Ultrafast Relaxation and Electron Transfer in Optically Prepared "Simple" Ion Pairs

Aldo Hörmann, Wlodzimierz Jarzeba,*,† and Paul F. Barbara*

Department of Chemistry, University of Minnesota, Minneapolis, Minnesota 55455

Received: November 10, 1994[⊗]

An extensive investigation of the ultrafast pump–probe spectroscopy of the charge-transfer band of the mesitylene/Br EDA complex and related complexes in various solvents and over a broad range of UV, visible, and near-IR probe wavelengths is described. The data allow for a measurement of the charge-recombination kinetics which exhibits a distribution of rate constants, including an initial very fast component ($\tau \approx 1$ ps), a factor of >1000 slower component, and intermediate-rate processes. The nonexponential kinetics may be associated with a distribution of arene$^+$/Br$^-$ acceptor geometries in the initially prepared state of the ion pair. The complex kinetics are discussed in terms of contemporary electron-transfer theory, which indicates that the most likely source of the dramatically nonexponential kinetics is an inner-sphere effect involving specific, configurationally dependent electronic interactions of the donor and acceptor. The reaction kinetics particularly at early times, is not strongly sensitive to solvent polarity or solvation dynamics, further supporting that mainly the donor/acceptor electronic interactions are dominating the kinetics. The data also reveal features due to the local transitions on the transient D$^+$ species in the ion pair and evidence of vibrationally unrelaxed absorption due to the initially re-formed complex subsequent to charge recombination.

Introduction

Ultrafast spectroscopy is leading to a new level of understanding of the dynamics of the primary events in electron-transfer reactions in solution. In particular, it is becoming possible to time resolve key dynamical processes such as solvation dynamics, vibrational relaxation, and even vibrational motion during the process of electron transfer. This is especially true for intramolecular electron-transfer reactions. The intramolecular case has been extensively investigated, and a close contact with theory has been established.[1–24] A detailed understanding of the role of vibrational and solvation dynamics is emerging. The situation is less developed for the more complex and less well studied intermolecular electron-transfer case, which is complicated by additional types of nuclear degrees of freedom, mainly reagent translational and rotational motions. Unfortunately, ordinary bimolecular electron transfer cannot be fruitfully investigated by ultrafast spectroscopy since the diffusion of the reagents is sufficiently slow that is washes out the ultrafast features of the dynamics.

The deleterious effects of diffusion can be circumvented by studying preformed reagent complexes, namely, electron donor–acceptor (EDA) complexes.[25–27] The optical excitation of the ground state of an EDA complex leads to formation of the geminate ion pair (D$^+$A$^-$), which subsequently can undergo both nonradiative charge recombination (k_{cr}) and separation (k_{sep}) to yield free ions:

$$D + A \overset{K}{\rightleftharpoons} [D/A] \underset{k_{cr}}{\overset{h\nu_{CT}}{\rightleftharpoons}} [D^+/A^-] \overset{k_{sep}}{\rightleftharpoons} D^+ + A^- \qquad (1)$$

Many time-resolved studies on EDA complexes have been published,[17,23,28–52] but we are concerned here with those that have sufficient time resolution to record the direct time domain consequences of vibrational, solvational dynamics, and reagent relative motion.[6–8,10,11,22,53–56] Detailed information on these processes would lead to a much better understanding of the microscopic aspects of intermolecular electron-transfer reactions. Ultrashort optical preparation of the ion pair is so rapid that it can prepare an ion pair with a highly nonequilibrium configuration of the donor, acceptor, and solvent sphere. The subsequent evolution including charge recombination, solvation dynamics, vibrational relaxation, molecular rotation, and translation of the ions, as well as ion separation, is a unique opportunity to resolve the nuclear motions that are involved in the actual event of electron transfer. Thus, experiments of this type are even relevant to the understanding of bimolecular reactions. In other words, ion pairs are intermediates along the reaction path of any bimolecular electron-transfer reaction. It should be noted that, while the specific nuclear and electronic configurations of the ion pairs that are created by optical excitation of EDA complexes may differ significantly from those involved in the ordinary bimolecular case, the investigation of this problem is directly relevant to how ions interact during an electron-transfer reaction. In particular, key issues in electron-transfer theory[57–61] arise in the investigation of EDA complexes, such as reaction adiabaticity, inner-sphere vs outer-sphere behavior, dynamical effects (solvation and vibrational),[3,18,62–64] and extraordinary complexity due to multiple excited states.[41,65,66]

The observed transient spectra can be extremely complex, and the individual steps in eq 1 may be a combination of processes. Charge recombination of the ion pair has been observed to be sufficiently fast to produce a significant nonequilibrium vibrational population in the donor, which can be observed in the transient spectra.[22] For example, the instantaneous photoexcited state has been reported to be only partially charge separated.[10,12,13] Subsequent vibrational and solvent relaxations are apparently necessary to produce the fully charge-separated ion pair D$^+$A$^-$.

Some evidence for a distribution of electron-transfer rates as a function of time and solvent configuration has been reported.[7,14] The kinetic role of contact vs solvent-separated ion

---

[†] Present address: Faculty of Chemistry, Jagiellonian University, Ingardena 3, 30-060 Krakow, Poland.

[⊗] Abstract published in *Advance ACS Abstracts,* January 15, 1995.

0022-3654/95/2099-2006$09.00/0

pairs has also been explored,[33-37,41,47,50,51,67-69] and electrolyte effects have been studied.[24]

An intriguing class of EDA complexes involve a halogen atom as the acceptor and various aromatic donors, including benzene (Bz) and methylated benzene derivatives. We will use the term arene throughout this paper to denote benzene and its methylated derivatives. This type of complex arises in photochemistry and radiation chemistry of halogen-containing precursors.[30,52,70] Such complexes have also been implicated in free-radical chlorination reactions.[40] In addition to aromatic donors, EDA complexes with simple alkane, alcohol, alkyl halide donors, and water have been studied and observed to have charge-transfer bands in the visible to ultraviolet region depending on the donor and halogen, i.e., Cl, Br, or I.[71,72]

We recently studied for the first time the ultrafast transient spectroscopy of the benzene/Br radical charge-transfer complex (Bz/Br).[54,56] From the standpoint of investigating the ultrafast processes involved in intermolecular electron transfer, the Bz/Br system is "simple", in principle, since the acceptor lacks molecular complexity, the donor is relatively small and conformationally simple, the charge-transfer band of Bz/Br is isolated from the locally excited states with much higher energy of the donor and acceptor, and, finally, the Bz/Br system lacks complications due to intersystem crossing. Intersystem crossing can be a complication when studying conventional D^+A^-, which are radical ion pairs which can be in the singlet or triplet state. Intersystem crossing and subsequent charge recombination in the radical ion pair can lead to population of locally excited triplets of the donor, but not in the Bz/Br system which is a doublet in the first two electronic states, DA and D^+A^-.[73]

An interesting related example of a charge-transfer complex, the ClO/Bz complex, was recently studied by Simon and coworkers.[28,29]

Ultrafast studies on the Bz/Br EDA complex in pure benzene and mixtures of Bz and other solvents revealed that the charge-recombination process is accelerated greatly at high Bz concentration.[54,56] Other studies have also seen charge-recombination rate enhancements at high donor concentrations.[38] The evidence for the Bz/Br system suggests that the rate acceleration is due to a complex involving a delocalized positive charge over both benzenes as shown in eq 2. The simpler process, charge recombination of the ion pair (eq 3), was observed to be considerably slower.[56]

$$D(D^+A^-) \xrightarrow{k_{cr}} D(DA) \tag{2}$$

$$D^+A^- \xrightarrow{k_{cr}} DA \tag{3}$$

The present paper is primarily concerned with the first detailed study of the charge recombination and dynamics of the process represented by eq 3. In order to investigate this process without complications from eq 2, it was necessary to study solutions at donor concentration ≤ 0.5 M and in some cases much lower. This was not possible with benzene as the donor since the equilibrium constant to form the Bz/Br complex is too small to obtain sufficient concentrations of the complex to study by ultrafast spectroscopy at the lower donor concentrations.[74] Fortunately, methylated benzenes such as mesitylene (Ms) form much stronger complexes[74] and can be investigated with good signal-to-noise ratio.

We present an extensive investigation of the ultrafast pump–probe spectroscopy of the charge-transfer band of the Ms/Br EDA complex and related complexes with other benzene derivatives in various solvents and over a broad range of UV, visible, and near-IR probe wavelengths. The main result of the paper is that the electron-transfer kinetics for charge recombination are not simple first order. The reaction is found to exhibit a distribution of rate processes over 3 orders of magnitude. The different kinetic components are interpreted as a manifestation of a distribution of arene$^+$/Br$^-$ geometries in the initially prepared state of the ion pair. The nature of these complex kinetics is discussed in terms of contemporary electron-transfer theory. The results are then related to the simple bimolecular reaction $Br^- + Bz^+$. The analysis suggests that strongly exothermic electron transfer involving organic ions may be quite different from the usual simple Marcus picture that applies for simple outer-sphere inorganic and organic electron-transfer reactions.[61]

Experimental Section

The experiments were performed with a laser system based on a synchronously pumped femtosecond dye laser and a regenerative Nd:YAG amplifier that resulted in 70–100-fs pulses at 790 nm, with an energy of 7–9 mJ/pulse and a 500-Hz repetition rate.[5] The pulses were used to generate a white light continuum in a 2-mm quartz cell through which water was flowed. The continuum was split into pump and probe pulses; their wavelengths could be independently varied between about 540 and 950 nm using 10-nm-bandwidth interference filters. Pump pulses were amplified in a two-stage dye amplifier and probe pulses in a one-stage amplifier. These amplifiers were pumped by the doubled output from the Nd:YAG regenerative amplifier. The time delay between the arrival of the pump and probe pulses was varied by changing the length of the optical path between them. The fwhm of the instrument response function measured using the optical Kerr effect in water was <150 fs. The pump–probe experiments were performed at the magic angle.

Br radicals were produced by photocleavage of α-bromoacetophenone,[52] using 100-ps, 7-mJ pulses at 355 nm obtained by frequency tripling of residual 1064-nm pulses from the regenerative amplifier. The time delay between the 355-nm synthesis pulse and pump–probe experiment was ~10 ns, allowing for the formation of the arene/Br complex. The experiment was performed in a 2-mm quartz cell through which the sample was circulating. The total volume of the circulating solution was 0.3–1 dm^3. The concentration of α-bromoacetophenone in all solutions was 0.05 M. The observed transient absorption kinetics was not dependent on α-bromoacetophenone concentration. α-Bromoacetophenone (98%, Aldrich and Lancaster) was used as received or recrystallized from hexanes or methanol, depending on the quality of the batch. All solvents were either of spectrophotometric or HPLC grade. Experiments were made at ambient temperature (21 °C).

There was only a weak pulse-duration-limited artifact observed when benzene or α-bromoacetophenone was not present in solution. The artifact is also observed when all three beams and all reagents are present. It was usually small enough, however, that it was negligible. This type of artifact appears as an absorption, a bleach, or some mixture of the two (with the shape of a derivative of the pulse), depending on experimental conditions. The type of artifact is due to a nonlinear optical interaction between the pump and probe, presumably due to phase modulation of the refractive index by the more intense pump pulse. The probe beam's frequency spectrum is altered by the time-varying refractive index induced by the pump. This frequency shift is detected as an apparent transient optical density change since the detection optics and/or sample has some static wavelength-dependent transmission, due for example to an optical filter installed before the detector. The artifact is a factor in some of the data because the magnitudes of the transient optical density changes are small, due to the small absorption of the Br/Ms complex, itself, and because many of the transients are recorded at the band edges where the transient optical density are small ($\Delta OD \leq 0.0005$) in some experiments. Due to the small signals, extensive signal averaging was required, in many cases for several hours for a single transient.

Experiments performed at a shorter or no delay between the UV synthesis pulse and the pump–probe experiment gave smaller signals, but the shapes of the transients were unaffected. This demonstrates that we were not probing secondary photoproducts other than arene/Br complexes.

Mesitylene/Br Complex

Static Absorption and Equilibrium Constant. Transient absorption studies have shown that Br atoms form a charge-transfer complexes with mesitylene (Ms) characterized by a broad charge-transfer absorption band centered at 525 nm (fwhm 6100 cm^{-1}).[70] Ms is a stronger electron donor ($I_D = 8.40$ eV)[75] than the more widely studied benzene ($I_D = 9.25$ eV)[75] and forms EDA complexes with different acceptors with formation constants of at least several times higher than those for respective benzene complexes. Based on analogy to other EDA complexes, DA as well as D(DA) complexes should be considered, as shown in eqs 4 and 5. The DA complex is the species of interest in this paper. Recent transient absorption studies gave

$$D + A \overset{K_1}{\rightleftharpoons} DA \qquad (4)$$

$$DA + D \overset{K_2}{\rightleftharpoons} D(DA) \qquad (5)$$

an estimate for K_1 of 59 dm^3/mol for Ms/Br in methanol, while K_2 was estimated to be 0.11 dm^3/mol.[74] In all of the transient absorption experiments reported herein the donor concentration was sufficiently low to ensure a bigger than 20:1 ratio of the DA to D(DA) complex. In several of the key experiments where it was particularly important to eliminate any complicating absorptions from D(DA), the Ms concentrations was ≤ 0.05 dm^3/mol, ensuring a bettter than 100:1 concentration ratio of DA to D(DA). These experiments were more difficult, however, since the DA concentration was lower and the resultant lower signal-to-noise ratio made it necessary to signal average for much longer periods.

Bleach Recovery Dynamics of Ms/Br in Methanol. Figure 1 portrays transient absorption kinetics of the Ms/Br EDA complex at ambient temperature in methanol at various probe wavelengths. The central wavelengths, 550 and 600 nm, exhibit an initial instantaneous bleach due to excitation of the charge-transfer band. This is followed by a recovery of ≈60% on the 1.2-ps time scale, an additional recovery to ≈80% on the ≈10-ps time scale, and slower recovery dynamics which will be discussed below. To ensure that these dynamics are due to the Ms/Br complex, and not complicated by high Ms concentration effects, we have studied the bleach-recovery dynamics at much lower Ms concentration. Figure 2 shows the transient spectroscopy of Br/Ms over a factor of 50 change in concentration. The kinetics are identical within experimental error, except at the highest concentrations and longest times where a small degree of Ms induced quenching is visible.[55]

The most likely interpretation of the bleach-recovery kinetics is charge recombination, i.e., ground-state return. Thus, the charge-recombination reaction occurs with a wide distribution of rate constants. Figure 3 shows the bleach-recovery dynamics

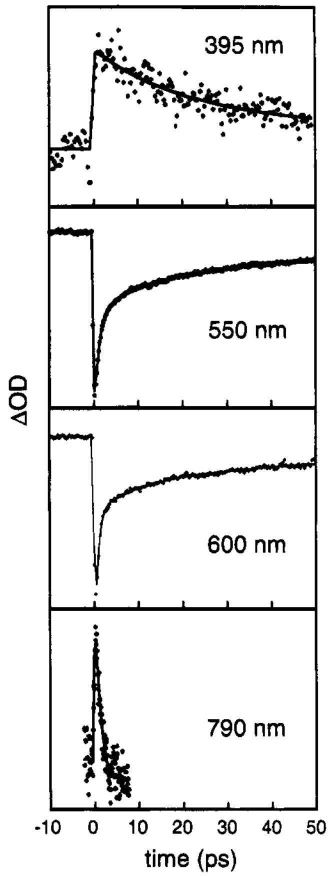

Figure 1. Transient absorption of Ms/Br complex in 0.5 M solution of mesitylene in methanol at 395, 550, 600, and 790 nm (pump wavelength 550 nm). Solid lines show multiexponential fits to the data (see parameters in Table 1).

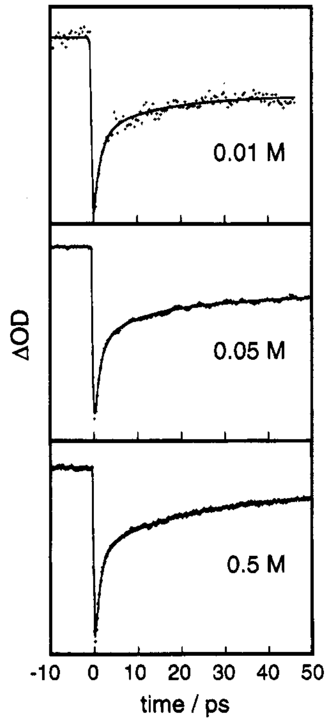

Figure 2. Bleach recovery of Ms/Br in methanol observed at 550 nm at various Ms concentrations after ultrafast 550-nm excitation.

of Ms/Br on the nanosecond time scale. In this figure the time spacing between points is too large to resolve the 1- and 10-ps decay components, but the longer decay component is now visible. For methanol, there is some evidence that the bleach

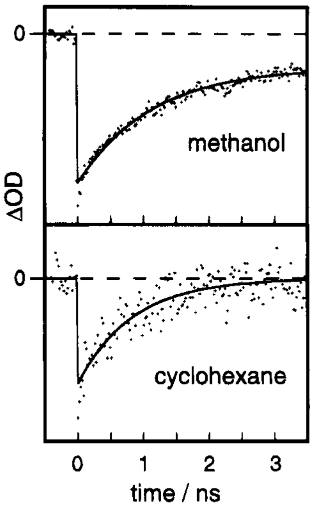

Figure 3. Bleach recovery of Ms/Br in methanol and cyclohexane on the nanosecond time scale. Ms concentration is 0.02 M, and pump and probe wavelengths are 550 nm.

TABLE 1. Best-Fit Parameters of Pump−Probe Transients of the Ms/Br Complex in Methanol at Different Mesitylene Concentrations *c* and Probe Wavelengths λ_{probe}[a]

λ_{probe}/nm	*c*/M	τ_1/ps	τ_2/ps	τ_3/ps	τ_{avg}/ps
390	0.5		16 (0.57)	100 (0.76)	
550	1.5	1.1 (0.66)	8.4 (0.18)	47 (0.16)	9.8
	1.0	1.1 (0.59)	9.8 (0.25)	59 (0.16)	12.5
	0.5	1.1 (0.60)	11.9 (0.18)	101 (0.22)	25.0
	0.3	1.2 (0.61)	14.5 (0.25)	≈200 (0.14)	32.4
	0.05	1.2 (0.51)	9.6 (0.19)	≥250 (0.31)	≥80
	0.02	(0.73)[b]		1100 (0.21)[c]	
600	0.5	0.6 (0.64)	10.2 (0.16)	100 (1.21)	
790	0.5	0.3 (−0.50)	1.0 (0.5)		

[a] Transients were fitted to one, two, or three exponentials with relaxation times τ_1, τ_2, and τ_3. The numbers in parentheses indicate the relative amplitudes *A* of the respective kinetic components. Negative amplitudes indicate a rising ΔOD component. τ_{avg} was calculated as $(A_1\tau_1 + A_2\tau_2 + A_3\tau_3)/(A_1 + A_2 + A_3)$. [b] No experiment was run to resolve the first two components. [c] After the 1100-ps recovery a residual bleach remained which accounted for ≈6% of the total signal.

TABLE 2. Best-Fit Parameters for Bleach Recovery of the Ms/Br Complex in Various Solvents at 0.05 M Mesitylene Concentration Observed at 550 nm after 550-nm Pump[a]

solvent	τ_1/ps	τ_2/ps	τ_3/ps
mesitylene	1.0		
propylene carbonate	1.2 (0.69)	6.4 (0.22)	135[b] (0.08)
cyclohexane	2.2 (0.64)	18.6 (0.17)	680[c] (0.19)
methanol	1.2 (0.51)	9.6 (0.19)	1100[c] (0.31)
acetonitrile[d]	1.3 (0.50)	7.4 (0.16)	>200[e] (0.34)
carbon tetrachloride		10.2 (0.42)	>200[e] (0.58)

[a] Transients were fitted to one, two, or three exponentials with relaxation times τ_1, τ_2, and τ_3. The numbers in parentheses indicate the relative amplitudes of the respective kinetic components. [b] Transient seems to return to base line within 250 ps. However, limited signal-to-noise ratio due to weak signal after 250 ps might prevent observation of slower components. [c] Relaxation time obtained from a 0.02 M mesitylene solution. [d] 5% acetone was added to prevent deposits on sample cell. [e] Maximum delay time between pump and probe was 250 ps in these experiments precluding an accurate determination of relaxation time.

recovery is not complete. Roughly, 6% bleach (including the fast and slow decay components) does not recover to Ms/Br. We assign the unrecovered component to separation of the ion pair to form free ions. In the case of cyclohexane full bleach recovery is observed.

Tables 1 and 2 summarize the results for the charge-recombination kinetics (electron-transfer times) and ion separation for the optically prepared ion pair state of Ms/Br in methanol and other solvents. The charge-recombination kinetics are extraordinarily time dependent as compared to typical photoinduced electron-transfer reactions. As discussed extensively below, we assign this extreme deviation from first-order behavior to a distribution of Ms^+/Br^- geometries in the initial (Franck−Condon) configuration of the complex. Thus, the initial distribution actually reflects a distribution of geometries in the equilibrated form of Ms/Br, which is frozen during the event of ultrafast optical excitation of the charge-transfer band. The coordinates of the Br atom relative to the Ms ring are the most obvious coordinates to explain this phenomenon. Theoretical calculations on halogen/aromatic complexes suggest that the Br coordinates should have a dramatic effect on the electronic interaction of the Br and Ms groups in the ion-pair state.[55] Furthermore, the force constants for the Br coordinates in the Ms/Br should be relatively small, so the Br coordinates should have a broad distribution in the equilibrated form of the Ms/Br complex.

Vibrationally Unrelaxed Absorption Transients, Excited-State Absorption, and the <1-ps Dynamics of Ms/Br in Methanol. In addition to the bleach-recovery dynamics, other spectral features are apparent in the ultrafast pump−probe spectroscopy of Ms/Br in methanol (Figure 1). At 790 nm, a short-lived absorption signal is observed. In Figure 4 this signal is shown on a shorter time scale, as is a lower signal-to-noise transient at 950 nm. Although the data is noisy and is distorted by significant contributions from the artifact mentioned in the Experimental Section, certain features are apparent. We have reproduced these observations on several occasions. The absorption signal appears with an apparent delay or rise time of ~300 fs. This rise time is obscured by the artifact and may be in error, nevertheless, the apparent rise time has been observed in multiple measurements, and it is also observed for other solvents and other donors. After the apparent delayed rise, the absorption signal decays and turns over to a small bleach. The bleach signal is probably due to the tail of the charge-transfer band which has recovery components on a much longer time scale; see above. The assignment of the weak long-time bleach to the charge-transfer band is confirmed below where other donors are described.

The most likely assignment of the 790-nm absorption transient is vibrationally excited Ms/Br complexes produced by the fastest component of the charge-recombination processes. Alternative interpretations will be discussed below. Transient absorption signals due to hot ground-state molecules produced by rapid ground-state return have been observed previously for charge-transfer bands of intramolecular donor/acceptor compounds as well as EDA complexes.[5,15,22] In the present situation, the vibrational relaxation rate of the hot ground-state molecules is apparently faster than the initial rate of charge recombination, since the delayed rise time is shorter than the electron-transfer time. Thus, the lifetime of the 790-nm absorption essentially reflects the electron-transfer process, while the rise time (~300 fs) manifests the vibrational relaxation dynamics. It is important to note that vibrational relaxation dynamics of charge-transfer bands due to rapid ground-state return can complicate the measurement of the electron-transfer rate. Previous results on the betaine system indicate absorption recovery at the band maximum is the least distorted by the vibrational relaxation dynamics and offer the best estimate for the electron-transfer kinetics.[5,15] The betaine system also indicates that, in addition to increased absorptions on the red edge, vibrationally-excited

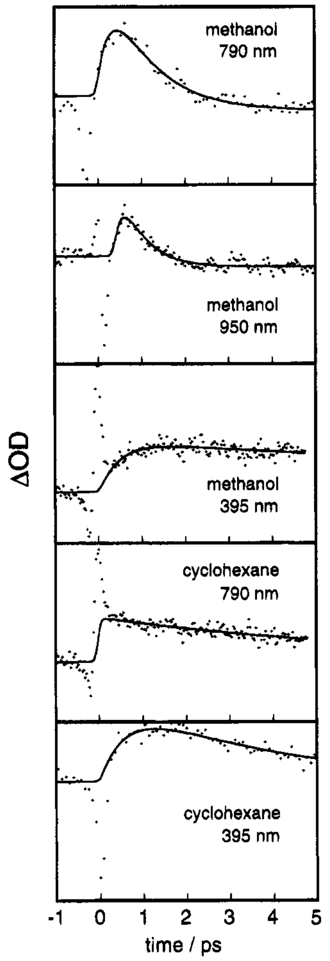

Figure 4. Transient absorptions of Ms/Br in methanol and cyclohexane at various probe wavelengths on the 5-ps time scale following ultrafast excitation at 550 nm. Ms concentration is 0.05 M, except at the 390-nm probe where it is 0.5 M.

ground states also are prominent on the blue (high energy) edge of the charge-transfer band. On the blue edge the hot molecules and subsequent cooling lead to a delay in the absorption recovery. This is apparently an important factor in the interpretation of the 395-nm probe data; see below.

The top panel in Figure 1 shows the transient absorption signal of Ms/Br probed in methanol at 395 nm. A measurement on a shorter time scale is shown in Figure 4. As in the case of the 790-nm data, the earliest time dynamics are obscured by the pump–probe artifact. After the artifact a clear delayed appearance of the absorption is observed. After the absorption signal is fully formed, it decays on a distribution of time scales, although the initial fast decay that is seen for 550 nm is not obvious. The 395-nm signal apparently probes both the blue tail of the charge-transfer complex and a local $\pi-\pi^*$ transition of Ms$^+$ in the ion pair. The $\pi-\pi^*$ transition has been observed in isolated arene cations previously ($\lambda_{max} = 475$ nm for Ms$^+$).[76] It is interesting that the 395-nm absorption, which should follow the kinetics of the ion-pair concentration if it were due to Ms$^+$ only, does not seem to show the initial decay that has been inferred by the bleach-recovery kinetics at 550 nm. This discrepancy between the 395- and 550-nm data is apparently due to the overlap of the $\pi-\pi^*$ absorption of Ms$^+$ in the ion pair and the blue edge of the charge-transfer absorption of the ground state of the complex. At early times, during the initial decay component of the electron transfer, the blue edge of the charge-transfer band has an apparent delayed rise due to vibrational relaxation effects. As mentioned above, delayed absorption components at the blue edge have been observed previously for charge-transfer bands. In the Ms/Br case the delay at the blue edge in the bleach recovery is apparently responsible for the delayed appearance of the 395-nm absorption. The complexity of the phenomena and the difficulty of these experiments make it exceedingly difficult to confirm these observations. Alternative interpretations are also possible; see below.

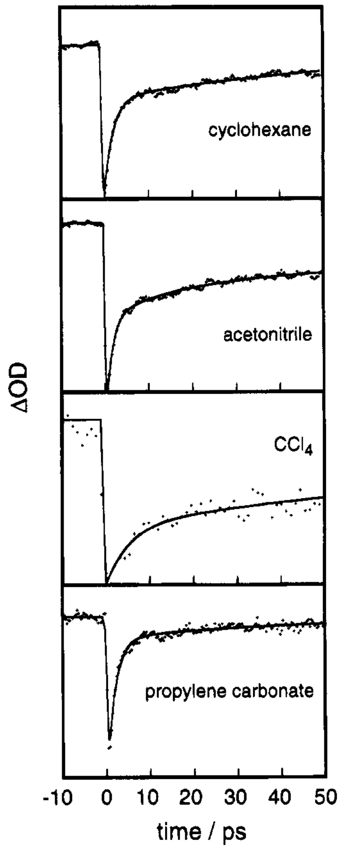

Figure 5. Transient bleach recovery observed at 550 nm of Ms/Br in various solvents. Ms concentration is 0.05 M.

Transient Spectroscopy of Ms/Br in Other Solvents. The bleach-recovery dynamics of Ms/Br in various solvents are shown in Figure 5. As in the case of methanol, a distribution of recovery times is apparent in the data. It is interesting that one of the solvents, CCl_4, lacks the fastest electron-transfer component that is observed in methanol and the other solvents. This is demonstrated in Figure 6. The component of ~1-ps recovery is absent for CCl_4 but clearly observed for propylene carbonate (Figures 5 and 6), methanol (Figure 4), and cyclohexane (Figure 5). Experiments on benzene and other donors also show that the ~1-ps component is missing for CCl_4.[56,74] Another chlorinated solvent, CH_2Cl_2, also suppresses the ~1-ps component in the one case studied (benzene). As discussed below, we believe that the CCl_4 effect should be ascribed to complexation of the solvent with the EDA complex, causing a change in the distribution of the donor/Br coordinates. Upon excitation of the complex the solvent effect on the structure of the complex is "copied" to the excited state by the ultrafast pump pulse. Thus, the initial geometry of the ion pair is altered, leading to an effect on the kinetics of ground-state return.

While CCl_4 seems to suppress the ~1-ps component, the solvent propylene carbonate actually amplifies the fast component. In propylene carbonate over 90% of the charge recombination occurs in ~20 ps while the remainder occurs much more slowly.

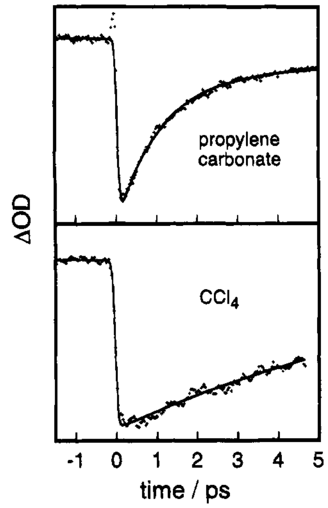

Figure 6. Comparison of early-time bleach recovery of Ms/Br in propylene carbonate and CCl_4.

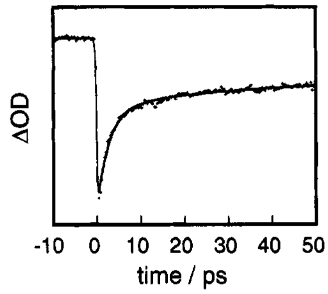

Figure 7. Transient bleach recovery of PMB/Br in methanol observed at 550 nm.

It is interesting to compare the least polar solvent studied, cyclohexane, to the more polar solvents, methanol, acetonitrile, and propylene carbonate. There is little effect of solvent polarity on the kinetics. For example, methanol and cyclohexane have nearly identical electron-transfer kinetics at early time. The long-time results are also similar within experimental error. As expected for a nonpolar solvent, the cyclohexane data lack a long-term bleach due to ion-pair separation which is observed in the more polar methanol. Despite the huge change in polarity, the time scales for the longest charge-recombination components are similar in cyclohexane and methanol.

Pentamethylbenzene/Br and Complexes with Other Donors

In an attempt to determine whether the different observations that were described in the previous section are specific to the Ms/Br complex or, alternatively, whether these effects are more general, we have investigated the pentamethylbenzene/Br (PMB/Br) charge-transfer complex. PMB is a stronger donor than Ms, and the absorption maximum of the Br atom complex is shifted to 565 nm.[70] In addition, the complex appears to have a significantly greater formation constant, since it was possible to study the complex at lower donor concentrations (0.005 M). Generally, the PMB results (Figures 7–9) are closely analogous to the Ms results. The bleach-recovery kinetics (Figures 7 and 8) in methanol exhibit kinetic components on the ~2-, ~13-, and >1000-ps time scales, with roughly the same amplitudes as for Ms/Br. The long-time bleach recovery kinetics were too slow to study with our spectrometer, but they show recovery on the nanosecond time scale with the possibility of a long-term bleach due to ion separation, as shown in Figure 8. As observed for Ms/Br, the fastest bleach-recovery component in methanol is considerably diminished in CCl_4; see Figure 9.

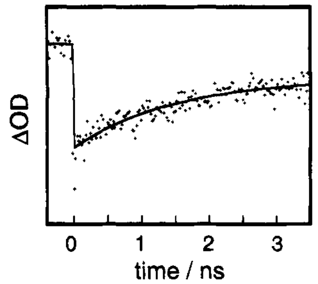

Figure 8. Long-term bleach of PMB/Br in methanol at 550 nm. PMB concentration is 0.005 M.

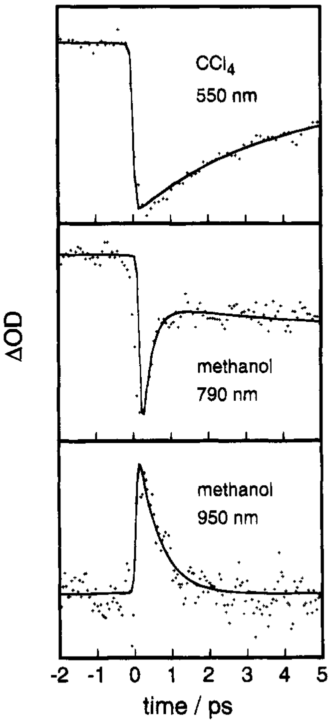

Figure 9. Transient absorptions of PMB/Br in methanol and CCl_4 at various wavelengths after ultrafast 550-nm excitation.

The transient data in the near-IR are particularly revealing. The 790-nm probe wavelength for PMB/Br in methanol probes on the red band edge on the charge-transfer absorption. This should be contrasted to the situation described above for Ms/Br, which has a more blue-shifted charge-transfer band. In the case of Ms/Br, 790 nm probes almost beyond the red band edge, Correspondingly, for PMB/Br the 790-nm transient is due to both bleach recovery and vibrational relaxation. After the laser-pulse-limited appearance of the bleach a very fast (~300 fs) recovery component is apparent. This recovery component is followed by a slight "overshoot" of the recovery which eventually evolves into the slowly recovering bleach component. The initial, fast bleach-recovery component should be assigned to absorption due to a combination of fast charge recombination and vibrationally unrelaxed ground state. There are two types of evidence that the vibrationally unrelaxed, "hot" absorption is contributing to the kinetics. First, the overshoot of the recovery followed by the decay of the overshoot is apparently due to the appearance and disappearance of the "hot" contribution to the absorption from the fast recombination process. Second, the observed time scale for the initial recovery, i.e., ~300 fs, is much shorter than the time scale for bleach recovery probed at 550 nm, i.e., ~2 ps. This behavior is very typical for bleach recovery followed by vibrational relaxation.[5,15]

An even longer probe wavelength, 950 nm, exhibits relatively more "hot" absorption signal and less bleach, as expected since this probe wavelength is far in the tail of the red edge of the charge-transfer absorption band. The "hot" absorption signal, which decays rapidly, is clearly apparent. The actual times for the transients are difficult to interpret. As the probe wavelength is increased, the time scale for the vibrational relaxation of the "hot" molecules should become faster since "redder" wavelengths probe "hotter" molecules. In addition, the dynamics of recovery may be correlated with the pump wavelength since different initial populations may exhibit significantly different absorption spectra. In other words, the charge-transfer absorption band may be inhomogeneously broadened. Although, studies on Bz/Br with different pump wavelengths suggest this is not the case.

Recent experiments on the Bz/Br complex reveal analogous behavior.[56] The benzene experiments, however, require higher donor concentrations due to a smaller formation constant for the complex and thus may be complicated by donor/donor interactions, as pointed out in the Introduction.

Finally, Jarzeba has recently observed bleach recovery kinetics at 550 nm for EDA complexes of Br with various donors at low concentration, including hexamethylbenzene, durene, *p*-xylene, and toluene.[74] All of these complexes exhibit a charge recombination on several time scales including an initial ~1-ps component.

Discussion

The Ion Pair Structure and the Multiexponential Kinetics. By analogy to the many other donor/acceptor complexes of various organic compounds and Br, the lowest excited state of arene/Br has been assigned to a charge-transfer state. Charge-transfer states between separate donors and acceptors are also equivalent to contact ion pairs in the limit of weak covalent interaction between the cation and anion. On the other hand, as the strength of the covalent interaction between the ions increase, the ion-pair description can become invalid. In the Mulliken description of charge-transfer states,[27] the nominal ion pair becomes inaccurate when the electron-exchange interaction between the ions is great enough to produce charge delocalization. Under those circumstances the ground and first excited states may be a mixture of both the D/A and D^+/A^- localized electronic states. *This type of electronic delocalization is consistent with the weak solvent dependence of the arene/Br charge-transfer band energy.*[70] *Another indication that the arene/Br complexes have very strongly interacting excited states is the large extinction coefficient, which is much larger than that typically observed for charge-transfer transitions between separate donors and acceptors.*[52] The state mixing and in turn the charge-transfer character have recently been shown to play an important role in electron-transfer processes of excited EDA complexes.[41,65,66]

The actual situation for arene/Br EDA complexes may even be more complex than simple charge delocalization would suggest. *Ab initio* calculations on Bz/Cl reveal strong covalent interactions between Cl and Bz in the ground state of the complex.[55] This interaction can even lead to a σ-radical-like complex rather than to a π complex, depending on the position of the Cl atom with respect to the benzene ring. The excited states of the σ complex are completely different than the excited states of the π complex, according to these calculations. While the σ complex is unlikely the ground state of the Bz/Br complex,[77] specific covalent interaction may become an important factor in the nominal charge-transfer state, which has a more reactive benzene ring. Thus, the very weak solvent dependence of the absorption energy of the charge-transfer band may indeed reflect some charge delocalization and strong covalent cation/anion interaction in the nominal charge-transfer state due to state mixing.

In addition to strong charge delocalization via mixing of the D/A and D^+A^- states, it is also important to consider the involvement of the locally excited states, D*A and DA*. An excited state of one of the partners can interact with the ground state of the other partner to produce an exciplex via charge-transfer interactions. For the arene/Br system the most likely candidate is the locally excited state of the arene. There are several known examples of polar exciplexes of locally excited aromatic donors and strong electron acceptors.[78,79] In the case of the arene/Br complexes, whether the locally excited state is strongly involved is unknown. The absorption spectrum of this type of complex seems to indicate that the locally excited state maintains its relatively high transition energy and identity, thus casting doubt on the locally excited-state exciplex interaction, but a more careful analysis and investigation are warranted.

It is interesting that the observed transient spectroscopy of the arene/Br complexes do vary with solvent, but the variations are not consistent with a conventional solvent polarity effect. The proposal that the "ion-pair state" is highly delocalized and that the donor and acceptor species are strongly interacting covalently is consistent with the lack of any obvious correlation of the ground-state recovery dynamics with the solvent polarity, which in turn affects the driving force.[41,42,48,61,65,69,80,81] For example, the kinetics for Ms/Br are nearly identical for methanol and cyclohexane, except for the ion separation yield. In addition, there is no evidence of a correlation of the charge recombination or relaxation dynamics with polar solvation dynamics, which varies tremendously with the solvents studied herein: acetonitrile, methanol, propylene carbonate, etc. Solvation dynamic effects have been observed for a variety of other systems including the charge recombination of betaine 30, an intramolecular donor/acceptor compound.[5,15,20] Analogous effects are not present for arene/Br.

The most obvious solvent effect observed for the arene/Br excited-state recovery kinetics is the diminution of the initial fast component in the chlorinated solvents, CCl_4 and CH_2Cl_2. Chlorinated solvents are known to interact with Br atoms differently than alkanes and alcohols.[71] The chlorinated solvents apparently form a π complex with Br atoms while the other solvents tend to form a conventional charge-transfer complex. It may be that a π type of interaction between the solvent and the Br atom in CCl_4 is responsible for a different equilibrium structure of the arene/Br complex in chlorinated solvents than in the other solvents investigated herein. For example, the chlorinated solvents may favor a different location of the Br atom over the benzene ring.

Theoretical calculations on the related Bz/Cl system show that the electronic structure, charge distribution, geometry, and other properties of the ground and excited states of the Bz/Cl complex vary dramatically with small sub-angstrom variation in the position of the Cl atom.[55] The structure switches between a σ and a π complex as the Cl−Bz geometry is only slightly varied. It seems reasonable to expect that such effects should have a profound effect on the rate of excited-state decay (charge recombination). Thus, by analogy to the Bz/Cl complex, the different kinetic components of the excited-state decay of the arene/Br complexes may be due to different initial Br−arene coordinates.

While the electronic structure of the Bz/Cl complex is extremely sensitive to Cl−benzene geometry, the variation in potential energy of the complex is relatively mild. It seems reasonable that solute/solvent interactions might be able to modify the ground-state geometry of the Bz/Cl complex and

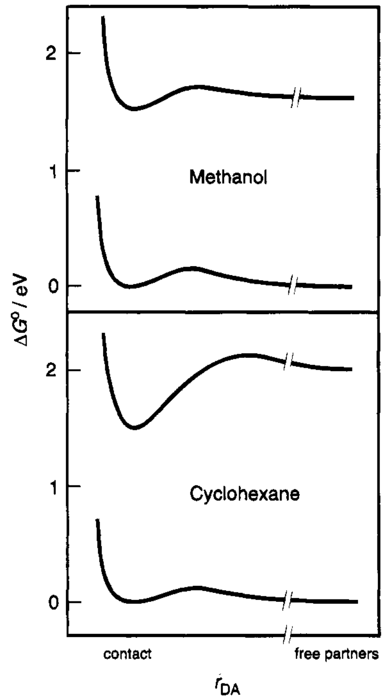

Figure 10. Schematic representation of standard free energy surfaces of Bz/Br and the Bz^+/Br^- ion pair in methanol and cyclohexane as a function of the Br−Bz separation. Note the difference of the energies of the free ion pair in polar and nonpolar solvents. The free energy difference between the Bz/Br complex and the separated Bz and Br is close to zero, corresponding to an equilibrium constant of 0.4.[74] The energies of the contact ion pair and of the free ions were estimated as outlined in the Appendix. All activation barriers are for illustrative purposes only, and their heights do not reflect actual values. A solvent-separated ion pair is not considered in this graph.

analogously the arene/Br complexes. This may explain the variation in the importance of the different rate processes as a function of solvent.

Relationship to the Bimolecular Electron Transfer and Conventional Models for Electron Transfer. Figure 10 is a schematic representation of the energetics of the charge-transfer complex and the ion-pair state as a function of the Br−Bz separation in a polar (acetonitrile) and nonpolar solvent (CCl_4 or cyclohexane). The energies of the separated ions were estimated by the methods described in the Appendix. The energy of the ion-pair state of the complex, which we denote as contact ion pair, was crudely approximated by using the spectroscopic energy of the red band edge of the charge-transfer complex (i.e., ~800 nm), which for arene/halogen complexes is known to not vary strongly with solvent.[70]

The relative energies of the contact ion pair and the free ions in polar solvent are consistent with the observation of charge separation to yield free ions in the polar solvent methanol. As expected from the relative energetics in nonpolar solvents, no separation of the ions occurs or is possible.

For nonpolar solvents the nominal contact ion pair energy, as determined spectroscopically ($\approx$1.5 eV), is considerably lower than predictions ($\approx$2 eV) based on the methods outlined in the Appendix which predict the energy of a pure ion pair structure. The apparent additional stabilization must reflect the interaction energy of the complex, probably as a result of charge delocalization and perhaps additional covalent interactions as a result of specific binding effects involving a rearrangement of the benzene ring and developing σ-bonding character.

The estimate for the ion-pair energy in polar solvents using the results above for the separated ions and an additional Coulomb term gives a value ($\approx$1.4 eV) which is similar to the spectroscopic value. This may be a coincidence, since the Bz/Br electronic interactions may be so strong that they dictate the energy of the excited complex.

One of the exciting aspects of the arene/Br system is that it potentially offers spectroscopic information on contact ion pairs, which themselves are important intermediates in electron-transfer reactions in solution; see Introduction. Conventional nonadiabatic electron-transfer theory involves diffusion of the free ions together to form a contact ion pair, followed by charge transfer in the ion pair. In Figure 10 this would involve starting at large separation in the free ion states and then remaining on the first excited surface until the contact ion pair is formed. Finally, electron transfer occurs; i.e., the system undergoes radiationless decay. However, the states in Figure 10 are not the diabatic states of conventional electron-transfer theory; rather, they apparently represent adiabatic states that may already be strongly mixed Bz/Br $\leftrightarrow$ Bz^+/Br^-.

Due to the strong mixing, i.e., charge delocalization, the actual event of electron transfer could in principle precede the formation of the contact ion pair. The branching ratio of forming the contact ion pair state vs electron transfer from a more separated configuration of the ions, a so-called encounter complex (or potentially a solvent-separated ion pair), depends on both the formation rate of the contact ion pair and the rate of electron transfer in the encounter complex, which is probably at most 10^9 s^{-1}, the slowest rate process observed in the present experiments for the contact ion pair. The key issue here is whether the formation of the contact ion pair is rapid compared to this rate or whether it is slow due to a barrier to formation of the contact ion pair from the encounter complex. The energetics in Figure 10 suggest that the overall process of forming the contact ion pair is energetically downhill, making a small barrier plausible in both polar and nonpolar solvents. This would suggest that the contact ion pair is an intermediate in the electron transfer of the separated ions.

Another potential difference between the arene/Br system and the conventional, so-called outer-sphere model for electron transfer is the evidence that the arene/Br contact ion pair involves strong covalent interactions between the ions leading to a rearranged structure and large changes in the vibrational modes. Thus, this back electron transfer should be classified as an inner-sphere reaction, rather than the simpler outer-sphere class.

Conclusions and Summary

This paper reports an extensive investigation of the ultrafast pump−probe spectroscopy of the charge-transfer band of the Ms/Br EDA complex and related complexes with other benzene derivatives in various solvents and over a broad range of UV, visible, and near-IR probe wavelengths. In addition to the charge-recombination kinetics, which were measured by absorption recovery, the spectroscopy also reveals features due to the locally excited transitions on the transient D^+ species in the ion pair and clear evidence of vibrationally unrelaxed absorption features in the initially re-formed complex subsequent to charge recombination. One of the main results of the paper is that the electron-transfer kinetics for charge recombination are not simple first order. Rather, the reaction has a distribution of rate processes, including an initial very fast component ($>10^{12}$ s^{-1}) and a factor of >1000 slower component. The slowest component of electron transfer is sufficiently slow that it is difficult to obtain a reliable value for its rate constant due to complications from eq 2 and other kinetic processes.

The different kinetic components may be associated with a distribution of arene−Br geometries in the initially prepared state of the ion pair. Interestingly, the initial distribution can apparently be altered by varying the solvent which, in turn, alters the equilibrium arene/Br complex structure, i.e., the precursor to the optically prepared ion pair. The nature of these complex kinetics is discussed in terms of contemporary electron-transfer theory which indicates the reaction should be classified as an inner-sphere reaction. It is concluded that the most likely source of the dramatically nonexponential kinetics is an inner-sphere effect involving specific, configurationally dependent electronic interactions of the donor and acceptor. This may be a common feature of bimolecular organic electron transfer reactions in solution, even though it has rarely been identified. Unexpectedly, the reaction kinetics, particularly at early times, is not strongly sensitive to solvent polarity or solvation dynamics, further supporting that the acceptor/donor electronic interactions are dominating the kinetics.

The results of this paper suggest that the mechanism of strongly exothermic electron transfers involving organic ions may be quite different from the usual simple Marcus picture that applies for simple outer-sphere electron-transfer reactions.

Acknowledgment. This research was supported by the Basic Energy Sciences program of the Department of Energy. A.H. thanks the Swiss National Science Foundation for a postdoctoral grant.

Appendix

The standard free enthalpy $\Delta G^{\ominus}_{\rm SI}$ of the two separated ions $\rm Bz^+$ and $\rm Br^-$ with respect to the free energy of the neutral precursors Bz and Br can be approximated as the difference of their respective standard oxidation and reduction potentials, eq A1.

$$\Delta G^{\ominus}_{\rm SI} = e(E^{\ominus}_{\rm Bz^+/Bz} - E^{\ominus}_{\rm Br/Br^-}) \qquad \text{(A1)}$$

While the standard oxidation potential of many aromatic hydrocarbons in acetonitrile have been published,[82] the situation is more complicated for the standard reduction potential of the acceptor because it involves the Br radical. However, from a thermodynamic cycle that includes the Br radical in the gas phase, liquid $\rm Br_2$, and $\rm Br_2$ in solution, we can estimated $E^{\ominus}_{\rm Br/Br^-} = 1.31$ V. In this estimate we assumed that the free enthalpy change in transferring the Br radical from solution to gas phase is small and roughly cancels out the free enthalpy of formation of $\rm Br_2$ in solution. The free enthalpy of formation of Br radicals in the gas phase,[83] and the standard reduction potential of $\rm Br_2/Br^-$ is known.[84]

Using this estimate and the standard oxidation potential of benzene (2.86 V),[82] we obtain $\Delta G^{\ominus}_{\rm SI} = 1.55$ eV in acetonitrile.

To estimate $\Delta G^{\circ}_{\rm SI}$ for other solvents, we apply a Born-type expression (eq A3),[7]

$$\Delta G^{\ominus}_{\rm SI}(\text{solvent}) = \Delta G^{\ominus}_{\rm SI}(\rm CH_3CN) + \Delta G_s \qquad \text{(A2)}$$

$$\Delta G_s = \frac{e^2}{8\pi\epsilon_0}\left(\frac{1}{r_+} + \frac{1}{r_-}\right)\left(\frac{1}{\epsilon_r} - \frac{1}{37.5}\right) \qquad \text{(A3)}$$

where r_+ and r_- are the radii of $\rm Bz^+$ and $\rm Br^-$, respectively, and ϵ_r is the dielectric constant of the solvent. Assuming[83] $r_- = 196$ pm and $r_+ = 250$ pm, we obtain $\Delta G^{\ominus}_{\rm SI} \approx 4$ eV for cyclohexane and 1.6 eV for methanol.

The free enthalpy $\Delta G^{\ominus}_{\rm CIP}$ of the $\rm Bz^+/Br^-$ contact ion pair (with respect to the neutral precursors Bz and Br) can be estimated from the free enthalpy of the separated ions by adding the Columb energy release (eq A4). This approximation is valid in the limit of weak covalent interactions between Bz and Br and between $\rm Bz^+$ and $\rm Br^-$.

$$\Delta G^{\ominus}_{\rm CIP} = \Delta G^{\ominus}_{\rm SI} - \frac{e^2}{4\pi\epsilon_0\epsilon_r r_{\rm DA}} \qquad \text{(A4)}$$

Equation A4 is valid for any solvent. $r_{\rm DA}$ denotes the distance between the ions in the contact ion pair. *Ab initio* calculations on the Bz/Cl complex predict a distance of 270 pm between the Cl atom and the benzene plane.[55] Using this value for $r_{\rm DA}$ in the $\rm Bz^+/Br^-$ contact ion pair, we obtain $\Delta G^{\ominus}_{\rm CIP} = 1.4$ eV in methanol and $\Delta G^{\ominus}_{\rm CIP} = 2.0$ eV in cyclohexane.

References and Notes

(1) Bagchi, B.; Fleming, G. R. *J. Phys. Chem.* **1990**, *94*, 9.

(2) Barbara, P. F.; Jarzeba, W. *Adv. Photochem.* **1990**, *15*, 1.

(3) Barbara, P. F.; Walker, G. C.; Smith, T. P. *Science* **1992**, *256*, 975.

(4) Fonseca, T. *J. Chem. Phys.* **1989**, *91*, 2869.

(5) Johnson, A. E.; Levinger, N. E.; Jarzeba, W.; Schlief, R. E.; Kliner, D. A. V.; Barbara, P. F. *Chem. Phys.* **1993**, *176*, 555.

(6) Mataga, N.; Kanda, Y.; Okada, T. *J. Phys. Chem.* **1986**, *90*, 3880.

(7) Mataga, N.; Shioyama, H.; Kanda, Y. *J. Phys. Chem.* **1987**, *91*, 314.

(8) Mataga, N.; Nishikawa, S.; Asahi, T.; Okada, T. *J. Phys. Chem.* **1990**, *94*, 1443.

(9) *Dynamics and Mechanisms of Photoinduced Transfer and Related Phenomena*; Mataga, N., Okada, T., Masuhara, H., Eds.; Elsevier: Amsterdam, 1992.

(10) Miyasaka, H.; Ojima, S.; Mataga, N. *J. Phys. Chem.* **1989**, *93*, 3380.

(11) Miyasaka, H.; Tabata, A.; Kamada, K.; Mataga, N. *J. Am. Chem. Soc.* **1993**, *115*, 7335.

(12) Ojima, S.; Miyasaka, H.; Mataga, N. *J. Phys. Chem.* **1990**, *94*, 4147.

(13) Ojima, S.; Miyasaka, H.; Mataga, N. *J. Phys. Chem.* **1990**, *94*, 5834.

(14) Ojima, S.; Miyasaka, H.; Mataga, N. *J. Phys. Chem.* **1990**, *94*, 7534.

(15) Reid, P. J.; Barbara, P. F. *J. Phys. Chem.*, submitted.

(16) Reid, P. J.; Silva, C.; Barbara, P. F.; Karki, L.; Hupp, J. T. *J. Phys. Chem.*, in press.

(17) Rentzepis, P. M.; Steyert, D. W.; Roth, H. D.; Abelt, C. J. *J. Phys. Chem.* **1985**, *89*, 3955.

(18) Rossky, P. J.; Simon, J. D. *Nature* **1994**, *370*, 263.

(19) Tominaga, K.; Walker, G. C.; Kang, T. J.; Barbara, P. F. *J. Phys. Chem.* **1991**, *95*, 10485.

(20) Walker, G. C.; Akesson, E.; Johnson, A. E.; Levinger, N. E.; Barbara, P. F. *J. Phys. Chem.* **1992**, *96*, 3728.

(21) Wasielewski, M. R. *Chem. Rev.* **1992**, *92*, 435.

(22) Wynne, K.; Galli, C.; Hochstrasser, R. M. *J. Chem. Phys.* **1994**, *100*, 4797.

(23) Yabe, T.; Kochi, J. K. *J. Am. Chem. Soc.* **1992**, *114*, 4491.

(24) Thompson, P. A.; Simon, J. D. *J. Am. Chem. Soc.* **1993**, *115*, 5657.

(25) Foster, R. *Organic Charge Transfer Complexes*; Academic: New York, 1969.

(26) Foster, R. *J. Phys. Chem.* **1980**, *84*, 2135.

(27) Mulliken, R. S.; Person, W. B. *Molecular Complexes*; Wiley-Interscience: New York, 1969.

(28) Dakhnovskii, Y. I.; Doolen, R.; Simon, J. D. *J. Chem. Phys.* **1994**, 101, 6640.

(29) Doolen, R.; Simon, J. D. *J. Am. Chem. Soc.* **1994**, *116*, 1155.

(30) Bühler, R. E. *Radiat. Res. Rev.* **1972**, *4*, 233.

(31) Bockman, T. M.; Karpinski, Z. J.; Sankararaman, S.; Kochi, J. K. *J. Am. Chem. Soc.* **1992**, *114*, 1970.

(32) Förgeteg, S.; Bérces, T. *J. Photochem. Photobiol. A: Chem.* **1993**, *73*, 187.

(33) Gould, I. R.; Ege, D.; Mattes, S. L.; Farid, S. *J. Am. Chem. Soc.* **1987**, *109*, 3794.

(34) Gould, I. R.; Moody, R.; Farid, S. *J. Am. Chem. Soc.* **1988**, *110*, 7242.

(35) Gould, I. R.; Moser, J. E.; Armitage, B.; Farid, S. *J. Am. Chem. Soc.* **1989**, *111*, 1917.

(36) Gould, I. R.; Young, R. H.; Moody, R. E.; Farid, S. *J. Phys. Chem.* **1991**, *95*, 2068.

(37) Gould, I. R.; Farid, S. *J. Phys. Chem.* **1992**, *96*, 7635.

(38) Gould, I. R.; Farid, S. *J. Am. Chem. Soc.* **1993**, *115*, 4814.

(39) Hilinski, E. F.; Masnovi, J. M.; Amatore, C.; Kochi, J. K.; Rentzepis, P. M. *J. Am. Chem. Soc.* **1983**, *105*, 6167.

(40) Ingold, K. U.; Lusztyk, J.; Raner, K. D. *Acc. Chem. Res.* **1990**, *23*, 219.

(41) Gould, I. R.; Young, R. H.; Mueller, L. J.; Farid, S. *J. Am. Chem. Soc.* **1994**, *116*, 8176.

(42) Gould, I. R.; Noukakis, D.; Gomez-Jahn, L.; Young, R. H.; Goodman, J. L.; Farid, S. *Chem. Phys.* **1993**, *176*, 439.

(43) Masnovi, J. M.; Kochi, J. K.; Hilinski, E. F.; Rentzepis, P. M. *J. Phys. Chem.* **1985**, *89*, 5387.

(44) Masnovi, J. M.; Kochi, J. K.; Hilinski, E. F.; Rentzepis, P. M. *J. Am. Chem. Soc.* **1986**, *108*, 1126.

(45) Hilinski, E. F.; Masnovi, J. M.; Kochi, J. K.; Retzepis, P. M. *J. Am. Chem. Soc.* **1984**, *106*, 8071.

(46) Angel, S. A.; Peters, K. S. *J. Phys. Chem.* **1991**, *95*, 3606.

(47) Goodman, J. L.; Peters, K. S. *J. Am. Chem. Soc.* **1985**, *107*, 6459.

(48) O'Driscoll, E.; Simon, J. D.; Peters, K. S. *J. Am. Chem. Soc.* **1990**, *112*, 7091.

(49) Pienta, N. J.; Kessler, R. J.; Peters, K. S.; O'Driscoll, E. D.; Arnett, E. M.; Molter, K. E. *J. Am. Chem. Soc.* **1991**, *113*, 3773.

(50) Peters, K. S.; Lee, J. *J. Phys. Chem.* **1992**, *96*, 8941.

(51) Peters, K. S.; Lee, J. *J. Am. Chem. Soc.* **1993**, *115*, 3643.

(52) McGimpsey, W. G.; Scaiano, J. C. *Can. J. Chem.* **1988**, *66*, 1474.

(53) Jarzeba, W.; Hörmann, A.; Barbara, P. F. *Ultrafast Phenom.*, in press.

(54) Jarzeba, W.; Schlief, R. E.; Barbara, P. F. *J. Phys. Chem.* **1994**, *98*, 9102.

(55) Jarzeba, W.; Thakur, K. A. M.; Hörmann, A.; Barbara, P. F. *J. Phys. Chem.* **1995**, *99*.

(56) Schlief, R. E.; Jarzeba, W.; Thakur, K. A. M.; Alfano, J. C.; Barbara, P. F. *J. Mol. Liq.* **1994**, *60*, 201.

(57) Song, X.; Marcus, R. A. *J. Chem. Phys.* **1993**, *99*, 7768.

(58) Marcus, R. A.; Sutin, N. *Biochem. Biophys. Acta* **1985**, *811*, 265.

(59) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155.

(60) Sumi, H.; Marcus, R. A. *J. Chem. Phys.* **1986**, *84*, 4894.

(61) Newton, M. D.; Sutin, N. *Annu. Rev. Phys. Chem.* **1984**, *35*, 437.

(62) Maroncelli, M.; MacInnis, J.; Fleming, G. R. *Science* **1989**, *243*, 1674.

(63) Bixon, M.; Jortner, J. *Chem. Phys.* **1993**, *176*, 467.

(64) Jortner, J.; Bixon, M. *J. Chem. Phys.* **1988**, *88*, 167.

(65) Gould, I. R.; Young, R. H.; Mueller, L. J.; Albrecht, A. C.; Farid, S. *J. Am. Chem. Soc.* **1994**, *116*, 8188.

(66) Gould, I. R.; Young, R. H.; Mueller, L. J.; Albrecht, A. C.; Farid, S. *J. Am. Chem. Soc.* **1994**, *116*, 3147.

(67) Goodman, J. L.; Peters, K. S. *J. Am. Chem. Soc.* **1986**, *108*, 1700.

(68) Peters, K. S.; Li, B. *J. Phys. Chem.* **1994**, *98*, 401.

(69) Li, B.; Peters, K. S. *J. Phys. Chem.* **1993**, *97*, 13145.

(70) Raner, K. D.; Lusztyk, J.; Ingold, K. U. *J. Phys. Chem.* **1989**, *93*, 564.

(71) Alfassi, Z. B.; Huie, R. E.; Mittal, J. P.; Neta, P.; Shoute, L. C. T. *J. Phys. Chem.* **1993**, *97*, 9120.

(72) Treinin, A.; Hayon, E. *J. Am. Chem. Soc.* **1975**, *97*, 1716.

(73) The maximum of the charge-transfer band of the Bz/Br complex is located at ≈550 nm (220 kJ mol^{-1}), which is at much lower energy than the triplet state of benzene (E_T = 352 kJ mol^{-1}; Carmichael, I.; Hug, G. L. In *Handbook of Organic Photochemistry*; Scaiano, J. C., Ed.; CRC Press: Boca Raton, FL, 1989; Vol. 1) making intersystem crossing energetically unfavorable.

(74) Jarzeba, W. Manuscript in preparation.

(75) Watanabe, K.; Nakayama, T.; Mottl, J. *J. Quant. Spectrosc. Radiat. Transfer* **1962**, *2*, 369.

(76) Sehested, K.; Holcman, J.; Hart, E. J. *J. Phys. Chem.* **1977**, *81*, 1363.

(77) Benson, S. W. *J. Am. Chem. Soc.* **1993**, *115*, 6969.

(78) *The Exciplex*; Gordon, M., Ware, W. R., Eds.; Academic Press: New York, 1975.

(79) Beens, H.; Weller, A. In *Organic Molecular Photophysics*; Birks, J. B., Ed.; Wiley: London, 1975; Vol. 2.

(80) Gould, I. R.; Noukakis, D.; Goodman, J. L.; Young, R. H.; Farid, S. *J. Am. Chem. Soc.* **1993**, *115*, 3830.

(81) Weller, A.; Schäfer, F. P.; Röllig, K.; Knibbe, H. *J. Chem. Phys.* **1967**, *47*, 1184.

(82) Howell, J. O.; Goncalves, J. M.; Amatore, C.; Klasinc, L.; Wightman, R. M.; Kochi, J. K. *J. Am. Chem. Soc.* **1984**, *106*, 3968.

(83) *Handbook of Chemistry and Physics*, 66th ed.; Weast, R. C., Ed.; CRC Press: Boca Raton, FL, 1985–1986.

(84) *Encyclopedia of Electrochemistry of the Elements*; Bard, A. J., Ed.; Marcel Dekker: New York, 1973; Vol. 1.

JP943029W