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Ion Pairs from Photoexcited, "Random" Electron Donors and Acceptors: Alkylbenzenes and Tetracyanoethylene

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Transient photocurrent experiments are used to measure the free radical ion quantum yield of a number of alkylbenzene electron donors with the electron acceptor tetracyanoethylene (TCNE). These experiments are performed at a variety of photoexcitation wavelengths in dichloromethane, a moderately polar solvent. It is found that the free ion yields often exhibit a very strong dependence on the excitation wavelength and may decrease markedly in the center of the charge-transfer band. For example, the free ion yield of the donor−acceptor system, pentamethylbenzene−TCNE, increases more than 100-fold when the excitation wavelength is switched from 532 to 397 nm! We show that this result and others are understandable from the following model. While closely associated electron donor−acceptor (EDA) complexes account for most of the absorption, there is an additional, usually small, absorption due to unassociated random donor and acceptor pairs. The Franck−Condon (vertical) excitation of these random pairs results in radical ion pairs which have center-to-center distances greater than contact and which have high probabilities for separation. Quantitative analysis based on Onsager theory indicates that only distantly separated radical ion pairs (ca. 1 nm or more) created by photoexcitation can escape each other's Coulombic attraction to produce the free ion yields observed in our experiments. The photoexcitation of ground-state EDA complexes plays little essential role in this process. The observed wavelength dependence then corresponds both to variation in the ratio of random pair to EDA complex absorption and to the distance distribution of radical ion pairs produced. Free ion yields calculated using Onsager theory and a simple excitation function for the random pairs fit our experimental results quite well and support this model.

1. Introduction

Photoinduced electron transfer is a fundamental process in many chemical and biological reactions and has been a major topic of research for more than 4 decades. Relationships between electron transfer (ET) rates and the energy gap, the separation distance, the reorganization parameters, and the coupling element have been found to be important. Basic theories concerning these relationships have been established and confirmed experimentally for many systems.[1−7] For example, for systems with weak interactions between donors and acceptors, ET processes involving radical ion pairs (RIPs) can be described well by Marcus theory and its extensions in which there is a "bell shaped" correlation between ET rates and the driving force for ET.[4,6,7]

The RIPs generated by ET quenching of excited states at a relatively long distance are "loose" radical ion pairs (LRIPs),[8a] i.e. solvent-separated radical ion pairs (SSRIPs),[7e,f] and it is believed that, in this case, the electronic coupling interaction between the donor cation (D^+) and acceptor anion (A^+) is relatively weak. When the RIPs are generated by direct excitation of electron donor−acceptor (EDA) complexes, contact radical ion pairs (CRIPs) with a center-to-center D^+/A^- separation distance of ~3.5 Å are produced in which there is very strong electronic coupling.[8−10] In such pairs, the charge recombination (CR) and charge separation (CS) rates and the free radical ion (FRI) yields are generally more sensitive to changes in the types of electron donors and acceptors,[11] to molecular size[7] and relative orientation, to solvent polarity, and to temperature[12] than they are in typical long-distance ET quenching systems. For complexes formed by relatively small π-donors and π-acceptors, EDA interactions show a strong dependence on the distance between donor and acceptor.

While there is considerable evidence for long-range optical charge transfer in bridged donor/acceptor systems,[4d,e] the implications of the distance distribution for photoinduced ET in unattached EDA systems has not been well-addressed. In an earlier work the implications of the distribution of donor−acceptor separations for the rate constants of thermal bimolecular electron transfers were analyzed.[13] In this work, we will consider the implication of the distribution of donor−acceptor separations for FRI formation in photoinduced ET processes involving unattached EDA systems. We have chosen tetracyanoethylene (TCNE) and alkyl-substituted benzenes as the acceptor and the donors, respectively, for this study, because TCNE is a well-known strong electron acceptor with a very compact structure.[14] Additionally, TCNE complexes with alkylbenzenes exhibit a large range of formation equilibrium constants.

So far, most studies of electron-transfer dynamics involving LRIPs and CRIPs[7,8,12,13] have been conducted in polar solvents, in which CS of the RIPs competes with CR. For CR processes in many systems, experimental findings have been generally in accord with theoretical predictions, but for the CS process, no simple relationship between CS rate constants and driving force has been observed.[8c,15] The difference in the dependence of CS

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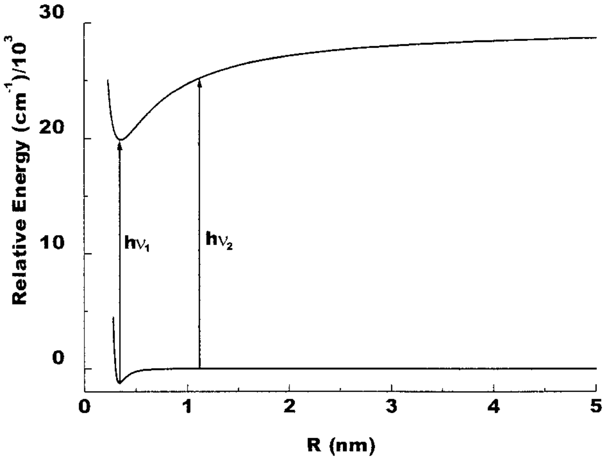


Figure 1. Potential energy curves for ground and excited EDA pair. The lower curve is schematic for a D−A pair that forms a weakly bound EDA complex, while the upper curve is scaled to give a CT absorption band at ca. 20 000 cm^{-1}. For donor cation D^+ and acceptor anion A^- separations greater than about 0.4 nm, the upper curve is Coulombic with a dielectric constant of 2.03 which corresponds to the optical dielectric constant (square of refractive index) for dichloromethane. $h\nu_1$ represents excitation in the CT band, while $h\nu_2$ represents excitation of a random D···A pair to give a $D^+\cdots A^-$ excited state of the same separation.

and CR processes on driving force has led to the conclusion[16] that the interionic distance distribution in the RIPs should be taken into consideration as a significant factor for the understanding of the mechanisms of subsequent reactions of RIPs.[11] Given that interionic Coulomb interaction in weakly polar solvents is stronger than that in strongly polar solvents, CS and CR rates and FRI yields will be more sensitive to interionic distances in weakly polar solvents. However, a disadvantage in using nonpolar or weakly polar solvents is that the CS process will be too slow to compete with CR and the FRI yield will be very small. In fact, for EDA complex photoexcitation in weakly polar solvents, the CRIPs after relaxation undergo simple single-exponential CR decay, and time-resolved transient absorption cannot detect any dissociation to free ions.[8c]

However, the transient photocurrent technique is a very sensitive method for unambiguous detection of free ions in photoinduced electron-transfer reactions and offers an attractive alternative to transient absorption. It is capable of measuring FRI quantum yields as small as 10^{-6}, depending on the solvent.[17] In recent work, FRI yields from the excitation of the ground-state complex of *trans*-stilbene/fumaronitrile in a variety of solvents were measured.[18] It was found that the observed FRI yield is much greater than that expected for CRIPs separating in a Coulomb field. To understand such a phenomenon, it was proposed that some kind of "initial" LRIP might be important in the FRI formation process. Given that the formation of LRIPs might be determined by the distance distribution of ground-state D−A pairs, we could achieve different FRI yields within the same D−A system if we could find a way to excite D−A pairs of various separations selectively. As suggested by Figure 1, we will demonstrate that selective excitation of D−A pairs of varying separation can be achieved.

Suppose D and A form a 1:1 EDA complex, while free D and A species are present in the solution only as random or "statistical" pairs. The random pairs will have, in general, a range of donor/acceptor separations from a fraction of a nanometer to infinity, and their binding energy will be smaller than their thermal energy, k_BT. Upon Franck−Condon photoexcitation, an electron is transferred from D to A to form a radical ion pair D^+/A^- with the same initial separation as in the ground-state D−A pair. In such D^+/A^- pairs there is strong Coulomb and other interactions, and all interactions show a strong dependence on $D^+\cdots A^-$ separation. Figure 1 makes clear our view that low photon energies excite primarily short-distance D−A pairs (EDA complexes), while in general, the excitation of long-distance pairs requires higher photon energies and forms LRIPs directly.

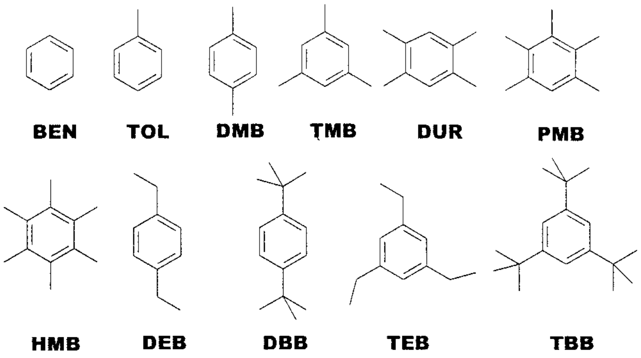
In our present work, transient photocurrent experiments are used to measure the FRI yields of several donor/acceptor systems at different excitation wavelengths in dichloromethane. It is found that FRI yields often exhibit a very strong dependence on excitation wavelength. As the excitation wavelength approaches the center of a charge-transfer band, the FRI yield may be dramatically reduced. We will show that this decrease is due to a decrease in the ratio of random pair to EDA complex absorption as well as variation in the distance distribution of the random ion pairs created. When D−A pairs which contribute to the absorption in or near a CT band are excited by photons, only the long-distance $D^+\cdots A^-$ pairs which are produced have a chance to separate into free ions. Because all electronic excitations obey the Franck−Condon principle, i.e., are vertical, photoexcitation of D−A pairs that happen to be distantly separated (ca. 1 nm or more) makes a large contribution to the FRI yield by resulting in distantly separated radical ion pairs which can escape each other's Coulombic attraction.

2. Experimental Section

Tetracyanoethylene (TCNE) from Acros was used as acceptor in this study. Donors used were benzene (BEN; Fisher, 99.9%), toluene (TOL; Fisher, 99.8%), 1,4-dimethylbenzene (DMB; Fisher, 99.8%), 1,4-diethylbenzene (DEB; Aldrich, 96%), 1,4-di-*tert*-butylbenzene (DBB; Aldrich, 98%), 1,3,5-trimethylbenzene (TMB; Aldrich, 98%), 1,3,5-triethylbenzene (TEB; Aldrich, 98%), 1,3,5-tri-*tert*-butylbenzene (TBB; Aldrich, 97%), 1,2,4,5-tetramethylbenzene (DUR; Aldrich, 98%), pentamethylbenzene (PMB; Aldrich, 98%), and hexamethylbenzene (HMB; Aldrich, 99%). Dichloromethane (Aldrich, 99.9%) was used as the solvent.

Absorption spectra were recorded using a Perkin-Elmer Lambda 9 Spectrophotometer. In transient photocurrent experiments, excitation of sample solutions was performed by using a nitrogen laser (337 nm) (Laser Science Inc. VSL-337), or third harmonic generation (THG, 355 nm), or second harmonic generation (SHG, 532 nm) from an MPB Technologies Orion SE-R Nd:YAG laser with full width at half-maximum (fwhm) of 0.4 ns, or a Spectra Physics Quanta Ray GCR-11 Nd:YAG laser with fwhm of 8 ns. Raman shifted pulses (397 nm) were obtained by focusing THG from the Quanta Ray GCR-11 Nd:YAG laser into cyclohexane. Dye laser pulses (441 or 485 nm) were obtained by pumping Coumarin 440 or 485 solutions with THG output from the Quanta Ray laser. Pulse energies were between 10 and 40 μJ within a 0.015 cm^2 spot size. A continuous-flow cell consisting of two parallel stainless steel electrodes, separated by 0.96 mm, with a 1.0 cm optical path length was used in the present study. The experiment was conducted in the charge displacement mode using a high impedance probe (1 MΩ) as the load resistor. A detailed description of the photoinduced current measurement has been reported previously.[17b,18] All experiments were performed at room temperature (21 ± 1 °C). The concentrations of donors and acceptors used depended on the formation constants of the EDA complexes. The usual concentration of TCNE was 0.006−0.012 M; the concentrations of donors ranged from 0.004 to

CHART 1



0.12 M, depending on the equilibrium constants of complexes. In 1 cm cells, such concentrations gave absorbances of 0.3–1.0 at wavelengths used for transient photocurrent experiments. Neither the concentrations of donors or acceptor nor changes in laser pulse energy or intensity had a noticeable effect on FRI yields.

3. Results

By themselves, TCNE and the alkylbenzenes of Chart 1 have no absorption in the visible region. However, TCNE can form EDA complexes with alkylbenzenes which exhibit broad absorption bands in the visible and near-UV. Figure 2 gives the absorption spectra of EDA complexes of TCNE with the alkylbenzenes used in this work (see Chart 1). The transition energy maxima of these complexes decrease as the number of methyl substituents on the benzene ring increases and the alkylbenzene becomes easier to oxidize. Some of the spectra exhibit two peaks, which arise from electronic transitions from the a_1 and b_1 orbitals of the benzene ring to the π^* orbital of TCNE.[14] This is obvious in the spectra of DMB, DEB, DBB, and DUR. For BEN, TMB, TEB, TBB, and HMB, the a_2 and b_1 orbitals are degenerate, and the CT bands have only one maximum. A fully optimized calculation for the BEN–TCNE complex at the HF/6-311G** level with GAUSSIAN 90 indicates that the complex has a symmetrical structure with a center-to-center separation of 3.724 Å in the optimized geometry.[19] A Gaussian fits the BEN–TCNE spectrum well on its low-energy side, but, on the high-energy side, the fit reveals a long tail. For other systems, such as TMB, TEB, TBB, and HMB with single-peak CT bands, similar results are observed. As suggested by Figure 1, such a deviation from Gaussian band shape can come from the excitation of distantly separated D···A pairs in the high-energy region of a CT band.

TMB and TBB have similar structures and their oxidation potentials are nearly the same (2.11 vs SCE for TMB, 2.10 for TBB).[20] The main difference between them is that TMB can form an EDA complex with TCNE but TBB does not appear to form a stable complex. For TMB–TCNE, ν_{max} of the CT band appears at 21 300 cm^{-1}, while ν_{max} of the random pairs of the TBB–TCNE system appears at 23 300 cm^{-1} and the absorption band is much weaker. That is, the random pairs produce an absorption "band" that is blue-shifted from that of the TMB complex by 2000 cm^{-1} (see Figure 2B). The small difference in oxidation potentials would contribute only 80 cm^{-1} to such a shift; the major contribution to the blue shift appears to come from the fact that transition energy depends strongly on the distance between D and A in the D···A pairs (Figure 1). A greater photon energy is needed to excite a distantly separated pair. Another significant difference between the spectrum of random pairs and that of an EDA complex is that the bandwidth, $\Delta\nu_{1/2,}$ of the former is larger than that of the latter. For example, $\Delta\nu_{1/2}$ of TBB–TCNE whose spectrum appears to be dominated by random pairs is 9600 cm^{-1}, while $\Delta\nu_{1/2}$ for the TMB–TCNE CT band is 5500 cm^{-1}. Similarly $\Delta\nu_{1/2}$ of HMB–TCNE is 5400 cm^{-1}, while $\Delta\nu_{1/2}$ of the sterically hindered hexaethylbenzene (HEB) with TCNE is 8400 cm^{-1}.[14a] It is useful to introduce a parameter, α, which describes the contribution of the "random" pairs to a CT band.

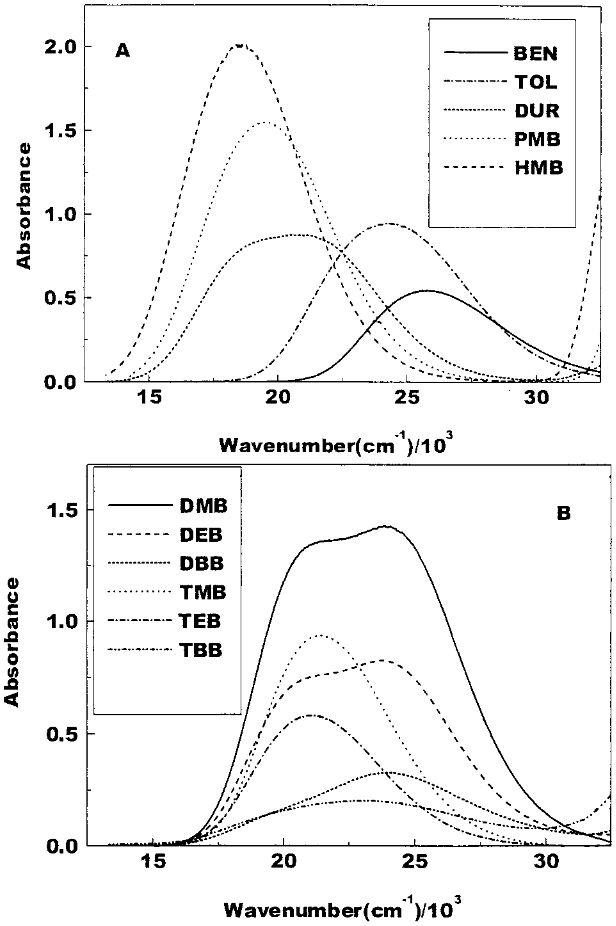


Figure 2. Absorption spectra of EDA complexes of alkylbenzenes with TCNE in dichloromethane at room temperature. Donor concentrations are 0.11, 0.11, 1.1 × 10^{-2}, 5.5 × 10^{-3}, 2.7 × 10^{-3}, 0.11, 0.11, 0.22, 2.4 × 10^{-2}, 4.4 × 10^{-2}, and 0.2 M for BEN, TOL, DUR, PMB, HMB, DMB, DEB, DBB, TMB, TEB, and TBB, respectively; while the TCNE concentration is 1.0 × 10^{-2} M except when the donors are DBB and TBB, where the TCNE concentrations are 2.0 × 10^{-2} and 4.0 × 10^{-2}, respectively.

For the systems studied here, the following equilibria exist:

$$\mathrm{D} + \mathrm{A} \rightleftharpoons \mathrm{DA} \quad K_{\mathrm{CP}} \tag{1a}$$

$$\mathrm{D} + \mathrm{A} \rightleftharpoons \mathrm{D}\cdots\mathrm{A} \quad K_{\mathrm{SSP}}(r) \tag{2a}$$

where DA and D···A denote EDA complexes and random (statistical) solvent-separated pairs, respectively. In the statistical pairs of interest, the donor and acceptor may be separated by either a part of a solvent molecule, a single solvent molecule, or several solvent molecules. At any wavelength, the absorbance, $A = A(\mathrm{DA}) + A(\mathrm{D}\cdots\mathrm{A})$. The fraction, α, of the photons incident at any wavelength which are absorbed by D···A pairs is given by

$$\alpha \equiv A(\mathrm{D}\cdots\mathrm{A})/A \tag{2a}$$

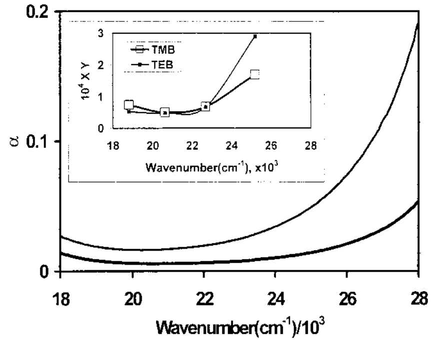


Figure 3. Values of α for TMB−TCNE and TEB−TCNE CT bands vs excitation wavenumber in dichloromethane. α, the probability that an absorbed photon excites a "random" D···A pair is computed as described in the text. Inset: plots of FRI yield (*Y*) against excitation wavenumber for the same two systems.

If we let $A(D\cdots A) = \kappa[D][A]$, where κ ($M^{-2}\ cm^{-1}$) = $\Sigma\epsilon_{SSP}(r)\ K_{SSP}(r)$ characterizes the absorbance by species D···A and [D] and [A] are the molar concentrations of free donor and acceptor, we have

$$\alpha = \kappa[D][A]/(\epsilon_{CP}[DA] + \kappa[D][A]) \qquad (2b)$$

where ϵ_{CP} ($M^{-1}cm^{-1}$) is the molar absorption coefficient of ground-state complexes and [DA] is their concentration. Using $K_{CP} = [DA]/[D][A]$, we have

$$\alpha = \kappa/(\epsilon_{CP}K_{CP} + \kappa) \qquad (3)$$

Thus the fraction α does not depend on the concentrations of DA, D, or A; i.e. it does not depend on dilution. Moreover, the relatively small values of K_{CP}, and [D] and [A] used in this study ensure that [DA] ≪ [D], [A]. Thus the stoichiometric concentrations of D and A can be used to calculate κ, once $A(D\cdots A)$ is known.

Since, for any D−A pair, K_{CP} is independent of wavelength and concentrations, and ϵ is independent of concentration, the only way to change α is to change K_{CP} by changing the donor or acceptor, the temperature or the pressure. For a typical CT band, this makes it difficult to separate the absorbance contributions of the random pairs from that by EDA complexes. Moreover, in an EDA complex, the electronic coupling between donor and acceptor is relatively strong, while such interaction within a random D···A pair is much weaker ($\ll k_BT$).

However, for systems with similar donor structures, the decay of electronic coupling with D−A separation should be similar from donor to donor. Thus, given that TMB, TEB, and TBB have similar structures and oxidation potentials, it is reasonable to use the absorption spectrum of TBB−TCNE to calculate κ for 1,3,5-trialkylbenxene−TCNE random pairs. Such values of κ are then used to calculate α for TEB−TCNE and TMB−TCNE. Figure 3 shows the variation of α with excitation energy for TMB−TCNE and TEB−TCNE; κ in eq 3 is calculated from the spectrum of TBB−TCNE by dividing each absorbance in Figure 2B by [D][A]. In Figure 3 it is seen that α shows a very strong dependence on excitation energy. At the high-energy side of a CT band, the random pair excitation probability is high, while α is at a minimum at the maximum of a CT band, and then rises again at lower energy.

The electronic coupling matrix element H_{ab} is expected to exhibit an exponential dependence upon the distance *r* between donor and acceptor[21,22]

$$H_{ab2}/H_{ab1} = \exp[-\beta(r_2 - r_1)/2] \qquad (4)$$

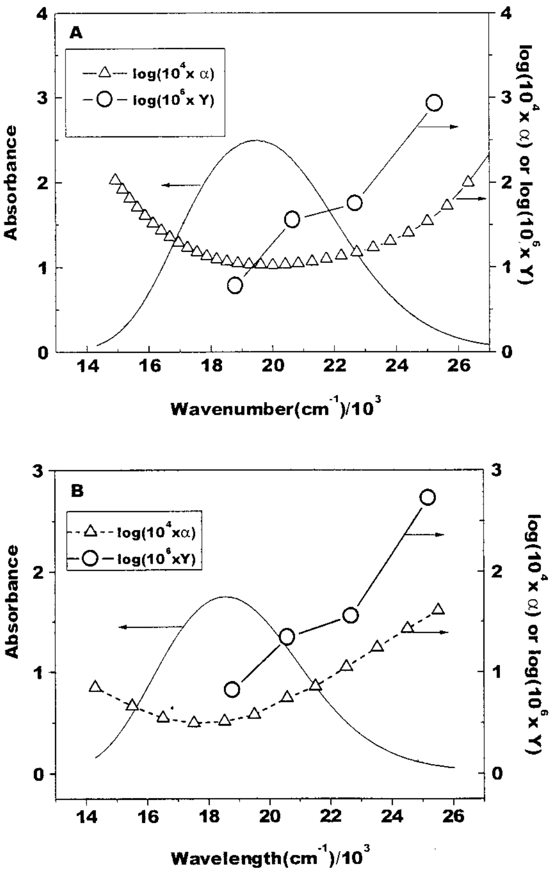


Figure 4. (A) Absorption spectrum, log plot of FRI yield (*Y*) and log α vs excitation wavenumber for PMB−TCNE in dichloromethane. (B) Absorption spectrum, log plot of FRI yield (*Y*) and log α vs excitation wavenumber for HMB−TCNE in dichloromethane.

We will assume that, for all the D−A pairs of this study, *β* values are the same. Maxima in the random pair absorption spectra are expected to be shifted from that of TBB−TCNE for other donors. But under the assumption of constant *β*, we will assume that the spectral shape for random pairs is donor-independent if the spectrum of the TCNE complex of the donor is similar to that of TMB−TCNE or TEB−TCNE. Thus we will obtain the spectra of other random pairs by appropriately shifting the spectrum of TBB−TCNE which we assume to be that of random pairs alone. For example, the maxima in the EDA bands of PMB−TCNE and TMB−TCNE are located at 19 500 and 21 500 cm^{-1}, respectively. Therefore, the spectrum of the random pairs of PMB−TCNE was obtained by shifting the spectrum of TBB−TCNE to lower energy by 2000 cm^{-1} prior to calculating the α curve by the procedure described above. Parts A and B of Figure 4 show plots of the logarithm of α against excitation energy for PMB−TCNE and HMB−TCNE.

For DMB−TCNE, DEB−TCNE, DBB−TCNE, and DUR−TCNE, CT spectra exhibit two bands, i.e, CT_1 and CT_2, which as discussed above arise from electronic transitions from the a_1 and b_1 orbitals of the benzene ring to the π^* orbital of TCNE, respectively.[14] In these cases, α_1 and α_2 for the two CT bands are calculated by using the procedure above and Gaussian fits to the two absorption bands; then α values for the observed CT band are obtained from eq 5.

$$\alpha = (\alpha_1 A_{CT_1} + \alpha_2 A_{CT_2})/A \qquad (5)$$

From Figures 3−5, it can be seen that all α curves have similar shapes. In other words, the random pair excitation

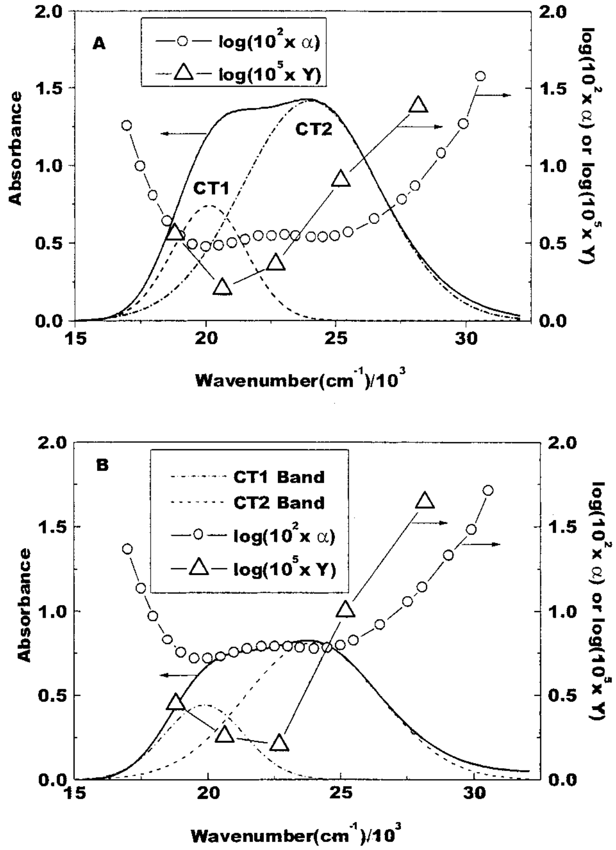


Figure 5. (A) Absorption spectrum, log *Y*, and log α vs excitation wavenumber for DMB−TCNE in dichloromethane. (B) Absorption spectrum, log *Y* and log α vs excitation wavenumber for DEB−TCNE in dichloromethane.

probability α is always greater on the high-energy side of a CT band, while, at the band maximum, α is at a minimum before recovering at lower energy. This behavior provides us the opportunity to study the effect of the D···A pair distance distribution on the free ion yield.

The experimental FRI quantum yield, *Y*, is calculated from photocurrent measurements as $Y = N_c/N_{abs}$, where N_{abs} is the number of photons absorbed by the solution and N_c is the number of free ion pairs produced; N_c is obtained from the extrapolated signal amplitude, v_{max} by using[18]

$$N_c = d^2 v_{max}\,[(\mu_+ + \mu_-)eV_0R]^{-1} \tag{6}$$

where *d* is the distance between the two electrodes, *e* is the charge of the electron, V_0 is the voltage applied, *R* is the load resistor, and μ_+ and μ_- are the positive and negative ion mobilities.[23] The FRI yields (*Y*) of different D−A pairs at various wavelengths are collected in Table 1. It is clear that, apart from BEN−TCNE, which shows no detectable wavelength dependence in *Y*, all other systems exhibit a strong wavelength dependence. To allow comparison of the wavelength dependence of *Y* with that of α, the variation of log *Y* with excitation energy is also plotted in Figures 3−5.

4. Discussion

The data presented above offer evidence that photogeneration of ion pairs in alkylbenzenes−TCNE solutions in dichloromethane depends principally on photoexcitation of relatively distant donor−acceptor pairs that interact via an incident photon. This photoinduced ET is a vertical excitation that produces a donor cation D^+ and an acceptor anion A^- at the same initial separation as in the original ground-state pair. As developed in Results, the wavelength-dependent factor, α, is the probability that a photon is absorbed by a “random” donor−acceptor pair even though most photons are usually absorbed by close-contact EDA complexes.

Figures 3−5 show that, for all alkylbenzene donors, the FRI quantum yield *Y* increases as α increases, especially on the high-energy side of CT absorption bands. Photoexcitation of ground-state EDA complexes appears to be *counter*productive to free ion formation, at least in a solvent of medium dielectric constant like dichloromethane.

To further understand the relationship between *Y* and excitation energy, it is helpful to show that FRI formation depends on the history of the RIPs which are initially formed after laser excitation in a CT band. It is well-known that the CR processes of RIPs produced by excitation of CT complexes show a strong dependence on the polarity of the solvent. CR is relatively slow in nonpolar solvents, but it is very fast in polar solvents.[24] On the other hand, in highly polar solvents, the solvation of photoinduced RIPs is exoergic, which makes SSRIPs more stable than CRIPs and enables further separation to produce FRIs. As solvent polarity is reduced, the CRIPs are more important, since solvation to form SSRIPs becomes endoergic[7f,25] and is thus less likely to occur.

A consequence of these solvation effects is, of course, higher FRI yields in polar solvents than in nonpolar solvents. In the medium-polarity solvent, dichloromethane, picosecond transient absorption experiments on CT complexes indicate that the

TABLE 1: Free Ion Quantum Yields (*Y*) of D−A Pairs for Alkylbenzene Donors with TCNE in Dichloromethane at Different Wavelengths

donor molecule	λ_{max}	K^a (M^{-1})	Y(337nm)^b (29 700 cm^{-1})	Y(355nm) (28 200 cm^{-1})	Y(397nm) (25 200 cm^{-1})	Y(441nm) (22 700 cm^{-1})	Y(485nm) (20 600 cm^{-1})	Y(532nm) (18 800 cm^{-1})
BEN	385	0.12	1.6×10^{-4}	1.9×10^{-4}	1.8×10^{-4}	1.2×10^{-4}		
TOL	410	0.28	3.2×10^{-4}	1.6×10^{-4}	5.3×10^{-5}	1.6×10^{-5}		
DMB		0.41		2.4×10^{-4}	8.0×10^{-5}	2.3×10^{-5}	1.6×10^{-5}	3.6×10^{-5}
DEB		0.16		4.4×10^{-4}	1.0×10^{-4}	1.6×10^{-5}	1.8×10^{-5}	2.8×10^{-5}
DBB				1.1×10^{-3}	5.3×10^{-4}			
TMB	465	1.56			1.7×10^{-4}	6.8×10^{-5}	5.0×10^{-5}	7.4×10^{-5}
TEB	473	0.27			2.9×10^{-4}	6.7×10^{-5}	4.9×10^{-5}	5.2×10^{-5}
TBB	429				1.5×10^{-3}	7.6×10^{-4}		
DUR	480	4.27			2.3×10^{-4}	2.0×10^{-5}	1.9×10^{-5}	1.2×10^{-5}
PMB	510	4.49			5.9×10^{-4}	3.9×10^{-5}	2.5×10^{-5}	4.2×10^{-6}
HMB	540	20.74			3.8×10^{-4}	2.6×10^{-5}	2.6×10^{-5}	4.7×10^{-6}

[a] Taken from ref 14a. [b] Values are preliminary and are corrected to zero applied electric field according to theory. In all transient photocurrent experiments, locally excitation of alkyl benzenes or TCNE gives a contribution of less than 0.5% to the total absorption; its effect on the FRI yield can be ignored.

formation of the "ion pair" is instantaneous, and the decay of the ions is also very rapid (within 60 ps).[26] A similar result was observed in time-resolved fluorescence studies of tetracyanobenzene (TCNB) EDA complexes by Gould et al. in other medium-polarity solvents.[27] For EDA complexes formed between the strong acceptor TCNE and arenes, recent work indicates that the CR processes of the photoinduced ion pairs are even faster with CR rates of $\sim 10^{11}$ s^{-1} in dichloromethane.[9,24b] Early work of Masuhara et al. indicates that CS processes proceed, at least in part, from unrelaxed excited states.[28] In this case, it is frequently assumed that, if a typical EDA complex is excited at a given wavelength, FRI formation comes from the direct competition between the CS and CR processes.

According to many previous investigators of charge pair escape and recombination,[7f,11] the escape probability ($P_{\rm esc}$) of RIPs is given by

$$P_{\rm esc}{}^{\rm kin} = k_{\rm CS}/(k_{\rm CS} + k_{\rm CR}) \qquad (7)$$

where $k_{\rm CS}$ and $k_{\rm CR}$ are time-independent, first-order rate constants for CS and CR. In nonpolar or medium polarity solvents, $P_{\rm esc} \ll 1$, i.e. $k_{\rm CS} \ll k_{\rm CR}$, so that

$$P_{\rm esc}{}^{\rm kin} = k_{\rm CS}/k_{\rm CR} \qquad (8)$$

When the EDA complex of TOL with TCNE in dichloromethane is excited at either 375 or 400 nm, recent work of both Tachiya's group and Kochi's group indicates that $k_{\rm CR}$ of the CRIP is 1.0×10^{11} s^{-1}.[9,24b] From Table 1, we can see that the FRI yield for the TOL−TCNE system is 5.3×10^{-5} if it is excited at 397 nm and, using eq 8, we calculate that $k_{\rm CS}$ is 5.3×10^{6} s^{-1}. According to Eigen's[29] or Tachiya's treatment,[30] $k_{\rm CS}$ for a D$^+$/A$^-$ pair may be estimated from

$$k_{\rm CS} = Dr_{\rm c}/\{r^3[\exp(r_{\rm c}/r) - 1]\} \qquad (9)$$

where $r_{\rm c}$ is the Onsager radius, it equals $e^2/(D_{\rm s}\epsilon_0 k_{\rm B}T)$, and it is 63 Å for dichloromethane at 293 K,[18] D is the sum of the diffusion coefficients for donor cation D$^+$ and acceptor anion A$^-$ and is calculated to be 1.4×10^{-9} m^2 s^{-1} in dichloromethane, and r is the distance between D$^+$ and A$^-$.

If excitation results in the formation of CRIPs with a separation distance of 3.5 Å, $k_{\rm CS}$ is estimated to be 3.2×10^{3} s^{-1} from eq 9. This is more than 10^3 times smaller than that required by eq 8 in order to give the measured value of $Y = 5.3 \times 10^{-5}$! Clearly, by itself, the direct separation of CRIPs cannot compete with the CR process and give much contribution to the FRI yields measured in this work. CR rates are very sensitive to the extent of electronic coupling, and both CR and CS rates depend on D$^+\cdots$A$^-$ separation; stronger coupling in CRIPs will result in much higher CR rates than for relatively long-distance pairs. At the same time, the CS rate will increase steeply as the initial pair separation increases because of decreased Coulombic attraction at long distances. An approximate relationship between the FRI yield and the separation of the D$^+$/A$^-$ pair for TOL−TCNE can be obtained as follows. If the distance dependence of the energy gap and the reorganization energies are neglected compared with the distance dependence of the electron-transfer coupling element (a poor assumption particularly for electron transfer in the inverted region[13]), the result for $k_{\rm CR}$ is [21,22]

$$k_{\rm CR} = k_{\rm CR}{}^0 \exp[-\beta(r - r_{\rm m})] \qquad (10)$$

where $r_{\rm m}$ is the van der Waals contact radius. Assuming that the main contribution to the CR rate in the transient absorption experiments[9,24b] on the TOL−TCNE EDA complex comes from CRIPs with a separation distance of 3.5 Å, and that $\beta = 1.1$ Å^{-1}, then introducing eqs 9 and 10 into eq 7 (with $D = 1.4 \times 10^{-9}$ m^2 s^{-1} and $r_{\rm c} = 63$ Å for TOL−TCNE in dichloromethane), gives values of the theoretical FRI yield ($P_{\rm esc}$) vs initial separation r as shown in Figure 6. Obviously, $P_{\rm esc}$ shows a very strong dependence on the initial separation of the D$^+$/A$^-$ pair which is produced by excitation. Note also that when r is larger than 1.2 nm, $P_{\rm esc}$ is approximately unity. Such calculated values of $P_{\rm esc}$ are clearly wrong, and we conclude that eq 10 is useful only for short-distance pairs. For these the ET coupling element is the main factor in determining the CR rate; i.e. diffusion can be neglected. But for long-distance pairs, the coupling between D$^+$ and A$^-$ is weak and diffusion is as important for the CR process as for CS.

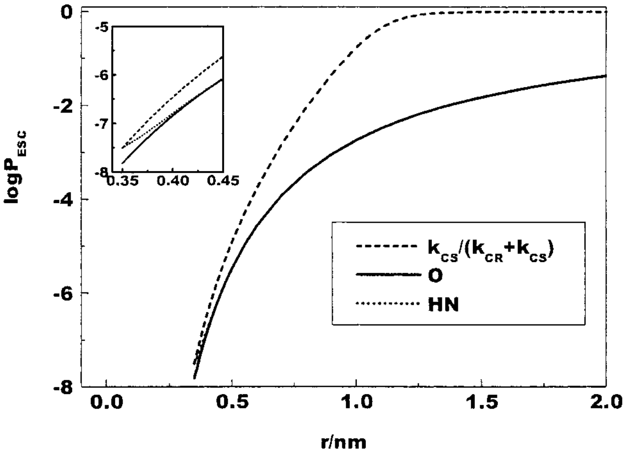


Figure 6. Calculated escape probabilities ($P_{\rm esc}$) for D$^+$/A$^-$ pairs of TOL−TCNE in dichloromethane as a function of initial separation distance r using eqs 7, 12, and 13. The solid line is calculated from eq 11, the dotted line is calculated from eq 12, and the dashed line is calculated from eq 7 in combination with eqs 9 and 10.

A more realistic alternative to eq 7 is based on the work of Onsager[31] who found a steady-state solution for the fate of a cation and an anion which are allowed to diffuse on the potential energy surface provided by their mutual Coulomb and any applied electric field. Onsager's equation for the escape probability of a charge pair which is initially separated by r_0 has been used in radiation chemistry[32] and in our work.[33] A key virtue[31b] is that Onsager's result provides a test of its applicability, which has no adjustable parameters. The applied electric field and temperature dependence predictions of Onsager's theory agree with photocurrent quantum yield experiments for holes and electrons photogenerated in single-crystal anthracene[33b] and for cation−electron pairs produced by photoionizing a solute in several liquids.[33d,e] Solutions to the Onsager diffusion equation for the time dependence of charge pair separation were provided by the work of Hong and Noolandi (HN).[34] The HN result was first applied to picosecond geminate charge pair recombination in the early 1980s.[35] The geminate pair decay observed in those experiments was highly nonexponential; fitting the data required the work of HN. Both the data and HN theory exhibit the "long-time tails" which are characteristic of the diffusive-recombination of geminate charge pairs. Moreover, the picosecond data provided values of the "initial" radius r_0 which are in general agreement with those obtained by applying Onsager theory to the earlier quantum yield data.

However, the electric field dependence of the free charge carrier quantum yields for donor−acceptor pairs in various polymers could be fit only if r_0 values of 2−3 nm were assumed.[36] Such large initial separations were difficult to reconcile with a photoexcitation process that was thought to produce a nearest-neighbor charge pair.[36] It is now known that the charge pairs in many polymer photoconductivity experiments were produced by long-distance electron transfer and that photogeneration of D^+/A^- pairs which were favorably oriented in the applied electric field[37] probably also played a role in charge pair separation. Evidently similar considerations also apply in the present study.

Under zero applied field, the following equations for predicting P_{esc} can be derived using the work of Onsager (O) or Hong and Noolandi (HN):

$$P_{esc}{}^{O} = \exp(-r_c/r_0) \tag{11}$$

$$P_{esc}{}^{HN} = \frac{\mathrm{esp}(-r_c/r_0) + (z-1)\exp(-r_c/r_m)}{1 + (z-1)\exp(-r_c/r_m)} \tag{12}$$

In both eqs 11 and 12, r_0 is the initial separation at which a RIP begins diffusing, and r_m is a critical reaction radius; we chose $r_m = 3.5$ Å for the RIP of TOL−TCNE, $z = Dr_c/\chi r_m{}^2$, where χ is the surface CR rate constant defined as r_m/τ, where τ is the lifetime of the ion pair when separated by r_m. For TOL−TCNE, z is calculated to be 2.09. With the parameters provided above, Figure 6 includes log P_{esc} vs initial formation distance r_0 for TOL−TCNE in dichloromethane according to eqs 11 and 12.

From Figure 6, it is interesting to note that when $r_0 \leq 5$ Å, diffusion is not important for CR; eqs 7, 11, and 12 give similar FRI yields. As pointed out earlier for another system,[18] the difference between the FRI yield predicted by Onsager theory (eq 11) and that by HN (eq 12) is small, and no difference can be seen for TOL−TCNE when r_0 is larger than 5 Å. However, when r_0 is larger than 5 Å, diffusion cannot be ignored and the popular eqs 7−10, which are usually used with the assumption that rate constants are independent of time, fail completely.

A better estimate is based on the data from TBB−TCNE and eq 11. Using $Y = 1.5 \times 10^{-3}$ at 397 nm and equating Y and $P_{esc}{}^{O}$ from eq 11, the initial Onsager separation $r_0 = 9.8$ Å, while using $Y = 7.6 \times 10^{-4}$ at 441 nm gives $r_0 = 8.8$ Å. For TBB−TCNE, the EDA interaction in the ground state is very weak. This allows us to ignore absorption by D−A pairs which might be transiently bound and to assume that only pairs, i.e. random pairs, exist when the donor is the sterically hindered TBB.

Next, we calculate the probability for excitation of such D···A random pairs of various radii and their contribution to Y and then compare the results with the Onsager separations obtained above. The random pair radius distribution function, $P(r)$ around a given A with a D−A "contact" radius r_m is simply

$$P(r)\,\mathrm{d}r = 4\pi n_D(r^2 - r_m{}^2)\,\mathrm{d}r \tag{13}$$

where n_D is the number density of the donor.

The general relationship between the electronic coupling matrix element and the intensity of the charge-transfer transition can be written as[2b,38,39]

$$\mathrm{H}_{ab}(r) = |\nu_{max}(r)\,\mu_{ge}(r)/(\mu_b(r) - \mu_a(r))| \tag{14}$$

where $\nu_{max}(r)$ is the band maximum for random pairs with a center-to-center distance of r, $\mu_{ge}(r)$ is the transition dipole moment, and $\mu_b(r) - \mu_a(r)$ is the difference between the dipole moments of the initial and final diabatic states. Substituting for the transition dipole moment of a Gaussian-shaped band and noting that $|(\mu_b(r) - \mu_a(r)| = re$ yields the familiar Mulliken−Hush equation:[21,38,39]

$$\mathrm{H}_{ab}(r) = 2.06 \times 10^{-2}[\epsilon_{max}(r)\,\nu_{max}(r)\,\Delta\nu_{1/2}(r)]^{1/2}/r \tag{15}$$

where ν_{max} and the bandwidth $\Delta\nu_{1/2}$ are in wavenumbers, ϵ_{max} is the molar absorptivity, and r is in angstroms.

In terms of the above formalism, the molar absorptivity for D···A at a given separation r can be calculated from

$$\epsilon_{max}(r) = 2.36 \times 10^3\mathrm{H}_{ab}(r)^2 r^2/[\nu_{max}(r)\,\Delta\nu_{1/2}(r)] \tag{16}$$

From eqs 13 and 16, the normalized absorption distribution, $P_A(r)$, of D···A pairs of various radii for excitation at ν_{max} can be written as

$$P_A(r) = \frac{\epsilon_{max}(r)\,P(r)}{\int_{r_m}^{\infty}\epsilon_{max}(r)\,P(r)} = \frac{(r^2 - r_m{}^2)r^2\exp[-\beta(r - r_m)]}{N\,\nu_{max}(r)\,\Delta\nu_{1/2}(r)} \tag{17}$$

where $\boldsymbol{N}$ is the normalization constant. Using eq 11 the distribution $\boldsymbol{P_Y(r)}$ of initial radii for those radical ion pairs that eventually separate into free ions is

$$P_Y(r) = P_A(r)\exp(-r_c/r) \tag{18}$$

The maximum of the charge-transfer absorption band at a given donor−acceptor separation can be calculated from[39b,c]

$$\nu_{max}(r) = \lambda_s(r) + \lambda_v + \Delta G°(r) \tag{19}$$

and the corresponding bandwidth $\Delta\nu_{1/2}(r)$ in wavenumbers is given by

$$\Delta\nu_{1/2}(r) = [2310(\lambda_s(r) + \lambda_v)]^{1/2} \tag{20}$$

where $\lambda_s(r)$ and λ_v are the solvent and intramolecular (vibrational) reorganization energies, respectively. The solvent reorganization energy is a function of the radii of the donor and acceptor, their separation, and optical (D_{op}) and static (D_s) dielectric constants of the medium. It can be calculated from the Marcus two-sphere model.[1] $\Delta G°(r)$ is the standard free-energy change for the optical transfer at the separation distance r. It equals the value at infinite separation corrected for the electrostatic work required to bring the separated RIPs from infinity to the separation distance r.

$$\Delta G°(r) = [E_{1/2}(D^+/D) - E_{1/2}(A/A^-)]F - e^2/D_s r \tag{21}$$

where F is Faraday constant. For TBB−TCNE in dichloromethane, $r_m = \sim 0.48$ nm, r_D and r_A are 0.41 and 0.30 nm, respectively, D_{op} and D_s are 2.02 and 9.08, respectively, $E_{1/2}$(D$^+$/D) for TBB and $E_{1/2}$(A/A$^-$) for TCNE are 2.11 and 0.24 V vs SCE, respectively. For consistency with other work,[7d] λ_v is assumed to be 0.2 eV in the present calculation. Figure 7 shows plots of $P_A(r)$, and $P_Y(r)$ against r for $\beta = 0.9$, 1.0, 1.1, and 1.2 Å^{-1}. It can be seen that, in all four cases, the absorption is caused mainly by small-radius pairs with separation distances < 0.8 nm, while FRIs are produced mainly by large-radius pairs with separation distances > 0.8 nm; the small radius pairs make very little contribution to the formation of FRIs. For $\beta = 0.9$, 1.0, 1.1, and 1.2 Å^{-1}, the $P_Y(r)$ vs r plots show maxima at 1.09, 1.03. 0.97, and 0.92 nm, respectively. The FRI yields for the four cases may be calculated by integrating the $P_Y(r)$ vs r plots

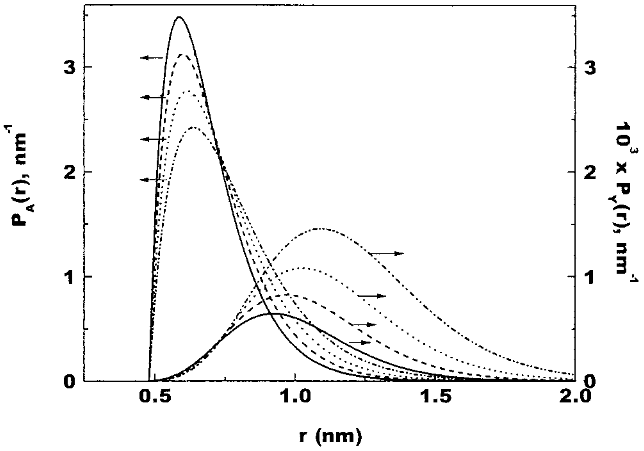


Figure 7. Calculated absorption distribution ($P_A(r)$) from eq 17 and FRI formation distribution ($P_Y(r)$) from eq 18 for random D···A pairs of TBB−TCNE in dichloromethane as a function of separation distance (r)—for excitation at λ_{max} given by eq 19. The electronic coupling parameters β used for the calculations are 0.9 (− ·· −), 1.0 (···), 1.1 (--), and 1.2 Å^{-1} (—), respectively.

to give 9.9×10^{-4}, 6.8×10^{-4}, 4.7×10^{-4}, and 3.4×10^{-4}, respectively.

These calculated quantum yields may be compared with experimental values of Y. For excitation at 441 nm, near λ_{max} of the TBB−TCNE CT band, $Y = 7.6 \times 10^{-4}$. This fits the calculated FRI yield with typical β values of 0.9 or 1.0 Å^{-1} and indicates the plausibility of our assumption that only random pairs exist in the TBB−TCNE system. If there were EDA complexes in that system, the experimental Y would be smaller than that predicted from the calculation of Figure 7, because the short-distance EDA complex makes almost no contribution to FRI formation. For excitation at 397 nm, the FRI yield is 1.5×10^{-3}—somewhat larger than that predicted under the random pair assumption; the reason for this will be discussed later.

In work of Jones' group[40] and Hoffman's group[41] on photochemistry of ground-state EDA complexes, it was observed that, for many EDA systems in various solvents, the quantum yields of chemical product formation were lower for excitation at long wavelengths in a CT band than for excitation at short wavelengths. The wavelength dependence was interpreted to be associated with excitation to upper vibrational levels in a CT band with the resulting enhancement of ionic photodissociation. In a typical work of Jones' group,[40c] the photoisomerization of EDA complexes of hexamethyl (Dewar) benzene with tetracyanobenzene TCNB and fumaronitrile was studied in dichloromethane. They found that the efficiency of rearrangement (i.e. the yield of ionic photodissociation) for irradiation at shorter wavelengths (CT excitation) approaches, but does not surpass, the yield found for irradiation of uncomplexed TCNB. For the methyl viologen EDA complex with oxalate, Hoffman's group found that there is a low plateau in the conversion quantum yield near the visible region.[41a,42] This is not expected from Jones' model and implies that a full understanding of the wavelength dependence, apart from excitation energy effects, requires that the initial structure after excitation should also be considered.

The results presented here clearly indicate that the exciting photon energy is not the only factor to affect the FRI yield. There is also a clear relationship between FRI yields and α which can be seen by comparing the profiles of Y and α vs excitation energy in Figures 3−5. On the high-energy side of a CT band, the random pair excitation probability increases as the excitation energy increases, while Y exhibits the same tendency. α is at a minimum at the maximum of a CT band and then rises again in the lower-energy region; the Y curves in Figures 3 and 5 exhibit a similar change. While this increase in Y on the low-energy side is not understood at this time, the significant increase in Y on the high-energy side is clear evidence that photoexcitation of random pairs dominates the production of ionic species which are able to separate and form FRIs.

However, quantitative analysis indicates that there is no simple linear relationship between Y and α—the Y curve is much steeper than that of α, especially on the high-energy side of CT absorption bands. The reason for this is that α gives only the probability of random pair excitation; it does not provide information about the separation−distribution of the random pairs which are excited, while the FRI yield is very sensitive to the distance distribution of the photoexcited random pairs. Figure 7 indicates that only long-distance random pairs with a separation of ∼1 nm make a large contribution to FRI formation.[18] From Figure 1 it is clear that excitation on the high-energy side of a CT band provides a higher probability for the excitation of long-distance random pairs than does excitation at a CT band maximum. This can probably explain why TBB−TCNE—in which only random pairs are postulated to exist—exhibits a weak wavelength dependence of Y. It also may explain why, on the high-energy side of the "CT band", Y for TBB−TCNE is even larger than that calculated by using the random pair model with $\beta = 0.9$ Å^{-1}. In eqs 17 and 18, excitation coefficients at maxima for different distance random pairs are used for the calculation of $P_A(r)$ and $P_Y(r)$. The excitation energy dependent distributions of both $P_A(r)$ and $P_Y(r)$ are ignored. When eq 18 is used to predict the FRI yield (Y) at the lower energy side of the peak, the contribution of the long-distance pairs will be overweighted. This will make the calculated P_{esc} value larger than that of the experimental one, while, at the high-energy side of the peak, the contribution of the short distance pair will be overweighted. This will make the calculated P_{esc} value smaller than that of the experimental one. The excitation energy dependent distributions of $P_A(r)$ and $P_Y(r)$ calculated by modeling the spectra is in progress and will be reported later.

Consistent with our assumptions, Table 1 shows that, in general, Y decreases as K_{CP} increases from one donor to another. This is most noticeable near the center of CT absorption bands for EDA complexes with a large value of K_{CP} and, thus, small values of α, i.e. when most incident photons are absorbed by EDA complexes rather than by random D···A pairs. Unfortunately, while the trend of Y vs K_{CP} is clear, we have been unable to derive a quantitative relationship between Y and K_{CP} that includes results for all donors. This will be the subject of future work. Moreover, while the theory underlying eq 17 provides semiquantitative values of κ for TBB−TCNE, detailed calculations also await further work.

5. Conclusion

Transient photocurrent experiments are used to measure the free radical ion (FRI) separation quantum yields Y of a number of alkylbenzene electron donors with the electron acceptor tetracyanoethylene (TCNE) at a variety of wavelengths in dichloromethane. The results indicate that, in general, Y decreases as K increases from one donor to another. To analyze the wavelength dependence of Y, the probability α that a photon is absorbed by a "random" donor−acceptor pair is introduced. The data presented show that, for all alkylbenzene donors, Y increases as a increases, especially on the high-energy side of

CT absorption bands. Thus photogeneration of FRI pairs arises principally by photoexcitation of relatively distant random donor−acceptor pairs that interact via an incident photon. Photoexcitation of ground-state EDA complexes appears to be *counter*productive to FRI formation, at least in a solvent of medium dielectric constant like dichloromethane. Quantitative analysis of FRI formation via random pair excitation based on Onsager theory indicates that excitation of random pairs with a separation of ca. 1 nm dominates the FRI yield of our systems. Free radical ion quantum yields calculated from a simple theory of random pair excitation fits experimental results for TBB−TCNE well.

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Abbreviations

CR	charge recombination
CRIP	contact radical ion pair
CS	charge separation
CT	charge transfer
EDA	Electron donor−acceptor
ET	electron transfer
FRI	free radical ion
HN	Hong and Noolandi
LRIP	loose radical ion pair
O	Onsager
RIP	radical ion pair
SSRIP	solvent-separated ion pair
Y	experimental free ion yield

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