Electrolyte Effects on the Energetics and Dynamics of Intermolecular Electron Transfer Reactions

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Abstract: Picosecond absorption spectroscopy is used to examine the effects of added electrolytes on the electron transfer reaction between the *trans*-stilbene radical cation and the radical anion of fumaronitrile in acetonitrile and ethyl acetate solutions formed by photoexcitation of the corresponding ground state complex. The salts studied are $LiClO_4$, $NaClO_4$, and Bu_4NClO_4. Contrary to previous reports, the yield of ion-pair separation following photolysis of the ground state complex is small. Greater than 90% of the photogenerated ion-pairs undergo back electron transfer. The electron transfer rates are dependent on the particular electrolyte present in solution. Thus, the driving force of the reaction cannot be quantified by any general models which solely consider the concentration of dissolved salt. A model is proposed which parametrizes the energetics of the electron transfer reaction in terms of the photophysical behavior of 3-aminofluoren-9-one in the salt solutions studied. Using this approach, the dependence of the reaction rate on exothermicity is quantitatively determined. For the salt solutions studied, the driving force changes by ~15 kcal/mol. Excellent agreement between the experimental data and the predictions of the Marcus inverted region are observed. The influence that added salts have on the outer-sphere reorganization energy and solvent dynamic contributions to the electron transfer rate are also discussed.

Introduction

Electron transfer (ET) reactions occupy a central role in chemistry. The mechanisms of many organic reactions, e.g., Grignard reactions,[1] Wittig reactions,[2] hydride transfers,[3] and condensation reactions,[4] involve electron transfer reactions. As a result, there has been and continues to be a considerable theoretical and experimental effort aimed at understanding the role solvents play in determining reaction rates and efficiencies. Medium effects on ET reactions are usually classified as static or dynamic. Static interactions between the solvent and reacting solutes affect the free energetics, thereby exerting influence by changing the activation energy and exothermicity with changing dielectric properties of the fluid. Solvent dynamics affect motion along the reaction coordinate and can result in many interesting kinetic effects, e.g. polarization caging in which the solvent polarization traps the reacting system at the transition state resulting in multiple barrier crossings.[5] Many excellent reviews and monographs on electron transfer in homogeneous solutions have appeared.[6]

Less understood, but of equal importance, are the factors which control electron transfer processes in electrolyte solutions. The reaction dynamics can still be thought of as being effected by static and dynamic influences of the solvating medium of the reacting molecules. While these effects can, in principle, be measured, a molecular description of how salts influence liquid properties is not well understood. Salt solutions differ in several important ways from homogeneous liquids, all of which could contribute to the medium's effect on the reaction coordinate of the solute molecule.

In this paper salt effects on the intermolecular charge transfer reaction of the photogenerated *trans*-stilbene (TS) radical cation and fumaronitrile (FN) radical anion ion-pair are examined. This molecular system was chosen for two major reasons. First, excitation of the ground state charge-transfer complex (CTC) between TS and FN selectively forms a contact ion-pair (CIP) between $TS^{\bullet+}$ and $FN^{\bullet-}$.[7] Back electron transfer only occurs from the CIP intermediate; therefore, the reaction dynamics are free of diffusional components. Second, the reaction dynamics in neat liquids are well characterized. The energetics and reorganization energies associated with this ET reaction are known for several solvents.[8] This enables quantitative comparison of the reaction rates in electrolyte solutions to theoretical models.

Previous picosecond studies of this reaction in polar aprotic solvents support the reaction model shown in Scheme I.[8]

Scheme I

$$\mathrm{CTC} \underset{k_{et}}{\overset{h\nu}{\rightleftharpoons}} \mathrm{CIP} \xrightarrow{k_{ips}} \mathrm{FI}$$

Photoexcitation of the ground state charge-transfer complex (CTC) results in the formation of the $TS^{\bullet+}/FN^{\bullet-}$ contact ion-pair (CIP). Ion-pair separation to form free ions (FI) competes with the back electron transfer process. In acetonitrile solution, Peters and co-workers[8] have reported that nearly half of the initially formed ions dissociate, with a rate constant of 2.9×10^9 s^{-1}. This result is somewhat surprising. For molecules of this size, ion-pair separation should occur with a rate constant on the order of 1×10^8 s^{-1},[9] over an order of magnitude slower than what has been observed. In this paper, we show that the yield of free ions in dry acetonitrile is dependent on the intensity of the excitation laser pulse. At excitation pulse energies which are

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$\sim 10^4$ less intense than those used in previous picosecond studies,[8] almost no ion-pair separation is observed. This result is consistent with the relative rates of back electron transfer in the CIP and diffusion constants of similar sized molecular ions.[10] In the absence of ion-pair separation, no approximations of the kinetics are needed to determine the rate constant of electron transfer between $TS^{\bullet+}$ and $FN^{\bullet-}$.

The back electron transfer dynamics from the photogenerated $TS^{\bullet+}/FN^{\bullet-}$ CIP are examined in acetonitrile and ethyl acetate salt solutions. These two solvents were chosen as they represent prototypical high ($\epsilon \sim 37$) and low ($\epsilon \sim 6$) dielectric polar aprotic solvents. The salts studied are the perchlorates of Li^+, Na^+, and Bu_4N^+. These salts were chosen as the ion-pair equilibria in both acetonitrile and ethyl acetate solutions and have been studied over a large concentration range using a variety of experimental techniques.[11] Comparison of the reaction dynamics in these two solvent systems allows several important questions to be addressed.

First, previous work[8] has established that this particular ET reaction lies in the Marcus inverted region,[12] $-\Delta G° > \lambda$. In this limit, increased exothermicity should lead to a decreased rate constant. Addition of salts provides a means by which the driving force of the reaction can be altered without changing the liquid. Thus, this approach provides a means of testing the Marcus expression for reactions in the inverted region over a reasonably large range of reaction exothermicity. For the salts/solvents studied in this paper, the driving force ranges from 2.69 to 2.95 eV, mapping out a significant range of exothermicities in the inverted region.

Second, the contribution of the ionic atmosphere to the outer-sphere reorganization energy of the reaction is quantified. In the solutions studied, the ionic atmosphere can, in principle, play an important role. This can be seen by considering the distance over which the ion exerts an electrostatic potential. The distance that corresponds to a reduction in the charge density of a solvated ion to $1/e$ of its original value is referred to as the Debye length.[13] As this length is based on a continuum model, it is independent of the atomic or molecular nature of the ion. For example, a 0.2 M solution of a one-to-one electrolyte has a Debye length of 4.7 Å. Thus, the electric field of the ion strongly polarizes more than one solvent shell. This can result in significant restructuring of the liquid as well as substantial changes in the time scales of the molecular dynamics of the liquid molecules. Either effect can influence ET reaction rates. Thus, in addition to influencing the reorganization energy, it is important to consider the potential importance of the ion-atmosphere dynamics on the reaction rate.

Experimental Section

Materials. *trans*-Stilbene, fumaronitrile, and 3-aminofluoren-9-one (3-AF) were purchased from Aldrich. *trans*-Stilbene was purified by recrystallization from ethanol; fumaronitrile and 3-AF were purified by sublimation. Solvents of spectrograde quality were purchased from Fisher Scientific. Acetonitrile was refluxed several hours with CaH to remove trace amounts of water. Ethyl acetate was used as received. All salts were purchased from Aldrich and dried in a vacuum oven at 110 °C for at least 12 h. Samples were prepared in a drybox under an inert nitrogen atmosphere. The concentrations of *trans*-stilbene and fumaronitrile were 0.025 and 0.125 M, respectively. All experiments were performed at room temperature.

Solvent Polarity. The solvent polarity was determined by measuring the absorption maximum of Reichardt's dye in the solvents of interest. From these measurements, the $E_T(30)$ polarity parameter can be calculated using eq 1.[14] It was not possible to measure $E_T(30)$ values for many of the salt solutions studied. To determine the polarity in electrolyte solutions, the energy gap of the $S_1 \leftarrow S_0$ intramolecular charge transfer band of 3-aminofluoren-9-one was used. As described in detail below, this molecule provides a polarity scale for electrolyte solutions which can be linearly related to the more common $E_T(30)$ scale.

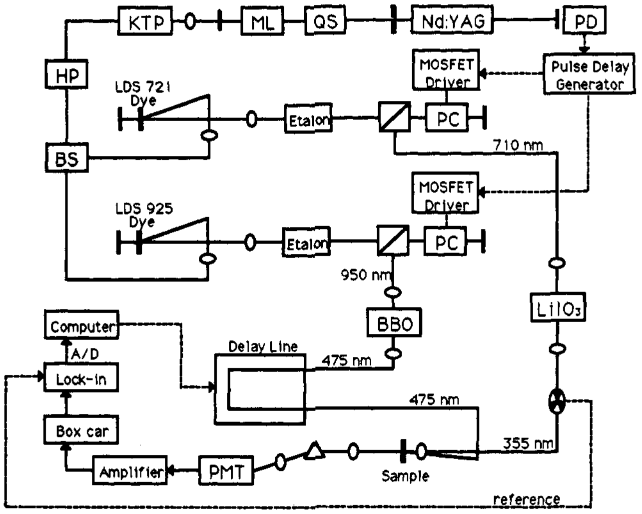

Figure 1. Schematic of the picosecond absorption spectrometer. Abbreviations: PD, FND-100 (EGG) photodiode; ML, acousto-optic mode-locker; QS, acousto-optic Q-switch; PH, pinhole; KTP, potassium titanium phosphate, second harmonic generator; HP, half-wave plate; BS, 80:20 beamsplitter; PC, pockels cell; $LiIO_3$, lithium iodate, second harmonic generator; β-BBO, β-barium borate, second harmonic generator; PMT, photomultiplier tube.

$$E_T(30)(\text{kcal/mol}) = 2.86 \times 10^4/\lambda_{\max}\ (\text{nm}) \qquad (1)$$

Time-Resolved Spectroscopy. Transient absorption experiments of the *trans*-stilbene and fumaronitrile complex in electrolyte solutions were carried out using a high repetition rate picosecond laser system. A schematic of this laser system is shown in Figure 1. The CW Nd:YAG laser oscillator (Quantronix) was mode-locked at 38 MHz (Quantronix) and Q-switched at a repetition rate of 1 kHz (IntraAction Corp.). The 1064-nm output was frequency doubled in a 2 × 2 × 9 mm³ KTP crystal (CSK), generating 0.7 W of 532-nm light. The green light was used to synchronously pump two cavity dumped infrared dye lasers: 80% pumped at LDS 721 dye laser and the remaining 20% pumped a LDS 925 dye laser. The output pulses of the LDS-721 (30 ps fwhm at 710 nm) dye laser were frequency doubled in a 10 × 10 × 5 mm³ $LiIO_3$ crystal (Quantum Technology, Inc.) to generate <2-μJ pulses at 355 nm. These ultraviolet pulses were optically chopped at 250 Hz and were used to pump the sample. The output pulses of the LDS 925 (30 ps fwhm at 950 nm) were frequency doubled in a 2 × 2 × 3 mm³ β-BBO crystal (Quantum Technology, Inc.), generating submicrojoule pulses at 475 nm. These light pulses, tuned to the absorption maximum of the *trans*-stilbene radical cation, were used to probe the reaction dynamics. The 475 nm probe pulses travelled a computer controlled optical delay line and were combined with the 355-nm pump pulses and focussed collinearly with the excitation pulses into a 2 mm sample cell. The 475 nm probe pulses were separated from residual pump light after the sample using a prism. The intensity of the probe beam was detected by a water-cooled photomultiplier tube (PMT). The PMT output was amplified and processed using a boxcar and lock-in amplifier. This combination greatly enhances the sensitivity allowing very small absorption signals to be detected.[15]

The lock-in amplifier output, S_{LIA}, is a root mean square of the voltage difference of the PMT output at the chopping frequency given by

$$S_{LIA} = \sqrt{2}(\Delta V)/\pi \qquad (2)$$

where ΔV is the transient absorption induced voltage difference. The change in absorption signal for the sample is

$$\Delta A = (\Delta\epsilon)cl = \Delta\ln(I)/2.303 \qquad (3)$$

In the limit of a small absorption change, eq 2 can be rewritten as

$$\Delta A = \Delta\ln(I)/2.303 \approx \Delta I/(2.303I) = \Delta V/(2.303V) = 0.964S_{LIA}/V \qquad (4)$$

where V is the voltage of the boxcar output. In our experiment, $\Delta A \leq 10^{-3}$. Therefore, the output of the lock-in is a measure of the absorption signal.

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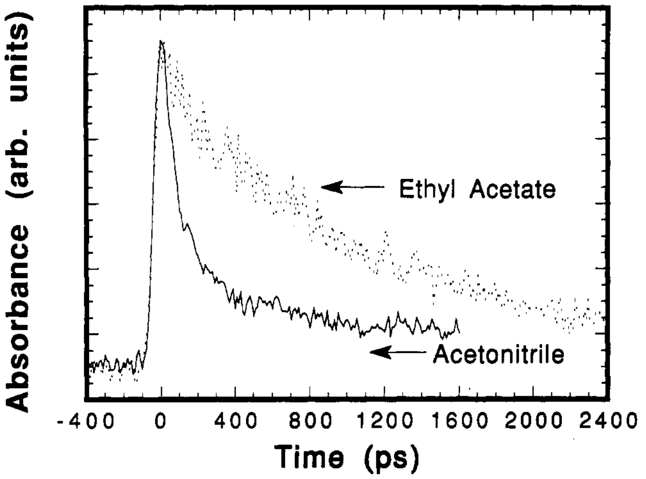

Figure 2. Transient absorption dynamics probed at 475 nm (monitoring the *trans*-stilbene radical cation) following excitation of the TS/FN ground state complex at 355 nm. The decay times are 1180 and 40 ps for neat ethyl acetate and acetonitrile, respectively. A nearly complete decay in the absorption signal on the nanosecond time scale is seen for both solvents.

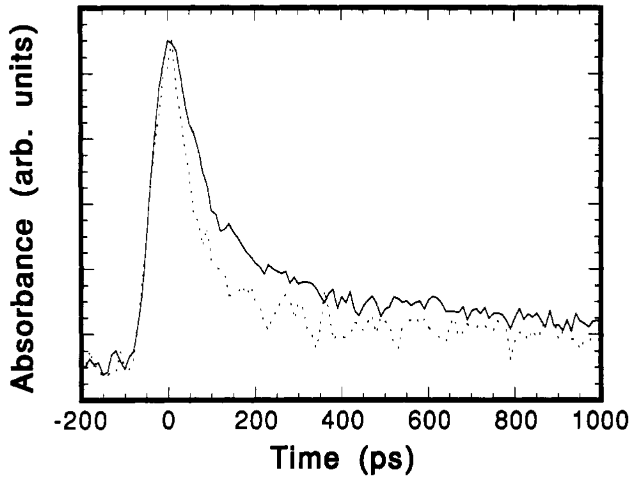

Figure 3. The transient absorption dynamics at 475 nm following excitation of the TS/FN ground state complex at 355 nm are compared for neat acetonitrile (solid line) and acetonitrile with 1.0 M $LiClO_4$ added (dashed line). 1.0 M $LiClO_4$ decreases the lifetime of the *trans*-stilbene radical cation to 10 ps, compared to 40 ps for the neat solvent.

Results

Transient Absorption Studies in Neat Liquids. The time dependent absorption of the *trans*-stilbene radical cation (probed at $\lambda_{max} = 475$ nm)[7a,b,8a] following excitation of the TS/FN ground state complex at 355 nm in neat acetonitrile and ethyl acetate is shown in Figure 2. The transient signal in both solvents is well-described by a single exponential function. In previous reports, the signal levels out at $\sim$40% of its original value.[8] The data shown in Figure 2 indicate nearly complete decay of the absorption signal.

Transient Absorption Studies in Salt Solutions. The transient absorption dynamics observed at 475 nm following excitation of the TS/FN complex in acetonitrile solutions containing 1.0 M $LiClO_4$ and 1.0 M Bu_4NClO_4 are shown in Figures 3 and 4, respectively. Addition of $LiClO_4$ results in an increase in the rate of decay of the absorption signal. In contrast, added Bu_4NClO_4 has no effect. The transient absorption dynamics observed at 475 nm following excitation of the TS/FN complex in ethyl acetate solutions containing 1.0 M $LiClO_4$ and 0.5 M Bu_4NClO_4 are shown in Figures 5 and 6, respectively. In ethyl acetate, unlike acetonitrile, both electrolytes increase the rate of decay of the transient absorption signal.

Power Dependency Studies. In Figure 7, the absorption kinetics of the 475-nm transient signal following excitation of the TS/FN complex in neat acetonitrile solutions are examined as a function of photolysis energy. At low excitation energies, the signal essentially decays to zero on the time scale of the delay shown. Increasing the photolysis pulse energy results in the observation of a long time constant signal, which persists for at least 5 ns, the longest delay time possible. With increasing photolysis power, the relative intensity of the long time component to the intensity observed immediately following photoexcitation increases. This observation is important in light of the fact that previous picosecond studies[8] used several hundred microjoules of excitation energy. In those studies, the data reflect a significant contribution of this long time constant signal. The current results clearly show that this absorption feature is produced by a nonlinear process. For an $\sim$100-μm spot size, it is necessary to use photolysis energies of $\sim$2 μJ or less to remove these unwanted nonlinear optical processes.

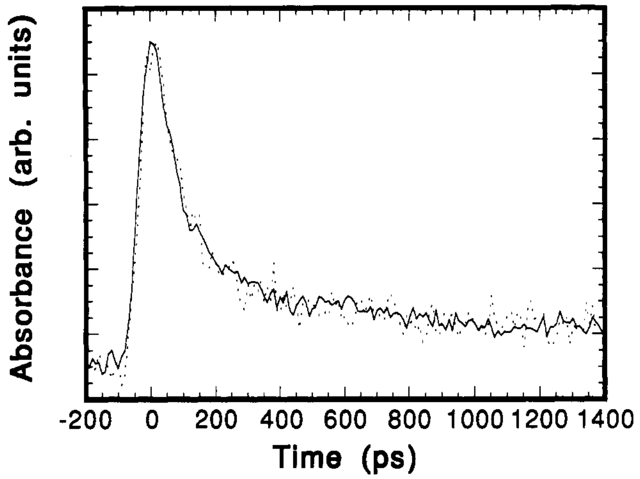

Figure 4. The transient absorption dynamics at 475 nm following excitation of the TS/FN ground state complex at 355 nm are compared for neat acetonitrile (solid line) and acetonitrile with 1.0 M Bu_4NClO_4 added (dashed line). No change in the decay time is observed with the addition of up to 1.0 M Bu_4NClO_4.

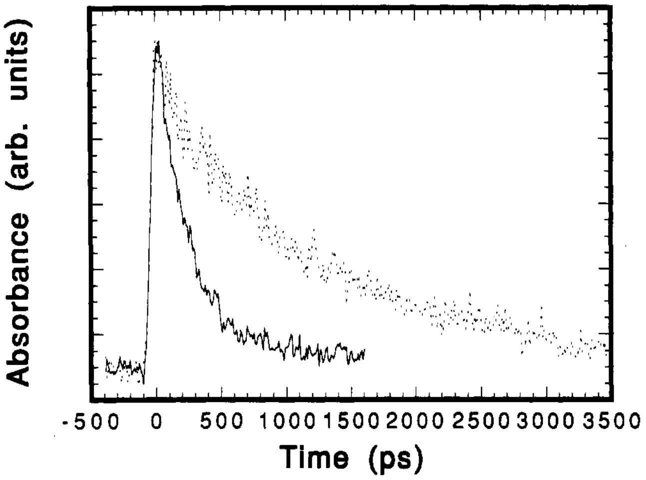

Figure 5. The transient absorption dynamics at 475 nm following excitation of the TS/FN ground state complex at 355 nm are compared for neat ethyl acetate (dashed line) and ethyl acetate with 1.0 M $LiClO_4$ added (solid line). 1.0 M $LiClO_4$ decreases the lifetime of the *trans*-stilbene radical cation to 200 ps, compared to 1180 ps for the neat solvent. Complete decay of the absorption signal in the neat solvent is observed within a few nanoseconds.

Discussion

Photoexcitation of the TS/FN ground state complex results in the formation of a contact ion-pair (CIP). The energy gap between the CIP and the neutral ground state CT complex is solvent dependent. As this energy gap determines the driving

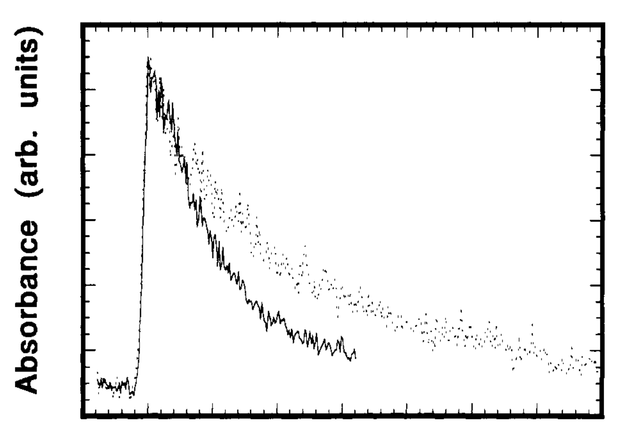

Figure 6. The transient absorption dynamics at 475 nm following excitation of the TS/FN ground state complex at 355 nm are compared for neat ethyl acetate (dashed line) and ethyl acetate with 1.0 M Bu$_4$NClO$_4$ added (solid line). 1.0 M Bu$_4$NClO$_4$ decreases the lifetime of the *trans*-stilbene radical cation to 500 ps, compared to 1180 ps for the neat solvent. This contrasts the acetonitrile study, where addition of Bu$_4$NClO$_4$ does not effect the transient dynamics. Complete decay of the absorption signal is observed within a few nanoseconds.

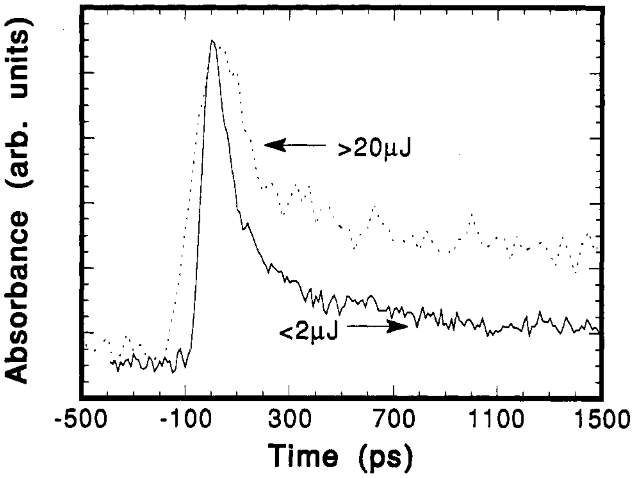

Figure 7. The absorption kinetics of the TS/FN complex are examined as a function of photolysis energy in neat acetonitrile. With low excitation energies, <2 μJ, (30 ps fwhm) the absorption signal essentially decays to zero. At high excitation energies, >20 μJ, (80 ps fwhm) a long time component is observed, which arises from multiphoton processes in the sample. Since different excitation pulse widths were used in the two experiments, it is important to note that the spot sizes were controlled so that the peak power per area was increased by over a factor of 10.

force for the ET reaction, the reaction rate will be effected by any changes in the solvating medium which influence this gap.

Electrolytes stabilize the equilibrium free energy of the solvation of molecular ions.[16] Thus, in salt solutions, the energy gap between the CIP and the neutral complex will decrease. Electrolytes alter bulk (e.g. dielectric constant, viscosity, polarizability) and molecular-based solvent properties (e.g. polarity).[17] In understanding the influence of dissolved salts on reaction processes in solution, it is necessary to determine which of these variables, if any, provide useful information concerning how electrolytes influence the reaction rate. One of the goals of the present paper is to address this question. The results and analysis presented indicate that some of the general concepts used to analyze ET reactions in neat liquids are applicable to salt solutions. However, as will be discussed in detail, current theoretical approaches for modeling salt solutions are not able to account for a large number of experimental observations. Clearly, new approaches for modeling these complicated solutions are needed. The rest of this discussion section is organized as follows. First, the primary photochemical processes are delineated and the electron transfer rate constants are determined. Second, solvent effects on the energetics of the electron transfer process are determined. This section critically examines the predictions of free energy models that are based on solvent static dielectric constant and molecular polarity scales for parametrizing reaction exothermicity. Third, the reorganization energy of the TS/FN electron transfer reaction in salt solutions is examined. This provides insight into the role that the ionic atmosphere plays in affecting the reaction driving force. Finally, the potential importance of frequency dependent friction in determining reaction rates in salt solutions is examined.

A. Reaction Mechanism and Rate Constants. Irradiation of the TS/FN charge transfer complex (CTC) with 355-nm light directly produces the *trans*-stilbene radical cation and fumaronitrile radical anion CIP. Largely based on the picosecond absorption work of Peters and co-workers,[8] the accepted reaction scheme for the subsequent chemical processes involves competition between back electron transfer and ion-pair separation as seen in Scheme I. In acetonitrile solution, the conclusion that free ions formed with a quantum efficiency of ~0.4 was based on the observation that the dynamics at 475 nm could not be described by first-order kinetics. In the present study, the power dependent experiments reported do not support this model.

At high pump energies, >20 μJ/pulse, the time dependence of each of the transient signals is comparable to those observed by previous workers.[8] However, upon decreasing the energies by another order of magnitude, ~2 μJ/pulse, the long time constant absorption that has been attributed to the free *trans*-stilbene radical cation vanishes. The data shown in Figure 7 provide an upper bound for the potential amount of free ion yield. For photolysis energies less than 2 μJ, the noise in the data increased, making it impossible to determine if there is any residual absorption on the nanosecond time scale. Figure 7 suggests that the maximum yield is about 5–10%. The decay of the transient absorption signal due to back electron transfer is comparable with the instrument response. Thus, it is likely that the initial signal amplitude is underestimated and that essentially no ion-pairs separate. The signals observed at longer times when using high-energy photolysis are likely to arise from the one-photon ionization of the fumaronitrile radical anion. This intermediate has a strong absorption at the pump wavelength. The ionization potential of FN$^{\bullet-}$ is 1.36 eV,[18] far less than the photon energy of 3.5 eV. Photoionization should result in electrons with substantial kinetic energy. A large percentage should escape the Onsager radius,[19] leaving a population of TS$^{\bullet+}$ which will persist well onto the nanosecond time scale. Those electrons which remain close to the initial ion-pair could, in principle, recombine with either the FN radical or the TS$^{\bullet+}$, complicating the reaction kinetics. The low photolysis energies used in the present study eliminate these complications, allowing for quantitative determination of the electron transfer kinetics.

The electron transfer rates were determined by fitting the time dependent absorption data for TS$^{\bullet+}$ to a single exponential function convolved with an instrument response function. For all solutions studied, excellent fits were obtained. There were no indications of any multiexponential character to the decays. Table I lists the reaction rates determined for the neat solvents and salt solutions studied.

B. Medium Effects on Reaction Energetics. In general, the electron transfer rate (k_{et}) is given by eq 5,[20] where κ_{el} is the electron transmission coefficient, ν_n is the nuclear frequency factor, and ΔG^* is the activation energy. κ_{el} is assumed to be one for

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Table I. Energy Gaps and Nonradiative Rates, k_{nr}, for 3-AF for All Salt Solutions Studied[a]

solvent	salt concn, mol/L	energy gap, cm^{-1}	$E_T(30)$, kcal/mol	k_{nr}, 10^8 s^{-1}	k_{et}, 10^9 s^{-1}
ethyl acetate	$LiClO_4$				
	0.0	22 002.1	38.2	2.1	0.85
	0.01	21 917.7	38.9	2.2	1.22
	0.10	21 695.6	40.8	5.1	1.72
	0.50	21 206.5	44.9	9.9	3.45
	1.0	20 807.0	48.3	14.2	5.0
	$NaClO_4$				
	0.0	22 002.1	38.2	2.1	0.85
	0.01	21 937.1	38.7	2.3	0.99
	0.10	21 683.5	40.9	4.3	1.33
	0.50	21 381.7	43.4	6.9	2.21
	Bu_4NClO_4				
	0.0	22 002.1	38.2	2.1	0.85
	0.01	21 928.0	38.8	2.2	1.05
	0.10	21 772.7	40.1	2.9	1.43
	0.50		42.5		2.0
acetonitrile	$LiClO_4$				
	0.0	21 315.0	46.0	3.1	25.0
	1.0	20 637.0	51.7	10.0	100.0
	$NaClO_4$				
	0.0	21 315.0	46.0	3.1	25.0
	1.0	21 050.5	48.2	8.3	66.7
	Bu_4NClO_4				
	0.0	21 315.0	46.0	3.1	25.0
	1.0	21 353.5	45.6	3.1	25.0

[a] The corresponding $E_T(30)$ values derived from the 3-AF data as described in the text are also tabulated. The rate constant, k_{et}, is that for the $TS^{\bullet+}/FN^{\bullet-} \rightarrow TS/FN$ back electron transfer reaction following photoexcitation of the ground state bimolecular complex.

$$k_{et} = \kappa_{el}\nu_n \exp(-\Delta G^{\ddagger}/RT) \qquad (5)$$

adiabatic reactions and less than one for nonadiabatic reactions. $\Delta G^{\ddagger}$ contains contributions from both the solvent (outer-sphere) and the reactant vibrations (inner-sphere). For the TS/FN system, photoexcitation prepares the CIP, from which back electron transfer directly occurs. The product $\kappa_{el}\nu_n$ provides information on the role of solvent dynamics in the reaction process. In the limit of solvent controlled adiabatic electron transfer, various theoretical models predict a correlation between $\kappa_{el}\nu_n$ and the inverse of the solvent longitudinal relaxation time, τ_L^{-1}.[21]

Much of the theoretical development for understanding the influence of energetic factors on bimolecular ET kinetics is based on the original ideas of Marcus.[22] Marcus theory provides a free energy relationship that connects the activation energy of the ET reaction to a function of the reaction exothermicity ($\Delta G°$) and the reorganization free energy (λ).

$$\Delta G^{\ddagger} = (\Delta G° + \lambda)^2/4\lambda \qquad (6)$$

λ is a measure of the free energy that is required to move all the atoms constituting the precursor complex, including the solvent shell, from their equilibrium positions to the equilibrium positions of the successor complex without transferring the electron. In most bimolecular systems, one also needs to consider the work associated with formation of the precursor complex and stabilization/solvation of the products from the successor complex. The two reactants in the TS/FN reaction are initially cosolvated and the products undergo essentially quantitative back electron transfer. Thus, these work terms can be ignored in any quantitative analysis of the data.

The free energy of reorganization is commonly partitioned into two types of contributions.[20,22]

$$\lambda = \lambda_i + \lambda_o \qquad (7)$$

The inner-sphere reorganization energy (λ_i) represents contributions arising from activation of the vibrational modes of the reactants, and the outer-sphere reorganization energy (λ_o) represents changes in solvent structure, which effect the electrostatic environment around the reactants.

This free energy relationship predicts a parabolic dependence between the natural log of the electron transfer rate and the reaction exothermicity ($\Delta G°$). The maximum rate is predicted when $-\Delta G° = \lambda$. There have been several elegant studies reported in recent years that address the validity of the Marcus free energy expression.[23] Originally observed by Closs and Miller,[23a] the parabolic dependence of k_{et} on $\Delta G°$ was determined for a variety of ET reactions. Many of these studies have used molecules that contain donor and acceptor groups which are connected by rigid spacers. Small modifications of either the donor or acceptor groups enable a systematic change in $\Delta G°$.

In addition to changing the donor or acceptor group, the driving force for a particular ET reaction can be altered by changing the solvent. This general approach has been used by several researchers in evaluating the role of the solvent (both static and dynamic) in determining ET rate constants.[23] For example, Weaver and co-workers have used this approach to elucidate dynamical effects of liquids on the rate constants for electron-exchange reactions in various metallocene systems.[24] In principle, for the TS/FN reaction, the $\Delta G°$ values can be directly determined from the charge-transfer absorption spectra. Unfortunately, the charge-transfer absorption band overlaps the $\pi^* \leftarrow \pi$ absorption band of fumaronitrile. The small equilibrium constant for complex formation, $K_{eq} = 0.13$ M^{-1},[25] coupled to the large difference in absorption intensities of the $\pi^* \leftarrow \pi$ band of FN and the CT complex, and the unknown shape of the CT absorption band make is impossible to quantitatively determine $\Delta G°$ from the optical spectra. In the absence of a direct measurement, it is necessary to parametrize the medium effects on $\Delta G°$. In many studies, the change in free energy relative to a particular solvent can be determined using continuum theoretical models. If we were to choose acetonitrile as the reference solvent, a Born solvation model could, in principle, be used to estimate changes in the oxidation potential of the donor and reduction potential of the acceptor in the salt solutions studied. The free energy change, referenced to acetonitrile, would be given by[26]

$$\Delta G° = (E_D^{ox} + E_A^{red})_{37.5} + e^2/2(1/r_A + 1/r_D)(1/\epsilon_S - 1/37.5) - e^2/\epsilon_S r_{DA} \qquad (8)$$

where E_D^{ox} and E_A^{red} are the oxidation and reduction potentials for *trans*-stilbene and fumaronitrile. In this expression, r_A, r_D, and r_{DA} are the radii of the acceptor and donor and the

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intermolecular distance between the donor and acceptor, respectively. For the molecules studied, these values are $\sim$5, $\sim$8, and $\sim$3.5 Å.[8,18] ϵ_S is the static dielectric constant of the solution. E_D^{ox} and E_A^{red} for TS and FN in acetonitrile are 1.5 and −1.36 eV,[18] respectively. The second term in eq 8 is the Born correction to the free energy that arises in going from acetonitrile to a medium of dielectric constant ϵ_S. The last term is the Coulombic attraction between the ions, which is generally assumed to be small. Many treatments ignore this value; however, uncertainty over the appropriate value to use for the dielectric constant has resulted in various discussions over the importance of this term. Dielectric saturation effects suggest that ϵ_S in the vicinity of the ion-pair may be substantially altered compared to the neat solvent.[27] Since this correction term depends on the inverse of ϵ_S, such effects will increase the importance of this term to the calculated $\Delta G°$ values. Using experimentally determined parameters in acetonitrile solutions, $\Delta G°$ for the $TS^{•+}/FN^{•-}$ electron transfer reaction is calculated to be −66 kcal/mol (2.86 eV). Using eq 8, the corresponding value of $\Delta G°$ for ethyl acetate solutions is −73.3 kcal/mol (3.18 eV). Previous studies report a reorganization energy of $\sim$46.1 kcal/mol (2 eV) for this reaction.[8] Thus, in neat solvents $-\Delta G° > \lambda$, and the reaction falls in the Marcus inverted region. The free energy relationship given in eq 5 predicts that the ET rate constant will decrease with increasing reaction exothermicity. For the two solvents studied, the reaction rate should be slower in ethyl acetate than in acetonitrile. This is what is observed.

In order to use this relationship to calculate the free energy change in electrolyte solutions, it is necessary to know the dielectric constants. Unfortunately, outside of aqueous solutions, there is not much tabulated data on the dielectric properties of salt solutions. Thus, a different approach is needed.

In recent years, it has become common to parametrize electron transfer reaction energetics in neat liquids in terms of the $E_T(30)$ molecular polarity scale.[14,28] This scale quantifies solvent polarity by a charge-transfer absorption transition of a dissolved dye molecule. As the energy gap in the TS/FN system is also based on a CT transition, one expects that the $E_T(30)$ scale would be an appropriate measure of solvent effects on $\Delta G°$. Unfortunately, only a few measurements on $E_T(30)$ values in electrolyte solutions have been reported.[17] In measuring $E_T(30)$ values for the salt solutions studied in the present paper, two problems were encountered. First, it was difficult to prevent the formation of dimers.[29] Second, for many electrolyte solutions, the CT band was observed upon dissolution of the dye molecule, but it disappeared within a short period of time, indicating that the dye was unstable in the perchlorate salt solutions. This made any scale of polarity in electrolyte solutions based on empirical $E_T(30)$ values unreliable.

This result necessitated finding a molecular system on which we could establish a polarity scale in electrolyte solutions. Ideally, one still wants a probe molecule which undergoes an intramolecular charge transfer (ICT) excitation. In addition, it is important that the spectral characteristics of the probe molecule depend on bulk properties of the electrolyte solutions. A probe molecule that does not form any specific complexes with dissolved ions in either the ground or excited electronic state is needed. We have previously demonstrated that the molecule 3-aminofluoren-9-one (3-AF) satisfies these criteria in acetonitrile–salt solutions.[30] Before using the spectral properties of this molecule to establish a polarity scale relevant to the $TS^{•+}/FN^{•-}$ ET reaction, it is necessary to demonstrate that 3-AF satisfies the above criteria in ethyl acetate–salt solutions. To check this, we measured the steady-state spectra (absorption and emission), quantum yield for emission, and excited state lifetime of 3-AF in the ethyl acetate–salt solutions of interest. In our previous study in acetonitrile solutions, the relationship between the nonradiative rate constant, k_{nr}, and the $S_1 \leftarrow S_0$ energy gap, ΔG(3-AF), was quantitatively described by the energy gap law.[30] This combined with the steady-state spectroscopy argued strongly that 3-AF was probing bulk properties of the solution.

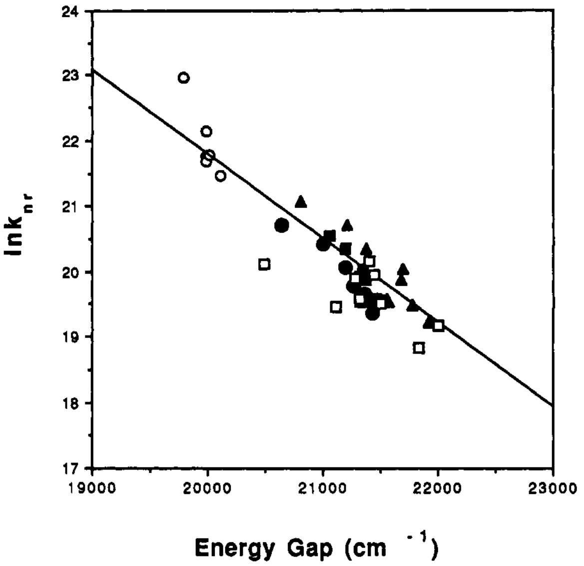

Figure 8. The natural log of the nonradiative rate constant, k_{nr}, is plotted as a function of the experimentally determined energy gap for 3-AF in neat solvents. The nonradiative rate increases with decreasing energy gap, as predicted by the energy gap law. Open circles, protic solvents; open squares, aprotic solvents; closed small triangle, ethyl acetate/salts; closed circle, acetonitrile/LiClO$_4$; closed square, acetonitrile/NaClO$_4$; closed large triangle, acetonitrile/Bu$_4$NClO$_4$. See refs 30 and 31 for a list of solvents.

In Figure 8, the dependence of k_{nr} on the energy gap, ΔG(3-AF), is plotted for the entire set of acetonitrile and ethyl acetate salt solutions studied. All data fall on a single line, indicating that the nonradiative properties of this molecule in both solvent–salt systems (which involves an ICT process) are controlled by the energetics. In addition, as reported earlier, the 3-AF data in neat polar solvents also fall on this line.[31]

In neat solvents, an excellent linear correlation is observed between ΔG(3-AF) and $E_T(30)$ values, see Figure 9. Using the linear relationship between ΔG(3-AF) and $E_T(30)$ obtained in these neat liquids, the ΔG(3-AF) measured in salt solutions can be converted into corresponding $E_T(30)$ values. The resulting polarities for the salt solutions are reported in Table I. As anticipated, added salt increases solution polarity in both acetonitrile and ethyl acetate.

The relationship between the solution polarity, $E_T(30)$, and the reaction exothermicity $\Delta G°$ remains to be derived. An empirical relationship can be established using reported emission spectra of the photoexcited TS/FN ground state charge transfer complex in nonpolar solvents.[8] In benzene and chlorobenzene, the CT complex emits at 527 and 540 nm, respectively.[8b] The $E_T(30)$ values of benzene and chlorobenzene are 34.5 and 37.5 kcal/mol, respectively.[14] Assuming that the shift in emission maximum is linearly related to the change in the $0 \leftarrow 0$ band of the emission spectrum, the reaction energy gap decreases by 1.3 kcal/mol for an increase in the solvent polarity parameter of 3.0 kcal/mol. Using this result, the salt solutions studied collectively span a reaction exothermicity range from $\sim$62 to $\sim$68 kcal/mol. In addition to the data reported in this paper, independent measurements of the electron transfer rates (kcal/mol) in benzene ($E_T(30)$ = 34.5), chlorobenzene ($E_T(30)$ = 37.5), dimethoxyethane ($E_T(30)$ = 38.2), acetone ($E_T(30)$ = 42.2), dimethyl

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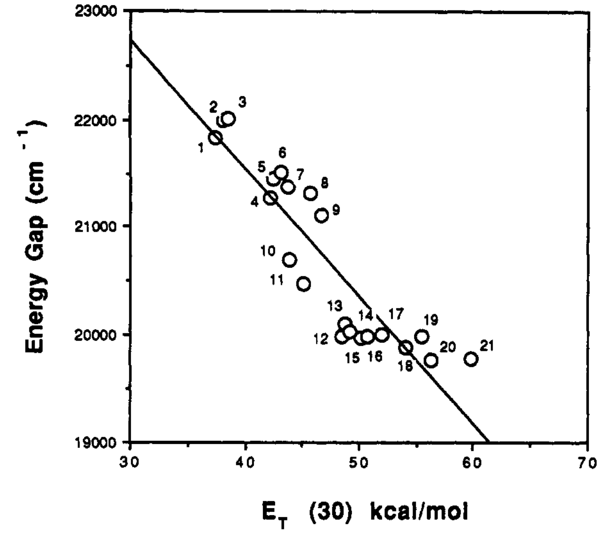

Figure 9. The energy gap of 3-AF in neat solvents is plotted as a function of the $E_T(30)$ solvent polarity parameter. Using this linear relationship, the $E_T(30)$ values in electrolye solutions are determined. The solvents listed are the following: (1) tetrahydrofuran; (2) ethyl acetate; (3) butyl acetate; (4) acetone; (5) valeronitrile; (6) butyronitrile; (7) propionitrile; (8) acetonitrile; (9) propylenecarbonate; (10) dimethylformamide; (11) dimethyl sulfoxide; (12) 2-propanol; (13) hexanol; (14) pentanol; (15) butanol; (16) 1-propanol; (17) ethanol; (18) propanediol; (19) methanol; (20) ethylene glycol; (21) trifluoroethanol.

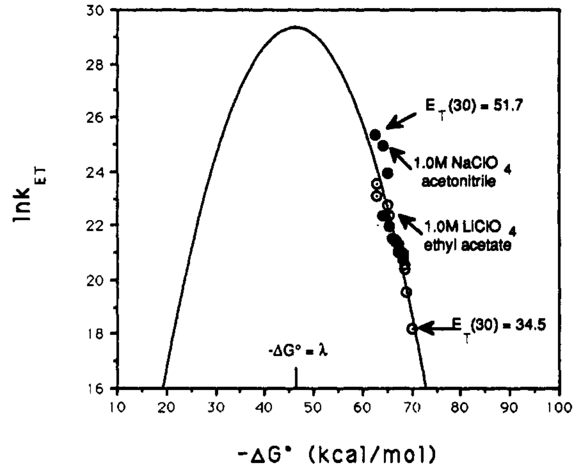

Figure 10. The natural log of the electron transfer rate constants, k_{et}, of the TS/FN complex is plotted as a function of reaction exothermicity, $\Delta G°$, for both neat solvent and salt solution data. The solid line is the best fit of the experimental data to the Marcus expression, using a reorganization energy of 2 eV. All rates occur within the inverted region.

sulfoxide ($E_T(30)$ = 45.0), 1-propanol ($E_T(30)$ = 50.7), and ethanol ($E_T(30)$ = 51.9) have been published.[8] The rate data for the entire set of neat solvent and salt solutions are plotted as a function of reaction exothermicity in Figure 10.

Using the Marcus free energy relationship, a parabolic dependence is predicted with a maximum rate occurring at $-\Delta G° = \lambda = {\sim}46$ kcal/mol, eq 6.[23] The solid line in Figure 10 is the best fit of the experimental data to the Marcus expression, assuming that eq 5 and 6 are valid. In applying the Marcus theory, only the prefactor was varied to obtain the best fit. The value of λ was fixed to be 2 eV, as previously reported. The validity of this assumption is discussed later. Good agreement is observed between theory and experiment.

While the agreement in Figure 10 is impressive, closer examination of the data reveals evidence that understanding salt effects on ET reactions requires more than just determining the reaction energetics. For example, the rate of electron transfer is about thirteen times faster in 1.0 M $NaClO_4$/acetonitrile solutions as compared to 1.0 M $LiClO_4$/ethyl acetate solutions even though these two solutions have the *same* polarity ($E_T(30)$ = 48.3 kcal/mol). These two solutions are highlighted in Figure 10. While the Marcus curve qualitatively describes the entire set of data, a detailed understanding of electrolyte effects will certainly require molecular models. For example, consider the effect of added Bu_4NClO_4. In acetonitrile, addition of this salt does not effect the solution polarity,[17,30] and hence the reaction rate constant is independent of this salt up to 1.0 M. However, in ethyl acetate, addition of 0.5 M Bu_4NClO_4 increases the solution polarity and results in an increase in k_{et} of a factor of 2.6. While this observation is accountable for by the changes in solution polarity, it is inconsistent with ionic strength models,[12,30] which are commonly used to explain electrolyte effects.

As stated above, in generating the theoretical curve in Figure 10, the reorganization energy was assumed to be constant. This is clearly an approximation. Since addition of electrolytes in the concentration range studied significantly affects the dielectric constant of the solvent,[32] the outer-sphere reorganization energy must be affected. In ethyl acetate, where dielectric constant data have been measured, a 1.0 M $LiClO_4$ solution has a dielectric constant of 17.0, in comparison to 6.2 for neat ethyl acetate.[32] In addition, the outer-sphere reorganization energy has contributions from both the solvent and the ionic atmosphere, $\lambda_o = \lambda_S + \lambda_{IA}$.[33] Thus, it is important to try and access the magnitudes of the reorganization energies and their dependence on changes in the molecular makeup of the electrolyte solutions. The parabolic curve in Figure 10 also assumes that the pre-exponential factor $\kappa_{el}\nu_n$ is constant for the solutions studied. The value of this term depends, in part, on the liquid dynamics.[21] Simple theories of electrolyte solutions suggest that relaxation dynamics associated with the ionic atmosphere are strongly concentration dependent.[34] In addition, it is expected that the dynamical motions of the liquid molecules themselves will be altered by added salt. This suggests that one needs to critically examine the assumptions made in generating the comparison between the reaction rates and the overall energetics shown in Figure 10. The next two sections examine and discuss these issues.

C. Reorganization Energies. Previous determination of the reorganization energy of the $TS^{\bullet+}/FN^{\bullet-}$ electron transfer reaction indicated approximately equal contributions from inner- and outer-sphere terms.[8] It is impossible to experimentally measure the effect of salt on the inner-sphere contribution. Since there is no evidence that added salt affects the vibrational modes of the ground state complex, it is reasonable to conclude that this part of the total reorganization energy is constant for the solutions studied. This may not be the case for the outer-sphere contribution.

Within a continuum solvent model, the effect of changes in the static dielectric constant on the solvent reorganization energy, λ_S, can be evaluated using eq 9.[20,35] In this expression r_D, r_A, and

$$\lambda_S = e^2(1/2r_D + 1/2r_A - 1/r_{DA})(1/n_S^2 - 1/\epsilon_S) \qquad (9)$$

r_{DA} are the radii of the donor and acceptor and the intermolecular distance, respectively. ϵ_S and n_S are the dielectric constant and index of refraction of the solution.

Using reported data for ϵ_S in ethyl acetate/$LiClO_4$ solutions, λ_S increases from 0.6554 to 0.8370 eV upon addition of 1.0 M $LiClO_4$. This suggests that λ_S may change by ~20%. Unfortunately no dielectric data are available for the acetonitrile/salt solutions so a comparable calculation cannot be made. In addition to λ_S, the contribution arising from the reorganization of the

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ionic atmosphere, λ_{IA}, contributes to λ_o. This effect can be calculated using eq 10.[36]

$$\lambda_{IA} = e^2/r_{DA}\epsilon_S[(2a\Gamma - 1 + \exp(-2a\Gamma))/(1 + 2a\Gamma)] \quad (10)$$

In the above expression, $a = r_{DA}/2$, and Γ is a screening parameter. Within a mean spherical approximation Γ is given by $[(1 + 2\kappa\sigma)^{1/2} - 1]/2\sigma$, where σ is the average diameter of the ion and κ^{-1} is the Debye length.[12,36] For a 1.0 M $LiClO_4$/ethyl acetate solution, λ_{IA} is 0.006 eV. This value is negligible compared to λ_S. Thus, the effect of λ_{IA} on the total reorganization energy, λ, is not of concern for the set of solutions studied. Assuming that λ_i is constant, λ will vary by less than 15%. Thus, assuming a constant value for λ in deriving the Marcus curve shown in Figure 10 may not be a reasonable approximation.

D. Dynamical Effects of Electrolyte Solutions. Since the frequency factor $\kappa_{el}\nu_n$ (eq 2) depends on the relaxation time(s) of the solvent, its value should also change with added salt. To determine the magnitude of this effect, it is necessary to quantify the relaxation dynamics of electrolyte solutions. Recently Chapman and Maroncelli[37] and Huppert and co-workers[32] reported studies which address this question. In addition to other solvents, these workers measured the time dependent Stokes shift for several polar solute molecules in a variety of acetonitrile and ethyl acetate–salt solutions. In all cases, the dynamic Stokes shifts revealed multiple relaxation times. Compared to the neat liquid, an additonal small amplitude, long time component is observed to contribute to the relaxation process. Huppert and co-workers have attributed this relaxation time to the ion atmosphere, τ_{IA}.[32] In 10 mM and 400 mM $LiClO_4$/acetonitrile solutions, this component had a relaxation time of 33.9 and 0.93 ns, respectively. The corresponding values in ethyl acetate are 25.6 and 1.2 ns. In contrast, Chapman and Maroncelli assigned these long time dynamics to the exchange between ions and solvent molecules in the first solvent shell of the probe molecule.[37]

The general time scale observed (ns) is consistent with theoretical predictions of ionic atmosphere relaxation, e.g. using the model of Debye and Falkenhagen (DF).[34] Such a slow relaxation time for the ion atmosphere raises an interesting question about the electron transfer reaction dynamics. While the above measurements and theoretical predictions focus on the dynamics associated with the ionic atmosphere of the dissolved salts, it is important to consider that photoexcitation also produces ions in solution. The instantaneously generated $TS^{\bullet+}/FN^{\bullet-}$ ion-pair also generates an ionic atmosphere. The transient Stokes shift measurements suggest that it may require nanoseconds for the solvent molecules in the vicinity of this photogenerated ion-pair to establish equilibrium. This is longer than the back electron transfer dynamics and suggests that the reaction may not be occurring in equilibrium solvation.

Even though a quantitative understanding of relaxation dynamics in electrolytes requires further experimental and theoretical work, it is of interest to try and compare trends in the experimentally determined prefactor, $\kappa_{el}\nu_n$, for the $TS^{\bullet+}/FN^{\bullet-}$ reaction to predicted values of τ_{IA}. $\kappa_{el}\nu_n$ for the solutions studied are given in Table II. The values obtained for $\kappa_{el}\nu_n$ do not appear to vary significantly with added salt. In addition, if either the measured values of Huppert and co-workers[32] or the theoretical DF models[34] are used as a gauge of the relaxation dynamics of the ionic atmosphere, then $\kappa_{el}\nu_n > 1/\tau_{IA}$. This suggests that the slow relaxation of the ionic atmosphere does not contribute to any appreciable extent to the magnitude of the kinetic prefactor. It is unknown at this time whether or not there are fast relaxation channels associated with the ionic atmosphere. Further experimentation is required to address this possibility. The magnitude of $\kappa_{el}\nu_n$ observed supports the conclusion that relaxation modes of the solution which are faster than that currently associated with the ionic atmosphere are dominant in determining the reaction rate.

Table II. Prefactors, $\kappa_{el}\nu_n$, for the $TS^{\bullet+}/FN^{\bullet-} \rightarrow TS/FN$ Back Electron Transfer Reaction following Photoexcitation of the Ground State Bimolecular Complex as a Function of Added Salt[a]

solvent	salt concn	τ_L^{-1}, s^{-1}	$\kappa_{el}\nu_n$, s^{-1}
acetonitrile	0.0	2.5×10^{12}	7.0×10^{11}
	1.0 M $LiClO_4$		1.2×10^{12}
	1.0 M $NaClO_4$		1.3×10^{12}
	1.0 M Bu_4NClO_4		7.0×10^{11}
ethyl acetate	0.0	3.9×10^{11}	8.0×10^{10}
	0.01 M $LiClO_4$		1.0×10^{11}
	0.10 M $LiClO_4$	9.3×10^{9}	1.0×10^{11}
	0.50 M $LiClO_4$	1.1×10^{10}	1.1×10^{11}
	1.0 M $LiClO_4$	1.3×10^{10}	9.3×10^{10}
	0.01 M $NaClO_4$		8.6×10^{10}
	0.10 M $NaClO_4$		7.8×10^{10}
	0.5 M $NaClO_4$		8.5×10^{10}
	0.01 M Bu_4NClO_4		8.7×10^{10}
	0.1 M Bu_4NClO_4		9.8×10^{10}
	0.5 M Bu_4NClO_4		8.9×10^{10}

[a] The solvent longitudinal relaxation times, τ_L^{-1}, are given where data were available.[32,37]

Conclusions

Electron transfer from the photogenerated contact ion-pair between *trans*-stilbene and fumaronitrile was studied in acetonitrile and ethyl acetate/salt solutions. In general, the effects of added electrolytes on the rate of electron transfer arise from changes in solution polarity. Addition of electrolytes increases the solution polarity in all cases studied except acetonitrile/Bu_4NClO_4 solutions, where no change in polarity was observed. With increased solvent polarity, the electron transfer rate increases.

Using the probe molecule 3-AF as a measure of solvent polarity, the reaction exothermicities, ΔG°, of the $TS^{\bullet+}/FN^{\bullet-} \rightarrow TS/FN$ reaction were determined. For the electrolyte and neat solvent systems studied, a change in ΔG° by 10 kcal/mol was achieved. Correspondingly, the rate constant varied by 3 orders of magnitude. For all the data, an increase in k_{et} is observed with a decrease in ΔG°, behavior characteristic of the Marcus inverted region. Excellent agreement is observed between the experimental data and the Marcus free energy relationship.

The contribution of the ionic atmosphere to the reorganization energy was determined to be about 2–3 orders of magnitude less than the solvent reorganization energy. Therefore contributions from the ionic atmosphere on energetic factors appear to be negligible. In addition, based on time resolved Stokes shift measurements and various theoretical models, the relaxation of the ionic atmosphere is believed to occur on a much longer time scale (e.g., nanoseconds) than both solvent relaxation (a few picoseconds for acetonitrile and ethyl acetate) and the electron transfer reaction studied. This suggests that relaxation dynamics of the ionic atmosphere do not influence the rate of the $TS^{\bullet+}/FN^{\bullet-} \rightarrow TS/FN$ reaction.

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