

The solution dynamics of photoinduced geminate radical ion pairs: free ion formation

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Abstract

For geminate radical ion pairs (RIPs) formed by electron transfer quenching of excited 9,10-dicyanoanthracene (DCA) using benzene donors substituted with different bulky groups in several moderately polar solvents, the recombination rates at a variety of separation distances are measured. We used photocurrent techniques together with single photon timing measurements. For the first time, increased recombination rate constants with increasing RIP separation distance are observed. It is concluded that the dominant mechanism for the recombination of solvent separated radical ion pairs (SSRIP) involves a direct return electron transfer from SSRIPs by tunneling, thus by-passing the contact radical ion pairs (CRIP). © 2002 Elsevier Science B.V. All rights reserved.

1. Introduction

In homogeneous solutions, photoinduced electron transfer from a donor to an acceptor results in the formation of two kinds of geminate radical ion pairs, namely, contact radical ion pairs (CRIPs) and solvent separated radical ion pairs (SSRIPs) [1–3]. Time-resolved absorption spectroscopy was the main tool used in previous dynamics studies of RIPs and the free radical ions (FRIs) formed by further separation of SSRIPs [4–6]. So far very little is definitely known about the

dynamics of FRI formation, interconversion and recombination of CRIPs and SSRIPs, because time-resolved absorption spectroscopy by itself cannot easily distinguish the absorption caused by FRI, CRIPs and SSRIPs.

In our previous work, a transient photocurrent technique [7] was used together with single photon timing fluorescence. We found that, in moderately polar solvents [8,9], for geminate radical ion pairs (RIPs), whether formed by direct excitation in charge transfer absorption bands or by electron transfer quenching of excited electron acceptors by electron donors, the free ions formed arose mainly from loose radical ion pairs (LRIPs) i.e., solvent separated radical ion pairs (SSRIPs). The contribution of contact radical ion pairs (CRIPs) is very small. We also found that there is a potential barrier between CRIPs and SSRIPs and no equi-

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librium is reached between them during recombination and free ion formation [10]. For the recombination of SSRIPs, there are two possible mechanisms. First, they might collapse to CRIPs by overcoming the potential barrier and recombining to give the ground state; second, they might recombine directly from SSRIPs by electron tunneling and thus by-pass the barrier between CRIPs and SSRIPs. That is, it is unclear whether the dominant mechanism involves a thermally activated SSRIP collapse to CRIP which then recombines to the ground state, or a direct return electron transfer from SSRIPs by tunneling thus by-passing the CRIP.

The electronic coupling for CRIPs is much stronger than that for SSRIPs [11] but the solvent reorganization energy for recombination of RIPs at short separation distance is much smaller than that at long separation distances. Theoretical calculations indicate that, in the inverted region where most return electron transfers take place, rate constants should reach their maximum value at a separation distance larger than contact because of the opposing effects of separation distance on electronic coupling and solvent reorganization energy [12]. Such a prediction is difficult to test in solution, especially in moderately and weakly polar solvents. In these solvents, most of the RIPs formed by direct CT excitation or electron transfer quenching are CRIPs. In this case, the weak transient absorption signal by SSRIPs will be overlapped by the strong absorption of CRIPs. This makes difficult the detection and kinetic analysis of SSRIPs. The ambiguity can be overcome by using the transient photocurrent technique which can selectively detect the decay of SSRIPs or the formation of FRIs. If the recombination of SSRIPs is via electron-tunneling and no equilibrium exists between CRIPs and SSRIPs, [13] we should be able to measure the recombination rates of CRIPs and SSRIPs by single photon timing fluorescence and photocurrent risetime measurements, respectively. We can further regulate the separation distances of RIPs by using sterically hindered donors. This is the first systematic study of the separation distance dependence of electron transfer rates in solution for RIPs that are not

connected by chemical bonds. In this work, a series of experiments based on transient photocurrent measurements and single photon timing fluorescence is carried out in different solvents. Recombination rate constants at a variety of separation distances are reported for RIPs formed by electron transfer quenching of excited DCA using several benzene donors substituted with different bulky groups.

2. Experimental

9,10-Dicyanoanthracene (DCA) from Aldrich was used as the acceptor in this work. Donors used were durene (DUR; Aldrich, 98%), 1,2,4,5-tetraisopropylbenzene (TIPB; Aldrich, 96%), hexamethylbenzene (HMB; Aldrich, 99%) and hexaethylbenzene (HEB, Aldrich). Solvents used were ethyl acetate (Fisher, 99%), tetrahydrofuran (THF, Aldrich, 99%), dichloromethane (DCM; Fisher, 99%), 1,2-dichloroethane (Aldrich, 99%), 4-methyl-2-pentanone (Aldrich, >99%), pentanone (Aldrich, >99%), acetone (Fisher, 99%).

A detailed description of the method used for photoinduced current measurements can be found in our previous work [7,8,10]. All experiments were performed at room temperature (21 ± 1 °C). The absorbance of the solutions used in the photocurrent experiment was about 0.6 at 355 nm in a 1 cm cell. The solutions were deoxygenated by bubbling with nitrogen. The concentrations of donors were 0.02–0.2 M. The free ion yields were normalized to 100% quenching efficiency.

Fluorescence spectra were recorded using a PERKIN ELMER LS 50 luminescence spectrometer. Fluorescence lifetimes were measured using time correlated single photon counting. A 355 nm laser pulse from NV-20001-100 (Uniphase) was used for excitation. The pulses had a duration of 0.8 ns at 13 kHz and an average power of 1 mW. The emission was collected at 90° through a monochromator with a bandwidth of 3 nm located in front of the photomultiplier tube. The output from the single photon counting system was connected to a computer board module (Mca 32).

3. Results and discussion

3.1. Recombination rates at different separation distances

Under the condition used in the present study, no obvious EDA complex formation can be detected by absorption spectroscopy. Fig. 1a shows the emission spectra of 1.0×10^{-5} M DCA in the absence and presence of 0.1 M DUR in pentanone. It can be seen that, for solutions containing DCA and DUR, a new broad band ($\lambda_{em} \sim 530$ nm) appears in the long wavelength region. This is the characteristic exciplex emission. The decay of the exciplex emission is directly related to recombination of CRIPs. The time profile of the fluorescence intensity at 580 nm is shown in Fig. 1b and can be used to probe the formation and recombination processes of CRIPs. The decay at 580 nm is biexponential with a weak fast component from the unquenched DCA emission and a dominant component from the CRIPs. The lifetime of CRIPs can be determined to be 10.4 ns. Fig. 1c shows the photocurrent traces after quenching of excited DCA by 0.1 M DUR and TIPB in pentanone, respectively. The FRI yields can be determined to be 0.122, and 0.200, respectively. The risetime of the photocurrents which can be assigned to the decay times of SSRIPs are 7.4 and 4.0 ns, respectively. When the experiments are performed in less polar solvents such as 1,2-dichloroethane, the decay rates of CRIPs and SSRIPs decrease (Fig. 2). The photocurrent signals are smaller than those in pentanone. A photoinduced dipole signal following excitation can be observed (Fig. 2a). The FRI yield and photocurrent risetime can be calculated from the photocurrent which remains after subtraction of the dipole signal. The values are 0.0088 and 25 ns, respectively (for details on subtraction of the dipole signal see [10]). The free ion yields, exciplex lifetimes and photocurrent risetimes for DCA quenched by various donors in different solvents are collected in Table 1. For the solvents used, it is always true that the risetimes of the photocurrent are shorter than the decay time of the exciplexes for DCA–DUR and DCA–HMB. Furthermore, the photocurrent risetimes for DCA–DUR and DCA–HMB are generally longer

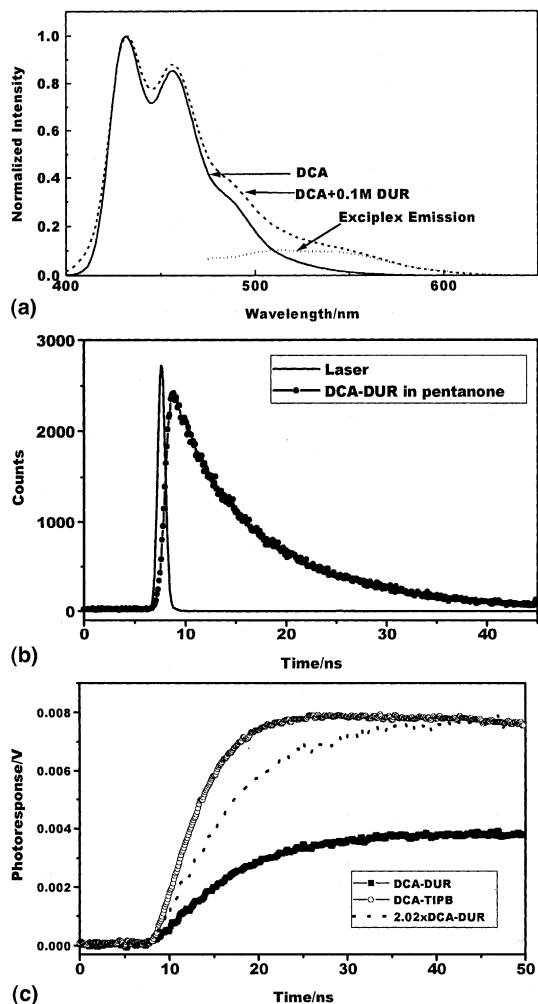


Fig. 1. (a) Emission spectra of 1.0×10^{-5} M DCA in absence and presence of 0.1 M DUR in pentanone. (b) Radiative decay curve of 1.0×10^{-5} M DCA with 0.1 M DUR in pentanone at 580 nm after excitation at 355 nm. (c) Photocurrents for 1.0×10^{-4} M DCA with 0.1 M DUR (solid square) and 0.1 M TIPB (open circle) in pentanone after absorption of 23 and 33.3 μ J at 355 nm, respectively. The transient DC photocurrent experiments are conducted in a continuous-flow 'fast' cell with electrodes separated by 0.96 mm. The applied voltage is 800 V, scope input is 50 Ω . For comparison of the risetimes, the photocurrent signal of DCA with DUR is enlarged to the same voltage as that of DCA with TIPB (dashed line).

than those of DCA–TIPB and DCA–HEB, respectively. In most cases, the risetimes of photocurrent for systems of DCA with 'bulky' donors TIPB and HEB are more than 30% shorter than those of systems of DCA with the corresponding

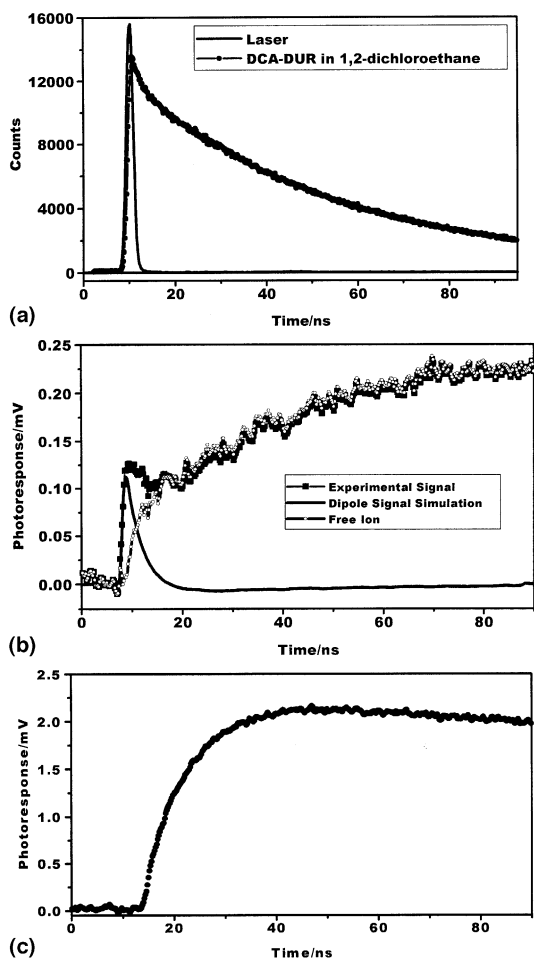


Fig. 2. (a) Radiative decay curve of 1.0×10^{-5} M DCA with 0.1 M DUR in 1,2-dichloroethane at 580 nm after excitation at 355 nm. (b) Photoresponses for 1.0×10^{-4} M DCA with 0.1 M DUR (solid square) in 1,2-dichloroethane after absorption of $39.3 \mu\text{J}$ at 355 nm with 800 V applied and a 50Ω scope input. The free ion component (open circle) is obtained by subtracting the simulated dipole signal (solid line) from the experimental signal (see text). (c) Photoresponses for 1.0×10^{-4} M DCA with 0.1 M TIPB in 1,2-dichloroethane after absorption of $47.3 \mu\text{J}$ at 355 nm with 800 V applied and a 50Ω scope input.

‘normal’ donors DUR and HMB. It is also clear that the free ion yields for DCA with bulky donors are always several times larger than for DCA with the corresponding normal donors (Table 1).

The obvious difference in exciplex decay time and photocurrent risetime for the same acceptor–donor combination in the same solvent indicates that there is no fast equilibrium between CRIPs

and SSRIPs. In other words, there is a potential barrier larger than $k_{\text{B}}T$ between CRIPs and SSRIPs. As concluded in our previous work (Scheme 1), [10] the free ions are mainly formed from SSRIPs, while the photocurrent risetime gives the total decay rate constant of the SSRIPs. The SSRIPs decay by one of the following three processes: (a) Direct recombination to ground state with a rate constant $k_{-\text{ET}}^{\text{SSRIP}}$, which can be estimated by Marcus theory [14]. Given the fact that the recombination process is in the Marcus inverted region, a stronger donor will have a larger recombination rate. (b) Collapse to the contact ion pair, followed by decay to the ground state by radiative or non-radiative charge transfer. The collapse is a diffusion controlled process in the Coulombic field of the two ions. The potential barrier for the diffusion is determined by the desolvation. For charge-separated radical ion pairs formed from donors and acceptors with similar structures and molecular sizes, this barrier should be similar in a given solvent. In this case, if no equilibrium is established between CRIP and SSRIP, and if the rate determining step is the collapse process with a rate constant k_{Coll} , we can expect decay rates for DCA–DUR and DCA–HMB to be very similar and to exhibit only a very weak dependence on the change in donor molecule. (c) Similar to b, the separation rate constant (k_{Sep}) should exhibit very weak dependence on a change in donors in a given solvent if all these donors have similar structures and molecular sizes.

If we assume that the free ion formation process competes directly with collapse or recombination at a critical separation distance r_{m} , the risetime of the photocurrent could be written simply as

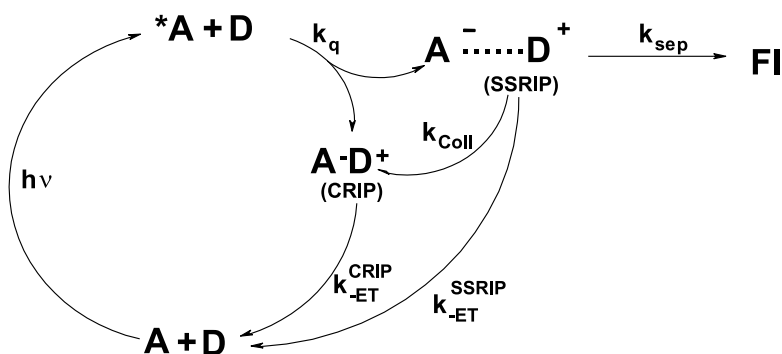
$$\tau_{\text{risetime}} = 1/(k_{\text{SEP}} + k_{\text{Coll}} + k_{-\text{ET}}^{\text{SSRIP}}). \quad (1)$$

For the medium polarity solvents used in our experiment, the FRI yield is less than 0.1. The ion pair separation does not determine the photocurrent risetime. Since DUR and HMB have very similar structures, if collapse is the key process in determining the total decay rate, we should see that the risetime exhibits little or no dependence on the change in donors from DUR to HMB in a given solvent. This is not true. The difference in photocurrent risetimes for DCA–DUR and DCA–

Table 1
Free ion yields (Y_{FRI}) and photocurrent risetimes (τ_{risetime}) for DCA quenched by various donors in different solvents

Donor	Solvent ^a	Viscosity (mPa s)	Y_{FRI}	τ_{exciplex} (ns)	τ_{risetime} (ns)
DUR	EA ($\epsilon = 6.02, r_c^0 = 96 \text{ \AA}$)	0.423		53.8	
TIPB	EA	0.423			ca. 10
HMB	EA	0.423		29.4	
HEB	EA	0.423			13
HMB	THF ($\epsilon = 7.58, r_c^0 = 74 \text{ \AA}$)	0.456	0.0107	34	6
HEB	THF	0.456	0.0634		15
DUR	DCM ($\epsilon = 8.93, r_c^0 = 63 \text{ \AA}$)	0.413	0.0043	32	21
TIPB	DCM	0.413	0.226		10
HMB	DCM	0.413	0.0048	28	7
HEB	DCM	0.413	0.138		7
DUR	DCE ($\epsilon = 10.36, r_c^0 = 54 \text{ \AA}$)	0.779	0.0088	48	25
TIPB	DCE	0.779	0.087		7
HMB	DCE	0.779	0.0069	21	5
HEB	DCE	0.779	0.073		4
DUR	MPT ($\epsilon = 13.11, r_c^0 = 43 \text{ \AA}$)	0.545	0.053	22.4	17.4
TIPB	MPT	0.545	0.214		6.4
HMB	MPT	0.545	0.030	14.1	6.4
HEB	MPT	0.545	0.161		4.1
DUR	PT ($\epsilon = 17.00, r_c^0 = 33 \text{ \AA}$)	0.444	0.122	10.4	7.4
TIPB	PT	0.444	0.200		4.0
HMB	PT	0.444	0.051	8.8	6.9
HEB	PT	0.444	0.205		4.2
DUR	AT ($\epsilon = 20.00, r_c^0 = 27 \text{ \AA}$)	0.306	0.087	3.2	3.5
TIPB	AT	0.306	0.162		2.9
HMB	AT	0.306	0.041		3.5
HEB	AT	0.306	0.165		2.8

^a EA = ethyl acetate, THF = tetrahydrofuran, DCM = dichloromethane, DCE = 1,2-dichloroethane, MPT = 4-methyl-2-pentanone, PT = pentanone, AT = acetone.



Scheme 1.

HMB is obvious and the risetime for DCA–DUR is always larger than that for DCA–HMB. This suggests that there exists a direct competition between direct recombination and separation in SSRIPs at large separation distance, and the recombination rate constant is far larger than the ion pair separation rate constant. The photocurrent risetime can, in fact, be used to probe the recombination rate constants of SSRIPs.

Gould and Farid [11] reported the FRI yields of electron transfer quenching of excited DCA by sterically hindered alkylbenzenes in acetonitrile. They found that the yields are 1.5–4 times larger than those for unhindered alkylbenzenes. It is concluded that the main reason for this comes from the steric-hindrance-induced decrease in the magnitude of electronic coupling for electron transfer, thus decreasing the return electron transfer rate and increasing the FRI yields. The effect of separation distance induced solvent reorganization energy change on return electron transfer rate was largely ignored. For an electron transfer reaction in the inverted region, theoretical calculation by Brunschwig et al. [12] indicates that the unique first-order rate constant reaches a maximum at separation distance larger than contact. This is attributed to the opposing effects of separation distance on electron coupling, H_{ab} , and solvent reorganization energy, λ_{out} . The free energies for the recombination reaction ($-\Delta G_{ET}$) for RIPs of DCA–DUR, DCA–TIPB, DCA–HMB and DCA–HEB are 2.69, 2.68, 2.50 and 2.55, respectively [11,15]. All of them are located in the inverted region.

When the donors are changed from the ‘normal’ donors DUR or HMB to sterically hindered TIPB or HEB, there are no significant changes in free energies for the recombination reactions. The main effect on the recombination rate constant of using sterically hindered TIPB or HEB to replace DUR or HMB is caused by separation distance-induced changes in electronic coupling or solvent reorganization energies. According to Brunschwig et al. [12] increased recombination rates should be observed at larger separation distances. The data presented in Table 1 show that, consistent with the above Brunschwig calculation, the recombination rate constants of SSRIPs of DCA–DUR and

DCA–HMB, measured by the reciprocals of photocurrent risetimes, are larger than those of CRIPs of the same acceptor–donor pairs measured from the reciprocals of the exciplex lifetime. When sterically hindered donors TIPB and HEB are used in the electron transfer quenching of DCA, the separation distances of SSRIPs formed are expected to be larger than those of SSRIPs formed from DCA–DUR and DCA–HMB. It is obvious from Table 1 that a steric hindrance induced increase in separation distances of SSRIPs results in further increases of recombination rate constants or decreases in the photocurrent risetimes. This indicates that a decrease in recombination rate is not the key for increasing FRI yield when sterically hindered donors are used in electron transfer quenching.

3.2. The key for FRI formation: initial charge separation distribution or rate constant

In order to get high FRI yields, bimolecular photoinduced electron transfer experiments are usually conducted in polar solvents like acetonitrile. In such solvents, it is much easier for geminate RIPs to overcome the coulomb interaction and to separate into FRIs. We note that, in acetonitrile, the FRI yields for RIPs formed by quenching of excited acceptor molecules using substituted benzene donor molecules are several times larger than those for RIPs from the same donor/acceptor combinations but formed by direct excitation of EDA complexes [16]. This clearly indicates that the initial charge separation distance is very important for FRI formation. On the other hand, even in acetonitrile, emission by CRIPs can be observed following both direct EDA complex excitation and electron transfer quenching. Interestingly, the emission yields in the latter cases are always more than half of those for EDA complex excitation [17,18]. This means that not all RIPs formed by electron transfer quenching are SSRIPs. However, the general lack of detailed knowledge of the separation distribution of electron transfer processes makes it difficult to address separation effects on exciplex and FRI yields quantitatively.

To study CRIPs/SSRIPs interconversion, Gould et al. [16] assumed that, in the polar solvent

acetonitrile, all the electron transfer quenching resulted in the formation of SSRIPs. However, this led them to report a more than 6-fold change in desolvation rates for SSRIPs with very small changes in donor structures, which is clearly unreasonable [19]. We find that allowing a donor/acceptor dependent probability for CRIP formation in quenching fits their data without such a strained conclusion. Thus, we wish to learn the distribution of donor cation/acceptor anion pair separations formed by quenching because this distribution controls the complete dynamics of the problem.

FRI yields are determined by the recombination and separation rates of RIPs. Both exhibit strong dependence on separation distance and solvent polarity. In weakly polar solvents, the separation rate is slow, but the recombination rate is also slow. For some RIPs, the recombination rate in a less polar solvent is more than 100-fold smaller than that in a more polar solvent [20]. It is also true that the FRI yield is always higher in strongly polar solvents than in weakly polar solvents. There are two reasons for this: (1) for RIPs with the same initial separation distance, the separation rate in a polar solvent is larger than that in a less polar solvent and (2) more importantly, for electron transfer quenching, long distance quenching which will result in the formation of SSRIPs is more probable in the polar than in non-polar solvents. However, the second reason has been largely ignored in the analysis of solvent effects on FRI formation. Our calculation based on Hong–Noolandi theory [21] indicates that, for SSRIPs, when the polarity of the solvent is decreased, the significant decrease in recombination rate could well balance the decrease in separation rate and make the FRI yield in a less polar solvent even larger than that in a more polar solvent.

For DCA quenching by normal donors such as DUR and HMB in the five solvents with polarity between DCM and acetone, the FRI yields increase by a factor of more than 10 as the solvent is changed from the less polar DCM (Onsager radius², $r_c^O = 63 \text{ \AA}$) to more polar acetone and

pentanone ($r_c^O = 27 \text{ \AA}$ and 33 \AA , respectively). The FRI yield exhibits a continuous increase as the solvent polarity increases. Note, however, that from pentanone to acetone the polarity of the solvent increases while the FRI yield decreases. This is true for both DUR and HMB as donor. A possible reason for this may be that the polarities of both solvents are very large and there is only a very small change in initial separation distance distribution of RIPs formed after quenching. The Coulombic interaction within the SSRIPs is weak and has very a limited effect on ion pair separation and FRI formation. But in more polar solvents such as acetone, there is an obvious increase in the decay rate of both contact and solvent separated RIPs (as can be seen from the shorter exciplex lifetime and faster photocurrent risetime in acetone compare with that in pentanone), and this in turn causes an obvious decrease in FRI yield.

For the five medium polarity solvents (from DCM to acetone) used in the experiments, the FRI yields of DCA with bulky donors exhibit no obvious change. The free ion yield values are between 0.13 and 0.24. The variation is less than a factor of 2. The only exception is that of 1,2-dichloroethane, in which the free ion yield is less than 0.1. A possible reason for the latter case may be that the viscosity of 1,2-dichloroethane is about twice that of other solvents (see the Table 1). Once again, the FRI yield in the most polar solvent, acetone, is not the highest. Actually, for DCA–TIPB, FRI yields decrease as the solvent polarity increases. As pointed out previously, most RIPs formed after quenching by bulky donors are long-distance separated SSRIPs, and there is a direct competition between separation and recombination during FRI formation. The effect of solvent polarity on FRI yield depends on its opposing effect on both separation and recombination rates of SSRIPs. For SSRIPs in the medium polarity solvents used in our work, the Coulombic interaction between donor cation and acceptor anion is weak; a change in solvent polarity has only a limited effect on separation rate.

On the other hand, both exciplex lifetime and photocurrent risetime increase significantly as the polarity of the solvent decreases. The increased lifetimes in SSRIPs of DCA with sterically hin-

² r_c^O is the Onsager radius, $r_c = e^2/(4\pi\epsilon_r\epsilon_0kT)$.

dered donors TIPB and HEB will provide the SSRIPs a greater chance to escape. The small range in the changes of FRI yield values accompanying the changes in solvent polarities proves that, when the polarity of the solvent is decreased, its effect on both recombination rate and separation rate of SSRIPs are comparable. Based on the above analysis, we can expect a very weak solvent polarity dependence of FRI yields if most electron transfer quenching by normal donors such as DUR and HMB takes place at long separation distances and results in the formation of SSRIPs. With these normal donors, the more than 10-fold increase in FRI yields as the solvent is changed from less polar DCM to more polar acetone indicates that there is a significant increase in SSRIP formation probability as the solvent polarity increases.

Since the steric hindrance induced recombination rate change is not the key factor that makes the FRI yields for DCA with bulky donors much greater than that for DCA with corresponding normal donors, the steric effect on FRI yields in different solvents can be used to evaluate the changes in the separation distance distribution of the initially formed RIPs after electron transfer quenching. For example, the FRI yield of sterically hindered DCA–TIPB is less than twice that of the sterically unhindered DCA–DUR in the most polar solvent, acetone. This means that a large portion of the quenching in DCA–DUR takes place at long separation distances and results in the formation of SSRIPs. In DCM, the FRI yield of DCA–TIPB is more than 50 times larger than that of DCA–DUR, this means that a very small portion of the quenching (<2%) results in the formation of SSRIPs.

4. Conclusions

For geminate radical ion pairs (RIPs) formed by electron transfer quenching of excited 9,10-dicyanoanthracene (DCA) using benzene donors substituted with different bulky groups in several moderately polar solvents, the recombination rates at a variety of separation distances are measured by using photocurrent techniques together with

single photon timing measurements. The results presented here might well imply that in homogeneous solutions, for electron transfer recombination processes in the inverted region, the recombination rate increases as the separation distance increases. The driving force dependence of recombination rate constants of SSRIPs suggests that the dominant mechanism for the recombination of SSRIPs involves a direct return electron transfer from SSRIPs by tunneling, thus by-passing the CRIPs. There is a direct competition between electron transfer recombination and separation during FRI formation processes. For moderately to strongly polar solvents used in the present study, the FRI yields of RIPs of DCA with bulky donors exhibit weak dependence on solvent polarity. The strong dependence on solvent polarity of FRI yields of DCA with sterically unhindered donors is attributed to the solvent polarity induced change in the separation distance distribution of the initially formed RIPs after electron transfer quenching.

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