Intersystem Crossing in Charge-Transfer Excited States[†]

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Absolute rate constants for intersystem crossing (ISC) in exciplexes formed between cyanoanthracenes as acceptors and alkylbenzenes as donors in solvents with low to moderate polarity have been measured. The extent of charge transfer in these particular exciplexes has been determined previously, and thus the dependence of the ISC rate constant on this parameter is obtained. A smooth transition of exciplexes with high locally excited state character to those with essentially pure charge-transfer character argues in favor of a mechanism of intersystem crossing involving a spin-forbidden return electron transfer process to form the locally excited triplet directly. The proposed mechanism is supported by the observed energy gap dependence of the rate constant, and by deuterium isotope effects. External heavy-atom effects in chlorinated solvents are observed. Analysis of the rate constant for intersystem crossing for the pure charge-transfer exciplexes using electron-transfer theory allows determination of the matrix element for the spin-forbidden electron-transfer reaction. It is found to be roughly 3000 times smaller than the matrix element for corresponding spin-allowed electron transfer in similar systems. General principles for the factors that control the mechanisms of intersystem crossing in excited charge-transfer states are discussed.

I. Introduction

Exciplexes (Ex) are bimolecular excited states formed between electron acceptor and donor molecules that are characterized by varying degrees of charge-transfer (CT) character.[1] Their usual description is as a mixture of pure locally excited, pure charge (electron) transfer and pure ground states.[1] This is illustrated in eq 1 for the case of an electron acceptor (A) and an electron donor (D).

$$\Psi(Ex) = c_1\Psi(A^*D) + c_2\Psi(A^{\bullet-}D^{\bullet+}) + c_3\Psi(AD) \quad (1)$$

In this example, the locally excited state of the acceptor (A*) is lower in energy than that of the donor (D*), and the pure CT state is a radical-ion pair ($A^{\bullet-}D^{\bullet+}$), corresponding to complete transfer of an electron from the donor to the acceptor. Usually, ($c_1 + c_2$) is much greater than c_3, and the exciplex may be described qualitatively as a resonance mixture of locally excited and ion-pair states; see Scheme 1. The exciplex in Scheme 1 would be formed via bimolecular reaction of the locally excited singlet state of the acceptor, $^1A^*$, with the donor D.

The photophysical processes that characterize exciplexes are the same as those of excited states in general, i.e., radiative and nonradiative decay (k_{nr} and k_f) and intersystem crossing (k_{isc}), Scheme 1.[2] In polar solvents, exciplexes can also undergo a

SCHEME 1
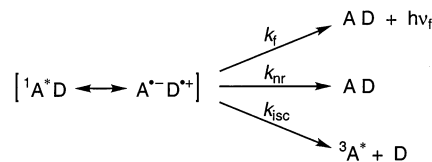
solvation process that may result in the formation of separated radical ions,[3] and in other cases, chemical reactions may occur.[4] However, the processes in Scheme 1 are those that most likely to be encountered for exciplexes in less polar solvents. Ideally, the factors that control the rates of these various processes should be understood so that the reactivity of exciplexes can be predicted. However, with the possible exception of the radiative rate, k_f, very few systematic studies of these processes have been reported.[1,5] In particular, there have been essentially no quantitative studies of the way that these processes depend on changes in the extent of charge transfer and upon the driving force for pairs with high CT character.[5]

Previously we described a series of exciplexes formed between 9,10-dicyanoanthracene (DCA) and 2,6,9,10-tetracyanoanthracene (TCA) as electron acceptors and various methyl-

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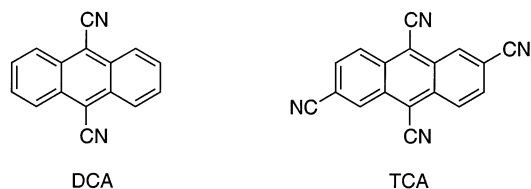
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substituted benzenes as donors in homogeneous solution at room temperature.[6] Depending on the particular acceptor/donor/solvent combination, exciplexes with varying extents of charge-transfer character were obtained, ranging from essentially zero (i.e., for the pure cyanoanthracene locally excited states, A*D) to essentially 100% as cyanoanthracene radical anion/alkylbenzene radical cation pairs, $A^{\bullet-}D^{\bullet+}$.[6] The radiative rate constants (k_f) decreased smoothly with increasing charge-transfer character. A complete theoretical analysis of the data was possible, and from this a quantitative determination of the extent of charge transfer in each exciplex was obtained.[6]

Intersystem crossing as illustrated in Scheme 1 is possible when the energy of the exciplex is higher than that of a locally excited triplet state.[1,7,8] The energies of the cyanoanthracene triplet states are lower than those of the corresponding alkylbenzene exciplexes in a wide range of solvents, and indeed formation of the cyanoanthracene triplet states can be detected as one of the decay paths of DCA exciplexes.[9,10] Here we describe the results of a detailed and quantitative study of the triplet-forming process in cyanoanthracene exciplexes, with an emphasis on the mechanism of the intersystem crossing process, the factors that control the intersystem crossing rate constants, k_{isc}, and the influence of the extent of charge transfer on the intersystem crossing mechanism. General conclusions concerning the mechanisms of intersystem crossing in excited CT states are given.

II. Results and Discussion

II.A. Detection of Intersystem Crossing in Cyanoanthracene/Alkylbenzene Exciplexes. All of the experiments discussed in the present work were performed in solvents of sufficiently low polarity (cyclohexane, carbon tetrachloride, trichloroethylene, dioxane, and fluorobenzene) that separation to form separated radical ions is not important.[3] Detection of the cyanoanthracene triplet states formed from decay of the exciplexes was accomplished in a number of ways. Nanosecond transient absorption spectroscopy results in observation of a species with a lifetime of several microseconds, and with absorption maxima at ca. 670, 735, and 810 nm, and another shorter wavelength absorption with a maximum lower than 450 nm that could not be accurately determined due to absorption by the DCA ground state. Picosecond excitation of DCA in methylene chloride results in formation of the DCA singlet state with an absorption maximum at ca. 620 nm; see Figure 1. In the presence of 0.1 M hexamethylbenzene and 1 M iodoethane, this absorption is rapidly replaced with the same absorption observed on the microsecond time scale in the nanosecond experiments (Figure 1). This absorption is assigned to the triplet DCA based on the following observations. The species is relatively long-lived, with a lifetime of several microseconds in deaerated solution, and has an absorption spectral feature in common with those from previous observations.[11] The species is also readily quenched by oxygen.[12] It is formed from the singlet state of DCA by the addition of hexamethylbenzene and the heavy-atom-containing iodoethane. Finally, addition of rubrene results in an increase in the rate of decay of the species observed at 810 nm and the corresponding formation of the known rubrene triplet state at 490 nm at the same rate.[11a] This process is assigned to energy transfer from ^{3}DCA* to rubrene.[11a] Corresponding experiments using TCA gave a spectrum for the triplet state that was similar to that shown in Figure 1 for DCA, except that the absorption peaks for DCA at ca. 670, 735, and 810 nm were red shifted to ca. 700, 770, and 850 nm for TCA.

Relative quantum yields for formation of the cyanoanthracene triplet states from different exciplexes were determined using
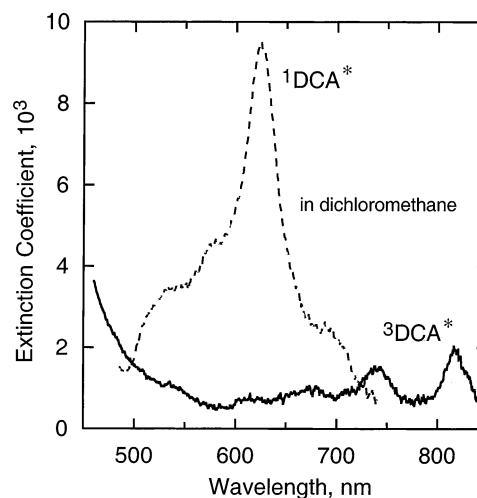

Figure 1. Quantitative absorption spectra of (upper dashed curve) the first excited singlet state and (lower solid curve) first excited triplet state of 9,10-dicyanoanthracene in dichloromethane solvent at room temperature.

several methods. In initial experiments, relative quantum yields were obtained by directly observing the signals due to ^{3}DCA* and ^{3}TCA* for various combinations of DCA or TCA with different alkylbenzenes in different solvents using nanosecond transient absorption spectroscopy. The small extinction coefficients of these species (Figure 1), however, meant that the experiments were difficult to perform accurately when the quantum yields were low. Higher accuracy, however, was achieved by carrying out the experiments in the presence of rubrene, capitalizing on the higher extinction coefficient of its triplet state at 490 nm.[13] The relative quantum yields for formation of locally excited cyanoanthracene triplet state from the corresponding exciplexes were obtained simply as the relative amounts of rubrene triplet formed. Furthermore, yields from DCA exciplexes could be compared directly to those from TCA exciplexes, since the same transient, rubrene triplet, was observed in each case.

As a check on the relative quantum yields, time-resolved photoacoustic calorimetry experiments were also performed on exciplexes of DCA with alkylbenzenes in various solvents.[5d,14] Under the conditions of the experiment, the energy release due to the reaction of the DCA excited singlet and formation of the exciplex was not resolved, but the energy retained by the long-lived triplet state was determined (see Experimental Section). Measurements of the relative amounts of energy stored by the triplet states allowed relative quantum yields for triplet formation to be determined. The photoacoustic, direct triplet observation, and rubrene trapping methods were in good agreement.

Using these three methods, relative quantum yields for formation of DCA and TCA triplet states for a variety of exciplexes, and also from the ^{1}DCA* and ^{1}TCA* states in various solvents in the absence of added alkylbenzene donors, were determined. The relative quantum yields were converted into absolute yields using triplet sensitization actinometry. Triplet energy transfer to rubrene from the triplet state of the ketocoumarin **1**[15] in trichloroethylene solvent was measured
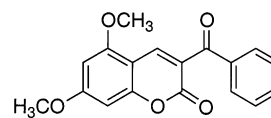
ISC in Charge-Transfer Excited States

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TABLE 1: Average Emission Frequency, ν_{av}, Lifetime, τ, Intersystem Crossing Quantum Yield, Φ_{isc}, and Rate Constant for Intersystem Crossing, k_{isc}, for the First Singlet Excited States of 9,10-Dicyananthracene (DCA) and 2,6,9,10-Tetracyanoanthracene (TCA) in Various Solvents at Room Temperature

acceptor	solvent[a]	ν_{av} (10^3 cm^{-1})	τ (ns)	Φ_{isc}	k_{isc} (10^6 s^{-1})
DCA	CHX	22.27	11.5	0.012	1.04
DCA	Diox	21.58	12.8	0.012	0.94
TCA	Diox	21.27	6.9$_3$	0.021	3.03
DCA	FB	21.57	12.3	0.014	1.14
TCA	FB	21.16	15.7	0.020	1.27
DCA	CTC	21.88	11.3	0.012	1.06
DCA	TCE	21.63	11.2	0.023	2.05
TCA	TCE	21.47	11.8	0.08	6.78

[a] CHX = cyclohexane, Diox = dioxane, FB = fluorobenzene, CTC = carbon tetrachloride, and TCE = trichloroethylene.

under identical light absorption conditions to the DCA/hexamethylbenzene/rubrene system in the same solvent.

The intersystem crossing quantum yield for **1** was determined to be 0.96 ± 0.02 (see Experimental Section), and thus the absolute quantum yield for the DCA/hexamethylbenzene/trichloroethylene exciplex was determined to be 0.58. Using this number, absolute yields for all of the other exciplexes studied, Φ_{isc}, were determined by averaging the relative yields

obtained using the different methods described above. Intersystem crossing quantum yields for the DCA and TCA acceptors in the different solvents in the absence of added donors were also determined. The results are summarized in Tables 1−3.

As a check, another method was also used to determine the absolute quantum yields for triplet formation. Excitation of DCA in trichloroethylene in the presence of 0.2 M pentamethylbenzene resulted in formation of the DCA triplet on the microsecond time scale. Experiments were performed in which the absorbance of the triplet state at 450 nm was measured as a function of added iodoethane. Heavy atoms are well-known to enhance intersystem crossing,[2] and indeed, increased yields of triplet DCA were obtained with increasing iodoethane concentration, as shown in Figure 2. In an independent experiment, iodoethane was found to quench the fluorescence of this exciplex with a bimolecular rate constant, k_q, of 3.8×10^8 M^{-1} s^{-1}. We make the reasonable assumption that quenching of the exciplex by the iodoethane results in formation of the locally excited triplet state with 100% efficiency. A mechanism that explains these observations is given in Scheme 2, which is the same as Scheme 1 with the addition of the iodoethane-induced transition from the exciplex to the triplet state. On the basis of Scheme 2, the dependence of the measured intersystem crossing quantum yield on the iodoethane concentration shown in eq 2 is obtained.
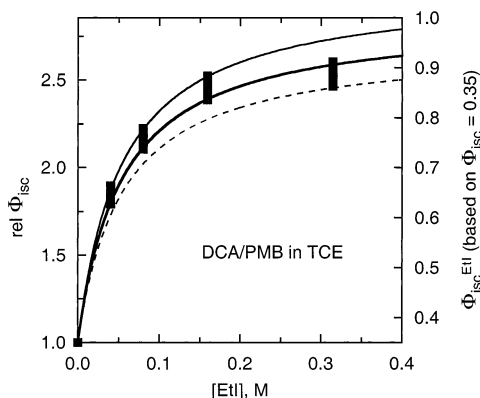
TABLE 2: Average Emission Frequency, ν_{av}, Lifetime, τ, Intersystem Crossing Quantum Yield, Φ_{isc}, Intersystem Rate Crossing, k_{isc}, and Percentage Charge Transfer, % CT, for Exciplexes of 9,10-Dicyananthracene (DCA) and 2,6,9,10-Tetracyanoanthracene (TCA) with Alkylbenzene Donors in Various Solvents at Room Temperature

acceptor	donor[a]	solvent[b]	ν_{av} (10^3 cm^{-1})	τ (ns)	Φ_{isc}	k_{isc} (10^6 s^{-1})	% CT
DCA	Dur	CHX	20.33	(37.5)	0.044	1.17	57
DCA	PMB	CHX	19.80	49.5	0.074	1.50	71
DCA	HMB	CHX	18.97	70.4	0.074	2.49	83
DCA	Dur	Diox	18.99	(67.7)	0.133	1.97	83
DCA	PMB	Diox	18.21	78.5	0.169	2.15	88
DCA	HMB	Diox	17.31	69.9	0.223	3.19	92
TCA	p-Xy	Diox	16.85	24.7	0.095	3.85	93
TCA	TMB	Diox	15.97	16.8	0.082	4.88	95
TCA	Dur	Diox	14.91	8.7	0.058	6.67	96
TCA	PMB	Diox	14.45	5.2	0.051	9.81	96
TCA	HMB	Diox	13.74	2.6	0.043	16.5	97
DCA	Dur	FB	18.71	(69.4)	0.098	1.41	85
DCA	PMB	FB	18.04	78.3	0.135	1.72	89
DCA	HMB	FB	17.08	68.5	0.180	2.63	93
TCA	p-Xy	FB	17.20	22.5	0.071	3.16	91
TCA	TMB	FB	16.21	14.7	0.057	3.88	94
TCA	Dur	FB	14.91	7.2	0.040	5.56	96
TCA	PMB	FB	14.45	4.6	0.035	7.61	96
TCA	HMB	FB	13.52	2.1	0.026	12.4	97

[a] Dur = durene, PMB = pentamethylbenzene, HMB = hexamethylbenzene, p-Xy = p-xylene, and TMB = 1,2,4-trimethylbenzene. [b] CHX = cyclohexane, Diox = dioxane, and FB = fluorobenzene.

TABLE 3: Average Emission Frequency, ν_{av}, Lifetime, τ, Intersystem Crossing Quantum Yield, Φ_{isc}, Rate Constant for Intersystem Crossing, k_{isc}, and Percentage Charge Transfer, % CT, for Exciplexes of 9,10-Dicyananthracene (DCA) and 2,6,9,10-Tetracyanoanthracene (TCA) with Alkylbenzene Donors in Chlorinated Solvents at Room Temperature

acceptor	donor[a]	solvent[b]	ν_{av} (10^3 cm^{-1})	τ (ns)	Φ_{isc}	k_{isc} (10^6 s^{-1})	% CT
DCA	Dur	CTC	19.83	(39.0)[c]	0.15	3.85	70
DCA	PMB	CTC	19.25	44.3	0.297	6.70	79
DCA	HMB	CTC	18.46	40.3	0.53	13.2	87
DCA	Dur	TCE	19.42	(39.7)[c]	0.20	5.04	77
DCA	PMB	TCE	18.82	48.1	0.349	7.26	84
DCA	HMB	TCE	18.02	41.0	0.58	14.2	89
TCA	p-Xy	TCE	18.41	51.8	0.31	5.99	85
TCA	TMB	TCE	17.53	54.8	0.326	5.95	90
TCA	Dur	TCE	16.27	46.6	0.256	5.49	94
TCA	PMB	TCE	15.83	26.2	0.206	7.86	95
TCA	HMB	TCE	14.75	12.2	0.194	15.9	96

[a] Dur = durene, PMB = pentamethylbenzene, HMB = hexamethylbenzene, p-Xy = p-xylene, and TMB = 1,2,4-trimethylbenzene. [b] CTC = carbon tetrachloride and TCE = trichloroethylene. [c] An equilibrium was observed between the exciplex and the locally excited state and the exciplex lifetime was extrapolated to infinite donor concentration.

Figure 2. Plot of (left-hand vertical axis) the relative quantum yield for formation of locally excited triplet state (solid bars indicating experimental error, Φ_{isc}^{EtI}), versus concentration of added iodoethane, for the exciplex of 9,10-dicyanoanthracene (DCA) with pentamethylbenzene (PMB) in trichloroethylene solvent (TCE). The curves through the data are calculated using eq 2 for the absolute quantum yield, with values for the parameters given in the text, and three different values for Φ_{isc}: 0.37 (thin solid line), 0.35 (bold solid line), and 0.33 (dashed line). The best fit to the relative yield data is obtained using 0.35 for Φ_{isc}. The absolute yields at the various iodoethane concentrations for this value of Φ_{isc} are indicated on the right-hand vertical axis.

SCHEME 2

$$\Phi_{isc}^{EtI} = \frac{\Phi_{isc}\tau^{-1} + k_q[\text{EtI}]}{\tau^{-1} + k_q[\text{EtI}]} \qquad (2)$$
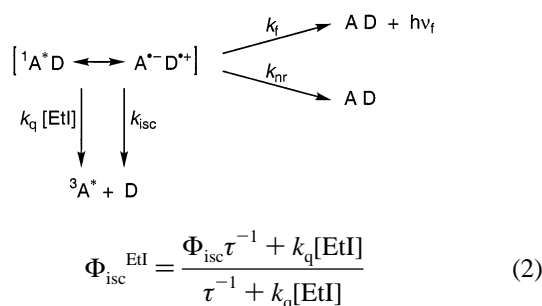
Here, Φ_{isc}^{EtI} is the triplet yield in the presence of iodoethane, Φ_{isc} is the triplet yield in the absence of iodoethane, and τ is the lifetime of the exciplex in the absence of iodoethane, which was measured to be 48.1 ns (Table 3). Fits to the data of Figure 2 using eq 2 are shown for three different values of Φ_{isc}. It is clear that the predicted variation in quantum yield is quite sensitive to the value of Φ_{isc} and that the best fit is for Φ_{isc} of 0.35, which is the same value obtained using the ketocoumarin actinometry described above (Table 3).

II.B. Rate Constants for Intersystem Crossing: A Method for Comparing Reactions in Different Solvents. The rate constants for intersystem crossing in the exciplexes and the cyanoanthracene excited singlet states in the various solvents, k_{isc}, were obtained from the lifetimes of the exciplexes (or excited states), τ, together with the quantum yields as shown in eq 3 (Tables 1−3).

$$k_{isc} = \Phi_{isc} \cdot \tau \qquad (3)$$

The lifetimes for the exciplexes studied here were determined previously,[6] or as part of the present work (see Experimental Section), and are included in the tables.

Shown in Figure 3 is a plot of log k_{isc} versus the average emission frequency, ν_{av}, for the DCA and TCA exciplexes in cyclohexane, fluorobenzene, and dioxane as solvents, together with the corresponding values for the locally excited singlet states, ^{1}DCA* and ^{1}TCA*, in the same solvents (see Tables 1 and 2). Evaluation of ν_{av} is described in ref 6, and its meaning
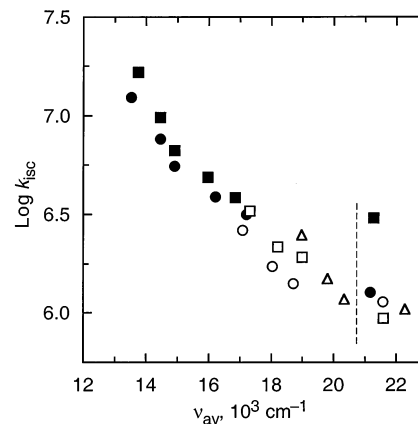

Figure 3. Plot of the logarithm of the intersystem crossing rate constant, k_{isc}, as a function of average emission frequency, ν_{av}, for (points to the left of the dashed line) exciplexes of 2,6,9,10-tetracyanoanthracene (TCA) and 9,10-dicyanoanthracene (DCA) with alkybenzene donors in various solvents, and (points to the right of the dashed line) the excited states of DCA and TCA in various solvents in the absence of added donor (data from Tables 1 and 2). Filled squares, TCA in dioxane; filled circles, DCA in dioxane; open squares, TCA in fluorobenzene; open circles, DCA in fluorobenzene; open triangles, DCA in cyclohexane.
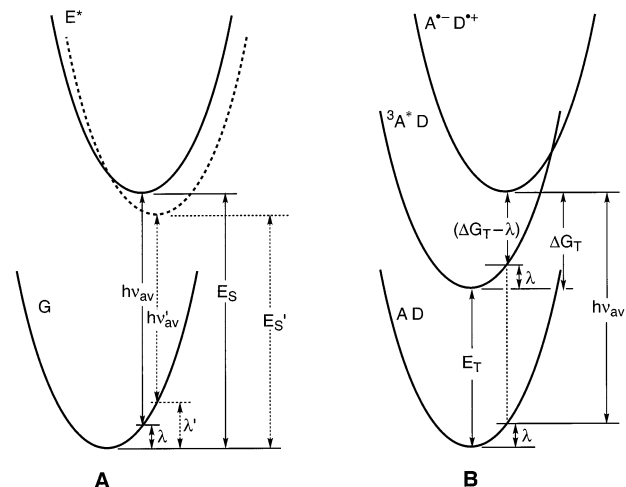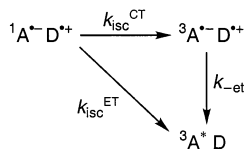

Figure 4. Energy curves illustrating (A) the relationship between the average emission energy of an excited state, ν_{av}, and the energy of an excited state in a nonpolar (solid upper curve, E_S) and a polar (dashed upper curve, E_S') and the reorganization energy for an excited state (E*) to ground state (G) transition, λ, and (B) the relationship between ν_{av}, the energy of a pure charge-transfer exciplex ($A^{\bullet-}D^{\bullet+}$), the corresponding locally excited triplet state (^{3}A*D), the ground neutral state (AD), and the reorganization energy for the exciplex to triplet and exciplex to ground-state transitions, λ.

is illustrated in Figure 4. As shown in Figure 4A, $h\nu_{av}$ represents the vertical energy difference between the excited state in its equilibrium geometry and the ground state at the same geometry. This energy is equal to the excited-state energy, E_S, minus the reorganization energy for the excited state to ground-state transition, λ. For different excited states in the same solvent, $h\nu_{av}$ decreases with decreasing excited-state energy, E_S. For the same excited state in different solvents, $h\nu_{av}$ decreases with increasing solvent polarity. This situation is illustrated in Figure 4A for an excited state in a less polar solvent (solid upper curve) and a more polar solvent (dashed upper curve). The average emission frequency is smaller in the more polar solvent ($h\nu_{av}'$ < $h\nu_{av}$) both because the excited-state energy is smaller (E_S' < E_S) and also because the reorganization energy is larger (λ' > λ).

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SCHEME 3

$$^1A^{\bullet-}D^{\bullet+} \xrightarrow{k_{isc}^{CT}} {}^3A^{\bullet-}D^{\bullet+}$$

$$k_{isc}^{ET} \searrow \qquad \downarrow k_{-et}$$

$$^3A^* D$$

For the excited states of Figure 3, we have shown previously that there is a quantitative relationship between the average emission frequency ν_{av} and the charge-transfer character of the emitting species.[6] The extent of charge transfer ranges from zero for the pure locally excited (LE) states to essentially complete for the exciplexes that emit with low values of ν_{av}. For the DCA and TCA exciplexes, the energy of the pure radical-ion-pair state $(A^{\bullet-}D^{\bullet+})$ decreases with increasing solvent polarity or by the use of donors with decreasing oxidation potential. Decreasing the energy of the $(A^{\bullet-}D^{\bullet+})$ state decreases mixing with the locally excited state (A*D) which increases the extent of charge transfer, and also decreases ν_{av}. For an exciplex with the same donor and solvent, the energy of the $(A^{\bullet-}D^{\bullet+})$ state is lower for TCA compared to DCA, and the TCA exciplex will have a lower value of ν_{av} and a higher extent of charge transfer. The extents of charge transfer for the various exciplexes studied here are given in Tables 2 and 3, and range from ca. 57% to greater than 95%. For the exciplexes with ν_{av} less than ca. 17.5×10^3 cm^{-1}, the extent of charge transfer is greater than 90%, and the species can be considered to be essentially pure contact radical-ion pairs, $(A^{\bullet-}D^{\bullet+})$.

For singlet excited charge-transfer states, two basic mechanisms for intersystem crossing can be considered, as illustrated in Scheme 3.[5,7,16,17] In the first, the CT state undergoes intersystem crossing to the triplet CT state, k_{isc}^{CT}, which is followed by return electron transfer in the triplet manifold to give the locally excited triplet, k_{-et}. In the second, intersystem crossing occurs as a result of a simultaneous spin-flip and electron-transfer process, k_{isc}^{ET}, and the singlet CT state is converted directly into the locally excited triplet state in a spin-forbidden electron-transfer reaction. Unless an intermediate state can be directly detected, or some specific spectroscopic information obtained, distinguishing between these mechanisms can be difficult. For several covalently linked donor/acceptor excited CT states, direct experimental evidence has been obtained using time-resolved ESR spectroscopy that demonstrates that either mechanism may operate, depending upon the system.[17] For the bimolecular systems studied here, however, such experiments are difficult, and useful mechanistic information is obtained in a different way, i.e., through the use of a near-homologous series of closely related systems. Specifically, the dependence of the rate of intersystem crossing on the reaction energetics and the extent of charge transfer is examined.

Figure 3 shows a reasonable correlation between the intersystem crossing rate constant and ν_{av}. The increase in log k_{isc} with decreasing ν_{av} is smooth, from essentially zero charge transfer (the DCA and TCA singlet states in the absence of added donor) to nearly complete charge transfer. The dependence of log k_{isc} on ν_{av} is very similar in both the high and low regions of CT character, which implies that the intersystem crossing mechanism does not change considerably as the extent of charge transfer changes.

Most theories of radiationless transitions describe the logarithms of the rate constants as a function of the energy gap between the states involved in the process.[18] The rate constants are predicted to decrease with increasing exothermicity, provided the energy of the excited state is larger than the reorganization
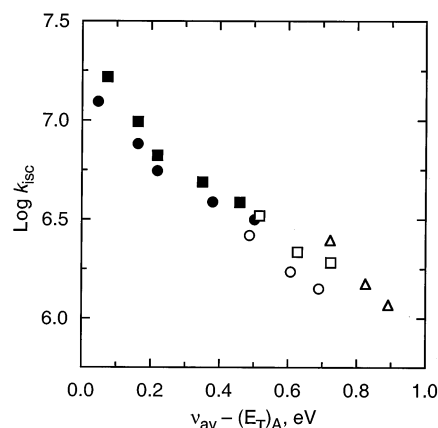

Figure 5. Plot of the logarithm of the intersystem crossing rate constant, k_{isc}, as a function of the energy gap for the exciplex to triplet state transition, $(\nu_{av} - (E_T)_A)$ for exciplexes of 2,6,9,10-tetracyanoanthracene (TCA) and 9,10-dicyanoanthracene (DCA) with alkylbenzene donors in various solvents (data from Table 2). Filled squares, TCA in dioxane; filled circles, DCA in dioxane; open squares, TCA in fluorobenzene; open circles, DCA in fluorobenzene; open triangles, DCA in cyclohexane.

energy for the transition, λ. This effect is known as the energy gap law, or the Marcus inverted region effect for electron-transfer processes.[18] As indicated in Figure 4, the reorganization energy is a measure of the extent to which the equilibrium positions of the nuclei of the excited-state molecules and the solvent are displaced in the excited- to ground-state transition. In ideal cases, λ can be measured spectroscopically from corresponding radiative processes.[18c,19] For excited states with extensive charge-transfer character, such as the exciplexes studied here, the reorganization energy is mainly due to differences in solvation between the excited and ground states.

The average emission frequency, ν_{av}, is related to the exciplex to ground-state transition, but can also be related to the corresponding transition to the locally excited triplet state $(^3A^*D)$. Because of the dominant solvent contribution to the reorganization energies for the exciplexes, we can assume that λ for the transition from the exciplex to the AD ground state is the same as that to the $(^3A^*D)$ triplet state, since both processes involve charge neutralization. This is illustrated in Figure 4B, where the ground and triplet states are shown at the same (nuclear) displacement on the horizontal (now solvation) axis. The ground and triplet excited states are displaced vertically by the triplet energy, $(E_T)_A$. Thus, the quantity $(\nu_{av} - (E_T)_A)$ represents the amount of energy that is in *excess* of the reorganization energy for the exciplex to triplet state transition, i.e., the amount of energy that must be dissipated in the transition. Because of the dominant solvent contribution, the reorganization energy λ will be different in different solvents. However, reactions in different solvents can be directly compared using $(\nu_{av} - (E_T)_A)$, because the reorganization energy is subtracted from the excited-state energy using ν_{av}, and only the *excess* energy beyond the reorganization energy is compared, as required in the energy gap/Marcus models of radiationless transitions.[18,20] Plots of log k_{isc} versus $(\nu_{av} - (E_T)_A)$ for the DCA and TCA exciplexes are shown in Figure 5. A value for $(E_T)_A$ of 37.5 kcal mol^{-1} is used for both cyanoanthracene acceptors. The method for determining $(E_T)_A$ is described in the Experimental Section.

The pure locally excited singlet state $(^1A^*D)$ obviously undergoes intersystem crossing directly to the locally excited triplet state $(^3A^*D)$. When the exciplex is still mainly locally excited, intersystem crossing presumably still occurs directly

to the (^{3}A*D) state, and the rate constant increases with decreasing ν_{av} as a consequence of the energy gap effect (see further below).[18] As the exciplex becomes more ion-pair like, the mechanism could change to one in which the initial product is a triplet charge-transfer state (^{3}A$^{•-}$D$^{•+}$) (k_{isc}^{CT}, Scheme 3). The energy difference between the pure singlet and triplet radical-ion-pair states is not known for the present systems. However, in the absence of mixing with LE states, this gap should not depend on the absolute energy of the pure (^{1}A$^{•-}$D$^{•+}$) and (^{3}A$^{•-}$D$^{•+}$) electron-transfer states; i.e., it should not vary with ($\nu_{av} - (E_T)_A$). Thus, if the mechanism of intersystem crossing does change from k_{isc}^{ET} to k_{isc}^{CT} (Scheme 3), it would be expected that the reaction should change from one for which the rate constant decreases with decreasing ($\nu_{av} - (E_T)_A$) (the energy gap effect for k_{isc}^{ET}) to one which becomes independent of ν_{av} (k_{isc}^{CT}). This obviously does not occur (Figure 5) since the rate constant varies smoothly with decreasing exciplex energy, even in the region of ν_{av} where the excited states are all essentially pure radical-ion pairs (their percent CTs are greater than 95).

Thus, we conclude that, for the exciplexes with high degrees of charge-transfer character, the intersystem crossing process can be understood as a spin-forbidden electron-transfer reaction from a state that is essentially (^{1}A$^{•-}$D$^{•+}$) to the (^{3}A*D) state, with k_{isc}^{ET}. This mechanism has been assumed in previous work on exciplexes;[5,16] the present data provide direct experimental support for this mechanism. The rate constants increase with decreasing energy gap between the (^{1}A$^{•-}$D$^{•+}$) and (^{3}A*D) states, which indicates that the reactions occur in the Marcus inverted region for the electron-transfer process.[21]

With very high CT character, it is possible that the mechanism may change again. As the energy of the ion pair decreases, mixing of the (^{1}A*D) and (^{1}A$^{•-}$D$^{•+}$) states decreases as the excited state becomes a pure radical-ion pair. However, as the energy of the pure ion-pair singlet state (^{1}A$^{•-}$D$^{•+}$) decreases, the energy of the corresponding triplet pair (^{3}A$^{•-}$D$^{•+}$) approaches that of the (^{3}A*D), and mixing between these two states should occur. It is unlikely that the (^{3}A$^{•-}$D$^{•+}$) decreases below the (^{3}A*D) state for the systems studied here, since the observed product of intersystem crossing is the separated ^{3}A*, which is readily observed by transient absorption spectroscopy. If the (^{3}A$^{•-}$D$^{•+}$) did become lower in energy than (^{3}A*D), then the product of intersystem crossing would be more ionic than locally excited, and it would not be expected to separate efficiently to give ^{3}A*. Furthermore, if the triplet radical-ion-pair state becomes lower than the ^{3}A* state, then the ^{3}A* that does separate should react with the D molecules in solution. This is not observed. Nevertheless, we cannot rule out the fact that intersystem crossing in the lowest energy exciplexes could involve a transition from (^{1}A$^{•-}$D$^{•+}$) to a triplet state with some charge-transfer character.

II.C. Isotope Effects on Intersystem Crossing. To further explore the intersystem crossing mechanism, we investigated the effects of deuterium isotopic substitution on the rate constants for this process. Our approach mirrors that described previously by Lim et al.[7] Exciplexes with DCA and TCA as the acceptors and hexamethylbenzene as the donor were studied. Comparison of the quantum yields for formation of locally excited triplet were compared for hexamethylbenzene and the fully deuterated analogue, and rate constants for intersystem crossing obtained as before. In both cases the k_{isc} values for the deuterated donors were smaller than those for the nondeuterated compounds, although the isotope effects were not large. Rate constant ratios, k_{isc}^H/k_{isc}^D, of ~1.3 were obtained for DCA/HMB

in fluorobenzene solvent and of ~1.5 for TCA/HMB in dioxane. Previously, we studied the effects of deuterium isotope substitution on the rate constants for inverted-region return electron transfer in solvent-separated radical-ion pairs.[22a] Deuterium substitution decreased the rate constants for electron transfer in those systems also, presumably because of a lowering of the average frequency of the vibrational modes that accept the energy associated with the process.[22] Qualitatively, the isotope effects are the same for both the intersystem crossing and the solvent-separated return electron transfer processes, and for other electron-transfer processes studied previously.[7,22] This provides further support for the proposal that intersystem crossing involves a spin-forbidden electron-transfer process.

II.D. Mechanisms of Intersystem Crossing. The intersystem crossing process k_{isc}^{ET}, Scheme 3, requires the electron-transfer process to be associated with a spin flip. In the absence of a strong external magnetic field, the most reasonable mechanisms for intersystem crossing in general involve either spin−orbit coupling[7,23] or hyperfine interactions.[24] Spin−orbit coupling is unlikely to induce the alternate intersystem crossing process k_{isc}^{CT} (Scheme 3). Lim has shown that in the one-electron approximation, spin−orbit coupling between the (^{1}A$^{•-}$D$^{•+}$) and (^{3}A$^{•-}$D$^{•+}$) states is zero, since the orbital occupation is the same in each system.[7] Thus, the hyperfine interaction is the most reasonable mechanism for (^{1}A$^{•-}$D$^{•+}$) to (^{3}A$^{•-}$D$^{•+}$) intersystem crossing. Indeed, direct evidence for this mechanism has been obtained in some covalently linked donor/acceptor systems.[17] In some favorable cases, the triplet radical pair state has been directly observed, confirming the mechanism.[17] However, the weak hyperfine interactions can only induce intersystem crossing when the energy difference between the singlet and triplet CT states is small, i.e., when electronic coupling is weak.[17] In both bimolecular and covalently linked donor/acceptor CT systems, electronic coupling tends to decrease with increasing separation distance between the radical sites.[25−27] In most of the covalently linked charge-transfer systems that have been studied, the distance between the donor and the acceptor is usually large, to reduce electronic coupling and thus enhance the lifetime of the final charge-separated states.[28] Interestingly, ESR experiments on a covalently linked donor/acceptor system in which the separation distance is small, and thus electronic coupling is correspondingly higher, suggest the spin−orbit coupling k_{isc}^{ET} mechanism.[17g]

In bimolecular CT systems, magnetic field effects have clearly demonstrated that the hyperfine mechanism is responsible for intersystem crossing in *solvent-separated* radical-ion pairs, SSRIP, i.e., k_{isc}^{CT}.[24c−e] Compared to the present contact radical-ion pairs, a solvent molecule separates the radical ions in the SSRIP,[24e,25] and thus the electronic coupling is much weaker in the latter compared to the former.[25] Thus, when the electronic coupling is weak, intersystem crossing seems to occur from singlet to triplet CT state via hyperfine coupling, k_{isc}^{CT}, and when the electronic coupling is large, it occurs from the excited CT state directly to the local triplet state via spin−orbit coupling, k_{isc}^{ET}. This is quite understandable. The spin−orbit mechanism is also an electron-transfer reaction, and will only be fast when the electronic coupling is large.[21] Under these conditions, the singlet triplet splitting in the CT states will be relatively large, which will preclude the hyperfine mechanism, k_{isc}^{CT}. The hyperfine mechanism can only take place when the electronic coupling is weak (when the singlet/triplet splitting in the CT state is small), and these are exactly the conditions under which the spin−orbit/electron-transfer process k_{isc}^{ET} will be slow. The choice between the mechanisms of Scheme 3 can thus be

accounted for by taking into account the strength of the electronic interactions.

II.E. Intersystem Crossing as an Electron-Transfer Reaction. The rate constant for the spin−orbit coupling induced electron-transfer process can be written as indicated in eqs 4.[21,29]

$$k_{-et}{}^{ET} = \frac{4\pi^2}{h} V_{isc}{}^2 \, \text{FCWD} \qquad (4a)$$

$$\text{FCWD} = \sum_{j=0}^{\infty} F_j (4\pi\lambda_s k_B T)^{-1/2} \exp\left[-\frac{(\Delta G_{isc} + jh\nu_v + \lambda_s)^2}{4\lambda_s k_B T} \right] \qquad (4b)$$

$$F_j = \exp(-S)\frac{S^j}{j!} \quad S = \frac{\lambda_v}{h\nu_v}$$

Here, λ_v and λ_s are the reorganization energies associated with a single averaged high-frequency vibrational mode, of frequency ν_v, and the low-frequency (mainly solvent) vibrational modes, and V_{isc} is the electron transfer/spin−orbit coupling matrix element responsible for the transition.[7,16] A value for V_{isc} can be obtained using the kinetic data and eqs 4, if values are known for the reorganization parameters λ_s, λ_v, and ν_v. The corresponding spin-allowed return electron transfer reaction ($^1A^{\bullet-}D^{\bullet+}$) to (AD) has been studied previously for cyanoanthracene/alkylbenzene contact radical-ion pairs.[25] Rate constants were measured as a function of reaction free energy, ΔG_{-et}, and inverted region behavior was observed. The data were analyzed according to eqs 4, substituting V_{-et} and ΔG_{-et} for V_{isc} and ΔG_{isc}. The values of the reorganization parameters that best describe the spin-allowed electron-transfer reaction are 0.2, 0.55, and 1400 cm^{-1} for λ_v, λ_s, and ν_v, respectively, and 1000 cm^{-1} for V_{-et}.[25] If we assume the reorganization parameters for the spin-forbidden electron-transfer reaction ($^1A^{\bullet-}D^{\bullet+}$) to ($^3A^*D$) are related to those for the spin-allowed process ($^1A^{\bullet-}D^{\bullet+}$) to (AD), a quantitative analysis of the intersystem crossing data can be made.

Consider intersystem crossing for the system TCA/hexamethylbenzene in fluorobenzene solvent as an example. The extent of charge transfer in this exciplex is high (>95%, Table 2). The energy of the exciplex above the neutral AD state is higher than the value of 2.03 eV for the previously studied CRIP ($^1A^{\bullet-}D^{\bullet+}$) in acetonitrile, because of the lower polarity of the fluorobenzene. Using a previously described relationship for the energies of radical-ion pairs,[3d] we estimate the exciplex energy to be ca. 2.13 eV. The free energy change for the exciplex to triplet state transition is equal to the exciplex energy minus the triplet energy; i.e., ΔG_{isc} is given by 2.13 eV − 1.63 eV = 0.5 eV. The average emission energy for this exciplex, ν_{av}, is 13 520 cm^{-1} (1.68 eV); see Table 2. The total reorganization energy for exciplex to neutral AD transition is the exciplex energy minus the average emission energy, i.e., 2.13 eV − 1.68 eV = 0.45 eV (Figure 4A). As discussed above, we can assume that the total reorganization energy for the exciplex to AD transition is the same as that for the exciplex to $^3A^*D$ transition. Taking the λ_v to be solvent independent and equal to 0.2 eV, and ν_v to be 1400 cm^{-1} (see above), we arrive at a value for λ_s for the intersystem crossing process of 0.25 eV. Substituting these values for the reorganization parameters and for ΔG_{isc} into eqs 4, together with 1.2×10^7 s^{-1} for k_{isc} (Table 2), we obtain a value for V_{isc} of 0.23 cm^{-1}. This calculation requires several assumptions and may not be very accurate; however, it is unlikely to be in error by more than a factor of 2. It is interesting
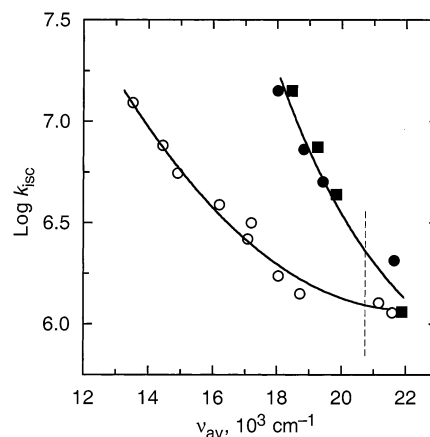
Figure 6. Plot of the logarithm of the intersystem crossing rate constant, k_{isc}, as a function of the average emission frequency (ν_{av}). The points to the left of the dashed line represent (open circles) exciplexes of 2,6,9,10-tetracyanoanthracene (TCA) and 9,10-dicyanoanthracene (DCA) with alkybenzene donors in fluorobenzene solvent, (closed circles) exciplexes of DCA in trichloroethylene solvent, and (closed squares) exciplexes of DCA in carbon tetrachloride solvent. The points to the right of the dashed line represent the excited states of DCA and TCA in the various solvents in the absence of added donor (data from Tables 1−3).

to compare this value with that obtained for the corresponding spin-allowed electron-transfer reaction V_{-et} of 750 cm^{-1}.[25] Clearly, the matrix element for the spin-forbidden process is much smaller than that for the spin-allowed process, by a factor of roughly 3000. In the only other direct comparison of matrix elements for spin-allowed and spin-forbidden electron transfer that we are aware of, the spin-forbidden and spin-allowed couplings differed by a factor of roughly 800.[30a]

As discussed elsewhere,[30] it is interesting that, even though the matrix element for the intersystem crossing process k_{isc} is much smaller than that for k_{nr} (V_{isc} is much smaller than V_{-et}), intersystem crossing still competes favorably to the extent that it can become one of the fastest decay processes for exciplexes. This is because although V_{isc} is small the FCWD term for intersystem crossing in eqs 4 can be much larger than the corresponding term for k_{nr}. In turn this is due to the difference in exothermicities; i.e., $-\Delta G_{isc}$ is much smaller than $-\Delta G_{-et}$. The efficiency of formation of the locally excited triplet state is determined by the competition between k_{isc} and the rate constants of the other processes of the exciplex.

II.F. External Heavy-Atom Effects on Intersystem Crossing. Experiments were also performed using trichloroethylene and carbon tetrachloride as solvents. The data are summarized in Table 3. The rate constants for intersystem crossing in these solvents do not fit well with those in the other solvents. The data are compared to data for comparable exciplexes in the nonchlorinated solvent fluorobenzene in Figures 6 and 7. In all cases, the rate constants in the chlorinated solvents are higher than those in the nonchlorinated solvents. We attribute this to an external heavy-atom effect associated with the chlorines.[2] Heavy-atom effects on intersystem crossing in radical-ion pairs are well-known, and have been studied previously.[31] The observed effects exhibit complex behavior. The effects on the pure locally excited states are quite different for DCA and TCA in the particular solvents studied. Intersystem crossing is considerably faster in trichloroethylene compared to the nonchlorinated solvents for TCA, whereas the increase in rate for DCA in trichloroethylene and in carbon tetrachloride compared to nonchlorinated solvents is much smaller for DCA. The reasons for this are not clear.
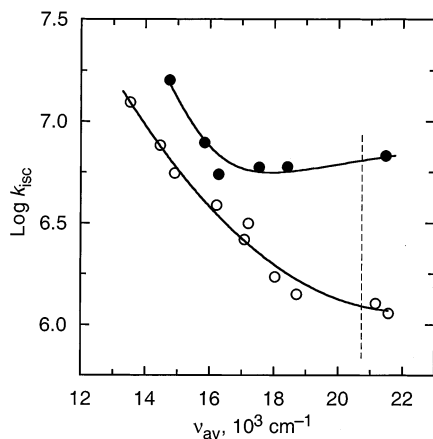
Figure 7. Plot of the logarithm of the intersystem crossing rate constant, k_{isc}, as a function of the average emission frequency (ν_{av}). The points to the left of the dashed line represent (open circles) exciplexes of 2,6,9,10-tetracyanoanthracene (TCA) and 9,10-dicyano-anthracene (DCA) with alkybenzene donors in fluorobenzene solvent, and (closed circles) exciplexes of TCA in trichloroethylene solvent. The points to the right of the dashed line represent the excited states of DCA and TCA in the two solvents in the absence of added donor (data from Tables 1−3).

The data in Figure 7 for the exciplexes of TCA in trichloroethylene show an interesting trend. The k_{isc} values for the TCA exciplexes in trichloroethylene are similar to those in the nonchlorinated solvents at comparable ν_{av} values. With increasing ν_{av} (decreasing percentage charge transfer), the intersystem crossing rate constants decrease, but trend to and level off at the value for ^{1}TCA*. Evidently, the influence of the trichloroethylene is largest when the extent of charge transfer is smallest for these systems. For the DCA exciplexes in trichloroethylene and carbon tetrachloride, the intersystem crossing rate constants also decrease with increasing exciplex energy and also trend to the values for DCA in the solvents alone. In these cases, however, the influence of the solvents in increasing the intersystem crossing rate constants seems to be greater for the exciplexes than for the locally excited state; i.e., the effect is largest when the percentage charge transfer is largest. These specific solvent heavy-atom effects are obviously quite interesting, but will require further study for a complete understanding.

III. Summary and Conclusions

Intersystem crossing rate constants have been obtained for exciplexes of cyanoanthracenes with alkylbenzene donors in various solvents at room temperature. In general, the rate constants exhibit energy-gap-law behavior, increasing with decreasing energy of the exciplex. Smooth trends are observed in the rate constants with changes in the extent of charge-transfer character. Together with the energy gap dependence observed even when the charge transfer is essentially constant, this is taken as support for a mechanism of intersystem crossing in these charge-transfer states as involving a spin−orbit coupling induced return electron transfer reaction to give the locally excited triplet state. Deuterium isotope effects on the rate constants are taken as further evidence in support of this mechanism. The spin−orbit coupling mechanism is expected for the systems studied here, which are characterized by strong electronic coupling. The alternate hyperfine-induced mechanism is only efficient when the electronic coupling is weak.

By combining this intersystem crossing data with that previously determined for the radiative rate constants, the dependence of the nonradiative rate constants on the extent of

charge-transfer character can now be determined for these exciplexes. This will be the subject of a future publication.

IV. Experimental Section

The cyanoanthracenes and alkylbenzenes were available from previous studies.[6] The solvents were all spectrograde and obtained from Aldrich and used as received. Rubrene was obtained from Aldrich and used as received. Exciplex and DCA and TCA fluorescence spectra and lifetimes were taken from ref 6, or were obtained using the methods described in that reference. Other steady-state fluorescence spectra were obtained using a Spex Fluorolog 2-1-2 spectrometer, and fluorescence lifetimes were measured using an instrument that has been described previously.[6] Picosecond time-resolved absorption spectroscopy was performed using an instrument that has been described previously.[32] The excitation wavelength was 355 nm. Spectra were recorded as a function of time and subject to global analysis using the commercial software package Specfit[33] to yield the absorption spectra and kinetics of the principal components formed upon excitation. The extinction coefficient of the singlet state of DCA in methylene chloride was determined relative to benzophenone triplet, observed at 525 nm.[11c] The extinction coefficient of the DCA triplet state was obtained assuming 100% conversion to the triplet state in the presence of 0.1 M hexamethylbenzene and 1 M iodoethane. Nanosecond transient absorption spectroscopy was performed using two instruments that have been described previously.[34] Excitation was either at 308 nm using an excimer laser or at 360 nm using an excimer pumped dye laser.

The time-resolved photoacoustic calorimetry experiment has been previously described.[14,35] Photoexcitation was performed at 420 nm (68.1 kcal/mol) using a nitrogen pumped dye laser and argon purged samples at room temperature. The acoustic waves are detected using a PZT transducer (∼0.5 MHz). The signal is amplified (Panametrics preamp, Model 5676), digitized (Tektronix TDS 620), and transferred to a laboratory computer for data analysis. The waveforms are the average of 50 laser pulses (<20 μJ). The transducer response function is obtained from photoexcitation of ferrocene. The optical densities of the calibration and sample compounds are ∼0.3 and are adjusted to be within 1% of each other. Sample absorbances did not change significantly during the experiment. The time resolution of the transducer is approximately 100 ns−5 μs. Heat depositions that occurred faster than 10 ns were not differentiated, whereas those slower than 5 μs were detected.

The triplet energy of DCA was obtained as follows. A DCA solution was excited in the presence of either hexamethylbenzene (HMB) or pentamethylbenzene (PMB) and 0.4 M iodoethane in trichloroethylene solvent. Under the reaction conditions, two heat depositions are observed: $\Delta H_a = -\alpha_a E_{hv}$ and $\Delta H_b = -\alpha_b E_{hv}$, where E_{hv} is the incident laser energy and α_a and α_b are the fractions of the incident photon energy released as heat in the depositions. The experimental enthalpic, α_a and α_b, and kinetic, $\tau_a \leq 10$ ns and τ_b, values are determined by deconvolution of the first 400 points of the acoustic waveforms. In the experiments, α_a corresponds to all the processes which lead to the formation of the DCA triplet state, and α_b corresponds to its decay. The triplet energy of DCA, $(E_T)_A$, is calculated from eq 5, where $(E_S)_A$ and $(E_T)_A$ are the singlet and triplet energies of DCA.

$$\alpha_a E_{hv} = (E_{hv} - (E_S)_A) + \Phi_{EX}((E_S)_A - E_{EX}) + \Phi_{IC} E_{EX} + \Psi_{ISC}^{EtI}(E_{EX} - (E_T)_A) \quad (5)$$

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E_{EX} is the energy of the exciplex, and Φ_{EX}, Φ_{IC}, and Φ_{ISC}^{EtI} are the quantum yields for exciplex formation, internal conversion of the exciplex, and intersystem crossing of the exciplex, respectively. These values are obtained from the extent of fluorescence quenching of the DCA singlet (Φ_{EX}), the quantum yield of exciplex fluorescence in the absence of iodoethane (Φ_{IC}), and the fluorescence quenching of the exciplex by iodoethane (Φ_{ISC}^{EtI}), assuming 100% conversion to the triplet state (see discussion above, and Figure 2). Under the reaction conditions, the following values are obtained for α_a, $(E_S)_A$, Φ_{EX}, Φ_{IC}, and Φ_{ISC}^{EtI}, respectively: 0.45, 61.7 (kcal/mol), 0.97, 0.01, and 0.94 with HMB as the donor. Because Φ_{EX} and Φ_{ISC}^{EtI} are close to unity, and Φ_{IC} is very small, eq 5 approximates to $\alpha_a E_{hv} = (E_{hv} - (E_T)_A)$. Under these conditions, the calculated value for $(E_T)_A$ is insensitive to the value chosen for E_{EX}, which is not known accurately. Thus, equating E_{EX} with ν_{av} (61.7 kcal/mol) gives a value for $(E_T)_A$ of 37.7 kcal/mol using eq 5. Changes in E_{EX} up to 5 kcal/mol result in changes in $(E_T)_A$ of less than 0.1 kcal/mol. The corresponding values for α_a, E_{EX}, Φ_{EX}, Φ_{IC}, and Φ_{ISC}^{EtI} with PMB as the donor are 0.43, 53.8 (kcal/mol), 0.97, 0.01, and 0.91. Using these values and eq 5, $(E_T)_A$ was calculated to be 37.7 and 37.0 kcal/mol from the PMB and HMB experiments, respectively. A value of 37.5 kcal/mol was thus taken for the DCA triplet energy. The same value was assumed for TCA.

Relative yields of triplet formation were obtained using nanosecond transient absorption spectroscopy with detection of the cyanoanthracene triplets at a variety of wavelengths, including 450, 735, and 810 nm for DCA and 450 and 770 nm for TCA. In the trapping experiments, rubrene triplet was monitored at 490 nm formed by energy transfer from the cyanoanthracene triplet states. Typically, the concentrations of the DCA and TCA were such that the optical density at the excitation wavelength was ca. 1.0, the concentrations of the alkylbenzenes were 0.1 M, and the rubrene concentration was 10^{-4} M. This concentration of rubrene ensures that essentially all of the DCA or TCA triplet states are trapped, and is sufficiently low that optical interference by the rubrene ground state is not important. Relative yields using photoacoustic calorimetry were obtained using the same cyanoanthracene/alkylbenzene solutions in the absence of rubrene. Absolute quantum yields were obtained using actinometry. Triplet energy transfer to rubrene from the triplet state of the ketocoumarin **1**[15] in trichloroethylene solvent was measured for a solution of the ketocoumarin in the presence of 10^{-4} M rubrene, and compared to the absorbance from a DCA/hexamethylbenzene/rubrene solution in the same solvent. Both solutions had the same optical density at 410 nm. Using an intersystem crossing quantum yield for the ketocoumarin of 0.96, the absolute quantum yield for the DCA/hexamethylbenzene/trichloroethylene exciplex was determined to be 0.58. Absolute quantum yields were checked as described above using iodoethane, with the assumption of complete conversion of exciplex to triplet in the presence of sufficient iodoethane. The intersystem crossing quantum yield for **1** was determined to be 0.96 ± 0.02 using time-resolved photoacoustic calorimetry as described previously,[36] using a value for the triplet energy of **1** of 56.8 kcal/mol.[15]

References and Notes

(1) (a) Weller, A. In *The Exciplex*; Gordon, M., Ware, W. R., Eds.; Academic Press: New York, 1975; p 23. (b) Mataga, N.; Ottolenghi, M. In *Molecular Association*; Foster, R., Ed.; Academic Press: New York, 1979; Vol. 2, p 1. (c) Jones, G., III. In *Photoinduced Electron Transfer. Part A. Conceptual Basis*; Fox, M. A., Chanon, M., Eds.; Elsevier: Amsterdam, 1988; p 245. (d) Kuzmin, M. G.; Soboleva, I. V. *Prog. React. Kinet.* **1986**, *14*, 157.

(2) Turro, N. J. *Modern Molecular Photochemistry*; Benjamin Cummins: Menlo Park, CA, 1978.

(3) (a) Weller, A. *Pure Appl. Chem.* **1982**, *54*, 1885. (b) Weller, A. *Z. Phys. Chem. (Wiesbaden)* **1982**, *133*, 93. (c) Arnold, B. R.; Noukakis, D.; Farid, S.; Goodman, J. L.; Gould, I. R. *J. Am. Chem. Soc.* **1995**, *117*, 4399. (d) Arnold, B. R.; Goodman, J. L.; Farid, S.; Gould, I. R. *J. Am. Chem. Soc.* **1996**, *118*, 5482.

(4) See, for example: (a) Lewis, F. D. *Acc. Chem. Res.* **1979**, *12*, 152. (b) Mattes, S. L.; Farid, S. *Science* **1984**, *226*, 917.

(5) (a) Soboleva, I. V.; Dolotova, E. V.; Kuz'min, M. G. *High Energy Chem.* **2002**, *36*, 29. (b) Davis, H. F.; Chattopadhyay, S. K.; Das, P. K. *J. Phys. Chem.* **1984**, *88*, 2798. (c) Watkins, A. R. *Chem. Phys. Lett.* **1976**, *43*, 299. (d) Van Haver, Ph.; Helsen, N.; Depaemelaere, S.; Van der Auwerer, M.; De Schryver, F. C. *J. Am. Chem. Soc.* **1991**, *113*, 6849. (e) Mataga, N. *Radiat. Phys. Chem.* **1983**, *21*, 83. (f) Adams, B. K.; Cherry, W. R. *J. Am. Chem. Soc.* **1981**, *103*, 6904.

(6) Gould, I. R.; Young, R. H.; Mueller, L. J.; Albrecht, A. C.; Farid, S. *J. Am. Chem. Soc.* **1994**, *116*, 8188.

(7) Lim, B. T.; Okajima, S.; Chandra, A. K.; Lim, E. C. *Chem. Phys. Lett.* **1981**, *79*, 22.

(8) See, for example: (a) Goldschmidt, C. R.; Potashnik, R.; Ottolenghi, M. *J. Phys. Chem.* **1971**, *75*, 1025. (b) Grellman, K. H.; Watkins, A. R.; Weller, A. *J. Phys. Chem.* **1972**, *76*, 3132. (c) Orbach, N.; Novros, J.; Ottolenghi, M. *J. Phys. Chem.* **1973**, *77*, 2831. (d) Nishimura, T.; Nakashima, N.; Mataga, N. *Chem. Phys. Lett.* **1977**, *46*, 334. (c) Kuzmin, M. G. *J. Photochem. Photobiol. A: Chem.* **1996**, *102*, 51. (d) Schneider, S.; Rehaber, H.; Schusslbauer, W.; Lewis, F. D.; Yoon, B. A. *J. Photochem. Photobiol. A: Chem.* **1996**, *99*, 103.

(9) (a) Soboleva, I. V.; Sadovskii, N. A.; Kuzmin, M. G. *Dokl. Akad. Nauk SSSR* **1977**, *233*, 635. (b) Soboleva, I. V.; Sadovskii, N. A.; Kuzmin, M. G. *Dokl. Akad. Nauk SSSR* **1978**, *238*, 400. (c) Takeda, Y.; Misawa, H.; Sakuragi, H.; Tokumaru, K. *Bull. Chem. Soc. Jpn.* **1989**, *62*, 2213.

(10) The energies of the locally excited cyanoanthracene triplet state are also lower than those of the alkylbenzene donors.

(11) (a) Darmanyan, A. P. *Chem. Phys. Lett.* **1984**, *110*, 89. (b) Kanner, R. C.; Foote, C. S. *J. Am. Chem. Soc.* **1992**, *114*, 678. (c) Carmaichael, I.; Hug, G. L. *J. Phys. Chem. Ref. Data* **1986**, *15*, 1.

(12) Gijzman, O. L. J.; Kaufman, F.; Porter, G. *J. Chem. Soc., Faraday Trans. 2* **1973**, *69*, 708.

(13) (a) As previously reported, quenching of ^{3}DCA* by rubrene results in formation of the rubrene triplet state.[11a,13b] We assume that the mechanism involves conventional triplet energy transfer,[2] since the triplet energy of rubrene is lower than that of DCA.[11a] However, we cannot rule out a mechanism involving electron transfer from the rubrene to ^{3}DCA*, followed by in-cage return electron transfer to form rubrene triplet. If this process does take place, overall energy transfer is likely to occur with 100% efficiency since separation of the DCA radical anion/rubrene radical cation pair will be too slow in the solvents used to compete with further formation of the rubrene triplet state via return electron transfer. We also assume that quenching of both ^{3}DCA* and ^{3}TCA* by rubrene occurs by the same mechanism, and that at the concentration of rubrene used, all of the ^{3}DCA* and ^{3}TCA* are trapped. (b) Darmanyan, A. P.; Kuz'min, V. A. *Dokl. Akad. Nauk SSSR* **1981**, *260*, 1167.

(14) (a) Cuppoletti, A.; Dinnocenzo, J. P.; Goodman, J. L.; Gould, I. R. *J. Phys. Chem. A* **1999**, *103*, 11253. (b) Rudzki, J. E.; Goodman, J. L.; Peters, K. S. *J. Am. Chem. Soc.* **1985**, *107*, 7849. (c) Herman, M. S.; Goodman, J. L. *J. Am. Chem. Soc.* **1989**, *111*, 1849. (d) Peters, K. S. In *Kinetics and Spectroscopy of Carbenes and Biradicals*; Platz, M. S., Ed.; Plenum: New York, 1990; p 37.

(15) Specht, D. P.; Martic, P. A.; Farid, S. *Tetrahedron* **1982**, *38*, 1203.

(16) Okada, T.; Karaki, I.; Matsuzawa, E.; Mataga, N.; Sakata, Y.; Misumi, S. *J. Phys. Chem.* **1981**, *85*, 3957.

(17) (a) Wiederrecht, G. P.; Svec, W. A.; Wasielewski, M. R.; Galili, T.; Levanon, H. *J. Am. Chem. Soc.* **2000**, *122*, 9715. (b) Wiederrecht, G. P.; Svec, W. A.; Wasielewski, M. R.; Galili, T.; Levanon, H. *J. Am. Chem. Soc.* **1999**, *121*, 7726. (c) Wasielewski, M. R.; Johnson, D. G.; Svec, W. A.; Kersey, K. M.; Minsek, D. W. *J. Am. Chem. Soc.* **1988**, *110*, 7219. (d) Carbonera, D.; Di Valentin, M.; Corvaja, C.; Agostini, G.; Giacometti, G.; Liddell, P. A.; Kuciauskas, D.; Moore, A. L.; Moore, T. A.; Gust, D. *J. Am. Chem. Soc.* **1998**, *120*, 4398. (e) Carbonera, D.; Di Valentin, M.; Agostini, G.; Giacometti, G.; Liddell, P. A.; Gust, D.; Moore, A. L.; Moore, T. A. *Appl. Magn. Reson.* **1997**, *13*, 487. (f) Carbonera, D.; Di Valentin, M.; Corvaja, C.; Giacometti, G.; Agostini, G.; Liddell, P. A.; Moore, A.

L.; Moore, T. A.; Gust, D. *J. Photochem. Photobiol. A: Chem.* **1997**, *105*, 329. (g) Willigan, H. v.; Jones, G. II; Farahat, M. S. *J. Phys. Chem.* **1996**, *100*, 3312.

(18) (a) Jortner, J. *Pure Appl. Chem*. **1971**, *27*, 389. (b) Marcus, R. A. *J. Chem. Phys.* **1984**, *81*, 4494. (c) Kober, E. M.; Caspar, J. V.; Lumpkin, R. S.; Meyer, T. J. *J. Phys. Chem.* **1986**, *90*, 3722.

(19) (a) Marcus, R. A. *J. Phys. Chem.* **1989**, *93*, 3078. (b) Gould, I. R.; Noukakis, D.; Gomez-Jahn, L.; Young, R. H.; Goodman, J. L.; Farid, S. *Chem. Phys.* **1993**, *176*, 439.

(20) The slope of the energy gap dependence or inverted region should be slightly different for different reorganization energies, but this effect is small and is ignored in the present discussion.

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

(22) (a) Gould, I. R.; Farid, S. *J. Am. Chem. Soc.* **1988**, *110*, 7883. (b) Martens, F. W.; Verhoeven, J. W.; De Boer, T. J. *Tetrahedron Lett.* **1979**, *31*, 2919. (c) Dresner, J.; Prochorow, J.; Sobolewski, A. *Chem. Phys. Lett.* **1978**, *54*, 292. (d) Prorochow, J.; Deperasinska, I.; Sobolewski, A. *J. Lumin.* **1979**, *18/19*, 105. (e) Lim, B. T.; Okajima, S.; Chandra, A. K.; Lim, E. C. *J. Chem. Phys.* **1982**, *77*, 3902. (f) Okijama, S.; Lim, E. C. *J. Phys. Chem.* **1982**, *86*, 4120. (g) Okijama, S.; Lim, B. T.; Lim, E. C. *J. Chem. Phys.* **1980**, *73*, 3512.

(23) (a) El-Sayed, M. A. *J. Chem. Phys.* **1963**, *38*, 2834. (b) Steiner, U. E.; Haas, W. *J. Phys. Chem.* **1991**, *95*, 1880. (c) Steiner, U.; Winter, G. *Chem. Phys. Lett.* **1987**, *55*, 364.

(24) (a) Closs, G. L. *Proc. Congr. Pure Appl. Chem.* **1971**, *4*, 9. (b) Kaptein, R. *Adv. Free Rad. Chem*. **1975**, *5*, 25. (c) Weller, A.; Staerk, H.; Treichel, R. *Faraday Discuss. Chem. Soc*. **1984**, *78*, 271. (d) Staerk, H.; Busmann, H. G.; Kuehnle, W.; Weller, A. *Chem. Phys. Lett.* **1989**, *155*, 603. (e) Weller, A. *Z. Phys. Chem. (Wiesbaden)* **1982**, *130*, 129. (f) Gould, I. R.; Turro, N. J.; Zimmt, M. B. *Adv. Phys. Org. Chem.* **1984**, *20*, 1.

(25) Gould, I. R.; Farid, S. *Acc. Chem. Res.* **1996**, *29*, 522.

(26) (a) Verhoeven, J. W. *Adv. Chem. Phys.* **1999**, *106*, 603. (b) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435.

(27) For an interesting exception, see: (a) Napper, A. M.; Read, I.; Waldeck, D. H.; Kaplan, R. W.; Zimmt, M. B. *J. Phys. Chem. A* **2002**, *106*, 4784. (b) Kaplan, R. W.; Napper, A. M.; Waldeck, D. H.; Zimmt, M. B. *J. Am. Chem. Soc.* **2000**, *122*, 12039.

(28) See, for example: Gust, D.; Moore, T. A.; Moore, A. L. *Acc. Chem. Res*. **1993**, *26*, 198.

(29) For a similar approach for the transition from triplet exciplexes (radical-ion pairs) to neutral ground state, see: (a) Levin, P. P.; Pluzhnikov, P. F.; Kuzmin, V. A. *Chem. Phys. Lett.* **1988**, *147*, 283. (b) Levin, P. P.; Naghavan, P. K. N. *Chem. Phys. Lett.* **1991**, *182*, 663. (c) Levin, P. P.; Pluzhnikov, P. F.; Kuzmin, V. A. *Chem. Phys.* **1989**, *137*, 331. (d) Ohno, T. *J. Phys. Chem.* **1985**, *89*, 5709. (e) Ohno, T.; Yoshimura, A.; Mataga, N.; Tazuke, S.; Kawanioshi, Y.; Kitamura, N. *J. Phys. Chem.* **1989**, *93*, 3546. (f) Ohno, T.; Yoshimura, A.; Mataga, N. *J. Phys. Chem.* **1990**, *94*, 4871. (g) Ohno, T.; Yoshimura, A.; Mataga, N. *J. Phys. Chem.* **1986**, *90*, 3295. (h) Ohno, T.; Yoshimura, A.; Shioyama, H.; Mataga, N. *J. Phys. Chem.* **1987**, *91*, 4365.

(30) (a) Morais, J.; Hung, R. R.; Grabowski, J. J.; Zimmt, M. B. *J. Phys. Chem.* **1993**, *97*, 13138. (b) Roest, M. R.; Oliver, A. M.; Paddon-Row, M. N.; Verhoeven, J. W. *J. Phys. Chem. A* **1997**, *101*, 4867.

(31) See, for example: (a) Steiner, U. *Chem. Phys. Lett.* **1980**, *74*, 108. (b) Pluzhnikov, P. F.; Levin, P. P.; Kuzmin, V. A. *Izv. Akad. Nauk SSSR* **1988**, *11*, 2627.

(32) Arnold, B. R.; Atherton, S. J.; Farid, S.; Goodman, J. L.; Gould, I. R. *Photochem. Photobiol.* **1997**, *65*, 15.

(33) Spectrum Software Associates, Chapel Hill, NC.

(34) (a) Gould, I. R.; Ege, D.; Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1987**, *109*, 3794. (b) Dockery, K. P.; Dinnocenzo, J. P.; Farid, S.; Goodman, J. L.; Gould, I. R.; Todd, W. P. *J. Am. Chem. Soc.* **1997**, *119*, 1876.

(35) Goodman, J. L. In *Energetics of Organic Free Radicals*; Simoes, J. A. M., Greenberg, A., Liebman, J. F., Eds.; Blackie Academic: London, 1996.

(36) Lavilla, J. A.; Goodman, J. L. *Chem. Phys. Lett*. **1987**, *141*, 149.