Kinetics of the Electroreduction and Electrooxidation of Tetrakis(dimethylamino)-*p*-benzoquinone in Polar Aprotic Solvents

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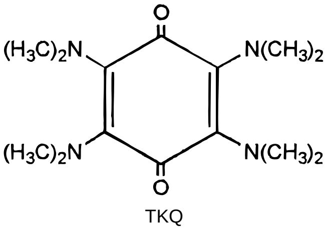
A high-frequency ac admittance technique capable of precisely measuring rate constants greater than 1 cm s^{-1} was used to collect kinetic data for both the one-electron reduction and one-electron oxidation of tetrakis(dimethylamino)-*p*-benzoquinone. This study was conducted at a gold ultramicroelectrode in seven polar aprotic solvents, with varying viscosity, in the presence of 0.1 M tetraethylammonium perchlorate. In addition, the temperature dependence of the standard rate constants was determined in three of these solvents. On the basis of an analysis of the solvent effects, it is shown that the kinetic data show a variation in the degree of reaction adiabaticity and the relative sizes of both the inner- and outer-sphere components of the Gibbs energy of activation. Solvent effects on diffusion coefficients and standard potentials were also investigated. The standard reduction potential is a linear function of the solvent acceptor number, a parameter reflecting molecular solvating properties, whereas the corresponding standard potential for oxidation is a linear function of solvent polarizability, a parameter that reflects nonspecific interactions between the reactant and the solvent. The significance of these results is discussed within the context of the current models for simple heterogeneous electron transfer reactions.

Introduction

During the past decade, considerable effort has been made toward understanding the role of reactant solvation in heterogeneous electron transfer reactions.[1−4] The simplest types of electrode reactions are those where only one electron is transferred to or from the reactant, no chemical bonds are formed or broken, and double-layer effects are minimal. In previous studies, it has been shown that molecular solvation effects can be explained through the dependence of the standard rate constant on the longitudinal relaxation time of the solvent and on the Gibbs free energy of activation. It has also been proposed that electrode reactions involving the formation of anions are somewhat slower than those involving cations and that the reorganization energy to form an anion from a given molecule is greater than that for a cation.[5] The latter can be examined in more detail by studying the temperature dependence of the two reactions and comparing experimental values of the enthalpy of activation.

The system chosen to test further these predictions is an organic compound, tetrakis(dimethylamino)-*p*-benzoquinone (TKQ), that can be both oxidized to form a cation radical and reduced to an anion radical.



The electrochemistry of TKQ has been the subject of some interest, especially with respect to structural changes that occur during a twofold oxidation to form the dicyanine salt.[6] This study also included calculations of charge distribution on both the parent molecule and the dication. Early work[7] showed that TKQ can undergo both electron transfer reactions in the solvent *N*,*N*-dimethylformamide, where the electron transfer rates are relatively fast. The first ionization energy of TKQ (7.1 eV), which is low due to the strong donor effect of the dimethylamino substituents, was also determined in this work. The distribution of spin density in the stable radical cation differed considerably from that of the corresponding stable semiquinone radical anion. These observations suggest that solvent effects for the kinetics of formation of the cation and anion radicals would be interesting to study. The kinetic parameters for these reactions should be quite different; more particularly, they should be affected by the solvent in quite different ways.

In this paper, kinetic data and activation parameters for the one-electron oxidation and one-electron reduction of TKQ in seven polar aprotic solvents are reported. The data were obtained by a high-frequency ac admittance technique at ultramicroelectrodes that can be used to determine fast electron transfer rate constants.[8−11] The goal of this study was to compare the solvent effects with those observed earlier for other systems and consider them in light of recent theoretical developments.

Experimental Section

Reagents. The solvents acetonitrile (AcN), butyronitrile (BuN), *N*,*N*-dimethylacetamide (DMA), *N*,*N*-dimethylformamide (DMF), hexamethylphosphoramide (HMPA), propylene carbonate (PC), and propionitrile (PrN) were purchased packed under nitrogen (anhydrous, 99+%, Aldrich) and were also handled under nitrogen. BuN was further purified using techniques described in the literature.[12]

Tetrakis(dimethylamino)-*p*-benzoquinone was used as received, courtesy of Prof. Dr. H. Bock (Frankfurt, Germany). Tetraethylammonium perchlorate (TEAP, GFS Chemicals) was purified and dried as described elsewhere.[9] Ferrocene (Aldrich) and silver perchlorate (Strem) were used as received.

Apparatus and Procedures. All measurements were performed with a reactant concentration of 1.5−2 mM and 0.1 M TEAP as electrolyte at 25 ± 0.5 °C, if not otherwise stated. A

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TABLE 1: Diffusion Coefficients of TKQ in Different Solvents at 25 °C in 0.1 M TEAP

solvent	$D/10^{-6}$ cm^2 s^{-1}	$\eta/10^{-3}$ Pa s	solvent	$D/10^{-6}$ cm^2 s^{-1}	$\eta/10^{-3}$ Pa s
AcN	22	0.341	HMPA	1.5	3.245
BuN	16.5	0.549	PC	6	2.513
DMA	10	0.88	PrN	17	0.41
DMF	13	0.802			

three-electrode system was employed with a gold ultramicroelectrode as the working electrode, a Pt sheet with an area of ~2 cm^2 as the counter electrode, and a silver wire immersed in acetonitrile containing 0.01 M $AgClO_4$ and 0.09 M TEAP as the reference electrode. The latter was separated from the working solution through a ceramic tip which provided the liquid junction (Bioanalytical Systems). All potentials were referred to the internal reference redox system ferrocene/ferricenium (Fc/Fc$^+$) at a concentration of 2 mM. Potentials of the Fc/Fc$^+$ couple were measured separately using the same electrolyte and temperature conditions as for the reactant under investigation. The Au ultramicroelectrode was prepared by sealing a gold wire with a radius of 12.5 μm (Goodfellow Metals) in a soft glass capillary in a Bunsen burner flame. The tip of the capillary was polished with fine carborundum paper (Buehler), rinsed with ethanol, and dried in a strong stream of compressed air. The smoothness of the electrode was confirmed in each experiment under an optical microscope (magnification 450×).

Data Analysis

The diffusion coefficient, D, for TKQ was calculated on the basis of cyclic voltammetric experiments at a normal size electrode (radius 0.25 mm) using convolution to obtain the semiintegrated limiting current.[13] The standard rate constant, k_s, and experimental transfer coefficient, α_{ex}, were determined using the ac admittance technique at ultramicroelectrodes as described elsewhere.[10] The experimental activation enthalpies, ΔH^*_{ex}, reported in the present study were measured in a totally isothermal cell; that is, the temperature of the reference electrode was kept the same as that of the cell. These quantities are often referred to as real activation enthalpies.[1] The peak separations in the cyclic voltammograms were usually in the range 62−82 mV. The error involved in estimating D, E(Fc), k_s, α_{ex}, and ΔH^*_{ex} did not exceed more than 10% for any given quantity.

Results and Discussion

The reduction and oxidation reactions involve the formation of anion and cation radicals as follows:

$$\mathrm{TKQ} + e^- \xrightarrow{k_{sr}} \mathrm{TKQ}^- \tag{1}$$

$$\mathrm{TKQ} \xrightarrow{k_{so}} \mathrm{TKQ}^+ + e^- \tag{2}$$

Solvent effects on diffusion coefficients and standard potentials were investigated, and kinetic data for both reactions were obtained at a Au ultramicroelectrode in seven polar aprotic solvents as a function of potential using 0.1 M TEAP as electrolyte at 25 ± 0.5 °C. In addition, the temperature dependence of the standard rate constants was determined in three of these solvents in order to estimate ΔH^*_{ex}.

Diffusion Coefficients. Diffusion coefficients for TKQ obtained in different solvents are reported in Table 1, together with values of solvent viscosity, η. It is apparent that the diffusion coefficients for TKQ vary considerably with solvent, being largest in the solvents with low viscosity.[10] According to the Stokes−Einstein theory, which relates D to η, one can calculate the effective radius, r, of the diffusing species modeled as a sphere:

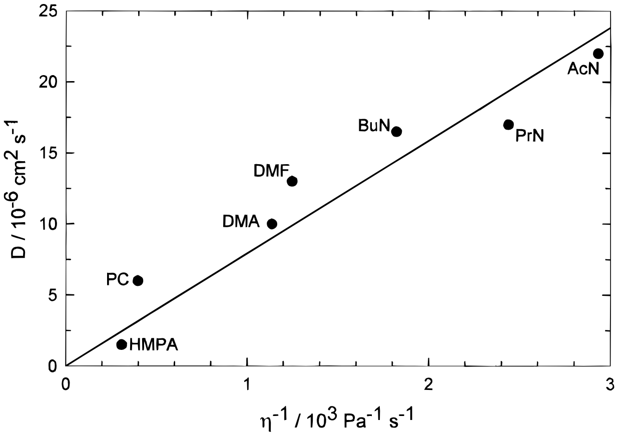

Figure 1. Plot of the diffusion coefficient, D, against the reciprocal of viscosity, η^{-1}, for TKQ in different solvents at 25 °C with 0.1 M TEAP as electrolyte.

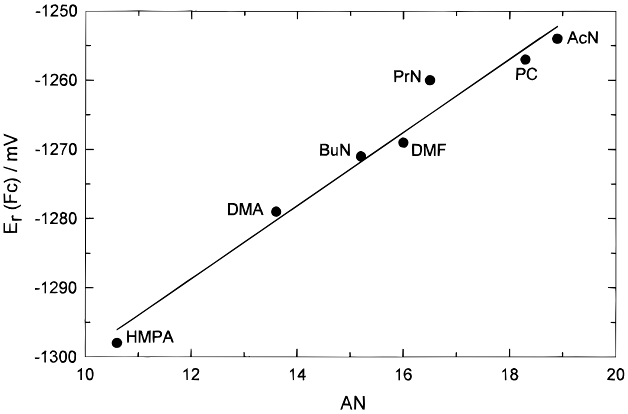

Figure 2. Plot of the standard potential for reduction in various solvents on the Fc/Fc$^+$ scale against the Gutmann acceptor number (AN).

$$D = kT/6\pi r\eta \tag{3}$$

In this one-parameter fit, the effective radius for TKQ estimated using eq 3 equals 0.28 ± 0.02 nm (Figure 1). The effective radius obtained from the present analysis is very similar to that calculated in an earlier study[14] for *p*-dicyanobenzene and anthracene (organic compounds of comparable size).

Standard Potentials. According to previous experimental results,[15−17] the standard potential for the formation of an anion is expected to have a strong dependence on the acidic properties of the solvent, that is, its ability to accept electrons. One scale measuring solvent acidity is the Gutmann acceptor number (AN).[15] Accordingly, the relationship between the standard potential and AN in the case of the formation of anions is given as

$$E(\mathrm{Fc}) = E_0(\mathrm{Fc}) + a\mathrm{AN} \tag{4}$$

where E(Fc) is the potential with reference to the ferrocinium$^{+/0}$ redox couple and E_0(Fc) is the standard potential in a solvent with zero acceptor number, which equals −1.35 V.

The relationship obtained on the basis of the present data is shown in Figure 2. The quality of the linear fit obtained is quite good with a correlation coefficient of 0.986. This result

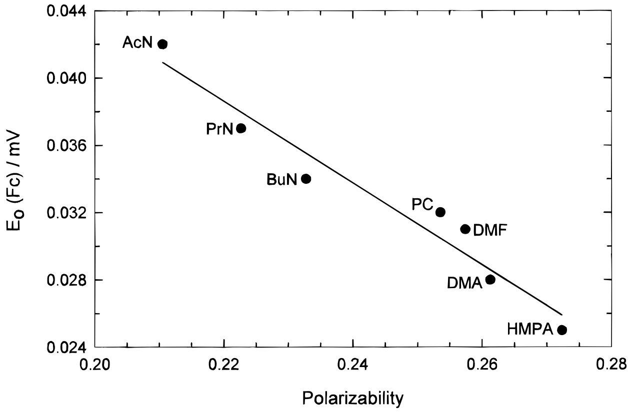

Figure 3. Plot of the standard potential for oxidation on the Fc/Fc$^+$ scale against solvent polarizability.

TABLE 2: Standard Potentials for Reduction E_r and for Oxidation E_o Scaled to the Fc/Fc$^+$ Reference Redox Couple Together with the Acceptor Number AN and Polarizability Parameter P

solvent	E_r(Fc/mV)	AN	E_o(Fc)/mV	polarizability
AcN	−1254	18.9	0.042	0.2105
BuN	−1271	15.2	0.034	0.2327
DMA	−1279	13.6	0.028	0.2613
DMF	−1269	16	0.031	0.2574
HMPA	−1298	10.6	0.025	0.2723
PC	−1257	18.3	0.032	0.2535
PrN	−1260	16.5	0.037	0.2227

is expected, since the negative charge on the anion radical is associated with the six-membered carbon ring,[7] so that it achieves stabilization as a result of specific solvent properties. Furthermore, the standard potentials for reduction become more negative as the acidity of the solvent decreases in the order AcN > PC > PrN > DMF > BuN > DMA > HMPA, indicating that the anion radical formed is most stable and thus most easily reduced in the solvent AcN (see Table 2). The values of the acceptor number for PrN and BuN are not available. Instead, they were estimated on the basis of a linear correlation between the Dimroth−Reichardt E_T parameter[15] and the Gutmann AN (correlation coefficient, 0.964). On the basis of this analysis, the estimates of AN are 16.1 and 15.2 for PrN and BuN, respectively. If the analysis is conducted with the addition of another term to eq 4 linear in a second solvent parameter such as the Gutmann donor number (DN), solvent polarizability (P), or solvent polarity (Y),[15] the quality of the fit is not improved, the dominant term in the regression analysis always being the AN.

According to previous experimental results for other systems,[4,11] when cation radicals are formed in an oxidation reaction, solvent donicity is the parameter of most importance, as it reflects the ability of the solvent to donate a pair of electrons and therefore stabilize cations. However, according to the present data the standard potential for the oxidation step in the case of TKQ is a linear function of solvent polarizability (P), with a correlation coefficient equal to 0.973 (Figure 3). Solvent polarizability is defined as

$$P = (n_D^{\,2} - 1)/(n_D^{\,2} + 2) \qquad (5)$$

where n_D is the refractive index of the solvent at the sodium D line, and it reflects the molecular polarizability of the solvent on the basis of the Lorentz−Lorenz model.[18] This result is connected with the fact that the charge on the cation radical is associated with the four dimethylamino groups (see TKQ structure). This is not at all suprising, as a previous study of the oxidation of TKQ to its semiquinone cation radical indicated that the extraordinary redox behavior of this sterically overcrowded and electron-rich compound is due to equal distribution of the positive charge over the four dimethylamino substituents.[7] The values of the standard potential for oxidation together with the solvent's polarizability are also summarized in Table 2.

TABLE 3: Standard Rate Constants for Both Reduction k_{sr} and Oxidation k_{so} Together with the Experimental Transfer Coefficients α_{ex} at a Au Ultramicroelectrode in 0.1 M TEAP at 25 °C

solvent	k_{sr}/cm s^{-1}	α_{ex}	k_{so}/cm s^{-1}	α_{ex}
AcN	1.25	0.47	1.05	0.52
BuN	0.83	0.49	0.85	0.48
DMA	0.52	0.48	0.68	0.46
DMF	0.62	0.5	0.74	0.51
HMPA	0.1	0.53	0.2	0.49
PC	0.43	0.49	0.52	0.51
PrN	0.9	0.52	0.87	0.43

Electron Transfer Parameters. Measured values of k_s and α_{ex} for both reactions are given in Table 3. The temperature dependence of the kinetic parameters was determined in DMA, PC, and PrN at five different temperatures. The values of ΔH^*_{ex} are given in Table 4, together with calculated values for the Gibbs energies and enthalpies of activation from current theories.

The k_s values for the studied reactions at 25 °C are considerably solvent dependent. They change by 1 order of magnitude for both systems when the solvent viscosity is changed. There is also some increase in ΔH^*_{ex} with increase in solvent viscosity. The values of α_{ex} are close to 0.5, the value that one would expect for a simple electron transfer reaction in the absence of double-layer effects. When reactions 1 and 2 are compared in a given solvent, the rate constants for the two processes are approximately the same whereas the value of ΔH^*_{ex} for the reduction reaction is somewhat larger than that for oxidation.

The expression for the standard rate constant considering dynamical solvent effects but ignoring double-layer effects[1] may be written as

$$\ln k_s + \Delta G^*_{os}/RT = -\theta \ln \tau_L + \ln A - \Delta G^*_{is}/RT \qquad (6)$$

where A is the part of the preexponential factor that is solvent independent, τ_L is the solvent's longitudinal relaxation time, θ is a fraction between 0 and 1 which depends on the degree of reaction adibaticity and/or the relative sizes of the inner- and outer-sphere reorganization energies, and ΔG^* is the Gibbs activation energy containing an inner-sphere reorganization energy component, ΔG^*_{is} (the amount of work done to change bond lengths and bond angles which accompany the activation process), and an outer-sphere reorganization energy component, ΔG^*_{os} (accounting for the work done to reorganize the solvent molecules around the reactant).

The outer-sphere contribution to the Gibbs activation energy is traditionally estimated on the basis of the Marcus model and is given in Table 4 assuming r_A is 0.28 nm. Assuming that image effects are absent, the expression for ΔG^*_{os} is

$$\Delta G^*_{os} = N_0 e_0 / 32\pi\epsilon_0 r_A (1/\epsilon_{op} - 1/\epsilon_s) \qquad (7)$$

where N_0 is the Avogadro constant, e_0 the fundamental electronic charge, ϵ_0 the permittivity of free space, r_A the radius of the reactant A represented as a sphere, ϵ_{op} the optical relative permittivity of the solvent, and ϵ_s the static value. This model is expected to overestimate ΔG^*_{os} especially for reactions involving cations.

TABLE 4: Estimates of the Outer-Sphere Contribution ΔG^*_{os} and ΔH^*_{os} to the activation Enthalpy According to the Marcus and MSA Model, Together with the Experimentally Observed Activation Enthalpy ΔH^*_{ex} and the Sum of the Inner- and Outer-Sphere Enthalpies ΔH^* [a]

		ΔG*os(MSA)			ΔH*os(MSA)			ΔH*ex		ΔH*	
solvent	ΔG*os (Marcus)	(+/0)	(0/−)	ΔH*os (Marcus)	(+/0)	(0/−)	ΔH_L	(+/0)	(0/−)	(+/0)	(0/−)
AcN	32.7	18.4	25	28.1	16.6	24.5	5.6				
BuN	29.9	16.4	21.7	27.2	16.3	23.2	6.5				
DMA	28.4	15.8	19.3	24.5	13.5	19.3	8	22.7	24.5	16.3	19
DMF	28.7	15.9	20.4	25.3	14.7	22.4	6.9				
HMPA	27.1	14.8	17.8	26.4	16.1	21	11.5				
PC	29.8	15.2	21.8	25.9	14.1	20.8	13.4	26.6	29.9	16.6	20.7
PrN	31.2	17.2	23.2	27.3	12.6	17.8	6.02	19.6	23.2	14.8	18.1

[a] All values of ΔG and ΔH are in kJ mol^{-1}.

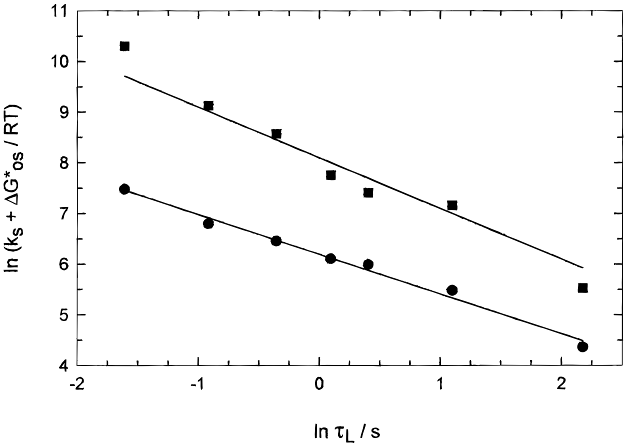

Figure 4. Plot of the logarithm of the standard rate constant corrected for the outer-sphere contribution to the Gibbs activation energy according to the MSA for both electroreduction (■) and electrooxidation (●) of TKQ in a given solvent against the logarithm of the longitudinal relaxation time for the solvent.

Another model used to estimate ΔG^*_{os} is the mean spherical approximation (MSA), which takes into account molecular solvation effects. In this approach, the expression for ΔG^*_{os} becomes

$$\Delta G^*_{os} = -N_0 e_0^2/32\pi\epsilon_0[(1 - 1/\epsilon_{op})r_A^{-1} - (1 - 1/\epsilon_s)(r_A + \delta_s)^{-1}] \quad (8)$$

where δ_s is a parameter which depends on solvent nature and whether the ionic product is a cation or an anion. Values of this parameter estimated from the Gibbs energy and entropy of solvation of monoatomic monovalent ions have been tabulated.[20] The estimates of ΔG^*_{os} on the basis of the MSA model for reactions 1 and 2 are also presented in Table 4. They are significantly smaller than the Marcus estimates.

ΔG^*_{os}(MSA) was used to correct the standard rate constant, and a plot of the logarithm of the corrected standard rate constant against the logarithm of the longitudinal relaxation time (eq 6) was used to determine the degree of reaction adiabaticity from the slope of the resulting straight line, as seen in Figure 4. On the basis of a linear least-squares analysis, θ equals 1.0 ± 0.2 for the case of reduction ($r = 0.895$) and 0.78 ± 0.04 for the case of oxidation ($r = 0.989$). These results indicate that the reduction reaction is adiabatic within experimental error. The lower value of θ for the oxidation reaction suggests this process is only weakly adiabatic. This result suggests that intramolecular reorganization is larger for this process than for the reduction reaction.

Activation Enthalpies. The experimental activation enthalpies, ΔH^*_{ex}, for both the reactions considered are also summarized in Table 4. They fall in the range 19−27 and 23−30 kJ mol^{-1} for oxidation and reduction, respectively. It is readily apparent that ΔH^*_{ex} depends on both the type of solvent and the nature of the reaction. In general, the values of ΔH^*_{ex} increase with solvent viscosity[10] for both cases considered, and the value of ΔH^*_{ex} for the reduction reaction is larger than that for oxidation, as expected.[11]

Just as for ΔG^*, there are two contributions to the activation enthalpy: the inner-sphere reorganization enthalpy, ΔH^*_{is}, and the outer-sphere reorganization enthalpy, ΔH^*_{os}. A third contribution, the longitudinal dielectric relaxation enthalpy, ΔH_L, comes from the preexponential factor which is temperature dependent through the temperature dependence of relaxation time τ_L. On the basis of the temperature dependence of ln k_s and neglecting double-layer effects, ΔH^*_{ex} is given by[1]

$$\Delta H^*_{ex} = \Delta H^*_{is} + \Delta H^*_{os} + \theta \Delta H_L \quad (9)$$

From eq 9, one can easily calculate the standard enthalpy of activation ΔH^*, which is the sum of the outer- and inner-sphere activation enthalpies, provided both θ and ΔH_L are known:

$$\Delta H^* = \Delta H^*_{ex} - \theta \Delta H_L = \Delta H^*_{os} + \Delta H^*_{is} \quad (10)$$

Values of ΔH_L, for most polar solvents, are available in the literature.[1] On the basis of both the Marcus model and the MSA,[1] one can estimate ΔH^*_{os}. If ΔS^*_{os} is assumed to be negligible, as in the case of other quinones studied previously,[2,3] then $\Delta H^*_{os} \approx \Delta G^*_{os}$. In the present study, estimates of ΔG^*_{os} and ΔH^*_{os} differ by only a few kJ mol^{-1}, a negligible difference with respect to the observed change in ΔH^*_{ex} with solvent nature. This aspect of the analysis of activation parameters for electron transfer reactions was emphasized in earlier work.[1,11]

Values of ΔH^* estimated using the values of θ determined on the basis of eq 6 (Figure 4) and previous estimates[1,11] of ΔH_L are also recorded in Table 4 for kinetic data obtained in DMA, PC, and PrN. First of all, a significant difference between values of ΔH^* is seen in reactions (1) and (2). Secondly, the experimental values of ΔH^* are all significantly less than the Marcus estimate of ΔH^*_{os}. This provides further evidence[1,11] that the Marcus estimates are too large.

On the other hand, the values of ΔH^* for the reduction reaction agree very well with the MSA estimates for a reaction involving formation of an anion. This suggests that the value of ΔH^*_{is} for this process is negligible. Such a conclusion is supported by the observation that the reduction process is adiabatic ($\theta = 1$) on the basis of the solvent effect observed in seven aprotic systems at 25 °C.

In the case of the oxidation process, the MSA estimates of ΔH^*_{os} for a reaction in which a cation is formed are all ~2 kJ mol^{-1} smaller than the observed values of ΔH^*. This suggests that ΔH^*_{is} for this reaction is ~2 kJ mol^{-1}. This conclusion is supported by the observation that the oxidation process is only weakly adiabatic ($\theta = 0.78$). It is also consistent with data obtained earlier[21] for simple redox reactions with small values of ΔH^*_{is}.

An alternative way of analyzing the experimental values of ΔH^*_{ex} on the basis of eq 9 is to plot $\Delta H^*_{ex} - \Delta H^*_{os}$ against ΔH_L and to determine ΔH^*_{is} and θ from the intercept and slope, respectively, of the resulting linear relationship. Such a procedure was used earlier[11] in the analysis of data for the electrooxidation and electroreduction of cobaltocene.[11] Application of this procedure to the present results yielded values of θ that are similar to those discussed above, but somewhat smaller. Since the linear analysis is based on only three data points, it is considered much less reliable and therefore is not presented here.

The differences between electron transfer kinetics in the two systems studied are related to the structural differences and changes accompanying electron transfer, as supported by ESR spectral data.[7] This is seen not only from the dependence of the standard rate constant on the nature of the solvent but also from the corresponding dependence of the enthalpy of activation. The present results support the notion that the formation of the cation radical requires significant intramolecular reorganization.

Conclusion

The present experiments clearly demonstrate that both electron transfer reactions studied are influenced by dynamic solvent effects. This is seen not only from the dependence of the standard rate constant on the nature of the solvent but also from the dependence of the enthalpy of activation on the solvent. The present analysis demonstrates that the reduction reaction is close to adiabatic since the coefficient θ is close to unity and that the oxidation reaction is only weakly adiabatic. Furthermore, analysis of the activation enthalpy data demonstrates that the outer-sphere reorganization energy to form an anion from the present reactant is greater than that to form a cation. A similar conclusion was reached earlier on the basis of experiments with cobaltocene.[11]

Using estimates based on the MSA model, we conclude that the inner-sphere reorganization for both reactions is small. Previous studies of aromatic compounds with a large effective radius indicate that the structural changes in these systems are small and that the major contribution to the activation energy is solvent reorganization.[21]

As expected, the standard potential for both reactions depends on solvent nature. However, the solvation of the cation radical does not depend significantly on the donor properties of the solvent but, instead, on solvent polarizability. This suggests that the charge distribution in the cation radical is important in determining the nature of the solvent effect.

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