exciplexes are *predicted* to be strongly dependent on the free energy change. For example, in the small range of $\Delta G_{-\mathrm{et}}$ from –2.5 to –2.7 eV, a plot of $\log(k_{-\mathrm{et}})^{\mathrm{c}}_{1:1}$ vs $\Delta G_{-\mathrm{et}}$ can be approximated by a linear relationship with a slope of –6.15 ± 0.15 eV^{-1}.

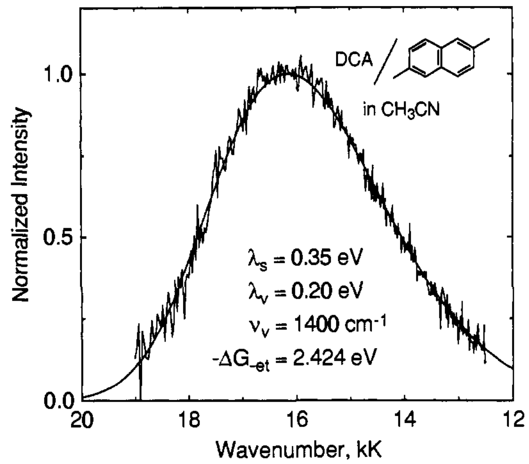

Figure 3. Emission spectrum (noisy line) of the 1:1 contact radical-ion pair (exciplex) formed between 9,10-dicyanoanthracene and 2,6-dimethylnaphthalene in acetonitrile and fit to the spectrum (smooth line) calculated using eq 9 and the parameters given in the figure.

ii. 1:1 Solvent-Separated Radical-Ion Pairs.

$$\boxed{A^{\bullet-}(S)D^{\bullet+}}\;\begin{array}{l}\xrightarrow{(k_{sep})^{ss}_{1:1}} A^{\bullet-} + D^{\bullet+} \\ \xrightarrow[(k_{-et})^{ss}_{1:1}]{} A + D\end{array} \tag{11}$$

From the plots of Φ_i vs [D] shown in Figure 2, values for α are obtained, as discussed above. The ratio $(k_{-\mathrm{et}})^{\mathrm{ss}}_{1:1}/(k_{\mathrm{sep}})^{\mathrm{ss}}_{1:1}$ can thus be obtained as $\{\alpha/(1-\alpha)\}$. If $(k_{\mathrm{sep}})^{\mathrm{ss}}_{1:1}$ is a constant for the SSRIP, then the driving force dependence for return electron transfer in the SSRIP is obtained from this ratio, as shown in Figure 4.[17] Fitting these data according to eq 8, using a λ_v value of 0.20 eV and a ν_v value of 1400 cm^{-1} as for the CRIP,[25] leads to a value for λ_s of 1.57 eV. Furthermore, a value of 5 × 10^8 s^{-1} has previously been estimated for $(k_{\mathrm{sep}})^{\mathrm{ss}}_{1:1}$,[1a] and therefore absolute values can be determined for $(k_{-\mathrm{et}})^{\mathrm{ss}}_{1:1}$ (Table II). From these data a value of 8 cm^{-1} is obtained for the electronic-coupling matrix element. We have discussed the reasons for the

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[19] (a) Hopfield, J. J. *Proc. Natl. Acad. Sci. U.S.A.* **1974**, *71*, 3640. (b) Van Duyne, R, P.; Fischer, S. F. *Chem. Phys.* **1974**, *5*, 183. (c) Ulstrup, J.; Jortner, J. *J. Chem. Phys.* **1975**, *63*, 4358. (d) Siders, P.; Marcus, R. A. *J. Am. Chem. Soc.* **1981**, *103*, 741, 748. (e) Marcus, R. A. *J. Chem. Phys.* **1984**, *81*, 4494. (f) Marcus, R. A.; Sutin, N. *Biochim. Biophys. Acta* **1985**, *811*, 265.

[20] (a) Marcus, R. A. *J. Chem. Phys.* **1965**, *43*, 1261. (b) Hush, N. S. *Prog. Inorg. Chem.* **1967**, *8*, 391. (c) Marcus, R. A. *J. Phys. Chem.* **1989**, *93*, 3078.

[21] (a) Gould, I. R.; Farid, S.; Young, R. H. *J. Photochem. Photobiol. A: Chem.* **1992**, *65*, 133. (b) Gould, J. R.; Noukakis, D.; Gomez-Jahn, L.; Young, R. H.; Goodman, J. L.; Farid, S. *Chem. Phys.*, submitted for publication.

[22] For the substituted benzene donors in acetonitrile, the CRIP emission spectra are broader than those of the naphthalenes, the best fits being for λ_s = 0.55 eV and λ_v = 0.2 eV.[2] In all of the solvents used, cyclohexane, trichloroethylene, fluorobenzene, ethyl acetate, and dichloromethane, the exciplex spectra of the alkyl-substituted benzenes are broader than the corresponding spectra of the naphthalenes. This supports the notion that the reorganization energies for return electron transfer are larger for the benzenes than those for the naphthalenes.

[23] (a) Gould, I. R.; Noukakis, D.; Goodman, J. L.; Young, R. H.; Farid, S. *J. Am. Chem. Soc.*, in press. (b) Gould, I. R.; Noukakis, D.; Gomez-Jahn, L.; Goodman, J. L.; Farid, S. *J. Am. Chem. Soc.*, in press.

[24] Integrating eq 9 allows V to be determined from the CT radiative rate, k_f, and the reorganization parameters (ref 21b). For the DCA/DMN 1:1 CRIP in acetonitrile, k_f can be estimated from the emission quantum yield (ca. 0.0054) and decay rate (k_E = 3.7 × 10^8 s^{-1}) to be ca. 2 × 10^6 s$_{-1}$, from which a value of ca. 880 cm^{-1} is determined for V.

[25] These values for λ_v and ν_v are smaller than those used previously to fit the $(k_{-\mathrm{et}})^{\mathrm{ss}}_{1:1}$ data;[1a] however, the current values should be more accurate, since they are obtained from fitting CRIP emission spectra. The influence of the relative magnitudes of these two parameters is much greater on the shape of the CRIP emission spectra than on the shape of the driving force dependence of $(k_{-\mathrm{et}})^{\mathrm{ss}}_{1:1}$.

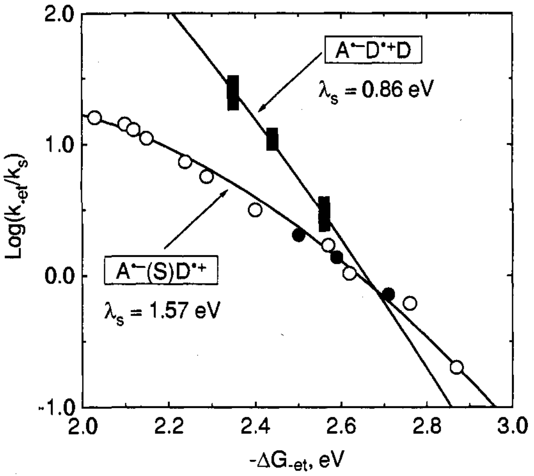


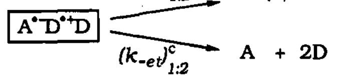
Figure 4. Plots of the ratios of the rates of return electron transfer (k_{-et}) to the rates of solvation (1:2 contact complexes, $A^{\bullet-}DD^{\bullet+}$, rectangles) and of separation (1:1 solvent-separated radical-ion pairs, $A^{\bullet-}(S)D^{\bullet+}$, closed circles) as a function of driving force ($-\Delta G_{-et}$) for the 9,10-dicyanoanthracene/naphthalene donor systems, in acetonitrile. The heights of the rectangles indicate the ranges of the values determined for the 1:2 contact complexes, as described in the text. The open circles are data for the solvent-separated pairs of the naphthalene donors with 2,6,9,10-tetracyanoanthracene as the acceptor and for other related donors with both acceptors, taken from ref 1a. The lines represent fits to the data and were calculated using eq 8 together with values of 0.20 eV and 1400 cm^{-1} for λ_v and ν_v, respectively, and values for λ_s given in the figure.

very different solvent reorganization energies for the SSRIP and the CRIP in an earlier publication.[2] The solvent reorganization energy is often estimated using a dielectric continuum model (eq 12).[26] In eq 12, r_D and r_A are the radii of the donor and the acceptor, R_{AD} is their center-to-center separation distance, and ϵ is the solvent dielectric constant. Although eq 12 is likely to be accurate only when R_{AD} is considerably larger than $r_D + r_A$, qualitatively the model predicts that λ_s should increase with increasing separation distance and that the change in λ_s with separation distance should be particularly large when the absolute values for R_{AD} are small (due to the reciprocal dependence on R_{DA}). If the plots of the data shown in Figure 4 are approximated

$$\lambda_s = \frac{e^2}{4\pi\epsilon_0}\left(\frac{1}{2r_D} + \frac{1}{2r_A} - \frac{1}{R_{AD}}\right)\left(\frac{1}{n^2} - \frac{1}{\epsilon}\right) \qquad (12)$$

to a linear relation over the range of ΔG_{-et} for the DCA/naphthalene, SSRIP, then a slope of ca. −2.2 eV^{-1} is obtained.

iii. 1:2 Contact Radical-Ion Complex.



(13)

From the analysis of the Φ_f and Φ_i data described above, values for k_9/k_6 are obtained for DCA with the three naphthalene donors (Table II) which are identical to $(k_{-et})^c_{1:2}/(k_{solv})^c_{1:2}$. As for the SSRIP, the driving force dependence for return electron transfer in the 1:2 contact complexes is obtained from this ratio. The stabilization energy associated with dimerization of the N and DMN radical cations ($D^{\bullet+} + D \rightarrow D^{\bullet+}D$) has been determined by Rodgers from pulse radiolysis studies to be ca. 0.14 eV.[9b] An estimate of 0.16 eV for this value for N has also been made from electrochemical studies.[9e] Thus, the ΔG_{-et} for the 1:2 complexes are expected to be lower than those for the 1:1 contact pairs by ca. 0.15 eV. A plot of $\log((k_{-et})^c_{1:2}/(k_{solv})^c_{1:2})$ vs $-\Delta G_{-et}$ is shown in Figure 4. Absolute values for $(k_{-et})^c_{1:2}$ can be obtained only by assuming a constant value for the rates of solvation for these species, $(k_{solv})^c_{1:2}$. This solvation process, $A^{\bullet-}DD^{\bullet+} \rightarrow A^{\bullet-}(S)DD^{\bullet+}$, appears to be closely related to the separation process of the 1:1 solvent-separated radical-ion pairs, $A^{\bullet-}(S)D^{\bullet+} \rightarrow A^{\bullet-} + D^{\bullet+}$, for which a rate constant of 5×10^8 s^{-1} has been estimated (see above). Taking this value for $(k_{solv})^c_{1:2}$ results in the estimates for $(k_{-et})^c_{1:2}$ given in Table II. The corresponding value for the electronic coupling matrix element for the 1:2 contact complexes is thus 400 cm^{-1}. If the $(k_{solv})^c_{1:2}$ were actually smaller or larger than 5×10^8 s^{-1} by a factor of 2, the corresponding values for the matrix element would be 280 and 570 cm^{-1}, respectively. When the plot of the 1:2 contact complex data in Figure 4 is approximated to a straight line, a slope of ca. −4.4 eV^{-1} is obtained.

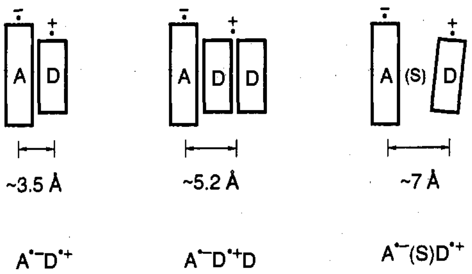


Figure 5. Schematic representations of the 1:1 contact radical ion pairs ($A^{\bullet-}D^{\bullet+}$), 1:2 contact radical-ion complexes ($A^{\bullet-}D^{\bullet+}D$), and 1:1 solvent-separated radical-ion pairs ($A^{\bullet-}(S)D^{\bullet+}$).

It is interesting to compare the λ_s values for the 1:1 CRIP and the SSRIP with the corresponding value for the 1:2 contact radical-ion complex. Again using the same λ_v value of 0.20 eV, as in the case of the radical-ion pairs, the observed dependence of $(k_{-et})^c_{1:2}$ on ΔG_{-et} can be explained using a value for λ_s of 0.86 eV (calculated curve shown in Figure 4). This value, being intermediate between those of 0.35 and 1.57 eV for ($A^{\bullet-}D^{\bullet+}$) and ($A^{\bullet-}(S)D^{\bullet+}$), respectively, suggests that the solvation of the contact 1:2 complex is approximately intermediate between those of the two radical ion pairs.

There are two possible factors that can influence the extent of solvation (and thus λ_s) of the 1:2 compared to the 1:1 contact species. First, it can be argued that the solvation of the dimeric radical cation in the 1:2 complex should be weaker than that in the 1:1 complex due to an increase in charge delocalization in the radical cation moiety, i.e., the effective radius for the dimeric radical cation (r_{DD}) is larger than that for the monomeric analogue (r_D) (cf. eq 12). Second, there is an effective increase in charge separation (R_{AD}) in the 1:2 complex compared to the 1:1 pair, which would increase λ_s for the same reasons that the solvent-separated pair has a much higher λ_s than the contact pair. The larger λ_s for ($A^{\bullet-}D^{\bullet+}D$) compared to ($A^{\bullet-}D^{\bullet+}$) suggests that the latter effect is more important in determining the λ_s value. To a first approximation, the increase in charge separation might be ca. 1.7 Å, i.e., if the positive charge is almost equally distributed between the two naphthalene donors in the 1:2 complex (see Figure 5).

Assuming such a symmetrical distribution of the positive charge between the two naphthalene molecules in the 1:2 complex, the electronic coupling matrix element, V_2, of the hamiltonian for return electron transfer in the 1:2 contact complex would be given by

$$\overset{\overset{-}{\bullet}}{A}\overset{\overset{+}{\bullet}}{D}D \xrightarrow{V_2} ADD$$

$$\left\langle \Psi(ADD) \,\middle|\, \mathcal{H} \,\middle|\, \frac{\Psi(\overset{\overset{-}{\bullet}}{A}\overset{\overset{+}{\bullet}}{D}D) \pm \Psi(\overset{\overset{-}{\bullet}}{A}D\overset{\overset{+}{\bullet}}{D})}{\sqrt{2}} \right\rangle$$

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(26) Marcus, R. A. J. Chem. Phys. 1956, 24, 966.

The corresponding matrix element, V_1, for the 1:1 contact pair is

$$\overset{\bar{\bullet}\,\overset{+}{\bullet}}{\mathrm{AD}} \xrightarrow{\mathrm{V_1}} \mathrm{AD}$$

$$\left\langle \Psi(\mathrm{AD}) \,\middle|\, \mathcal{H} \,\middle|\, \Psi(\overset{\bar{\bullet}\,\overset{+}{\bullet}}{\mathrm{AD}}) \right\rangle$$

As discussed above, the electronic coupling matrix element for the 1:1 CRIP of the DCA/naphthalene systems (V_1) can be estimated to be ca. 700–1000 cm^{-1}. The corresponding value for the SSRIP of the DCA/naphthalenes is ca. 8 cm^{-1}, i.e., about two orders of magnitude lower than for the contact pair. The CRIP ($A^{\bullet-}D^{\bullet+}$) and the SSRIP ($A^{\bullet-}(S)D^{\bullet+}$) can be considered to be good models for the species $A^{\bullet-}D^{\bullet+}D$ and $A^{\bullet-}DD^{\bullet+}$ that contribute to V_2. Accordingly, the contribution from $A^{\bullet-}DD^{\bullet+}$ to the matrix element V_2 is very small (the matrix element for $A^{\bullet-}(S)D^{\bullet+}$ is small), and thus the ratio of V_2 to V_1 would be expected to be ca. $1/\sqrt{2}$, i.e., ca. 0.7. The estimated value for V_2 of ca. 280–570 cm^{-1} is, therefore, in reasonable agreement with this prediction.

Thus, although the λ_s for the 1:2 contact complex is approximately an average of the values for the 1:1 CRIP and SSRIP, the electronic coupling matrix element is closer to, although still smaller than, that for the 1:1 CRIP. The smaller V for the 1:2 complex would be expected to decrease the rates of return electron transfer in these species compared to those in the 1:1 CRIP. However, the λ_s are larger for the 1:2 complexes and also the $-\Delta G_{-et}$ are smaller, both of which would be expected to increase the rate of return electron transfer. The actual rates of return electron transfer in the 1:2 complexes are indeed larger than those in the 1:1 CRIP. Specifically, the ratios of the rate constants for return electron transfer to separation (k_{-et}/k_{sep}) for the 1:1 contact pairs are all <0.02, i.e., return electron transfer is insignificant compared to separation, whereas the corresponding values for the 1:2 complexes range from 3 to 25 (Table II), resulting in significant energy wasting in these species. The larger return electron transfer rates in the 1:2 complexes compared to the 1:1 CRIP, therefore, are due to the fact that the influence of changing λ_s and $-\Delta G_{-et}$ is greater than the influence of changing V, thus further emphasizing the important role of the Franck–Condon factors in electron-transfer processes.[27]

iv. 1:2 Solvent-Separated Radical-Ion Complexes.

$$\boxed{A^{\bullet-}(S)D^{\bullet+}D}\ \begin{array}{l} \xrightarrow{(k_{sep})^{ss}_{1:2}} A^{\bullet-} + D^{\bullet+}D \\ \xrightarrow[(k_{-et})^{ss}_{1:2}]{} A + 2D \end{array} \qquad (14)$$

As discussed above, β, and therefore the rates of return electron transfer within the solvent-separated 1:2 complexes $A^{\bullet-}(S)D^{\bullet+}D$, cannot be determined from the kinetic data presented here, and therefore the dependence of $(k_{-et})^{ss}_{1:2}$ on driving force is not known. The ΔG_{-et} for the 1:2 solvent-separated complexes are presumably lower than those for the 1:1 solvent-separated pairs by ca. 0.15 eV (the stabilization energy associated with the dimer radical cation formation). Also, compared to the 1:1 SSRIP, it might be expected that both the electronic coupling matrix element and the λ_s would be smaller for the 1:2 complex due to the effective increase in charge separation and increase in the size of the radical cation (dimer vs monomer), respectively. These two factors will tend to decrease the rate constant for return electron transfer compared to the 1:1 SSRIP, although the effect of decreasing ΔG_{-et} would tend to increase the rate.

III. Concluding Remarks

This work illustrates that the rates of return electron transfer within the different primary radical-ion pair intermediates can vary significantly with stoichiometry and separation distance and that these differences can be understood at least qualitatively in terms of current electron-transfer theories. Differences in the behavior of the alkylbenzenes and naphthalenes can be understood as being a consequence of the higher tendency of the naphthalene radical cations to interact with the neutral donor to form dimeric radical cations. These reactions can be almost diffusion-controlled, and therefore the primary CRIP can be intercepted, resulting in lower free radical-ion quantum yields. The reactions are driven by the stability of the dimeric radical cation compared to that of the monomeric species. However, not all radical cations of naphthalene derivatives form dimers with equal efficiency. For example, the fluorescence efficiency of the CRIP of DCA/1,4-dimethylnaphthalene in acetonitrile is almost concentration independent, and the quantum yield for free radical-ion formation is essentially unaffected by the concentration of the donor. The tendency to form dimers for this radical cation appears to be lower than that for the other naphthalenes discussed here.[9e] We have also investigated the reactions of DCA with phenanthrene, 2-methylphenanthrene, and 3,6-dimethylphenanthrene. Very similar behavior to that of the naphthalenes was observed in these cases, namely self-quenching of the exciplex fluorescence and decrease in the quantum yield in free ions with increasing concentrations of the donor. The magnitudes of these concentration effects are also similar to those observed for the naphthalene derivatives.

IV. Experimental Section

The donors and acceptors used in this work were the same as those used previously.[1,2] Acetonitrile (Baker HPLC grade), cyclohexane (Baker HPLC grade), trichloroethylene (Aldrich spectro grade), and ethyl acetate (Aldrich HPLC grade) were used as received. Steady-state emission spectra were recorded using a Spex Fluorolog 2-1-2 spectrometer. Corrected spectra were obtained using a calibrated quartz–halogen light source as recommended by the spectrometer manufacturer. Emission lifetimes were determined using the technique of single photon counting using an apparatus that has been described previously.[28] The excitation wavelength was 380 nm. The exciplex kinetics were monitored at wavelengths ranging from ca. 600 to 700 nm, depending upon the particular acceptor/donor/solvent system. Oxygen was removed from all of the solutions by purging with argon. The DCA and TCA concentrations were ca. 5×10^{-5} M. Experiments were performed at room temperature.

Exciplex emission intensities at each donor concentration, Φ_f, were determined by subtracting the residual monomer emission (spectral distributions determined in the absence of donor) and dividing the remaining emission by $(1 - \Phi^{A^*}/\Phi_0^{A^*})$, where Φ^{A^*} is the intensity of the subtracted monomer emission and $\Phi_0^{A^*}$ is the intensity of the unquenched monomer emission, to correct for incomplete interception of $^1A^*$. For the exciplexes of DCA with the donors in cyclohexane and trichloroethylene, the Φ_f and also the fluorescence lifetimes determined using single photon counting were found to be constant over donor concentration ranges of ca. 0.002–0.02 M. The exciplex interception rate constants are thus estimated to be less than ca. 10^7 M^{-1}. For DCA in ethyl acetate and TCA in trichloroethylene, the exciplex lifetimes were determined over concentration ranges of ca. 0.005–0.04 M. In some cases the exciplex kinetics were analyzed as three exponentials, to take into account minor amounts of impurity emissions. Self-quenching rate constants were obtained from plots of the rate of the component corresponding to exciplex decay vs donor concentration. For DCA in acetonitrile the exciplexes decayed with rates that were comparable to their rates of formation. Only at very low concentrations of donor were the rates of exciplex formation and decay sufficiently different for accurate analysis. For example, at a naphthalene concentration of 0.0023 M, the exciplex emission monitored at 675 nm consists of a growth component with a time constant of 4.6 ns and a decay component with a time constant of 9.0 ns. Under these conditions the exciplex reacts more rapidly than it is formed (the exciplex decay is mainly due to solvation rather than self-quenching),

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[27] Closs, G. L.; Calcaterra, L. T.; Green, N. J.; Penfield, K. W.; Miller, J. R. *J. Phys. Chem.* **1986**, *90*, 3673.

[28] Gould, I. R.; Farid, S. *J. Phys. Chem.* **1992**, *96*, 7635.

and the exciplex lifetime is given by the growth component. The decay component in this case corresponds to the time constant for exciplex formation.[29] The exciplex lifetime is equivalent to $k_E + k_q[0.0023]$, in which k_q is the apparent self-quenching rate constant and k_E is the apparent exciplex decay rate in the absence of self-quenching. The ratio k_q/k_E was determined from plots of $(\Phi_f)_0/\Phi_f$ vs [N]. The individual k_q and k_E values were thus obtained (for all three naphthalenes) by combining the steady-state data with the time-resolved data at one or more concentrations of donor.

The quantum yields for formation of separated radical ions in acetonitrile solution were measured using transient absorption spectroscopy.[1a,2] The excitation source was an excimer/dye laser combination (Questek 2620/Lambda Physik FL3002). The excitation pulses were at 410 nm and ca. 20 ns in length. The excitation energies were kept below 0.5 mJ to avoid problems associated with nonlinear excitation.[1a] In a typical experiment, the DCA concentration was 10^{-4} M, which resulted in an absorbance of ca. 0.6 at 410 nm. The donor concentrations ranged from 0.005 to 0.5, M 0.012 to 0.5, and 0.005 to 0.19 M for N, MN, and DMN, respectively. 4,4′-Dimethoxystilbene (DMS) was added to the solutions, at a concentration of 5×10^{-4} M, to scavenge the donor radical cations ($D^{\bullet+}$) that separated from the geminate radical ion pairs by secondary electron transfer as indicated in eq 15. The relative absorbance of the $DMS^{\bullet+}$, monitored at 525 nm, was obtained by integrating the absorbance between ca. 250 and 500 ns after the pulse and was measured as a function of the donor concentration. The relative absorbances were taken to be directly proportional to the relative yields of separated radical cations at the different concentrations of donor. The relative yields were converted to absolute yields using the benzophenone triplet state as an actinometer, as described in ref 1a. Correction was made for incomplete interception of $^1A^*$ by determining the extent of fluorescence quenching as described above. For the example of naphthalene as the donor, the measured separation yield was 0.336 at a naphthalene concentration of 0.01 M. Steady-state emission experiments show that at this naphthalene concentration, 69.5% of the DCA fluorescence is quenched. The corrected separation yield, therefore, is 0.336/0.695, which is 0.484. Similarly, for 0.1 M naphthalene, the measured separation yield is 0.244 and 96.5% of the DCA fluorescence is quenched. The corrected separation yield is thus 0.244/0.965 which is equal to 0.253. The data obtained in this manner for the three donors are shown in Figure 4.

$$D^{\bullet+} + DMS \rightarrow D + DMS^{\bullet+} \qquad (15)$$

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