Solvent, Isotope, and Substituent Effects on the Bimolecular Electron Transfer Reaction between Chlorine Oxide and Benzenes

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The rate of back electron transfer following photoexcitation of ground-state complexes between ClO and aromatic molecules in nitrile solvents is examined. Both solvent effects on a single molecular complex and a series of complexes within a single solvent are analyzed in terms of commonly used theoretical models. For a single molecular complex (ClO-benzene), the rate of back electron transfer decreases with decreasing solvent dielectric constant and is temperature independent. This indicates that the reaction rate decreases with increasing exothermicity, behavior consistent with that expected for reactions in the Marcus inverted region. Investigation of the dependence of the reaction rate on exothermicity using a series of substituted benzenes as acceptor molecules in a single solvent revealed increasing reaction rates with increasing driving force, opposite to that observed upon varying solvent. Studies of deuteration effects on the reaction rate constant suggest that the origin of these disparate predictions arises from the assumptions made in carrying out the data analysis on the series of donor-acceptor complexes studied. In particular, both the inner-sphere and outer-sphere contributions to the reorganization energy are not constant for the set of molecules studied. This study demonstrates the difficulty in extracting accurate information on the reaction exothermicity, reorganization energy, and electronic coupling from measured rate constants.

Introduction

Electron-transfer reactions play a central role in chemistry. Due to their fundamental importance, there continues to be a great deal of theoretical¹⁻¹⁰ and experimental¹¹⁻²³ work dedicated to understanding the nature of electron-transfer kinetics in solution. In the adiabatic limit, electron-transfer reactions are considered to be thermally activated processes where the rate is related to the height of the reaction barrier. Quantum mechanical effects are assumed to be negligible. The rate constant, $k_{\rm et}$, is expressed as

$$k_{\rm et} = A \exp(-\Delta G^{\ddagger}/k_{\rm B}T) \tag{1}$$

where $k_{\rm B}$ is the Boltzmann constant, *T* is the temperature, ΔG^{\ddagger} is the height of the barrier, and *A* is the frequency factor. Marcus demonstrated that the barrier height can be related to the reaction exothermicity, ΔG° , and the reorganization energy, λ , by the following expression.¹

$$\Delta G^{\ddagger} = (\Delta G^{\circ} - \lambda)^2 / 4\lambda \tag{2}$$

The reorganization energy is the energy difference between the reactants at equilibrium and the reactants in the equilibrium solvation of the products. It is common to separate λ into contributions from the solvent, λ_s , and the reactants, λ_v ($\lambda = \lambda_s + \lambda_v$).

Combining eqs 1 and 2, one sees that the rate of electron transfer will increase with increased driving force as long as $-\Delta G^{\circ} < \lambda$. When $-\Delta G^{\circ} > \lambda$, the rate decreases with increasing driving force. This region of the exothermicity plot is referred to as the Marcus inverted region. In recent years,

several experimental studies have confirmed this predicted decrease in reaction rate constant with increasing exothermicity.¹¹⁻²³ However, most of the experimental observations exhibit behavior that cannot be explained as a thermally activated process. Many reactions that occur in the inverted region exhibit temperature-independent rates. In addition, the shapes of the plots of reaction rate versus exothermicity are not symmetric around the maximum. The observed falloff of the reaction rate with increasing exothermicity is generally less than that predicted by the parabolic dependence of eq 2. Accounting for the experimental difference of reactions that occur in the normal and inverted regions has been the subject of many theoretical studies.⁴⁻⁹ These works have led to the conclusion that reactions in the inverted region need to be modeled in terms of quantum mechanical tunneling (see Figure 1 and caption). In this case, the electron-transfer process is described as a radiationless transition; the rate constant is determined from a Golden Rule expression under the Born-Oppenheimer approximation. The rate constant depends on the square of the electronic matrix element, $|V|^2$, and a vibrational contribution that involves a thermally weighted sum of the Franck-Condon factors, FC (eq 3).

$$k_{\rm et} = (4\pi^2/h)|V|^2 {\rm FC}$$
 (3)

There are several different formulas for the rate constant depending on the approximations used to evaluate the electronic matrix coupling element and Franck-Condon terms. One expression derived by Jortner and Bixon (JB) has been used to model several experimental studies.⁵ In the JB model, the rate is given by

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Figure 1. Schematic potential energy surface for the electron-transfer reaction. The energy of the contact ion pair (ClO⁻ benzene⁺) and the ground-state complex (ClO⁻benzene) is plotted as a function of the nuclear configuration. The reorganization energy λ and exothermicity ΔG° are labeled. Excitation directly generates the CIP. Reaction (given by the rate constant k_{et}) occurs by tunneling from the CIP well to highlying vibrational levels on the ground-state complex. Depending on the relative rates of vibrational relaxation and reaction, tunneling can occur in the entire region (shaded area) from the bottom of the CIP well to that accessed by the excitation light, $h\nu$.

$$k_{\rm et} = e^{-s} |V_{\rm DA}|^2 \left(\frac{4\pi^3}{h^2 \lambda_{\rm s} k_{\rm B} T} \right)^{1/2} \sum_{j=0}^{\infty} \left(\frac{s^j}{j!} \right) (1 + H_j)^{-1} \times \exp\left(\frac{(\Delta G^{\circ} + \lambda_{\rm s} + jh\nu_{\nu})^2}{4\lambda_{\rm s} k_{\rm B} T} \right)$$
(4)

where $s = \lambda_v / h \nu_v$, $H_j = 8\pi^2 F_j |V|^2 \tau_L / (h\lambda_s)$, $F_j = e^{-sg/j!}$. λ_v is the reorganization energy due to one high-frequency mode of frequency $h\nu_v$, and τ_L is the longitudinal relaxation time of the solvent. This particular theory treats the high-frequency mode of the reactants quantum mechanically and the low-frequency fluctuations of the solvent classically. Using this formalism to calculate the reaction rate requires knowledge of the vibrational mode that couples to the reaction coordinate as well as the solvent reorganization and the electronic matrix coupling element. All of these parameters are necessary if one is to have a complete picture of the relative importance of the solvent and the internal vibrations in determining the reaction dynamics. Unfortunately, for most experimental systems, these values are difficult to determine with a high degree of accuracy.

Ground-state donor-acceptor charge-transfer complexes are useful model systems for advancing the fundamental understanding of electron-transfer reactions.11-23 In recent works, both bimolecular and unimolecular (donor and acceptor separated by a rigid spacer) systems have been examined. In many of these studies, light is used to excite a charge-transfer absorption band, which results in instantaneous electron transfer between the donor and acceptor molecules. The dynamics of the back electron transfer are then monitored. Most of the experimental systems studied to date have charge-transfer absorption bands in the visible or ultraviolet region of the spectrum. This suggests that the reverse charge transfer is highly exothermic ($\geq 2-3$ eV), and behavior consistent with the Marcus inverted region is generally found. As a result, most analyses of rate data for such systems model the back electron transfer rate constant in terms of quantum mechanical tunneling theories (eq 3). In many cases reported in the literature, a single arbitrary value is used to approximate the high-frequency mode



that couples to the reaction coordinate.^{11,12} Typically, a value of 1500 cm⁻¹ is used, representative of the carbon–carbon skeletal vibrations.¹¹

While this approximation has met with limited success, recent studies indicate that using a single average mode is likely to results in an incorrect assessment of the vibrational reorganization energy.14 This issue was addressed in detail in a recent resonance Raman study on the charge-transfer transition of the hexamethylbenzene-tetracyanoethylene complex.14 Raman signals are resonantly enhanced for vibrations that couple to the electronic transition being probed. Thus, this study provided direct insight into the mode(s) that couple to the electron-transfer reaction coordinate. The data reveal that both the low-frequency donor-acceptor intermolecular vibrational mode at 165 cm⁻¹ and the 1551 cm⁻¹ ring mode contribute to the reorganization energy. A related study reported deuteration effects on the rate constant for this complex that suggested the methyl C-H vibrations are major contributors to the reorganization energy.¹² These two studies taken together suggest several modes (ranging from \sim 150 to 3000 cm⁻¹) couple to the reaction coordinate. A complete understanding will necessitate the use of multimode theoretical models.

To assess the factors controlling electron-transfer reactions in the inverted region, one would like to systematically alter one variable while holding all others constant. One common approach along this line is to study the effect of solvent on k_{et} . It is generally assumed that this allows ΔG° to change while keeping |V| constant. Using theory (continuum and molecular), the effect of solvent on λ can be calculated (λ_v is generally assumed to be solvent independent so all changes in λ arise from λ_s). A second experimental approach involves altering the energetics of the electron transfer by using different, but related, donor-acceptor complexes in a single solvent. In analyzing this data, one generally assumes that the reorganization energy and electronic coupling are nearly constant for the series under study. Both approaches are useful, but in most cases the assumptions invoked in the data analysis have not been critically tested.

This paper examines back electron transfer following photoexcitation of ground-state donor-acceptor complexes between CIO and a series of substituted benzenes in polar aprotic solvents. Excitation of the charge-transfer band (in the region 450-600 nm) generates the contact ion pair (Scheme 1). Back electron transfer, k_{et} , competes with ion pair separation, k_s . Compared to many of the large molecules studied to date, the CIO-aromatic complexes present a simpler chemical system that is amenable to high-level quantum calculations. In addition, the vibrational modes of the reacting molecules are well-defined. By examining both solvent effects and the reaction rate constant for different acceptors, one can address the validity of common approaches used to compare experimental rate data to electrontransfer theory.

Experimental Section

Absorption kinetics were recorded using a kilohertz repetition rate picosecond laser system. A mode-locked, Q-switched, and cavity-dumped Nd:YAG laser was used to synchronously pump a cavity-dumped tunable dye laser.²⁴ The ClO-aromatic complexes were made by photolyzing OClO in the presence of the desired aromatic in the solvent of interest.²⁵ OCIO was generated by reaction of oxalic acid (Fischer) and potassium chlorate (Fischer) as previously described.²⁶ The gaseous OCIO was collected and bubbled through spectral grade acetonitrile (Fischer), proprionitrile (Aldrich), or butyronitrile (Aldrich). Photolysis of OClO at 355 nm (generated by frequency-tripling cavity-dumped infrared pulse from the YAG oscillator) gives high yields of ClO. In the presence of 0.1 M aromatic, the ClO-aromatic complex forms and achieves steady-state concentration on the nanosecond time scale. As the generation of ClO involves irreversible photochemistry, signal averaging was limited by the volume of sample that could be easily flowed through the system. A 4 L sample (the largest used) restricted data collection to approximately 6 min. After the ClO-aromatic complex achieved steady-state concentrations, it was excited at 532 nm; this light pulse was generated by frequency-doubling the cavity dumped infrared pulse from the YAG oscillator. The ensuing dynamics were probed at 556 nm, which measured repopulation of the ground-state complex. The probe beam was detected by a PMT, amplified, integrated by a sample-and-hold circuit (SRS Model 250), and sent to a lock-in amplifier (SRS digital lock-in). The pump beam was chopped at 500 Hz (half the repetition rate of the laser); the digital output from the chopper was used as the reference signal for the lock-in. The output from the lock-in was processed by a MAC-II computer running LabView. This computer also controlled a digital delay line (Compumotor) which enabled changing the relative timing of the pump and probe laser pulses. Delay times of up to 3 ns could be achieved in this manner. All laser beams were depolarized to remove coherence artifacts and any other signals which might arise from polarization-dependent properties of the sample. The absorption spectrum of the ground state complex was obtained by tuning the dye laser and fitting the experimental points to a log-normal distribution function.

Computational Methods

The conformational analyses of the ground state ClObenzene complex were predicted using the analytical gradient techniques in GAMESS.^{27a,b} Structures were calculated at the restricted open-shell Hartree-Fock (ROHF) self-consistent-field (SCF) level of theory using the TZV(2d,p) basis set,^{28,29} a triplevalence basis which is augmented by two sets of d orbitals on all heavy (non-hydrogen) atoms and a set of p orbitals on all hydrogen atoms. The inclusion of multiple sets of polarization functions is seen to be particularly important for proper description of polarizability. The nature of each SCF stationary point has been established by analytically calculating and diagonalizing the matrix of energy second derivatives (Hessian) to determine the number of imaginary frequencies. To accurately describe the complex intra- and intermolecular interactions, dynamical correlation treatments are essential. Moller-Plesset^{30a} perturbation theory has been shown to be a reasonable level of post-Hartree-Fock theory to treat systems with varying degrees of van der Waals types interactions.^{30b-f} Moller-Plesset perturbation calculations of order two have been performed in this study using GAUSSIAN92.^{27c}

Experimental Results

Figure 2 shows the absorption spectrum of the CIO-benzene complex in acetonitrile. The transient absorption dynamics of several CIO-aromatic complexes probed at 556 nm following 532 nm excitation in acetonitrile are shown in Figure 3. Excitation at 532 nm generates a contact ion pair (CIP). This



Figure 2. Charge-transfer absorption band for the ClO-benzene complex in acetonitrile.



Figure 3. Transient absorption dynamics at 556 nm plotted as a function of time following excitation at 532 nm for a series of ClOaromatic complexes in acetonitrile solutions. The decrease in the absorption at t = 0 corresponds to photogeneration of the CIP. The signal recovers as the CIP undergoes back electron transfer. The signal does not recover to zero due to the formation of solvent-separated ion pairs. The solid lines through the experimental data are calculated fits. Table 1 presents the rate constants derived from these fits. Data are shown for the aromatics (\times) benzene, (\bullet) toluene, and (O) xylene.

gives rise to the observed instrument response-limited bleach. Back electron transfer re-forms the ground-state complex, causing the signal to recover at the probe wavelength. An incomplete recovery (not returning to the value observed at negative delay time: probe before pump) indicates that ion separation competed with back electron transfer. The data clearly show that the relative rate of back electron transfer and ion pair separation depend on the acceptor molecule.

Here, we model the electron-transfer and ion pair separation rates as first-order kinetic processes. The resulting complex concentration as a function of time is given by eq 5

$$[C](t) = \left(\frac{k_{\rm et}}{k_{\rm et} + k_{\rm s}}\right)(1 - \exp[-t(k_{\rm et} + k_{\rm s})])$$
(5)

where k_{et} and k_{s} are the electron-transfer and ion pair separation rate constants. The experimental signal, S(t), is a convolution of the time-dependent concentration, $[\mathbf{C}](t)$, and the instrument response, I(t) (eq 6).

$$S(t) = I(t)^*[C](t)$$
(6)

The rate constants are determined by minimizing the residuals of a fit of eq 6 to the experimental data using a nonlinear leastsquares routine. The best fits are shown as solid lines through



Figure 4. Transient absorption dynamics at 556 nm plotted as a function of time following excitation for the ClO-benzene complex in a series of nitriles. The rate constants for electron transfer decreases with decreasing solvent polarity: $k_{\rm et} = 3.1 \times 10^9 \, {\rm s}^{-1}$ in acetonitrile (×), $1.3 \times 10^9 \, {\rm s}^{-1}$ in proprionitrile (\bigcirc), and $< 0.1 \times 10^9 \, {\rm s}^{-1}$ in butyronitrile (\bigcirc).

TABLE 1: Electron-Transfer Reaction Rate Constants, k_{et} , and Ion Pair Separation Rate Constants, k_s , for the ClO-Benzene Systems Studied

acceptor	temp (K)	solvent	$k_{\rm et} ({\rm s}^{-1})$	$k_{\rm s} ({\rm s}^{-1})$	IP (eV)
benzene-h ₆	295	CH ₃ CN	3.1×10^{9}	1.12×10^{9}	9.23
_	330	CH ₃ CN	3.1×10^{9}	1.12×10^{9}	
	295	CH ₃ CH ₂ CN	1.3×10^{9}	1.69×10^{9}	
	295	CH ₃ (CH ₂) ₂ CN	$< 0.1 \times 10^{9}$		
benzene-d ₆	295	CH ₃ CN	3.9×10^{9}	1.12×10^{9}	9.23
toluene	295	CH ₃ CN	1.50×10^{9}	1.15×10^{9}	8.82
o-xylene	295	CH ₃ CN	1.21×10^{9}	0.78×10^{9}	8.56
durene	295	CH ₃ CN	$\sim 0.14 \times 10^{9}$		8.05
p -xylene- h_{10}	295	CH ₃ CN	0.72×10^{9}		8.44
	330	CH ₃ CN	0.72×10^{9}		
p -xylene- d_{10}	295	CH ₃ CN	1.08×10^{9}		8.44

the data (see Figure 2). The rate constants k_{et} and k_s for the series of substituted benzenes studied are given in Table 1.

Figure 4 shows the transient absorption of the ClO-benzene complex probed at 556 nm following photoexcitation at 532 nm in acetonitrile, proprionitrile, and butyronitrile solutions. The rate constants determined using eqs 5 and 6 are also given in Table 1. $k_{\rm et}$ decreases with decreasing solvent polarity. In butyronitrile, the kinetics are dominated by ion pair separation; no back electron transfer is observed. This result requires that $k_{\rm et}$ be smaller than $0.1 \times 10^9 \, {\rm s}^{-1}$.

Figure 5 shows the transient absorption kinetics following excitation of the ground-state complexes of ClO with benzene (top) and *p*-xylene (bottom) at 295 and 330 K. Within the signal to noise, $k_{\rm et}$ is independent of temperature.

In Figure 6, the transient absorption kinetics following excitation of ClO complexes with benzene- h_6 and benzene- d_6 are compared. $k_{\rm et}$ for the deuterated complex is $3.9 \times 10^9 \, {\rm s}^{-1}$, corresponding to an inverse isotope effect, $k_{\rm et}^{\rm D}/k_{\rm et}^{\rm H}$, of 1.28. A larger inverse isotope effect of 1.49 is observed for the comparison of *p*-xylene- h_{10} and *p*-xylene- d_{10} .

Discussion

To determine the detailed mechanism of the intermolecular electron transfer that follows photoexcitation of the groundstate ClO-benzene donor-acceptor complex, the following issues will be discussed. Because ClO itself is a transient intermediate generated in these experiments, a determination of the structure of the donor-acceptor complex is not possible. We therefore have carried out quantum mechanical calculations



Figure 5. Transient absorption dynamics of ClO-p-xylene (top) and ClO-benzene (bottom) plotted as a function of time following excitation of these complexes in acetonitrile solutions at 295 K (solid) and 340 K (dashed). The dynamics are independent of temperature.



Figure 6. Transient absorption dynamics at 556 nm plotted as a function of time following excitation for the CIO-benzene- d_6 (dashed) and CIO-benzene- h_6 (solid) complexes in acetonitrile. The electron-transfer rate constant for the deuterated complex is $k_{\rm et} = 3.9 \times 10^9$ s⁻¹, faster than that found for the nondeuterated complex, $k_{\rm et} = 3.1 \times 10^9$ s⁻¹.

to gain insight into the structure of these complexes. Two sets of experimental data will be critically evaluated: the electrontransfer rate constants for (a) a single bimolecular system (ClO/ benzene) in a series of nitrile solutions and (b) a series of donor-acceptor complex in a single solvent (acetonitrile). Both approaches, in principle, provide a method for altering the reaction exothermicity. Both have been extensively used to develop insight into electron-transfer processes. Unfortunately, for the case considered here, these two approaches lead to contradictory conclusions. This calls into question the approximations used to compare experimental data to theoretical models. In particular, for both approaches, it is common to assume that the reorganization energy and electronic coupling matrix element are constant. We demonstrate that such assumptions are not justified for the ClO-benzene system.



Figure 7. Schematic of the interactions of the molecular orbitals of CIO and benzene. The molecular orbitals suggest donor-acceptor complexes where the CIO is either perpendicular or parallel to the plane of the benzene ring.

 TABLE 2:
 Summary of Computational Results on the

 CIO-Benzene Complex
 Image: Complex

type of calculation	sym	E (hartrees)	vibrational analysis	Cl-benzene distance (Å)
ROHF/TZV(2d,p)	C_1	-765.064 53	positive definite	4.326
ROHF/TZV(2d,p)	C_s	-765.065 54	positive definite	3.996
MP2/DZ(d)	C_1	-765.994 56	positive definite	2.197
MP2/DZ(d)	C_s	-765.995 18	positive definite	1.889

Structure of the CIO–Benzene Complex. The electronic ground state of CIO is ${}^{2}\Pi$, which is doubly degenerate between $(p_{x}^{*})^{2}(p_{y}^{*})^{1}$ and $(p_{x}^{*})^{1}(p_{y}^{*})^{2}$. Analysis of the molecular orbital diagrams for the bimolecular complex that forms between CIO and benzene distinguishes two possibilities for a ground-state configuration: an end-to-face interaction and a side-to-face interaction (Figure 7).

Calculations on the CIO-benzene complex [ROHF/TZV-(2d,p)] isolated both types of conformations as minima (see Table 2). We believe the particular end-to-face interaction observed in these calculations results from a Jahn-Teller distortion. The degeneracy of the e orbitals is raised as one drops from the highly symmetric C_{6v} (C_{2v}) to C_s structure. Classic examples of molecules which sustain Jahn-Teller distortions are positive and negative ions of benzene and symmetrically substituted benzenes.^{30e-g} As an electron-transfer species, ClO-benzene fits into this category. Although we were not able to specifically isolate the C_{6v} structure via calculations (supposedly due to the repulsive nature of the interaction in this orientation), we did find a C_{2v} structure which had two negative eigenvalues which then lead us to the C_s structure. The difference in energy between any of these structures is less than 1 kcal/mol, as is typically small for Jahn-Teller instabilities.

The energies of the two minimum structures, C_s and C_1 , differ by ca. 0.6 kcal/mol, with the end-to-face interaction being the more favorable interaction. Both conformations have rather long Cl-O bond distances, 4.326 and 3.996 Å for side-to-face and end-to-face, respectively. Note that the van der Waals radii of Cl is about 1.8 Å and that of benzene is about 1.4 Å.

In complexes such as these, where primary interactions are of the van der Waals type (electrostatic, induction, dispersion, and exchange type interactions), inclusion of dynamical correlation becomes essential. We have included dynamical correlation effects using Moller—Plesset theory of order 2. The results of the optimizations for both end-to-face and side-toface conformations are depicted in Figure 8. The major difference between the ROHF and MP2 results concerns the CIO to benzene distance, which decreased to 2.197 and 1.899 Å for the side-to-face and end-to-face conformation, respectively. The relevant parameters are given in Table 2. The calculated total spin (S^2) values for both electronic states is ~0.77, indicating that there is not a significant contamination of the states from higher multiplicities. The energies of the two structures differ by 0.39 kcal/mol at the correlative level, again with the C_s structure being the lowest energy. Figure 9 shows an electron density map on one of the bonding MOs between the CIO and benzene in the C_s conformation.

Solvent Effects on the Reaction Rate of ClO-Benzene. In this section, the effect of solvent on k_{et} is examined. In particular, the effects of solvent on ΔG° , λ_{v} , λ_{s} , and |V| are discussed. This analysis supports the conclusion that a change in solvent manifests itself most strongly in altering ΔG° . While information on relative exothermicities in the different solvents can be obtained, the absolute reaction exothermicity is difficult to evaluate.

First, we consider solvent effects on the reorganization energies, λ_s and λ_v . Modeling the reacting system as a sphere embedded in a dielectric continuum fluid, solvent effects on λ_s for the reaction in different solvents can be calculated using eq 7.¹

$$\lambda_{\rm s} = \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{\epsilon_{\rm op}} - \frac{1}{\epsilon_{\rm s}} \right) \left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r} \right) \tag{7}$$

Here e is the electron charge, ϵ_0 is the vacuum permittivity, ϵ_{op} and ϵ_s are the optical and static dielectric constants for the solvent, a_1 and a_2 are the radii of the donor and acceptor, and r is the center-to-center distance between the donor and acceptor. For the ClO-benzene complex, a_1 and a_2 were calculated assuming a sphere whose volume is equal to the molecular volume. This gives values of 2.18 and 1.1 Å for benzene and ClO, respectively. The contact distance, r, is set equal to 2.2 Å (the calculated value for the C_1 geometry). ϵ_{op} and ϵ_s are 1.9 and 38 for acetonitrile, 1.9 and 28.6 for proprionitrile, and 1.9 and 22.3 for butyronitrile. Using these parameters, eq 7 gives $\lambda = 1.64$, 1.61, and 1.57 eV for acetonitrile, proprionitrile, and butyronitrile, respectively. While the applicability of a continuum based model can be questioned, these calculations support the conclusion that, within this particular set of solvents, λ_s is essentially constant (changing less than 4%). This conclusion is supported by recent work of Li and Peters.²² In that study, different models for calculating the reorganization energy for the bimolecular reaction between stilbene and fumaronitrile were examined. Compared to a spherical cavity, the values λ_s decreased about 20% for an ellipsoidal cavity. While the absolute values of λ_s were found to be model dependent, the relative changes within the series of nitrile solvent were not. It is reasonable to conclude that our values would also be model dependent but that the overall insensitivity of λ_s to solvent would be retained for different cavity shapes.

The vibrational contribution to the reorganization energy, λ_v , depends on the equilibrium bond distances for the vibrational modes of the reactant, d_r , and product, d_p , and the average force constant, k_i , of the respective modes (eq 8).¹

$$\lambda_{\rm v} = \frac{1}{2} \sum_{i} k_i (d_{\rm r} - d_{\rm p})^2 \tag{8}$$

For polyatomic systems it is difficult to calculate the vibrational component of the reorganization energy. Within the nitrile series, the frequencies of the normal modes of the aromatic



Figure 8. Two views of the calculated C_s (a, b) and C_1 (c, d) structures of the ClO-benzene complex using Moller-Plesset theory (MP2) with GAUSSIAN92.

molecules are essentially independent of solvent. This is consistent with the predictions of various theoretical models for solvent polarity effects on vibrational spectra.³¹ Solvent effects on the stretching frequency of ClO are unknown. However, related studies on polar diatomics (NO⁺) suggest that, within the nitrile system, solvent effects on the stretching frequency will be insignificant.¹³ It is reasonable to conclude that, within this particular series of solvents, the magnitude of λ_v is essentially constant.

 $k_{\rm et}$ depends quadratically on the matrix coupling element, |V|. Small changes in |V| can therefore significantly alter the reaction rate. Experimental determination of |V| remains a difficult problem; however, recent theoretical studies are addressing this issue. Kim and Hynes have shown that in certain cases |V| is strongly dependent on solvent properties.⁶ Thus, it is not necessarily justified to assume that this parameter is unaffected by a change in solvent. To try and gain some insight into this question, |V| was determined from an analysis of the chargetransfer absorption band using the Hush and Miliken equation:³²

$$|V| (\text{cm}^{-1}) = (0.00206/r)(\epsilon_{\max}\nu_{\max}\Delta\nu_{1/2})^{1/2}$$
(9)

Here, ϵ_{max} is the extinction coefficient at the absorption maximum, ν_{max} , and $\Delta \nu_{1/2}$ is the full width at half-maximum. This expression assumes a Gaussian line shape, thereby giving a relationship between ν_{max} and $\Delta \nu_{1/2}$. For the CIO-benzene complex in acetonitrile, the experimentally measured values of ν_{max} , $\Delta \nu_{1/2}$, and ϵ_{max} are 17 250 cm⁻¹, 5500 cm⁻¹, and ~3000 M⁻¹ cm⁻¹, respectively (Figure 2). These values give a coupling constant of 0.61 eV. However, it needs to be pointed out that the charge-transfer absorption band is slightly narrower than that predicted for a Gaussian line shape (6300 cm⁻¹). By comparing the charge-transfer bands obtained for CIO-benzene in the nitrile solvents, eq 9 predicts that |V| is constant to within 5%. This solvent independence is also consistent with the results of Li and Peters for the stilbene-fumaronitrile complex.²² Here, the matrix coupling element changed by 0.01 eV (|V| = 0.08 for acetonitrile) when the solvent was changed from acetonitrile to butyronitrile.²²

The above observations suggest that the change in k_{et} found for the nitrile series does not arise from changes in λ or |V|. This leaves the reaction exothermicity, ΔG° . Solvent effects on ΔG° arise from the differential solvation energy of the ground-state complex and the photogenerated CIP. For a spherical cavity embedded in a dielectric continuum, solvation energies depend on the square of the solute dipole moment. For the systems under study here, the CIP has a larger dipole moment than the ground-state donor-acceptor complex. As solvent polarity in decreased, the CIP will be destabilized to a greater extent that the ground-state complex. This causes an increase in the driving force for the back electron transfer reaction. Quantitatively, this increase in exothermicity, $\Delta(\Delta G^{\circ})$, can be estimated using the Rehm-Weller expression:³³

$$\Delta(\Delta G^{\circ}) = \frac{-e^2}{4\pi\epsilon_0 r} \left(\frac{1}{\epsilon_{s1}} + \frac{1}{\epsilon_{s2}}\right) + \frac{e^2}{4\pi\epsilon_0} \left(\frac{1}{2a_1} + \frac{1}{2a_2}\right) \left(\frac{1}{\epsilon_{s1}} + \frac{1}{\epsilon_{s2}}\right)$$
(10)

Here, ϵ_{s1} and ϵ_{s2} are the dielectric constants for the two solvents. The other variables are defined above. Relative to acetonitrile, the reaction exothermicity increases by 0.14 eV for proprionitrile and 0.30 eV for butyronitrile. These relative changes in exothermicity along with the reaction rate constants (3.1×10^9 , 1.32×10^9 , and $< 0.1 \times 10^9 \text{ s}^{-1}$ for acetonitrile, proprionitrile, and butyronitrile, respectively) clearly exhibit that k_{et} decreases with increasing driving force. This behavior is characteristic of the Marcus inverted region.

For reactions in the Marcus inverted region, it is common to observe temperature-independent rate constants. The dynamics shown in Figure 4 clearly show that temperature-independent kinetics are observed for CIO complexes of both benzene and *p*-xylene.

Dependence of Reaction Rate on Substituted Benzenes.



Figure 9. Electron density map of one of the bonding MOs in the optimized MP2/DZ C_s structure of the ClO-benzene complex. Insert: same MO for the optimized C_1 structure.

In this section, the effect of different acceptors on the rate constant for electron transfer is considered. The rate of electron transfer is dependent on the specific acceptor (see Figure 3 and Table 1). If one assumes that the solvation energy is constant for the series of acceptors studied, then changes in the driving force only result from changes in the reduction potential of the aromatic cations. Thus, the reaction exotehrmicity relative to the reaction with benzene cation can be determined from the negative of the difference in ionization potentials: $\Delta(\Delta G^{\circ}) =$ $-[IP_{benzene} - IP_{aromatic}]$. A plot of $ln(k_{et})$ versus $-\Delta(\Delta G^{\circ})$ obtained in this manner for the series of benzenes studied (Figure 10) reveals that the rate increases with increasing exothermicity. The solid line in Figure 10 was generated using eq 3. ΔG° was arbitrarily set as 2 eV for the ClO/benzene complex, and the value of λ_s was fixed to 1.64 eV (from eq 7). As done in many past studies, we assumed a single vibrational mode of 1500 cm⁻¹ (0.18 eV).¹¹ The best fit was obtained for λ_v and |V| of 0.3 eV and 0.002 eV, respectively. Here |V| is over 2 orders of magnitude smaller than that obtained from the analysis of the charge-transfer absorption band. The observed dependence of $k_{\rm et}$ on $-\Delta(\Delta G^{\circ})$ suggests that $-\Delta G^{\circ} < \lambda$ (Marcus normal region), a conclusion that is in direct contrast to that derived for the analysis of a single complex in the series of nitrile solvents. In analyzing the data presented in Figure 10, $\lambda_{\rm s}, \lambda_{\rm v},$ and |V| are all assumed to be constant for the entire set



Figure 10. Logarithm of the electron-transfer rate constant, $\ln(k_{et})$, plotted as a function of driving force, $-\Delta(\Delta G^{\circ})$, for the various ClO–benzene complexes studied. The exothermicity of the ClO–benzene system was set to 2.0 eV, and the relative exothermicities of the complexes involving substituted benzenes were computed from known ionization potentials. The solid line is a fit of these data points to the theoretical model of Bixon and Jortner. The value of λ_s was fixed to 1.64 eV (see text for details). The best fit was obtained for λ_v and |V| of 0.3 and 0.002 eV, respectively.

of acceptor molecules studies. In light of the experimental charge-transfer bands recorded for the different complexes, this is a reasonable approximation for |V|; however, it is not clear what an accurate value for this parameter is. Furthermore, if we take the maximum of the charge-transfer band as a measure of reaction exothermicity, the difference between the driving force for the reaction involving benzene and durene is only 0.2 eV, not 1.5 eV as gauged by the ionization potentials and used in generating Figure 10. In generating single Marcus curves to a set of experimental data, one is really making the assumption that changes in λ_s , λ_v , and |V| are small compared to the overall energetic changes being studied. For example, if the range of driving forces spanned by the molecular complexes studies was small compared to changes that results in the reorganization energy through using different molecules, we would not be justified in fitting the experimental data to a single Marcus parabola.

For this particular set of molecules, the ionization energy may not be a good measure by which to gauge $\Delta(\Delta G^{\circ})$ in these systems as varying degrees of charge transfer are expected for the ground-state complexes of the various different aromatic molecules. Increased charge donation is expected with decrease ionization potential of the aromatic donor. This would lead to smaller driving forces with decreasing ionization potential than one would calculate using differences of ionization potentials as done in generating Figure 10. Thus, the energy scale used in Figure 10 overestimates the actual energetics. From the charge-transfer spectra, we would conclude that $\Delta(\Delta G^{\circ})$ varies only 0.2 eV between the benzene and durene complex. While extracting driving forces from donor-acceptor spectra is not that reliable, the data suggest that the range of driving forces is likely to be greater than 0.2 eV and significantly less than 1.5 eV. We need to critically examine whether or not the reorganization energy remains constant on the scale of the driving forces studied. Otherwise, a situation like Figure 11 can occur where we need to specify each complex by its own Marcus curve and cannot use a single value of the reorganization energy for the entire set of molecules studied. Note that Figure 11 displays a way in which the molecules can exhibit increased rates with increased driving force yet all the reactions actually occur in the Marcus inverted region. We shall see below that it is reasonable to conclude that the value of λ could be changing as much as ~ 0.5 eV for this set of reactions. This conclusions provides an explanation for the apparent different behavior observed in the molecule-dependent and solvent-dependent studies.

First consider the effect of varying the aromatic on the value of λ_s , λ_s depends inversely on molecular size (eq 7). In acetontrile, λ_s decreases from 1.64 eV for benzene to 1.50 eV for *p*-xylene, a change of 0.14 eV (over half of the range of $\Delta(\Delta G^\circ)$ determined spectroscopically). For the systems studied, the effect on λ_s is twice as large when the acceptor is varied than when the solvent is varied.

Next, consider the effect of varying the aromatic on the magnitude of λ_v . Unfortunately, the lack of information on the force constants and displacements for the large number of vibrations in these systems make the calculation of λ_v untenable. However, it is obvious that the number of vibrations increase with increasing number of atoms in the aromatic molecule. (Benzene has 30 normal modes; durene has 66 normal modes.) It is reasonable to assume that an increase in the number of vibrational modes could effect λ_v . To gain some insight into the potential magnitude of this effect, one would like to study a system at constant driving force, λ_s , and |V| but varying λ_v . This is possible using deuterated complexes. In particular, $-\Delta G^\circ$ for the CIO-benzene- h_6 and CIO-benzene- d_6 complexes are within 5 meV (the change in IP of the aromatic); λ_s is

unchanged (within continuum calculations), and |V| is constant (the charge-transfer bands are identical). However, the frequencies of the vibrational modes are affected, and thus one expects that λ_v will be different for the two complexes. The data in Figure 5 show that deuteration causes the rate of electron transfer to increase by 22%. Compared to p-xylene- h_{10} , a 50% increase in reaction rate is observed for the p-xylene- d_{10} complex. While these effects are currently difficult to quantify, it is clear that the Franck-Condon factors for the electron-transfer process are affected by deuteration. It is also possible that these results reflect a change in λ_{v} ; however, there is no experimental evidence to support such a conclusion. It is possible to address the effects of molecular size and shape on λ_v computationally. Several such studies on aromatic systems have been reported. Bondebey and co-workers³⁴ calculated the inner-sphere reorganization for vertical ionization of benzene and perfluorobenzene. At the Hartree-Fock level, the value of λ_v associated with the relaxation of the cation was 0.149 and 0.187 eV for benzene and perfluorobenzene, respectively. Recently, Klimkay and Larsson³⁵ reported a high-level calculations in which they used a UHF/MP2/6-31G approach to calculate λ_v associated with the relaxation of forming the benzene and naphthalene anions from the neutral molecules. They found values of 0.266 and 0.102 eV for benzene and naphthalene, respectively. While these calculations are for anions, not the cations as studied here, we can draw some conclusion from the data. We clearly see from these calculations that the reorganization energy is molecule dependent and can vary on the order of tenths of electronvolts. We expect that the values of λ_v will decrease with increasing number of vibrational modes. Thus, the smaller values of λ_v is expected for durene and largest for benzene. We found above that λ_s changes in the same direction, being smallest for durene and largest for benzene. Thus, both the inner-sphere and outer-sphere contributions to the reorganization energy exhibit the same trend in this series of molecules. It would not be surprising to find that the total reorganization energy may vary as much as 0.5 eV across the series of molecules studied.

The above comments establish that the total reorganization energy is not constant (both λ_s and λ_v change synergistically) for the series of acceptor molecules. The magnitude of change for λ is comparable to the range of driving forces studied, and hence we cannot describe the entire data set by a single Marcus parabola that assumes a constant value for λ . Likewise, the assumptions that underlie the fit presented in Figure 10 are not justified for the same reason, even though the Jortner-Bixon model can fit the data. These results can be brought into accord with the conclusions from the solvent study through the argument presented schematically in Figure 11. As discussed above, the reorganization energy for p-xylene complex will be less than that of the benzene complex. Thus, compared to benzene, the peak of the Marcus curve for *p*-xylene would be at a lower value of $-\Delta G^{\circ}$. If this change in the total reorganization energy, $\Delta \lambda$, is greater than the difference in reaction exothermicities, $\Delta(\Delta G^{\circ})$, then both reactions occur in inverted regions and the rate constant for the complex with *p*-xylene would be smaller than that with benzene. Such an effect could reconcile the entire set of experimental observations. Without accurate methods for determining $-\Delta G^{\circ}$ and λ this model, while reasonable, cannot be quantitatively verified.

Our future efforts will focus on using quantum calculations to address the issues raised in the above discussion. We are currently using such techniques to further characterize the ground state and ion pair structures in terms of geometry, energetics, molecular orbitals, vibrational, and electronic proper-



Figure 11. Schematic representation of the effect on the predicted behavior of k_{et} on driving force, $-\Delta G^{\circ}$, if each complex had a different reorganization energy. Here the two curves represent the situation for the benzene and *p*-xylene complexes. While the driving force for the *p*-xylene complex is less than that for benzene, the reaction rate constant is smaller owing to a reduction in the reorganization energy. In this model, both reactions occur in inverted regions, consistent with the observed temperature independence of the rate constants.

ties for the entire set of complexes studied herein. Our hope is to use this information to investigate (a) the effects of solvent on the reaction process using various solvent models and (b) the reaction dynamics of the electron transfer utilizing variational transition state theory. By combining quantum calculations with experimental data, we hope to develop a more detailed understanding of these multidimensional kinetic processes.

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