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Picosecond Dynamics of Stilbene–Olefin Contact and Solvent-Separated Radical Ion Pairs: Role of Electron Transfer and Radical Ion Pair Diffusion

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Abstract: Picosecond absorption spectroscopy is used to examine electron transfer and radical ion pair diffusional separation for the contact radical ion pair and solvent-separated radical ion pair for *trans*-stilbene/fumaronitrile, *trans*-4-chlorostilbene/fumaronitrile, *trans*-stilbene/dimethyl fumarate, and *trans*-4-chlorostilbene/dimethyl furmarate in acetonitrile. The decay of the solvent-separated radical ion pair proceeds by long-range electron transfer to form ground-state reactants and diffusional separation to form free radical ions. The rate of radical ion pair diffusional separation for the contact radical ion pair is independent of the structure of the diffusing species. However, the rate for ion pair diffusion for the solvent-separated radical ion pair is dependent upon the structure of the diffusing species.

Introduction

Recently we reported a study of the mechanism of the bimolecular quenching of the first excited singlet state of *trans*-stilbene by fumaronitrile in acetonitrile.[1-3] The reaction proceeds by the transfer of an electron from the first excited singlet state of *trans*-stilbene to fumaronitrile to form the radical cation of *trans*-stilbene and the radical anion of fumaronitrile. The intrinsic rate constant of the electron-transfer process was separated from the diffusion rate constant by applying the Collins and Kimball formalism for reactions with time-dependent rate constants.[1] Within this formalism, the rate of electron transfer is $k_{et} = 3.0 \pm 1.0 \times 10^{11}$ M^{-1} s^{-1}, and the distance over which the electron transfer occurs is 10.5 Å, suggesting that the electron is transferred over a distance greater than the contact distance between the reacting species. Thus diffusional quenching would appear to lead to solvent-separated radical ion pairs. However, upon examination of the ensuing radical ion pair dynamics by monitoring the time evolution of the radical cation of *trans*-stilbene, the nature of the ion pair formed upon diffusional quenching appears to be characteristic of the contact radical ion pair. It was thus concluded that the distance parameter contained within the Collins and Kimball formalism for time-dependent rate processes may lead to erroneous conclusions regarding reaction distances.

The kinetic characterization of the contact radical ion pair and the solvent-separated radical ion pair for *trans*-stilbene/fumaronitrile was developed from a study of the radical ion pair dynamics following irradiation of the ground-state charge-transfer complex between *trans*-stilbene and fumaronitrile.[3] Irradiation of the charge-transfer complex at 355 nm directly produces the contact radical ion pair which decays by two processes: back electron transfer forming the ground-state reactants and ion pair separation forming the solvent-separated radical ion pair, resulting in a lifetime for the contact radical ion pair of approximately 110 ps. In turn, the solvent-separated radical ion pair decays on the time scale of 1 ns. However, it was not possible to fully elucidate the reaction pathway for the decay of the solvent-separated radical ion pair.[3] In addition to diffusional separation to free ions, the solvent-separated radical ion pair could, in principle, decay by long-distance back electron transfer and/or collapse to the contact radical ion pair which decays by back electron transfer. From the kinetic modeling of the experimental data it was not possible to discern the relative contribution of these latter two processes to decay of the solvent-separated radical ion pair.

In this paper we extend our initial investigation by examining the dynamics for the *trans*-stilbene/dimethyl fumarate, *trans*-4-chlorostilbene/fumaronitrile, and *trans*-4-chlorostilbene/dimethyl fumarate radical ion pairs with the aim of determining the nature of the solvent-separated radical ion pair decay process as well as to examine the dependence of the diffusional separation of the contact radical ion pair and solvent-separated radical ion pair upon molecular structure. The decay of the solvent-separated radical ion pair appears to proceed by long-range electron transfer. Surprisingly, the diffusional separation of the contact radical ion pair into the solvent-separated radical ion pair is independent of molecular structure for these species, while the separation of the solvent-separated radical ion pair into free radical ions is dependent upon molecular structure.

Experimental Section

Picosecond Absorption Spectrometer. The picosecond absorption spectrometer has been described previously.[3] Briefly, a Continuum (PY61C-10) Nd:YAG laser is used to produce 35-ps light at 10 Hz. The third harmonic, 355 nm, is used for excitation. The 1060-nm light is used to produce continuum light, and a 5-nm band pass filter is used to select the 480-nm monitoring light. The I and I_0 beams are detected by a photodiode (EG&G DT100), measured by two box car integrators (SRS 250) and transferred to an IBM PC-AT. For each measurement at a given time, 50 laser shots are averaged with no excitation and then 50 laser shots are averaged with excitation. One hundred points in time are collected at 40-ps intervals. The absorbance at a given time is determined by

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

Samples. *trans*-Stilbene (Aldrich) was recrystallized from ethanol, and fumaronitrile (Aldrich) and dimethyl fumarate (Aldrich) were sublimed. *trans*-4-Chlorostilbene was prepared by the method outlined in ref 4. Acetonitrile (Mallinckrodt) was distilled over CaH. During the experiments the solutions were passed through a flowing sample cell by means of a syringe pump.

Data Analysis. The observed time-dependent absorbance, $A(t)$, results from the convolution of the instrument response function $I(t)$ with the underlying molecular kinetics, $F(t)$, and is given by[2]

$$A(t) = \int_{-\infty}^{t} I(\tau)F(t-\tau)\,d\tau \qquad (1)$$

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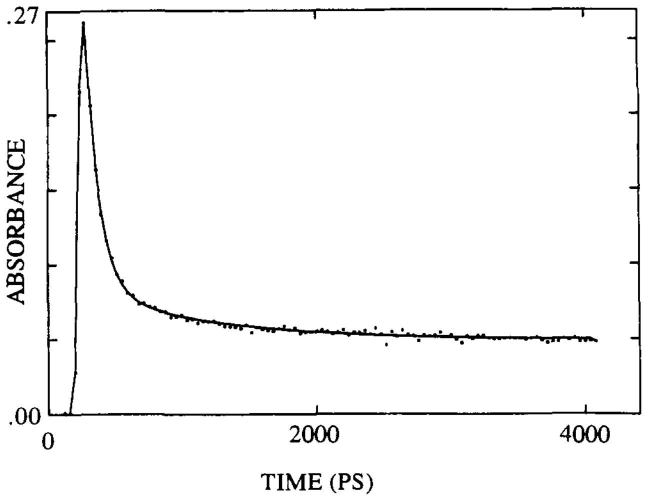


Figure 1. Dynamics of the *trans*-stilbene radical cation, monitoring at 480 nm following the 355-nm irradiation of a solution of 0.125 M FN, 0.025 M TS in acetonitrile. Points: experimental data which are the average of five experiments, 40-ps time increments. Solid curve: calculated kinetics based upon Scheme I and the associated rate constants given in Table I, set 2, and σ = 19 ps and t_0 = 105 ps.

where the instrument response function, $I(t)$, is produced by the convolution of the pump and probe pulse, and is assumed to have the analytical form of a Gaussian,[2]

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

where σ is the width and t_0 the position of the peak of the Gaussian. Monitoring the rise time of the $S_n \leftarrow S_1$ absorption of pyrene at 480 nm following 355-nm excitation, the value of σ is 19 ps which corresponds to a full width at half-maximum height of 45 ps and t_0 is 105 ps.

Results

In acetonitrile, *trans*-stilbene (TS) forms a ground-state charge-transfer complex with the electron-deficient olefins fumaronitrile (FN) and dimethyl fumarate (DF), with an association constant of 0.13 M^{-1} and 1.0 M^{-1}, respectively;[5] this complexation leads to a new absorption at 355 nm. Similarly, *trans*-4-chlorostilbene (TCS) forms a charge-transfer complex absorbing at 355 nm with FN and DF. The association constants for these complexes has not been determined. Irradiation of the ground-state charge-transfer complex at 355 nm will produce directly the contact radical ion pair (CRIP) whose dynamics are monitored through the time evolution of the radical cation absorption.[3] The radical cation of *trans*-stilbene (TS^+) has an absorption maximum at 472 nm, while the radical cation of *trans*-4-chlorostilbene (TCS^+) has an absorption maximum at 490 nm.[6]

The kinetics of the four CRIP (TS^+/FN^-, TS^+/DF^-, TCS^+/FN^-, and TCS^+/DF^-) in acetonitrile are examined. In each experiment the concentration of the stilbene is 0.025 M and the concentration of the electron-deficient olefin is 0.125 M. The dynamics of the radical ion pairs which are monitored at 480 nm following 355-nm excitation are shown in Figures 1–4. Each decay is monitored for 4 ns with 40-ps increments. The data displayed in each of the Figures 1–4 are the average of five separate experiments. Each decay is characterized by a fast decrease in absorbance at 480 nm during the first 400 ps, followed by a slower decrease in absorbance during the next 4 ns. The fraction of residual absorbance at 4 ns differs for each species.

In order to determine whether the observed kinetics in Figures 1–4 are dependent upon the concentration of the electron acceptors, the experiments were repeated where the concentration of the electron-deficient olefin was 0.25 M and the concentration of the stilbene was 0.025 M. Increasing the concentration of the electron-deficient olefin by a factor of 2 had no measurable effect upon the observed kinetics, suggesting that termolecular interactions do not contribute to the dynamics monitored at 480 nm.

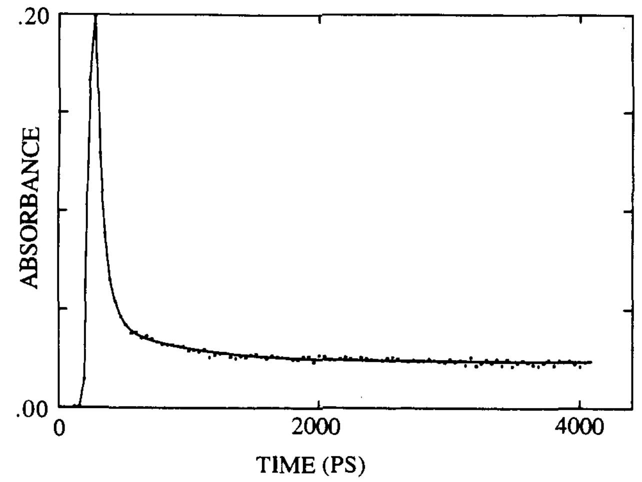


Figure 2. Dynamics of the *trans*-stilbene radical cation, monitoring at 480 nm following the 355-nm irradiation of a solution of 0.125 M DF, 0.025 M TS in acetonitrile. Points: experimental data which are the average of five experiments, 40-ps time increments. Solid curve: calculated kinetics based upon Scheme I and the associated rate constants given in Table I, set 2, and σ = 19 ps and t_0 = 105 ps.

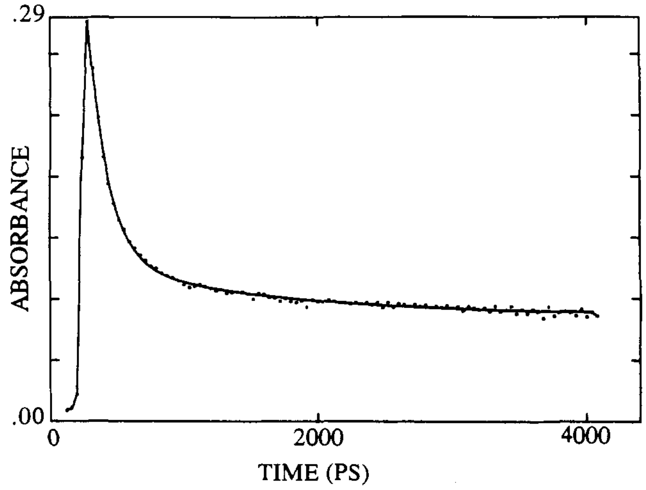
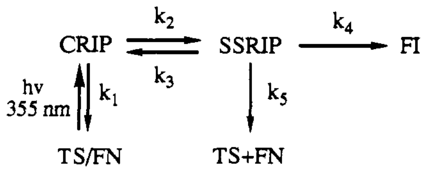


Figure 3. Dynamics of the *trans*-4-chlorostilbene radical cation, monitoring at 480 nm following the 355-nm irradiation of a solution of 0.125 M FN, 0.025 M TCS in acetonitrile. Points: experimental data which are the average of five experiments, 40-ps time increments. Solid curve: calculated kinetics based upon Scheme I and the associated rate constants given in Table I, set 2, and σ = 19 ps and t_0 = 105 ps.

Scheme I



To account for dynamic behavior monitored at 480 nm, we previously postulated[3] that at least three distinct radical ion species intervene: the CRIP, the solvent-separated radical ion pair (SSRIP), and free radical ions (FI). The following kinetic model, developed for TS/FN, is used in the analysis of the decay kinetics for each of the four experiments (Scheme I). Following the direct formation of the CRIP upon irradiation of the ground-state charge-transfer complex at 355 nm, the CRIP either undergoes back electron transfer to form the ground-state charge-transfer

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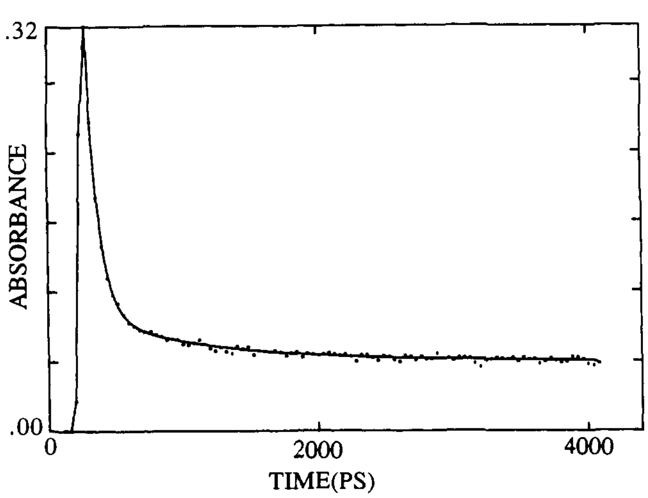

Figure 4. Dynamics of the *trans*-4-chlorostilbene radical cation, monitoring at 480 nm following the 355-nm irradiation of a solution of 0.125 M DF, 0.025 M TCS in acetonitrile. Points: experimental data which are the average of five experiments, 40-ps time increments. Solid curve: calculated kinetics based upon Scheme I and the associated rate constants given in Table I, set 2, and σ = 19 ps and t_0 = 105 ps.

Table I. Parameters for the Best fit of the Kinetic Model Depicted in Scheme I Holding $k_5 = 0$ and $k_3 = 0$

	$k_1 \times 10^9$, s^{-1}	$k_2 \times 10^9$, s^{-1}	$k_3 \times 10^9$, s^{-1}	$k_4 \times 10^9$, s^{-1}
	Set 1: $k_5 = 0$			
ST/DF	13.5 ± 1.43	1.84 ± 0.28	0.843 ± 0.242	0.905 ± 0.095
TCS/DF	9.14 ± 0.33	2.00 ± 0.18	0.521 ± 0.070	0.753 ± 0.122
ST/FN	6.90 ± 0.30	1.98 ± 0.18	0.508 ± 0.069	0.686 ± 0.115
TCS/FN	4.52 ± 0.24	1.85 ± 0.17	0.361 ± 0.084	0.541 ± 0.116

	$k_1 \times 10^9$, s^{-1}	$k_2 \times 10^9$, s^{-1}	$k_5 \times 10^9$, s^{-1}	$k_4 \times 10^9$, s^{-1}
	Set 2: $k_3 = 0$			
ST/DF	13.8 ± 1.42	2.01 ± 0.26	0.829 ± 0.222	0.859 ± 0.097
TCS/DF	9.29 ± 0.31	2.12 ± 0.16	0.469 ± 0.075	0.736 ± 0.127
ST/FN	6.89 ± 0.33	2.11 ± 0.15	0.439 ± 0.077	0.659 ± 0.110
TCS/FN	4.57 ± 0.24	2.00 ± 0.19	0.291 ± 0.087	0.516 ± 0.120

complex, k_1, or undergoes a diffusional separation to form SSRIP, k_2. The SSRIP may decay by three pathways: collapse to the CRIP, k_3; long-range back electron transfer, k_5; and further diffusional separation to form FI, k_4. In the analysis of the transient absorbance it is assumed that the extinction coefficient for the stilbene radical cation is independent of the radical ion pair structure. Thus the absorbance, at a given time, is given by the concentrations of each of the three radical ion species:

$$F(t)_{480\ \text{nm}} = \epsilon_{480}L([\text{CRIP}]_t + [\text{SSRIP}]_t + [\text{FI}]_t) \qquad (3)$$

The concentration of each molecular species is determined by direct numerical integration of the rate equations for Scheme I using fourth-order Runge–Kutta integration[7] to generate $F(t)$. The function $F(t)$ is convoluted with the instrument response function $I(t)$, previously determined from the analysis of the pyrene, to produce the calculated time-dependent absorbance, $A(t)_{\text{calc}}$. In order to eliminate the parameters ϵ_{480}, L, and $[\text{CRIP}]_0$, the function of $A(t)_{\text{calc}}$ is scaled to the experimental function $A(t)$. The fitting parameters, $k_1 - k_5$, are then optimized using an interative nonlinear least-squares technique.

In our previous investigation of the TS/FN radical ion pair dynamics, it was discovered that k_3 and k_5 could not be separated uniquely.[3] Therefore, two limiting cases are examined in fitting the kinetic model outline in Scheme I to the experimental data: set 1 with $k_5 = 0$ and set 2 with $k_3 = 0$. The results of the fitting procedure for the four experiments are given in Table I. It is observed for each experiment that the sum of the squares of the residuals are comparable and are within the error of the experiment; thus from the kinetic modelling alone it is not possible to delineate the relative contributions of k_3 and k_5.

Discussion

The aim of the present investigation is to determine the pathway by which the SSRIP decays. If collapse of the SSRIP to the CRIP, k_3, is significantly greater than the rate of long-range back electron transfer, k_5, then the appropriate set of rate constants for the model depicted in Scheme I is given by set 1 in Table I. Within this scheme, the ratio of the rate constants, k_2/k_3, represents the equilibrium constant for the conversion of the CRIP into the SSRIP. The free-energy change associated with this process would then be −0.46 kcal/mol for ST/DF, −0.79 kcal/mol for TCS/DF, −0.79 kcal/mol for ST/FN, and −0.95 kcal/mol for TCS/FN.

From the vantage of experiment, very little is known about the free-energy changes associated with the conversion of a CRIP into a SSRIP in polar solvents. However, Weller has developed a method for estimating the free-energy change for radical ion pair interconversion.[8] The formalism is based upon Kirkwood–Onsager model for the solvation of a dipole and the Born equation for the solvation of a ion. The free-energy change (in eV) as a function of the dielectric constant for the medium in the conversion of a contact radical ion pair to a solvent-separated radical ion pair is

$$\Delta G = (\mu^2/\rho^3)((\epsilon - 1/2\epsilon + 1) - 0.19) + 2.6\ \text{eV}/\epsilon - 0.51\ \text{eV} \qquad (4)$$

where μ is the dipole moment of the CRIP, ρ the radius of the solvation cavity of the CRIP, and ϵ the static dielectric constant of the solvent. This result assumes[8] that the mixing of the radical ion pair states with the ground-state reactants and the excited singlet state of stilbene is negligible; these conditions are fulfilled for these systems as the radical ion pair states are approximately 20 kcal/mol below the excited state of stilbene and 65 kcal/mol above the ground-state reactants.

For a typical charge-transfer complex between an aromatic compound and an olefin with a dipole moment of 15 D and a cavity radius of 6.5 Å in acetonitrile (ϵ = 35), the free-energy change associated with the conversion of a CRIP into a SSRIP is estimated[8] at −5 kcal/mol which is significantly greater than the values determined from corresponding rate constants in set 1. Furthermore, eq 4 contains the prediction that, as the dipole moment of the CRIP increases, assuming the radius of the cavity remains constant, the driving force associated with the conversion of the CRIP into the SSRIP will decrease. Thus, a free-energy change of −0.46 kcal/mol for ST/DF to −0.79 kcal/mol for ST/FN would be consistent with the ST/DF CRIP having a larger dipole moment that the ST/FN CRIP. However, experimentally Lewis has measured[9] the dipole moment of these complexes and found that TS/FN dipole (6.3 D) is larger than the TS/DF dipole (6.1 D). Therefore, based upon the expected magnitude of the free-energy change for the conversion of a CRIP into a SSRIP and the prediction of a decrease in driving force with an increase in the dipole moment of the CRIP, it would appear that k_3 is not the dominate pathway for loss of the stilbene radical cation in the SSRIP but rather long-range electron transfer, k_5, dominates.

Before discussing whether the observed changes in k_5 with changes in molecular structure are consistent with predictions of electron-transfer rate theory, the rate of back electron transfer, k_1, within the CRIP will be examined. To estimate the free-energy regime associated with the electron transfer within the radical ion pairs, the Weller equation[10] is employed utilizing the values for the oxidation of TS (1.48 eV)[4] and TCS (1.52 eV)[4] as well as the reduction potential of FN (−1.36 eV)[9] and DF (−1.54 eV).[9] The order of the radical ion pair energies relative to ground-state reactants is TCS$^+$/DF$^-$ (−2.96 eV), TS$^+$/DF$^-$

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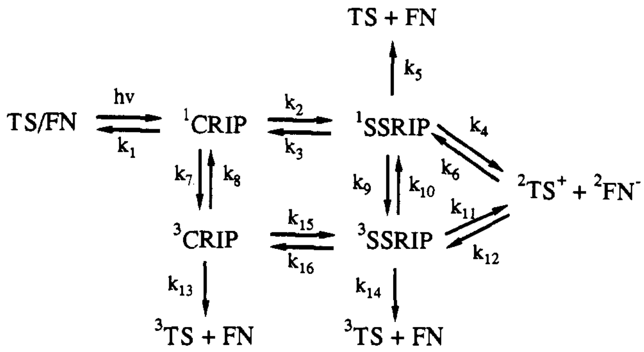
(−2.92 eV), TCS^+/FN^- (−2.78 eV), and TS^+/FN^- (−2.74 eV). These reaction free energies are sufficiently large that, whether one employs nonadiabatic electron-transfer theory[11] or adiabatic electron-transfer theory,[12] these reaction processes occur in the inverted energy regime so that the expectation is that, with an increase in free-energy change for the electron transfer, the rate of electron transfer should decrease. Indeed, increasing the free-energy change by the substitution of a chlorine onto stilbene, the rate of electron transfer decreases from 13.8×10^9 s^{-1} for ST/DF to 9.29×10^9 s^{-1} for TCS/DF, while the rate of electron transfer decreases from 7.67×10^9 s^{-1} for ST/FN to 4.57×10^9 s^{-1} for TCS/FN. Surprisingly, when comparing the rate of electron transfer with a change in the electron acceptor to increase the change in free energy associated with electron transfer, the rate actually increases, contrary to expectation, from 7.67×10^9 s^{-1} for ST/FN to 13.8×10^9 s^{-1} for ST/DF, and the rate also increases from 4.57×10^9 s^{-1} for TCS/FN to 9.29×10^9 s^{-1} for TCS/DF. The rationale for this latter observation is not that adiabatic or nonadiabatic electron transfer theories are invalid but rather that the magnitude of the electronic matrix element, V, between the CRIP state and the ground state is not constant for this series of compounds but rather depends upon nature of the molecular species involved in the electron-transfer process.

In view of the k_1 free-energy dependence, it is not possible to directly predict the dependence of k_5 upon the nature of the SSRIP as both the electronic coupling matrix element as well as the Franck–Condon factors will be different from those of the CRIP.[11,12] However, for electron-transfer processes occurring deep in the inverted regime, if each of the electronic coupling matrix elements decays with the same distance dependence, then the relative order of rates of electron transfer within the CRIP should be the same as in the SSRIP. Indeed, the relative ordering of k_1 and k_5 are the same (Table I) suggesting the decay process k_5 be ascribed to long-distance electron transfer.

Throughout the foregoing discussion, the role of the triplet CRIP and the triplet SSRIP has yet to be delineated. There have been several studies revealing that triplet radical ion pairs participate in the ensuing chemistry subsequent to irradiation of the charge-transfer complex of TS/FN. Arnold and Wong[13] found upon irradiation of TS/FN in benzene, that TS isomerizes to *cis*-stilbene (CS) and FN isomerizes to maleonitrile where the trans to cis isomerization of stilbene is the more efficient reaction. These authors postulate that isomerization of both TS and FN occur through their respective triplet states, which are formed from the triplet radical ion pair produced upon intersystem crossing of the singlet radical ion pair. This proposal received further support from the chemically induced nuclear spin polarization studies on TS/FN by Roth and Schilling on this system.[14] Lewis and Simpson[9] undertook an extensive study of the effect of solvent and O_2 upon the quantum yield for the isomerization of TS and FN and found that the predominate reaction is the isomerization of TS as the product ratio of CS/maleonitrile is 15/1. In benzene the quantum yield for TS isomerization is approximately 0.10 which greatly diminished to 0.001 in acetonitrile. No bimolecular reaction products are observed in these studies.

In view of the aforementioned studies of Lewis,[9] Scheme I is modified to account for role of the triplet radical ion pair (Scheme II). Within this scheme, the question arises as to what is the predominate pathway for the production of CS, formed with a quantum efficiency of 0.001. It is estimated that the energy of the ^{3}SSRIP is 2.74 eV and the ^{3}CRIP is 0.1 to 0.2 eV higher. The energy of the triplet state of TS, ^{3}TS, is 2.1 eV.[14] Thus the corresponding free-energy changes associated with back electron transfer to form ^{3}TS from ^{3}SSRIP and from ^{3}CRIP are −0.64 eV and −0.74 eV, respectively. For long-range electron transfer within the ^{3}SSRIP with a free-energy change of −0.64 eV, the rate of electron transfer, k_{14}, would be expected[15] to be of the order of 10^7 s^{-1}. However, for back electron transfer within the ^{3}CRIP with a free-energy change of −0.74 eV, the rate of electron transfer, k_{13}, may approach 10^{12} s^{-1}. Also, the rate of radical ion pair diffusion should be independent of the spin state so that $k_{15} = k_2 = 2 \times 10^9$ s^{-1} and $k_{11} = k_4 = 0.6 \times 10^9$ s^{-1}. Thus, if the ^{3}CRIP is formed through k_7, then the predominate reaction will be the formation of ^{3}TS as $k_{13} > k_{15}$. However, if the ^{3}SSRIP is formed through k_9, the predominate reaction will be radical ion pair separation as $k_{11} > k_{14}$. Assuming that all of CS is formed through the ^{3}CRIP, with a quantum yield of 0.001, and the quantum yield for the decay of ^{3}TS to CS is 0.55,[16] then the rate of intersystem crossing, k_7, is estimated to be 1.7×10^7 s^{-1} based on a lifetime of the ^{1}CRIP of 100 ps. This rate of intersystem crossing is very similar to the value of 1.4×10^7 s^{-1} determined by Lewis for TS/FN radical ion pair in benzene.[9]

Scheme II



The quantum yield studies of Lewis also support the previous conclusion that the rate of collapse of ^{1}SSRIP to ^{1}CRIP, k_3, is sufficiently smaller than k_5. Based upon the present picosecond kinetic studies, the fraction of ^{1}CRIP that escapes to FI is 0.19, Figure 1. Recalling that there are no bimolecular products formed from the FI, diffusional recombination of the FI, k_6 and k_{12}, will be distribution between 0.75 ^{3}SSRIP and 0.25 ^{1}SSRIP so that the overall yield of ^{3}SSRIP is 0.14. Since the rates k_3 and k_{16} are the same, if k_3 had a value of 0.5×10^9 s^{-1} (Table I, set 1), then approximately 43% of the ^{3}SSRIP would collapse to the ^{3}CRIP, as k_{16} would be larger than k_{10} and k_{14}. The ^{3}CRIP would then rapidly form ^{3}TS followed by isomerization to CS with a overall quantum yield of 0.033, contrary to experimental quantum yield determinations.

One of the more interesting observations of the present kinetic study is the structural dependence of the rate of diffusional separation for the CRIP, k_2, and the SSRIP, k_4 (Table I, set 2). The rate of diffusional separation for the CRIP, $k_2 = 2 \times 10^9$ s^{-1}, is independent of structure of the electorn donor–acceptor. In contrast, there is a rather strong dependence for the kinetics of diffusional separation of the SSRIP, varying from 0.51×10^9 s^{-1} to 0.85×10^9 s^{-1}. A similar observation was made by Mataga and co-workers[17] in their investigation of the dynamics of radical ion pair separation in tetracyanobenzene/alkylbenzene radical ion pairs in acetonitrile. Whether the radical anion is that of benzene, *m*-xylene, or *p*-xylene, the rate of diffusional separation for each CRIP is same, 4.6×10^9 s^{-1}, while the rate of diffusional separation for the SSRIP varies from 1.5×10^9 s^{-1} to 2.6×10^9 s^{-1}. At present, there are no theoretical formulations for radical ion pair diffusion which will guide our understanding of the molecular structural dependence of these processes.

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