

# Picosecond Decay Dynamics of the *trans*-Stilbene-Olefin Contact Ion Pair: Electron-Transfer vs. Ion-Pair Separation

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**Abstract:** The dynamics of the decay for the contact ion pair formed by irradiation of the ground-state charge-transfer complex of *trans*-stilbene with electron-poor olefins has been investigated by picosecond absorption spectroscopy. The contact ion pair decays by two pathways: back-electron transfer to form the ground-state complex and ion-pair separation to form the solvent-separated ion pair. The solvent dependence and salt effect of both processes has been examined.

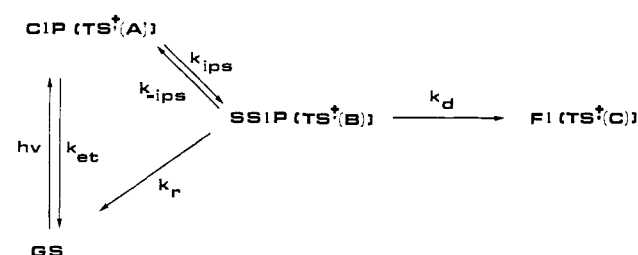
There have been numerous investigations of the role of ion pairs in organic reactions since the pioneering studies of Hughes and Ingold<sup>1</sup> and Winstein.<sup>2</sup> Some of the attention has been focused on the influence of the medium on the interchange of ion-pair forms. In recent years, there has begun to develop an understanding of how the solvent affects the distribution of ion pairs.<sup>3</sup> There is, however, virtually no experimental information or theoretical models relating to the parameters that control the dynamics of ion-pair interconversion.

Recently chemical systems have been developed that, in conjunction with picosecond absorption spectroscopy, allow for the dynamics of ion pairs to be directly probed.<sup>4</sup> For example, picosecond laser excitation of benzophenone induces an electron from an aromatic amine to be transferred to the excited triplet state of benzophenone to form an ion pair. The subsequent ion-pair dynamics are probed through the spectral shifts of the benzophenone radical anion absorption spectrum. With this chemical system, both solvent and salt effects upon the dynamics of ion-pair interchange have been examined.

One difficulty encountered with the benzophenone-aromatic amines picosecond studies is that following excitation of benzophenone there is a concentration gradient of aromatic amines about the excited ketone. Consequently, the ensuing electron transfer produces a spacial distribution of ion pairs which complicates the analysis of the ion-pair dynamics. A more satisfactory methodology would be the excitation of a ground-state charge-transfer complex that would produce only one form of ion pair, the contact form.

The photophysics and photochemistry of charge-transfer complexes of *trans*-stilbene with electron-poor olefins have been examined in great detail.<sup>5,6</sup> We recently reported a preliminary investigation into the picosecond dynamics of the excited *trans*-stilbene/fumaronitrile (TS/FN) charge-transfer complex.<sup>7</sup> Our studies support the reaction scheme developed by Lewis<sup>5</sup> for the subsequent chemical processes. Selective irradiation of the TS/FN ground-state charge-transfer complex directly produces the contact ion pair, a process independent of solvent, consisting of the *trans*-stilbene radical cation and the fumaronitrile radical anion (Scheme I). The contact ion pair (CIP) can undergo back-electron transfer,  $k_{et}$ , to the ground-state (GS) or ion-pair separation,  $k_{ips}$ , to the solvent-separated ion pair (SSIP). The SSIP can diffuse apart,  $k_d$ , to form free ions (FI), reform the CIP,  $k_{-ips}$ , or return to the ground state,  $k_r$ . Previous studies have shown that fluorescence and formation of triplet TS do not contribute significantly to the decay of the CIP.<sup>5b</sup>

Scheme I



In this paper, we present further studies of the dynamics of the CIP that is formed by the irradiation of *trans*-stilbene/electron-poor-olefin charge-transfer complexes. In particular we examine the solvent dependence and salt effect on both the rate of back-electron transfer,  $k_{et}$ , and contact ion-pair separation,  $k_{ips}$ .

## Experimental Section

**Materials.** *trans*-Stilbene (Aldrich) was vacuum sublimed. Fumaronitrile (Aldrich) was recrystallized from methanol and then vacuum sublimed. Dimethyl fumarate (Aldrich) was recrystallized from  $CCl_4$ . Maleic anhydride was recrystallized from  $CHCl_3$ . Inorganic salts ( $LiClO_4$  and  $(n-Bu)_4NClO_4$ ) were dried by heating under vacuum. 12-Crown-4 (Aldrich) was used as received. Benzene (Fischer), chlorobenzene (Aldrich), bromobenzene (Aldrich), dimethoxyethane (DME, Aldrich), acetonitrile (Baker), 1-propanol (Fischer), ethanol (US Industrial), acetone (Fischer), and dimethyl sulfoxide ( $Me_2SO$ , Fischer) were used as received.

**Picosecond Laser Apparatus.** The laser apparatus has been previously described in detail.<sup>8</sup> Briefly, the picosecond absorption spectrometer consists of a 10-Hz  $Nd^{3+}$ -YAG laser (Quantel International, YG-400) with a pulse width of 25 ps. The detector is an OMA II vidicon (PAR 1215, 1216, 1217) interfaced to a 200-mm spectrograph (JY-UFS-200). Each absorption spectrum is the average of at least 200 laser pulses. Irradiation was performed with 355-nm pulses on room temperature solutions which were 0.05 M *trans*-stilbene and 0.3 M olefin ( $OD > 1$ , 355 nm) unless otherwise noted. The irradiated solutions were rapidly stirred and frequently changed to prevent the buildup of photoproducts. The fluorescence experiments were conducted on the same apparatus with the excitation pulse, 355 nm, but without the interrogation beam.

## Results

Laser excitation (355 nm, 0.2 mJ) of the TS complexed with the olefins, fumaronitrile (FN), dimethyl fumarate (DMF), and maleic anhydride (MA), in several different solvents, generates a transient, with  $\lambda_{max}$  478 nm, within the laser pulse and has been assigned<sup>7</sup> to the radical cation of *trans*-stilbene in the contact ion pair,  $TS^+(A)$ . The  $\lambda_{max}$  of  $TS^+(A)$  does not change with solvent or olefin. However, the absorption spectrum of  $TS^+(A)$  does narrow with increasing solvent polarity. In nonpolar solvents,  $TS^+(A)$  decays completely (>97%) by first-order kinetics as monitored by absorption spectroscopy at several wavelengths. In polar solvents the decay displays at least two time components which may be fitted to a double exponential. As previously

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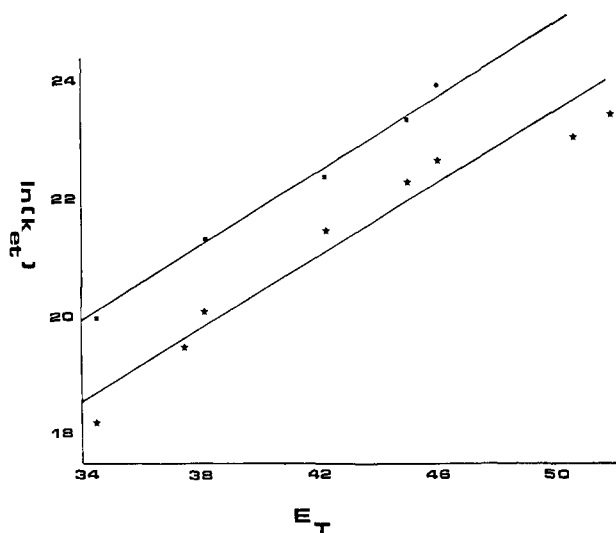
(7) Goodman, J. L.; Peters, K. S. *J. Am. Chem. Soc.* **1985**, *107*, 1441.

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**Table I.**  $\tau_1$  and  $\tau_2$  Values for the Decay of *trans*-Stilbene/Olefin Contact Ion Pair in Different Solvents<sup>1a</sup>

$E_T^b$	solvent	fumaronitrile		dimethyl fumarate		maleic anhydride	
		$\tau_1$	$\tau_2$	$\tau_1$	$\tau_2$	$\tau_1$	$\tau_2$
34.5	benzene	12500					
37.5	chlorobenzene	3300					
37.5	bromobenzene	3400					
38.2	dimethoxyethane	1400	>14000	537	5400	35	>350
42.2	acetone	469	990	195	400		
45.0	dimethyl sulfoxide	196	960	70	200		
46.0	acetonitrile	132	490	40	40	20	20
50.7	1-propanol	93	>900				
51.0	ethanol	60	>600			20	>150

<sup>a</sup>All lifetimes are  $10^{-12}$  s.  $\tau_1$  values are  $\pm 25\%$  and  $\tau_2$  values  $\pm 50\%$ . Measurements were made at  $298 \pm 3$  K. <sup>b</sup>Units of  $E_T$  are kcal/mol. See ref 17.



**Figure 1.** Plot of  $\ln k_{et}$  vs.  $E_T$  for the solvents listed in Table I: (☆) *trans*-stilbene/fumaronitrile,  $r = 0.971$ , and (■) *trans*-stilbene/dimethyl fumarate,  $r = 0.995$ .

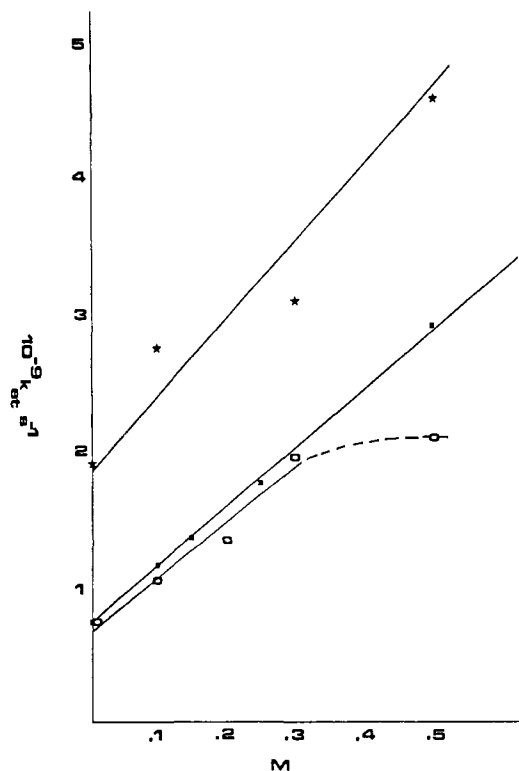
observed,<sup>7</sup>  $\tau_1$  ( $1/k_{et}$ ) is the fast decay of  $TS^+(A)$  to the ground state by back-electron transfer. The rate of ion pair separation  $k_{ips}$  of  $TS^+(A)$  to the solvent-separated ion pair  $TS^+(B)$  can be obtained from the kinetic data. Assuming the same extinction coefficients at 478 nm for  $TS^+(A)$  and  $TS^+(B)$ , then

$$\tau_2 = 1/k_{ips} = \tau_1(1 - a)/a$$

where  $a$  is the fraction of  $TS^+(A)$  that undergoes ion-pair separation. The fraction  $a$  is determined from the ratio of the  $y$  intercepts ( $t = 0$ ) from the double exponential fit. In Table I, values for  $\tau_1$  and  $\tau_2$  as a function of solvent for TS complexed with the olefins FN, DMF, and MA are given.

Both  $\tau_1$  and  $\tau_2$  decrease with increasing solvent polarity. A plot of  $\ln(k_{et})$  against the empirical solvent polarity parameter  $E_T$  for various solvents is linear for both TS/FN ( $r = 0.971$ ) and TS/DMF ( $r = 0.995$ ), Figure 1. The two plots have similar slopes of  $0.32 \pm 0.02$ .

The effect of added salts,  $LiClO_4$  and  $(n-Bu)_4NClO_4$ , on  $k_{et}$  for TS/FN and TS/DMF in dimethoxyethane is shown in Figure 2. For  $LiClO_4$ , the change in  $k_{et}$  with salt concentration (0–0.5 M) is linear with a slope of  $4.4 \pm 0.4$  for both TS/FN and TS/DMF. For  $(n-Bu)_4NClO_4$ , the dependence of  $k_{et}$  upon salt concentration (0–0.3 M) is linear, with slope  $4.4 \pm 0.4$ . However, there is a leveling of the salt effect on  $k_{et}$  from 0.3 to 0.5 M  $n-Bu_4NClO_4$ . The dependence of  $k_{ips}$  for TS/FN in dimethoxyethane upon the salts  $LiClO_4$  and  $(n-Bu)_4NClO_4$  was also investigated. Increasing the ionic strength increases the rate  $k_{ips}$  linearly with a slope of  $12 \pm 4$  for  $LiClO_4$  (0–0.5 M) and  $9 \pm 3$  for  $(n-Bu)_4NClO_4$  (0–0.3 M). The addition of equimolar 15-crown-4 to the  $LiClO_4$  solutions in dimethoxyethane yields the



**Figure 2.** Rate dependence,  $k_{et}$ , upon salt concentration: (■) *trans*-stilbene/fumaronitrile- $LiClO_4$ , (○) *trans*-stilbene/fumaronitrile- $n-Bu_4NClO_4$ , and (☆) *trans*-stilbene/dimethyl fumarate- $LiClO_4$ .

same  $k_{et}$  and  $k_{ips}$  dependence upon salt concentration for the TS/FN complex as is observed without the crown ether. In contrast, the addition of  $LiClO_4$  (0–0.5 M) to the solvent  $Me_2SO$  does not alter  $k_{et}$  and  $k_{ips}$  for TS/FN.

The emission spectrum for the TS/FN complex as a function of solvent was also examined. In benzene, the emission spectrum has a  $\lambda_{max}$  at 527 nm while in chlorobenzene the emission spectrum red shifts with a resulting  $\lambda_{max}$  at 540 nm. With the change in solvent from benzene to chlorobenzene, the integrated area of the emission spectrum is reduced by a factor of 0.3.

## Discussion

**Electron Transfer  $\tau_1$ .** In recent years there have been a large number of investigations<sup>9</sup> into the dependence of the rate of electron transfer upon the free energy change for the reaction. In its simplest form, the Marcus relationship<sup>10</sup> between the rate of electron transfer and the free energy change within an encounter complex is

$$k_{et} = v_{et} \exp[-\lambda(1 + \Delta G/\lambda)^2/4RT]$$

where  $\Delta G$  is the free energy change,  $v_{et}$  the frequency factor for electron transfer, and  $\lambda$  the solvent repolarization energy. A direct consequence of this relationship is that for free energy changes larger than the solvent repolarization energies, the rate of electron transfer decreases with increasing exothermicity, a relationship that has been termed the "inverted region". The actual existence of the inverted region has recently been demonstrated by Miller and Closs<sup>11</sup> in their investigation of the rate of electron transfer from 4-biphenyl that is linked to various  $\pi$ -conjugated hydrocarbons by a  $5\alpha$ -androstandane skeleton.

We have examined the rate of decay of the contact ion pair,  $k_{et}$ , via electron transfer as a function of  $E_T$ . Dimroth has proposed<sup>12</sup> a solvent polarity parameter  $E_T$  which is based upon a

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solvatochromic absorption band of pyridinium-*N*-phenoxide betaine dye. As there is a decrease in the molecular polarity on going from the ground state to the excited state, a change in solvent from nonpolar to polar increases the energy separation between the ground and excited state. The  $E_T$  value is a measure of the optical transition energy, in terms of kcal/mol, for a given solvent. For *trans*-stilbene/olefin complexes the ground state is a charge-transfer complex and the excited state corresponds to a contact ion pair. Thus there is a net increase in the molecular polarity upon excitation, so that increasing the solvent polarity decreases the energy gap between the GS and the CIP.

It is expected that the decrease in the energy separation between the GS and CIP will be a linear function with increasing  $E_T$ . However, it is not possible to directly quantify the energy decrease with increasing  $E_T$  from the absorption spectrum of the ground-state complex. There is no clear origin nor absorption maximum for the optical transition of the TS/FN or TS/DMF complex to the CIP. Similarly, the origin of the emission spectrum of the CIP in nonpolar solvents cannot be clearly discerned with the fluorescence apparatus. However, a  $\lambda_{\max}$  in the emission spectrum of the CIP in benzene and chlorobenzene can be measured. The emission spectrum for TS/FN shifts from 527 nm in benzene ( $E_T = 34.5$  kcal/mol) to 540 nm in chlorobenzene ( $E_T = 37.5$  kcal/mol). Therefore a change in the solvent polarity parameter by 3.0 kcal/mol corresponds to a decrease of 1.3 kcal/mol for the energy separation of GS-CIP. This analysis assumes that in the emission spectrum the Frank-Condon factors are independent of solvent and thus a change in the  $\lambda_{\max}$  for the emission reflects the same change in the energy of the origin for the transition. Consequently, a change in  $E_T$  value from 34.5 kcal/mol (benzene) to 51.9 kcal/mol (ethanol) should lead to a net decrease in the GS-CIP energy gap by  $\sim 7.5$  kcal/mol. This change leads to a  $k_{et}$  increase for TS/FN from  $0.8 \times 10^8$  to  $166 \times 10^8$  s $^{-1}$ , a factor of 200.

In examining the rate of decay of the CIP as a function of the solvent polarity, it is important to have an estimate of the energy separation between the GS and CIP. From the emission spectrum of TS/FN in benzene, the origin of the emission is approximately 70 kcal/mol (410 nm). Therefore, the energy gap is expected to vary from 70 kcal/mol in benzene ( $E_T = 34.5$  kcal/mol) to 62.5 kcal/mol in ethanol ( $E_T = 51.9$  kcal/mol). These changes in energy upon electron transfer are larger than those investigated by Miller and Closs (0 to 55 kcal/mol).<sup>11</sup>

As the change in the  $E_T$  parameter correlates with the change in the energy gap, the logarithm of  $k_{et}$  is found to be approximately a linear function with decrease in the energy gap for both TS/FN and TS/DMF (Figure 1).

For electron-transfer processes, there is a question as to the possible participation of solvent motion in the transfer process. Recently, the question of the coupling between charge transfer and solvent dynamics for adiabatic processes has been addressed.<sup>13</sup> One approach to this problem is to find solvents with different rotation correlation times but with the property that they do not change the overall energetics of the reaction. One set of solvent molecules that fulfill these criteria are chlorobenzene and bromobenzene. They both have the same  $E_T$  value, 37.5 kcal/mol. However, chlorobenzene and bromobenzene have rotation correlation times of 4.2 and 7.4 ps, respectively, a factor of 1.8 difference.<sup>14</sup> From Table I, the rate  $k_{et}$  of TS/FN is found to be the same for the two solvents. Thus, we conclude that the dynamics of solvent reorganization do not contribute to the  $k_{et}$  dynamics of the CIP for TS/FN.

**Ion-Pair Separation ( $\tau_2$ ).** The lack of monoexponential decay of TS<sup>+</sup>(A) in polar solvents suggests that there are at least two decay pathways for the CIP: back-electron transfer and ion-pair separation. The stabilizing ability of polar solvents to support ion-pair separation to free ions is well precedented. The ion-pair

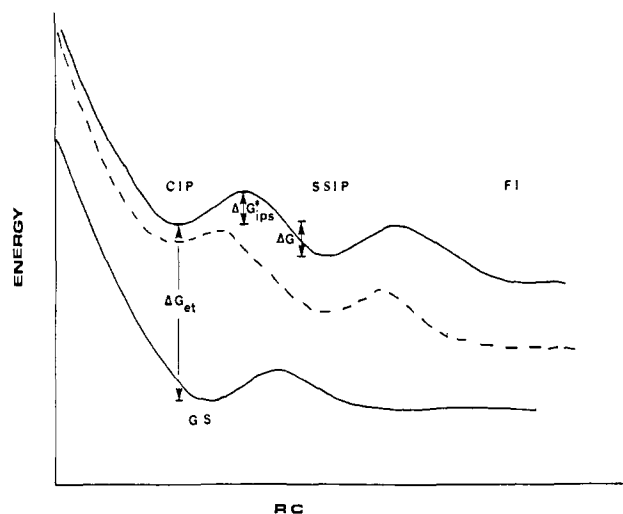


Figure 3. Reaction coordinate diagram: (—) less polar solvent, (---) more polar solvent.

reaction surface, Figure 3, in its simplest form, is comprised of intermediate stages by which the CIP separates. The barriers for the separation depend greatly on the CIP complex-solvent interactions. The relative thermodynamic,  $\Delta G$ , and kinetic,  $\Delta G_{ips}^*$ , properties of the intermediate are influenced by electrostatic interactions as well as by specific solvent-ion-pair interactions. Macroscopic solvent properties such as dielectric,  $\epsilon$ , dipole moment,  $\mu$ , Gutman's donor numbers, and the solvent polarity scales,  $E_T$  and  $Z$ , are useful but do not provide a detailed understanding of the dynamic and energetic relationship between the CIP and SSIP.<sup>15</sup> However,  $k_{ips}$  can provide insight into what factors are important for ion-pair separation in the TS/olefin complexes.

As is observed with  $\tau_1$ , there is both a solvent and an olefin dependence upon ion-pair separation,  $\tau_2$ , Table I. Although fluorescence data specifically from the SSIP are not available, it is reasonable to assume that as the solvent polarity increases the SSIP is stabilized and accordingly is lowered in energy (Figure 3). Importantly, from the rate data, it is implied that the SSIP is stabilized to a greater extent than the CIP when the solvent polarity is increased. As previously discussed, with an increase in solvent polarity, there is an increased stabilization of the CIP which is reflected in a decrease in  $\tau_1$ . If the CIP and SSIP were stabilized to the same extent with increasing solvent polarity, then it would be predicted that  $\tau_2$  would remain constant while  $\tau_1$  decreased. However, the ratio  $\tau_2/\tau_1$  is  $>10$  for the TS/FN complex in DME but is reduced to 3.4 for the same complex in acetonitrile. Therefore, if there is a Hammond relationship between the rate of CIP separation and overall energy change  $\Delta G$ , then with increasing solvent polarity there is greater increase in stability of the SSIP relative to the CIP.

In the above analysis, the dynamics of CIP separation is discussed in terms of an increase in rate with an increase in energy change. However, for time scales associated with the motion of solvent molecules this relationship may break down. Coupled to CIP separation is the concomitant reorganization of the solvent structure about the CIP so as to accommodate the SSIP. The relevant time scale for the solvent reorganization has not been established but may be of the order of the rotation correlation time of the solvent.<sup>13</sup> For the solvents listed in Table I, with the exception of ethanol, the rotation correlation times are less than 20 ps. However, one of ethanol's three relaxation times is long, 300 ps, which corresponds to the breaking of the hydrogen bond in the molecular aggregate followed by rotation. For CIP separation, it is anticipated that there should be significant restructuring of the hydrogen-bonding solvent. If the rate of back-electron transfer for the CIP is fast relative to solvent restructuring, then there should be little SSIP formation. Indeed, for TS/FN in

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ethanol, there occurs fast decay of the CIP via electron transfer,  $\tau_1 = 60$  ps, and no detectable SSIP formation.

**Salt Effect.** In the original investigation of Hughes and Ingold<sup>1</sup> into the unimolecular mechanism for the solvolysis of alkyl halides, the effect of added salt upon the rate of solvolysis was fundamental in elucidating the reaction mechanism. The salt effect was analyzed within a theoretical framework that paralleled the Debye-Hückel theory for the activity coefficient of an ion in the presence of an ionic medium. The Hughes-Ingold theoretical model assumed a permanent dipole moment for the transition state that would be stabilized by the interaction with surrounding ions. This analysis led to the relationship,

$$\log(k_1/k_1^0) = 0.916 \times 10^{16} \sigma c / \epsilon^2 T^2$$

where  $k_1$  is the rate of ionization in the presence of salt at a concentration  $c$ , and  $k_1^0$  is the rate in the absence of salt. The parameters  $\epsilon$ ,  $T$ , and  $\sigma$  represent the bulk dielectric constant of the solvent, temperature, and the degree of charge separation in the transition state, respectively. It was noted that the above relationship should be valid only in the low limit of salt concentration. Though the linear dependence of  $\log(k_1/k_1^0)$  upon the salt concentration  $c$  was found to hold for the solvolysis of *p*-tert-butylbenzhydride chloride, only two concentrations, 0.05 and 0.1 M, of sodium azide were employed. As noted by Winstein,<sup>2</sup> this relationship was "very inadequately tested".

Following this initial investigation, there was further activity in the area of the salt effect upon the solvolysis reactions, most notably the studies of Winstein and co-workers.<sup>16</sup> Surprisingly, the rate of solvolysis,  $k_1$ , of neophyl *p*-toluenesulfonate did not conform to the Hughes-Ingold relationship but rather  $k_1$  was found to be linear with concentration for a variety of added salts, leading to eq 1 for a normal salt effect. The slope of the linear plot  $k_1/k_1^0$

$$k_1 = k_1^0(1 + b[\text{salt}]) \quad (1)$$

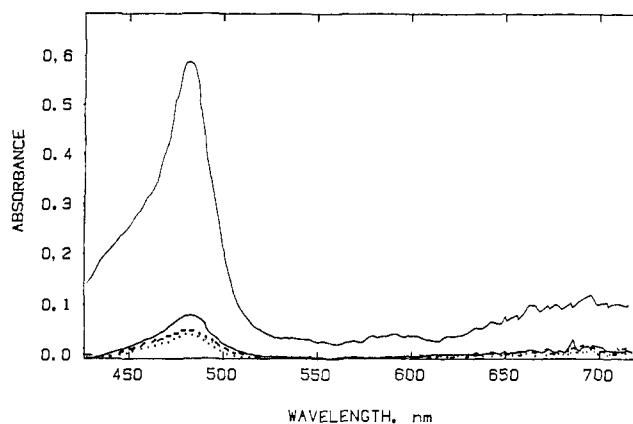
vs. [salt] is  $b$ , a constant that is dependent upon both the salt and solvent employed. This relationship was found to be general for a great variety of substrates, salts, and solvents. It must be emphasized, however, that this relationship is strictly empirical and has not been given theoretical justification. A special salt effect was also postulated to account for the large rate enhancements by very small concentrations of added salt. The prevention of return of the SSIP to the CIP by an ion-pair exchange reaction between the organic and salt ion pairs is believed to be the source of the special salt effect. The magnitude of the special salt effect is highly dependent on the types of ion pairs involved and also on the specific interactions between the ions and the solvent.

In recent years, there have been a limited number of investigations into the quenching of exciplex emission by inorganic salts. McCullough and Yeroushalmi<sup>17</sup> studied the quenching of 1-naphthionitrile/tetramethylethylene exciplex emission by LiClO<sub>4</sub> in DME. The authors proposed that the quenching mechanism was due to an ionic strength effect that enhanced the rate of ionic dissociation leading to a decrease lifetime of the exciplex. In a contrasting study, Tazuke<sup>18</sup> found that the quenching of exciplex emission of pyrene/*N,N*-dimethylaniline by quaternary ammonium salts, followed a Stern-Volmer relationship. This linear dependence, which has the same form as the Winstein relation for the normal salt effect, was taken as an indication that the quenching was bimolecular, proceeding through an association complex between the ammonium salt and the exciplex. Schuster<sup>19</sup> found a more complex behavior for the quenching of exciplex emission of pyrene/1,4-dicyanobenzene by tetra-*n*-butylammonium tetrafluoroborate in DME. At low salt concentration, the emission is quenched, but no free pyrene radical ions are observed. At 0.05 M salt, radical ion formation occurs. This led to the proposal that

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**Figure 4.** Transient absorption spectrum for *trans*-stilbene/fumaronitrile in dimethoxyethane as a function of LiClO<sub>4</sub> concentration at 4.2 ns: (—) 0.5 M, (---) 0.25 M, (···) 0.15 M. The intense peak, OD 0.6, is at 30 ps, the initial absorbance.

dipolar salt quenches exciplex emission through an undefined mechanism, and quadrupolar salt, due to aggregate formation, leads to ion-pair exchange producing free ions.

The TS/olefin complex is an ideal chemical system with which to investigate the nature of the influence of the salt upon the dynamics of the CIP as both  $k_{et}$  and  $k_{ips}$  can be directly monitored as a function of salt concentration. In accordance with the Winstein relationship for the normal salt effect, the increase in  $k_{et}$  is linear with increasing salt concentration (0–0.5 M), with a  $b$  value of  $4.4 \pm 0.4$  for both TS/FN and TS/DMF complexes in DME (Figure 2). Over this range in salt concentration, LiClO<sub>4</sub> exists as solvent-separated ion pairs or free ions.<sup>4</sup> For (*n*-Bu)<sub>4</sub>NClO<sub>4</sub>, the change in  $k_{et}$  is linear with an increase from 0 to 0.3 M salt and a  $b$  value of  $4.4 \pm 0.4$ . The salt effect decreases at higher concentrations of (*n*-Bu)<sub>4</sub>NClO<sub>4</sub> which may be attributed to possible ion aggregation.<sup>19</sup> Since the  $b$  coefficient is the same for both salts, LiClO<sub>4</sub> and *n*-Bu<sub>4</sub>NClO<sub>4</sub>, and independent of the olefin, this suggests that the increase in  $k_{et}$  is due to an ionic strength effect and not a specific interaction of the lithium cation with the CIP. This conclusion is further supported by the experiment where the addition of 12-crown-4, which specifically binds Li<sup>+</sup>, does not affect the  $b$  value for  $k_{et}$ . Finally the magnitude of the  $b$  coefficient is solvent dependent, in accordance with Winstein's observations. In Me<sub>2</sub>SO, the effect of LiClO<sub>4</sub> upon  $k_{et}$  for the CIP of TS/FN was not measurable ( $b \sim 0$ ).

For the  $k_{ips}$  of TS/FN, the  $b$  values are of the same magnitude,  $12 \pm 4$  for LiClO<sub>4</sub> and  $9 \pm 3$  for (*n*-Bu)<sub>4</sub>NClO<sub>4</sub>. The large range in  $b$  values reflects the inherently less accurate  $k_{ips}$  measurement. However, the  $b$  values for  $k_{ips}$  are greater than those for  $k_{et}$ . This implies that the normal salt effect is greater for ion-pair separation than for back-electron transfer. This is easily observed spectroscopically (Figure 4) by examining the [TS<sup>+</sup>] at longer times. At 4.2 ns, the TS<sup>+</sup> absorption for the TS/FN complex in DME is 14% of its initial absorbance in 0.5 M LiClO<sub>4</sub> and <3% in the absence of LiClO<sub>4</sub>. This effect can be rationalized in terms of the added salts increasing the ionic strength of the solution. As discussed earlier (Figure 3), the increased solvent polarity differentially stabilizes the SSIP more than the CIP, such that as the salt concentration is increased  $k_{ips}$  is accelerated more than  $k_{et}$ . The lack of a specific interaction for the Li<sup>+</sup> cation with the CIP causing an increase in ion-pair separation is again supported by the addition of 12-crown-4 having no effect upon the  $b$  value for  $k_{ips}$  of TS/FN in DME.

We therefore conclude that the decrease in the lifetime of the CIP upon the addition of salt is the result of an increase in  $k_{et}$  and a larger increase in  $k_{ips}$  resulting in an enhancement of solvent-separated ion-pair formation. The nature of this acceleration in  $k_{et}$  and  $k_{ips}$  appears to be due to an increase in the ionic strength and not a specific interaction of the cation with the CIP. Again

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we note the rather remarkable linear dependence of  $k_{et}$  and  $k_{ips}$  upon the concentration of salt ranging from 0 to 0.5 M for  $\text{LiClO}_4$ .

### Conclusions

The ground-state charge-transfer complex of *trans*-stilbene with electron-poor olefins is a chemical system that has yielded new information regarding the decay dynamics of the contact ion pair. For the decay via back-electron transfer there is a linear dependence of  $\ln k_{et}$  upon the solvent polarity parameter  $E_T$ . The rate of ion-pair separation is highly solvent dependent but could not be related to any particular solvent parameter. Finally both the rate of electron transfer and ion-pair separation are linear functions of ionic strength for the salts  $\text{LiClO}_4$  and  $(n\text{-Bu})_4\text{NClO}_4$  over the concentration range of 0–0.3 M salt.

Further studies will entail an examination of these processes as a function of temperature in order to obtain the thermodynamic activation parameters for ion-pair separation, quantities heretofore unknown.

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**Registry No.** *trans*-Stilbene–fumarionitrile, 70152-65-7; *trans*-stilbene–dimethyl fumarate, 98481-62-0; *trans*-stilbene–maleic anhydride, 63255-27-6.

## Electron-Donating Ability of Aliphatic and Aromatic Rings

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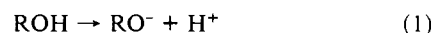
**Abstract:** Core-ionization energies and Auger kinetic energies of the halogens in halobenzenes and cyclohexyl halides and sulfur in thiophene, thiophenol, tetrahydrothiophene, and thiocyclohexanol have been used to determine the factors that affect the ability of the ring to accommodate a change in charge at the heteroatom in the ring or at a substituent position. This ability depends on the initial charge distribution in the molecule and on the rearrangement of this distribution when charge is added near the substituent. The results show that the aromatic ring is more electron withdrawing than the aliphatic ring. The effect of charge rearrangement is, however, nearly the same for both systems. Semiempirical calculations provide understanding of these results. The difference in initial-state charge distribution arises from the delocalization of  $\pi$ -electrons from the substituent to the ring. The lack of difference in charge rearrangement results from a cancellation of the effect of polarizability of the  $\pi$ -system in the aromatic ring by the effect of the greater number of electrons in the aliphatic system.

The ability of a molecule to accept charge at a particular site is a fundamental chemical property to which many other properties are closely related. Among these are acidity, basicity, ionization energy, rate of acid- and base-catalyzed reactions, and hydrogen bonding. This ability is closely related to the familiar concepts of electronegativity.

Organic chemists have devoted considerable effort to understanding this property in terms of field and resonance effects through the use of various  $\sigma$  parameters.<sup>2</sup> A somewhat different approach has been taken by physical and theoretical chemists, who have considered hydrogen-bond energies,<sup>3</sup> proton affinities,<sup>4–6</sup> gas-phase acidities,<sup>5,7,8</sup> and core-ionization energies<sup>9,10</sup> in terms of the effects of the charge distribution of the molecule before

reaction and the rearrangement of molecular charge as the reaction goes to completion.

We take acidity as an example to illustrate these ideas. We define  $A$  (for acidity) to be  $\Delta E$  for the reaction



and  $\Delta A$  to be the difference between the value of  $A$  for the compound of interest and that for some reference compound. We can divide  $\Delta A$  into two components, one  $\Delta V_A$ , an initial-state potential at the site of the acidic hydrogen due to the charge distribution in the unionized acids, and the other  $\Delta R_A$ , a final-state relaxation energy due to the rearrangement of charge on ionization. It can be seen that

$$\Delta A = -\Delta V_A - \Delta R_A \quad (2)$$

(The signs in eq 2 are easily understood. The more negative  $\Delta A$ , the stronger is the acid relative to the reference compound. A relatively positive potential at the hydrogen tends to force the hydrogen off; the negative of the potential is, therefore, a measure of acidity. The relaxation, or polarization effect, always favors the charge change, regardless of direction, and is, therefore, negative.) Similar expressions have been developed<sup>8,9,11,12</sup> for basicities,  $B$  (equal to the proton affinity), core-ionization energies,  $I$ , and Auger kinetic energies,  $K$

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(12) Expressions equivalent to eq 2, 3, and 4 have been presented in ref 8 and 9 and used in ref 5. The sign convention used here is different from that of the earlier references but is in keeping with the conventions now in use and is, in our opinion, easier to understand than the earlier convention.