and the sum of the H^+ contribution (reaction 3) and the known value of k_1 at room temperature,⁵ 880 s⁻¹, and scaling these differences to other temperatures with an assumed overall activation energy of 3.5 kcal/mol. At each temperature, these differences and the H⁺ contribution, calculated from the added NaOH and K_w , were subtracted from the data to obtain k_1 . They report values of k_{obsd} at each temperature and $e^{-}_{(aq)}$ concentration, so an attempt was made to reanalyze their data. First, it is apparent that the rate constants above 60 °C were dominated (>70%) by the reaction of $e^-_{(aq)}$ with H⁺ and should not be included in the data analysis. If just the data at 47 °C and below are used, then E_a is 5.8 kcal/mol using their method of data analysis. This method of data analysis is not adequate, however. If, instead, the first half-life is compared to the results of numerical integration of the mechanism of Table I, then the same data give $E_s = 6.5$ kcal/mol and k_1 at 25 °C as 930 s⁻¹. The 25 °C value is about 10% lower than that determined here and the activation energy 0.8 kcal/mol less, but there is no real disagreement between their work and the data presented here.

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Role of Contact and Solvent-Separated Radical Ion Pairs in the Diffusional Quenching of trans-Stilbene Excited Singlet State by Fumaronitrile

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Picosecond absorption spectroscopy is used to examine the question of whether contact radical ion pairs (CRIP) or solvent-separated radical ion pairs (SSRIP) are formed upon the quenching, by electron transfer, of the first excited singlet state of *trans*-stilbene (S_1) by fumaronitrile (FN). Prior to these experiments, it was generally believed that for exothermic reactions in polar solvents, SSRIP are formed upon quenching by electron transfer. However the present experiments reveal that the quenching of S_1 by FN in acetonitrile leads to the formation of CRIP. To establish the nature of the radical ion pair formed upon electron transfer, the kinetics for the decay of the CRIP and the SSRIP are established.

Introduction

One of the predominate mechanisms for the bimolecular quenching of electronically excited molecules is through electron transfer to form radical ion pairs. The molecular models used in discussing these reaction processes were developed through the pioneering studies of Weller and co-workers.^{1,2} Two distinct mechanisms for quenching are envisioned. In nonpolar solvents there is a charge transfer between the donor and acceptor to create a light-emitting species, termed an exciplex or contact radical ion pair (CRIP), with an interplanar separation of approximately 3.5 A 3

$${}^{1}\mathbf{A}^{*} + \mathbf{D} \rightarrow (\mathbf{A}^{-}\mathbf{D}^{+}) \tag{1}$$

Presumably, there are no solvent molecules situated between the radical ions. In polar solvents such as acetonitrile, the electron is transferred from the donor to acceptor to create a non-lightemitting species, a solvent-separated radical ion pair (SSRIP) with an internuclear separation of the order of 7 Å.¹ The radical ion pairs may decay by a variety of pathways including chemical reaction,⁴ charge recombination⁵⁻⁸ forming ground-state neutral reactants or triplet states of the neutrals, and radical ion pair separation.^{9,10} Each of these decay pathways has been studied

in some detail with most of the emphasis placed upon the free energy dependence of the kinetics of charge recombination.^{5,11}

This paper examines the proposal that in polar solvents, SSRIP are formed upon the quenching of an excited singlet state by an electron-transfer process. Specifically, the quenching of the first excited singlet state of *trans*-stilbene (TS) by fumaronitrile (FN) in acetonitrile is studied; the reaction proceeds by an electron transfer from the first excited singlet state (S_1) of TS to FN forming the radical cation of TS (TS⁺) and the radical anion of FN (FN⁻).¹² The free energy change for this reaction is estimated to be -0.76 eV. The paper begins with a brief discussion of our new picosecond absorption spectrometer where the signal-to-noise ratio has been improved by over an order of magnitude relative to our previous apparatus.¹⁰ Consequently, we have reexamined the dynamics of the CRIP formed by the irradiation of the ground-state charge-transfer complex between TS and FN. These experiments reveal new kinetic behavior for the decay of the CRIP that was not observed in the previous experiments.¹⁰ Finally, the kinetic behavior of the radical ion pair formed by the quenching of S_1 of TS by FN is measured and found to be identical with that of the CRIP suggesting that in the polar solvent acetonitrile a CRIP is formed exclusively contrary to previous proposals.¹

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Experimental Section

Picosecond Absorption Spectrometer. A Continuum (PY61C-10) Nd:YAG laser, 35-ps pulse width operating at 10 Hz, produces first (1064 nm), second (532 nm), third (355 nm), and fourth (266 nm) harmonic light. The 1060-nm light (20 mJ) is focused into a continuum cell to produce the monitoring light (380-850 nm). The transient absorbance, produced by either 355- or 266-nm excitation, is monitored at a single wavelength by passing the probe pulse through a 5-nm-bandpass filter. The excitation energies are 100 μ J focused down to 0.1 cm². The probe pulse may be continuously delayed up to 4 ns with respect to the pump pulse by a stepping-motor delay line (SLO-SYN Translator, Superior Electric Co.). To produce depolarized probe light, the probe pulse is passed through an optical fiber. Delays of up to 250 ns can be achieved by a change in the length of the optical fiber. A beam splitter is used to produce I and I_0 beams. The I probe beam is made collinear with the pump beam and focused into the sample. The I and I_0 beams are detected by a photodiode (EG&G DT100) and the output signals integrated by two boxcar integrators (SRS 250). The integrated signals are sent to a 12-bit analogue to digital converted controlled by an IBM PC-AT. For each position on the delay line, two hundred laser shots are averaged with no excitation passing through the sample and 200 laser shots are averaged with excitation passing through the sample. The computer controls the stepping motor delay line. The absorbance at a given time is calculated by

$$A(t) = \log (I_0/I)_{\text{with excitation}} - \log (I_0/I)_{\text{without excitation}}$$
(2)

All experiments are performed at 22 °C.

Samples. trans-Stilbene (Aldrich) was recrystallized from ethanol. Acetonitrile (Mallinckrodt) was distilled over CaH and stored over 4-Å molecular sieves. Fumaronitrile (Aldrich) was dissolved in dichloromethane, the solution filtered, and the solvent rotary evaporated and then sublimed. The samples were passed through a flowing sample cell by means of a syringe pump.

Data Analysis

The observed transient signal A(t) results from the convolution of the instrument response function I(t) with the transient signal, F(t):¹²

$$A(t) = \int_{-\infty}^{t} I(\tau) F(t-\tau) d\tau \qquad (3)$$

The instrument response function, I(t), results from the convolution of the pump and probe pulse, and is assumed to have the analytical form of a Gaussian:¹²

$$I(t) = (2\pi\sigma)^{-0.5} \exp(-(t-t_0)^2/2\sigma^2)$$
(4)

where σ is the width and t_0 the position of the peak of the Gaussian.

To obtain the parameters t_0 , which is wavelength dependent, and σ , the rise in the singlet state of pyrene is measured.¹³ The value of σ is 19 ps which corresponds to a full width at halfmaximum height for the instrument response function of 45 ps.

Results

To ascertain the nature of the radical ion pair formed by the quenching of S_1 of TS by FN, the kinetics for both the CRIP and the SSRIP must be characterized. In a prior study the kinetics of the CRIP, which decays by separation to the SSRIP and by charge recombination, were examined.¹⁰ However, with the significant improvement in the signal to noise of the picosecond absorption spectrometer, reexamination of the CRIP kinetics reveals dynamics previously not observed.

In acetonitrile, TS and FN form a ground-state charge-transfer complex, with an association constant of 0.13 M^{-1} , producing an new absorption at 355 nm.¹² Irradiation of a solution of 0.025 M TS and 0.125 M FN at 355 nm forms the CRIP directly as revealed by the appearance of the TS⁺ absorbing at 480 nm; spectral shifts in the absorption band of TS⁺ do not occur on the picosecond-nanosecond time scale.¹⁰ The S₁ of TS, λ_{max} 580 nm, is not observed following irradiation of the ground state chargetransfer band.¹⁰ The dynamics of the decay of the CRIP were



Figure 1. Dynamics of the *trans*-stilbene radical cation, monitoring at 480 nm, following the 355-nm irradiation of a solution of 0.125 FN, 0.025 M TS in acetonitrile. Points: experimental data, which are the average of five experiments, 20-ps time increments. Solid curve: calculated kinetics based upon Scheme II and the associated rate constants given in Table I, set 1, and $t_0 = 98$ ps and $\sigma = 19$ ps.



Figure 2. Dynamics of the *trans*-stilbene radical cation, monitoring at 480 nm, following the 355-nm irradiation of a solution of 0.125 FN, 0.025 M TS in acetonitrile. Points: experimental data, which are the average of five experiments, 60-ps time increments. Solid curve: calculated kinetics based upon Scheme II and the associated rate constants given in Table I, set 1, and $t_0 = 98$ ps and $\sigma = 19$ ps.

monitored at 480 nm for 600 ps with 20-ps increments, Figure 1, and for 3 ns with 60-ps increments, Figure 2. The data displayed in Figures 1 and 2 are the average of five separate experiments where in each experiment one point in time is the average of 200 laser shots. The decay kinetics are characterized by an initial rapid decrease in the absorbance during the first 300 ps, followed by a slower decrease in absorbance during the subsequent 3 ns.

There are two processes by which the CRIP may decay. The first process is back electron transfer to re-form the ground-state reactants. The second process is a structural rearrangement of the CRIP to form a new ion pair species, IP, a process which will not effect the magnitude of the absorption at 480 nm assuming that the extinction coefficient of the TS⁺ is independent of the nature of the radical ion pair. In principle there may be a third decay pathway, that of collapse to a biradicaloid species leading to the cycloadduct. However, since TS/FN quantum yield for photocycloaddition is negligibly small, it will be assumed that this latter process does not occur to a measurable extent.¹⁴ Thus Scheme I was initially assumed to describe the decay of the CRIP.

SCHEME I

$$TS/FN \xleftarrow{k_1} CRIP_{480 \text{ nm}} \xrightarrow{k_2} IP_{480 \text{ nm}}$$

It is assumed that the extinction coefficients for the TS⁺ in the



Figure 3. Points: same data as in Figure 2. Solid curve: calculated kinetics based upon Scheme I with $k_1 = 5.3 \times 10^9 \text{ sec}^{-1}$, $k_2 = 1.9 \times 10^9 \text{ sec}^{-1}$, $t_0 = 98 \text{ ps}$, and $\sigma = 19 \text{ ps}$.

SCHEME II

CRIP and IP are the same and the transient signal F(t) is given by¹⁰

$$F(t) = C\{[1 - k_2/(k_1 + k_2)]e^{-(k_1 + k_2)t} + [k_2/(k_1 + k_2)]\}$$
(5)

The resulting time-dependent function F(t) is convoluted with the instrument response function I(t) yielding $A(t)_{calc}$, eq 1. The parameters k_1 and k_2 are then varied to minimize the square of the residuals, $(A(t)_{calc} - A(t)_{exp})^2$.

The best fit of the kinetic model described in Scheme I to the averaged five sets of kinetic data is shown in Figure 3 where $k_1 = 5.3 \times 10^9 \text{ s}^{-1}$ and $k_2 = 1.9 \times 10^9 \text{ s}^{-1}$. The sum of the square of the residuals is 0.001 48 which corresponds to an average standard error for each data point of 0.0054 OD. It is estimated that the average error for each of the experimental data points is 0.000 65 OD. Thus, this simple decay model for the CRIP does not accurately describe the kinetic data. Extension of this two radical ion pair model where IP may return to CRIP, k_3 , or decay by back electron transfer to form ground-state reactants, k_4 , also does not accurately model the experimental data for in this model the sum of the square of the residuals is 0.000 108 leading to an average standard for each data point of 0.001 47 OD, which is greater than twice the signal to noise for a given data point in the five averaged experiments.

The minimum number of distinct species for TS^+ needed to describe the 480 nm decay kinetics is three. Following the suggestions of Winstein¹⁵ and Fuoss,¹⁶ the three radical ion species are distinguished as CRIP, the SSRIP, and free ions, FI. The kinetic model given in Scheme II is employed in the data analysis. Irradiation of the TS/FN charge transfer complex at 355 nm produces the CRIP which decays by two pathways: charge recombination, k_1 , and radical ion pair separation to the SSRIP, k_2 . The SSRIP decays by radical ion pair recombination to form the CRIP, k_3 , or separation to FI, k_4 , and charge recombination to uncomplexed TS and FN, k_5 . In developing kinetic model depicted in Scheme II, it is assumed that the extinction coefficients for the TS⁺ in the three radical ion species are the same and the transient signal, F(t), in eq 3 is given by

$$F(t)_{480 \text{ nm}} = \epsilon_{480} L([\text{CRIP}]_t + [\text{SSRIP}]_t + [\text{FI}]_t)$$
(6)

The concentration of each species is obtained by direct numerical integration of the rate equations using Runge-Kutta integration.¹⁷ The resulting time dependent function F(t) is convoluted with the instrument response function I(t) to generate $A(t)_{calc}$. The calculated $A(t)_{calc}$ is then scaled to the maximum absorbance of the

TABLE I: Rate Coefficients (s⁻¹) for the Decay of *trans*-Stilbene Radical Cation Produced upon 355-nm Irradiation of the *trans*-Stilbene/Fumaronitrile Charge-Transfer Complex Based upon Scheme II

	set 1 $(k_5 = 0.0)$	set 2 $(k_3 = 0.0)$
\boldsymbol{k}_1	$(6.90 \pm 0.32^{a}) \times 10^{9}$	$(6.89 \pm 0.35) \times 10^9$
k_2	$(1.85 \pm 0.09) \times 10^9$	$(2.05 \pm 0.18) \times 10^{9}$
k_3	$(4.25 \pm 0.72) \times 10^8$	0
k₄	$(5.48 \pm 1.40) \times 10^8$	$(5.90 \pm 2.15) \times 10^8$
k_5	0	$(3.47 \pm 1.08) \times 10^{8}$

^aErrors represent 1 standard deviation.

experimental curve, $A(t)_{exp}$, eliminating the parameters ϵ , L, and [CRIP]₀.

During the fitting procedures two limiting sets of rate constants were examined. The first set, set 1, assumes that the rate of charge recombination within the SSRIP, k_5 , is zero. The second set, set 2, assumes that the rate of SSRIP collapse to CRIP, k_3 , is zero. Both sets of conditions give the same quality of fit to the average of the five sets of experimental data; thus it is not possible to uniquely separate k_3 and k_5 . For the average of the five sets of experimental data the sum of the square of the residuals for set 1 is 0.000 023 which corresponds to the average standard error of each point of 0.000 68 OD, shown in Figures 1 and 2. For set 2, the sum of the square of the residuals is 0.000 026 which corresponds to the average standard error of each point 0.00072 OD. To estimate an error associated with the kinetic parameters listed in Table I, each of the five experiments where individually fit to set 1 and set 2 kinetic models.

Although the kinetic model depicted in Scheme II is a rather simplistic characterization, it does accurately describe the kinetic behavior of the three radical ion species within the signal to noise of the experiment. A more realistic model for the kinetic behavior of the various species of radical ions would incorporate a distant dependent rate constant of electron transfer, $k(r)_{et}$, for k_1 and k_5 . Such a model would entail knowledge of the potential of mean force for the distribution of the radical ion species, to account for their relative populations as a function of distance, as well as knowledge of the dependence of the rate constant for electron transfer upon distance and orientation of the reacting radical ions. At present such detailed information is not known for this molecular system.

Having characterized the kinetics for both CRIP and SSRIP, the dynamics of the radical ions produced by the quenching of the first excited singlet state of TS by FN are measured. In the absence of FN, the 266-nm irradiation of TS (0.6 mM) in acetonitrile produces the first excited singlet state (S_1) of TS; the rate constant for its decay, monitored at 570 nm, is (1.92 ± 0.29) $\times 10^{10}$ s⁻¹, Figure 4. In the presence of 0.2 M FN, S₁ is quenched by electron transfer and decays with a rate constant of $(2.63 \pm$ $(0.23) \times 10^{10} \,\mathrm{s}^{-1}$, Figure 4. Furthermore, the maximum absorbance for the S_1 decay curve decreases by a factor of 0.16 upon the addition of 0.2 M FN. This phenomenon has been observed in a prior study and is attributed to static quenching of S_1 by FN.¹² At high concentrations of FN a fraction of TS will have a molecule of FN within the first solvent shell while the remaining TS will be surrounded by solvent molecules. Upon irradiation those TS with FN within the first solvent shell will undergo rapid quenching by electron transfer with a rate of 3×10^{11} s⁻¹ (3.3 ps) generating CRIP.¹⁸ Those S_1 's not quenched by static electron transfer will decay by isomerization along the excited-state surface followed by internal conversion as well as quenching through diffusion limited electron transfer. From the rate of the S_1 decay in the absence $(1.92 \times 10^{10} \text{ s}^{-1})$ and in the presence $(2.63 \times 10^{10} \text{ s}^{-1})$ of FN, the fraction of S_1 quenched by diffusion-limited electron transfer is 0.27. Thus, the fraction of the total radical ions produced by static quenching and dynamic quenching is 0.32 and 0.68, respectively.

The kinetics of the radical ion pairs produced upon 266-nm irradiation of TS (0.6 mM) in the presence of FN (0.2 M) are monitored at 480 nm, Figure 5. Under these conditions, only 3% of TS forms a ground-state charge-transfer complex based



Figure 4. Top curve: dynamics of the S₁ decay, monitoring at 570 nm, following 266-nm excitation of 0.6 mM TS in acetonitrile. Points: experimental data, an average of three experiments. Solid curve: calculated decay with a rate constant of 1.92×10^{10} sec⁻¹. Bottom curve: dynamics of the S₁ decay following 266-nm excitation of 0.6 mM TS and 0.2 M FN in acetonitrile and monitoring at 570 nm. Points: experimental data, an average of three experiments. Solid curve: calculated decay with a rate constant of 2.63×10^{10} s⁻¹.

SCHEME III



upon an association constant of 0.13 M⁻¹.¹² In addition, the extinction coefficient at 266 nm for the charge-transfer complex is significantly less than that of TS; consequently it is assumed that 266-nm irradiation of the charge-transfer complex will not contribute to the formation of radical ion pairs. Scheme III is employed in the analysis of the data displayed in Figure 5. The diffusional quenching S₁ by FN may proceed by one of two pathways: k_6 , formation of CRIP, and k_7 , formation of SSRIP. In the data analysis, it is assumed that sum of the two rates, k_6 and k_7 , is 2.63 \times 10¹⁰ s⁻¹, obtained from the decay of S₁, Figure 4. In addition the rate constants $k_1 - k_5$ are held constant at values given as set 2 in Table I; only k_6 and k_7 are varied. In the fitting procedure, the amplitude of the calculated curve was scaled to the maximum absorbance of the experimental decay curve. The best fit of the model displayed in Scheme III to the experimental data in Figure 5 is for $k_6 = 2.63 \times 10^{10} \, \text{s}^{-1}$ or when the quenching of S₁ produces only CRIP. Thus it is estimated that the diffusional quenching of S₁ by FN leads to greater than 90% CRIP formation.

Discussion

The distinction between an excited-state charge-transfer complex (exciplex or CRIP) and ion pair (SSRIP) as intermediates in excited-state electron-transfer processes evolved from Weller's studies of fluorescence quenching of aromatic hydrocarbons by diethylaniline.¹ Quenching in nonpolar solvents leads to the formation of a new light-emitting species, the exciplex, where it is assumed that the interplanar separation is approximately 3.5 Å which is alternatively described as a CRIP.⁵ In a polar solvent such as acetonitrile, no new emission features are observed upon fluorescence quenching, suggesting that the intermediate formed upon electron transfer has an ion pair structure different from the exciplex. The internuclear separation for the ion pair species in polar solvent is estimated to be of the order of 7 Å. This distance is derived from the molar volume of diffusion, $V_{\rm D}$, obtained from the fluorescence quenching experiments. V_D is a function of the effective encounter distance, γ_a , diffusion coefficients of the donor,



TIME (PS)

1800

2400

3000

Figure 5. Dynamics of the *trans*-stilbene radical cation, monitoring at 480 nm, following the 266-nm excitation of 0.6 mM TS and 0.2 M FN in acetonitrile. Points: experimental data, an average of three experiments. Top solid curve: calculated decay based upon Scheme III with $k_6 = 0.0$ and $k_7 = 2.63 \times 10^{10} \text{ s}^{-1}$ and the rate coefficients listed in Table I, set 1. Lower solid curve: calculated decay based upon Scheme III with $k_6 = 2.63 \times 10^{10} \text{ s}^{-1}$ and the rate coefficients listed in Table I, set 1.

1200

.00

0

600

 $D_{\rm D}$ and the acceptor, $D_{\rm A}$, the lifetime of the excited molecule, τ_0 , and the number of molecules per milliliter, N⁴:

$$V_{\rm D} = 4\pi N'(\gamma_{\rm a})^2 [(D_{\rm D} + D_{\rm A})\tau_0]^{0.5}$$
(7)

For the fluorescence quenching of anthracene by diethylaniline, a process for which $\Delta G = -0.6$ eV, the effective encounter distance is $\gamma_a = 7.5$ Å. Since this is twice the interplanar separation of the exciplex, the ion pair formed in polar solvents appears to have an ion pair structure different from that of the exciplex.

The picture of two ion pair structures as intermediates in fluorescence quenching received further support from Mataga's studies of pyromelletic dianhydride (PMDA) quenching of excited pyrene;⁷ the change in free energy for this reaction is -1.3 eV. In acetonitrile, pyrene-PMDA forms a ground-state chargetransfer complex, which upon 532-nm irradiation produces a CRIP that decays by charge-recombination with a rate of $k_{CR} = 10^{11}$ s⁻¹; ion pair separation is not observed. Irradiating (355 nm) uncomplexed pyrene in the presence of PMDA produces a radical ion pair with substantially different kinetic behavior decaying by charge recombination, $k_{CR} = 2.5 \times 10^9$ s⁻¹ and by radical ion pair separation, $k_d = 2.6 \times 10^9$ s⁻¹. Therefore diffusional quenching by electron transfer produces a radical ion pair different in structure from the radical ion pair formed directly upon irradiation of the ground state charge complex.

The model that has emerged from Weller's and Mataga's studies is that in polar solvents, excited-state quenching by electron transfer leads to the direct formation of SSRIP with an internuclear separation of 7 Å.8,19 However, the generality of these conclusions has recently been questioned by Farid and co-workers.⁵ In their study of charge recombination processes in CRIP and SSRIP, they observe that quenching of the excited singlet state of tetracyanoanthracene (TCA) by m-xylene in acetonitrile leads to the formation of an exciplex (CRIP) as evidenced by weak emission. The efficiency of exciplex formation is dependent upon the driving force for the formation of the radical ion pair. The CRIP formation proceeds with near unit efficiency for TCA/mxylene to near zero efficiency for TCA/durene. The free energy change for these two reactions span a range -0.3 to -0.65 eV in driving force. Thus it appears that the nature of the ion pair formed upon quenching depends not only on the polarity of the solvent but also on the driving force for the reaction.

In a previous study, we examined the effective distance for the electron transfer from S_1 to FN.¹⁸ With utilization of a 1-ps absorption spectrometer, the dynamics of the S_1 decay in the presence of FN were measured. The quenching kinetics do not follow a simple exponential decay; rather the kinetics for S_1 decay

are time dependent. By application of the Collins and Kimball formalism for time-dependent rate constants, 20,21 the intrinsic rate of electron transfer, k_{et} , is separated from the diffusional component, k_d . The values are $k_{et} = 3 \times 10^{11} \text{ s}^{-1}$ and $k_d = 2.2 \times 10^{10}$ M⁻¹ s⁻¹. The diffusion rate is expressed as¹⁹

$$k_{\rm d} = 4\pi R N_{\rm A} (D_{\rm A} + D_{\rm D}) \tag{8}$$

where $D_A + D_D$ is the sum of the diffusion coefficients for the donor and acceptor molecules, N_A is Avogadro's number, and Ris the distance at which the reaction occurs. For $TS(S_1)/FN$ in acetonitrile, R is 8.7 Å, suggesting that quenching of S_1 by FN leads to SSRIP,¹⁸ which is in accord with Weller's observations.¹

In the present study the dynamics of the CRIP formed directly from the 355-nm irradiation of the TS/FN charge-transfer complex are measured. The development of a kinetic model for these processes necessitates the incorporation of at least three kinetically distinct radical ion species. Based on Scheme II with either k_3 = 0 or $k_5 = 0$, depending upon which kinetic model is used to analyze the data in Figures 1 and 2, the lifetime of the CRIP ranges from 105 to 120 ps, which decays by either charge recombination $(k_1 = 6.9 \times 10^9 \text{ s}^{-1})$ or radical ion pair separation $(k_2 = 2.2 \times 10^9 \text{ s}^{-1})$. Similarly, the lifetime of the second radical ion pair species ranges from 1.0 to 1.2 ns, depending upon which kinetic model is employed in the data analysis. Unfortunately, the present data do not allow for the determination of the relative contributions of k_3 and k_5 in the decay of the SSRIP.

At present, only the structure of the CRIP can be surmised. From the presumed structure of the ground-state charge-transfer complex, a sandwich type complex leading to maximum π -orbital overlap between ST and FN, the radical ion pair immediately produced upon irradiation, the CRIP, will have the same π -type complex structure as in the ground-state reactants.²² The second kinetically distinct radical ion pair, the SSRIP, has a structure yet to be defined. One possibility is that the two radical ions maintain a parallel relationship while the interplanar distance increases from 3.5 to 7.0 Å. Another possibility is that the two radical ions maintain contact while one radical ion pivots about the other, producing an end on coplanar species with an extended π -orbital system while maintaining maximum Coulombic interaction. This latter species could be considered another structure for a CRIP. Thus, the second radical ion pair species could have a layer of solvent molecules between the two species or still be in contact with an edge on interaction with no solvent molecules between the two species.

In summary, the present study brings into question the validity of deducing radical ion pair structures from the distance parameter contained within the diffusion rate equation, eq 8, or volumes of diffusions, eq 7. For the present system, the reaction distance for the diffusional quenching of S_1 by FN is 8.6 Å, which is consistent with the formation of a SSRIP. However, from the kinetic properties of the radical ion pair formed by FN diffusional quenching of S_1 , the predominate radical ion pair produced is the CRIP. Clearly great care must be exercised in deducing microscopic properties from theories that treat phenomena in terms of macroscopic parameters such as bulk diffusion coefficients.

The question that has not been resolved in the present study is the relative contributions of k_3 and k_5 , Scheme II, to the decay of the SSRIP. Studies are currently in progress that seek to resolve this issue.

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