verged with $R = 0.0540$ and $R_w = 0.487$ for 3763 unique reflections with $F_o > 4\sigma(F_o)$. The largest shift/esd in the final cycles was 0.415. A final difference synthesis showed no significant residual features (maximum and minimum electron densities 0.71 and −0.49 e Å^{-3}, respectively). Complex neutral-atom scattering factors[27] were used for all atoms.

Acknowledgments are made to the Natural Sciences and Engineering Research Council of Canada (NSERCC) and the Quebec Department of Education for financial support.

Supplementary Material Available: Fractional atomic coordinates and isotropic temperature factors of the calculated H atom positions (Table III), anisotropic temperature factors (Table IV), bond lengths and angles (Table V), a diagram of the structure of **2a** (Figure S1), a diagram of the unit cell (Figure S2), a description of product yields, elemental analyses, melting points, mass spectra, and IR and ^{1}H NMR data for 8-quinolinecarboxylic acid, **1b–e**, and **2b–e**, and NMR spectra of **1a**, **1c**, **2a**, and **2c** (Figures S3–6) (21 pages); observed and calculated structure factors (Table VI) (16 pages). Ordering information is given on any current masthead page.

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Temperature, Pressure, and Viscosity Dependence of Outer-Sphere Electron-Transfer Processes. Reduction of Aquapentaamminecobalt(III) by Hexacyanoferrate(II)

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Received June 3, 1988

The outer-sphere electron-transfer reaction between $Co(NH_3)_5H_2O^{3+}$ and $Fe(CN)_6^{4-}$ was studied as a function of temperature (20–35 °C), pressure (0.1–100 MPa), and solvent composition (water–glycerol mixtures up to 57 wt % glycerol). The experimental rate data were corrected for changes in viscosity with changes in temperature and pressure, and the resulting activation parameters were interpreted in terms of medium effects on the electron-transfer process. Both $\Delta H^{\ddagger}$ and $\Delta S^{\ddagger}$ increase significantly with increasing glycerol concentration, whereas $\Delta V^{\ddagger}$ remains constant within the experimental error limits. The results point to the importance of solvent rearrangement and collisional contributions in determining the rate of the electron-transfer process.

Introduction

Our general interest in the application of high-pressure techniques in the mechanistic analysis of inorganic and organometallic reactions[1] has led to some investigations involving typical outer-sphere electron-transfer (OSET) processes.[2-5] Earlier theoretical predictions revealed an apparently close correlation with experimentally observed volumes of activation,[6] but later work showed this to be wrong,[7] and the correlation is more complicated than originally predicted.[2,8] In an effort to gain more information on the intimate nature of the electron-transfer process itself, within the concepts of an outer-sphere mechanism, we have extended our earlier work to include an additional kinetic parameter, namely viscosity. This parameter should provide more information on the dynamic effect of the solvent on the electron-transfer process.

The role of solvent dynamics in electron-transfer processes has been realized for many years,[9-11] and the extensive theoretical treatments by Marcus[12-15] have quantified the solvent reorganization contribution toward the energy required for the electron-transfer process. Only a few studies have investigated the solvent dependence of such reactions.[16-20] The observed trends call for rather complex analyses since solvent variation affects a wide range of physical and chemical parameters that may affect the kinetics of the process in different ways. For this reason we prefer in the present study to examine the effect of viscosity on the process by varying the solvent composition of a water–glycerol mixture.

The reduction of $Co(NH_3)_5OH_2^{3+}$ by $Fe(CN)_6^{4-}$ follows an outer-sphere electron-transfer mechanism, and electron transfer occurs within the precursor ion pair.[3] The ion-pair-formation and electron-transfer rate constants can be determined kinetically and studied as a function of temperature, pressure, and viscosity. The kinetic separation of these constants enables a direct estimate of the electron-transfer rate constant within the ion pair, something that is not always possible. In cases where electron transfer is characterized by a second-order rate constant, it is usually a composite quantity and a detailed interpretation of the activation parameters is impossible. In addition, the results of this study allow us to comment on the adiabaticity versus nonadiabaticity of the OSET process.

Experimental Section

Materials. The complex $[Co(NH_3)_5H_2O](ClO_4)_3$ was prepared according to the method described in the literature.[21,22] Chemical analysis[23] and UV–vis spectral data were in agreement with the theoretically

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Table I. Viscosity as a Function of Temperature and Pressure for Water–Glycerol Mixtures[30,31]

		viscosity, cP			
T, °C	*p*, MPa	0[a]	19.4[a]	34.3[a]	57.2[a]
20	0.1	1.00	1.70	2.94	9.10
25		0.893	1.52	2.53	7.38
30		0.800	1.34	2.18	6.15
35		0.719	1.082	1.981	5.03
30	5	0.800	1.335	2.181	6.172
	25	0.800	1.330	2.189	6.393
	50	0.800	1.331	2.203	6.627
	75	0.800	1.335	2.227	6.889
	100	0.800	1.345	2.259	7.167

[a] Weight percent of glycerol.

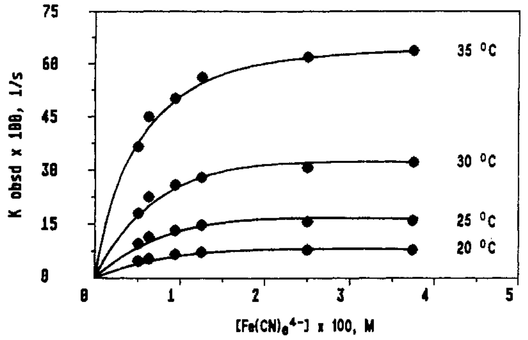

Figure 1. Plot of k_{obsd} versus $[Fe(CN)_6^{4-}]$ for the reaction in 34.3 wt % glycerol as a function of temperature. For experimental conditions see Table II.

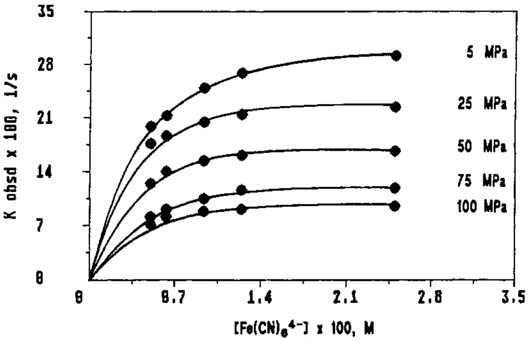

Figure 2. Plot of k_{obsd} versus $[Fe(CN)_6^{4-}]$ for the reaction in 34.4 wt % glycerol as a function of pressure. For experimental conditions see Table II.

expected values and those reported in the literature, respectively. All chemicals used were of analytical reagent grade, and doubly distilled water was used as the solvent throughout this study. The viscosity of the solvent was altered by the addition of glycerol, which was purified through vacuum distillation; its purity was checked by measuring its refractive index ($n^{20}_D = 1.475$). The water–glycerol solvent mixtures were saturated with Ar before being used in the kinetic work. The ionic strength of the medium was kept constant at 0.5 M with the aid of $NaClO_4$. The redox reaction was followed via the formation of $Fe(CN)_6^{3-}$, and H_2EDTA^{2-} (EDTA = ethylenediaminetetraacetate) was added to prevent the formation of $Co_3[Fe(CN)_6]_2$ by binding the produced Co^{2+} as Co(EDTA).[24,25] In addition, an acetate buffer was used to limit the drift in pH during redox reaction resulting from the release of NH_3.[3,24] Both of these precautions are, according to our experience, not very critical and are not affected significantly by changes in solvent composition, temperature, or pressure.

Recently Saito and co-workers[26] reported that a more accurate kinetic behavior (i.e. better pseudo-first-order plots) was observed when DTPA (diethylenetriaminepentaacetate) was used instead of H_2EDTA^{2-}, which especially affected the stability of the infinity absorbance value. We found that it did improve the stability of the infinity value, but with no significant effect on the value and accuracy of the observed rate constant. In addition, at higher [Fe(II)] ($>2 \times 10^{-2}$ M) we observed an influence of DTPA on the Fe(II) complex, which resulted in an unwanted absorbance increase around 420 nm, where the electron-transfer reaction was monitored. We assume that some complex formation reaction occurs between $Fe(CN)_6^{4-}$ and DTPA under such conditions and therefore preferred to use H_2EDTA^{2-} as in our earlier work.[3,4]

Instrumentation. UV–visible absorption spectra were recorded on a Shimadzu UV 250 spectrophotometer. pH measurements were performed on a WTW instrument equipped with a reference electrode filled with 3 M NaCl. Kinetic measurements were performed with an Aminco stopped-flow instrument at ambient pressure and a self-constructed high-pressure stopped-flow unit at elevated pressures.[27] All kinetic measurements were performed under pseudo-first-order conditions, and the observed rate constants were calculated in the usual way by using an on-line data acquisition system.[28] The corresponding first-order plots were linear for at least 3 half-lives of the reaction under all experimental conditions.

Results and Discussion

In a series of preliminary experiments the effect of the addition of glycerol to the solvent was analyzed in detail. Repetitive-scan spectra revealed no meaningful deviations, and the overall redox reaction followed the same pattern as in pure water. Even the spectral properties of the reactant and product species remained unchanged, from which it was concluded that glycerol at concentration levels up to 60% by weight did not affect the chemistry of the investigated system as detected by these techniques.

Addition of glycerol to water does affect a number of physical properties such as the dielectric constant, electrochemical parameters, and especially the viscosity. In comparison to water, glycerol has a lower dielectric constant and a lower dipole moment,[29] and it follows that these parameters will decrease on increasing the glycerol content of the solvent. For a dissolved electrolyte, the molar conductivity at infinite dilution also decreases with increasing glycerol concentration.[30] The viscosity dependence of water–glycerol mixtures as a function of temperature was extrapolated from literature data,[29] whereas that for the pressure dependence was determined by Küss.[31] The viscosity data employed in this study are summarized as a function of composition, temperature, and pressure in Table I.

The suggested mechanism for the outer-sphere electron-transfer reaction between $Co(NH_3)_5H_2O^{3+}$ and $Fe(CN)_6^{4-}$ can be summarized as in reactions 1 and 2. Under pseudo-first-order conditions, i.e. excess $Fe(CN)_6^{4-}$, the observed rate constant is a composite quantity as shown in (3). It follows that temperature,

$$Co(NH_3)_5H_2O^{3+} + Fe(CN)_6^{4-} \overset{K}{\rightleftharpoons} \{Co(NH_3)_5H_2O^{3+},Fe(CN)_6^{4-}\} \quad (1)$$

$$\{Co(NH_3)_5H_2O^{3+},Fe(CN)_6^{4-}\} \xrightarrow{k} Co^{2+} + 5NH_3 + H_2O + Fe(CN)_6^{3-} \quad (2)$$

$$k_{obsd} = kK[Fe(CN)_6^{4-}]/(1 + K[Fe(CN)_6^{3-}]) \quad (3)$$

pressure, and viscosity will affect the value of k_{obsd} through their influence on k and K and require detailed kinetic measurements to resolve the individual contributions. Plots of k_{obsd} versus $[Fe(CN)_6^{4-}]$ are strongly curved, and the double-reciprocal-plot procedure can be adopted to resolve the values of k and K.[3,4,24-26] This behavior was observed under all experimental conditions employed.

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Table II. Values of k and K as a Function of Solvent Composition and Temperature at Ambient Pressure[a]

	10^2k, s^{-1}			
T, K	0[b]	19.4[b]	34.3[b]	57.2[b]
293.2	7.1 ± 0.2[c]	6.9 ± 0.2	9.2 ± 0.4	12.1 ± 0.7
298.2	12.7 ± 1.0	15.6 ± 0.3	19 ± 1	25 ± 1
303.2	28 ± 2	29.4 ± 0.6	38 ± 3	52 ± 3
308.2	55 ± 5[c]	61.1 ± 0.9	74 ± 4	121 ± 5
$\Delta G^\ddagger$(298.2 K), kJ mol^{-1}	77.9	77.7	77.1	76.4
$\Delta H^\ddagger$, kJ mol^{-1}	102 ± 5	106 ± 3	102 ± 4	112 ± 4
$\Delta S^\ddagger$, J K^{-1} mol^{-1}	79 ± 15	93 ± 10	85 ± 13	121 ± 14

	K, M^{-1}			
T, K	0[b]	19.4[b]	34.3[b]	57.2[b]
293.2		182 ± 8	219 ± 8	324 ± 27
298.2	213 ± 13	205 ± 3	227 ± 11	348 ± 32
303.2	199 ± 10	240 ± 5	200 ± 37	276 ± 21
308.2		228 ± 2	212 ± 9	255 ± 11

[a] Data calculated from Table A (supplementary material): [Co(III)] = 5 × 10^{-4} M; [edta] = 1 × 10^{-3} M; [CH_3COOH] = [CH_3COONa] = 2.5 × 10^{-3} M; ionic strength 1.0 M ($NaClO_4$). [b] Weight percent of glycerol. [c] Extrapolated value.

Table III. Values of k and K as a Function of Solvent Composition and Pressure[a]

	10^2k, s^{-1}			
p, MPa	0[b]	19.4[b]	34.3[b]	57.2[b]
0.1	28.3 ± 0.1	29.4 ± 0.6	35.0 ± 0.3	55.0 ± 0.3
2.5		28.3 ± 0.2	33.4 ± 0.4	54.4 ± 0.2
25		22.0 ± 0.4	24.2 ± 0.1	44.7 ± 0.3
50		17.8 ± 0.1	18.9 ± 0.4	35.4 ± 0.4
75		13.4 ± 0.7	14.3 ± 0.1	25.9 ± 0.4
100		10.7 ± 0.2	10.7 ± 0.2	20.4 ± 0.3
$\Delta V^\ddagger$, cm^3 mol^{-1}	27 ± 2[a]	25.4 ± 0.5	29.6 ± 0.9	25.3 ± 0.8

	K, M^{-1}			
p, MPa	0[b]	19.4[b]	34.3[b]	57.2[b]
0.1	198 ± 10	240 ± 5	200 ± 37	276 ± 21
2.5		242 ± 7	281 ± 29	232 ± 18
25		303 ± 7	534 ± 36	277 ± 22
50		291 ± 9	411 ± 38	335 ± 22
75		323 ± 8	271 ± 48	450 ± 34
100		294 ± 11	432 ± 77	353 ± 32

[a] Data calculated from Table B (supplementary material): T = 303.2 K; [Co(III)] = 5 × 10^{-4} M; [edta] = 1 × 10^{-3} M; [CH_3COOH] = [CH_3COONa] = 2.5 × 10^{-3} M; ionic strength 1.0 M ($NaClO_4$). [b] Weight percent of glycerol.

Values for k_{obsd} as a function of [Fe(II)] in four different water–glycerol mixtures are summarized as a function of temperature (293–308 K) and pressure (0.1–100 MPa) in Tables A and B (supplementary material), respectively. Typical examples of plots of k_{obsd} versus [Fe(II)] are given in Figures 1 and 2 for 34.3 wt % glycerol as a function of temperature and pressure, respectively. The data were treated according to the double-reciprocal-plot procedure described above, and the resulting values of k and K for various solvent compositions are summarized in Tables II and III, as a function of temperature and pressure, respectively. The activation parameters $\Delta G^\ddagger$, $\Delta H^\ddagger$, $\Delta S^\ddagger$, and $\Delta V^\ddagger$ were calculated in the usual way and are included in these tables.

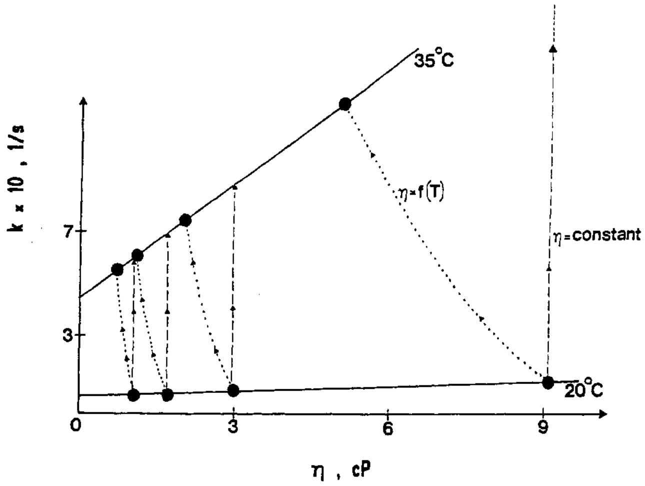

Figure 3. Schematic presentation of the correction procedure of k for the temperature dependence of the viscosity of the medium.

The values of K are subject to large errors, as discussed before,[3,4] and are not interpreted in more detail. Their magnitude is in good agreement with that reported before. More important for the mechanistic interpretation are the values of k and the associated activation parameters.

The interpretation of k as a function of solvent composition at various temperatures and pressures is complicated by the fact that solvent viscosity does not remain constant during the variation of these physical parameters (see Table I). This means that the viscosity dependences of these parameters are partly due to the influence of the variation in viscosity on the value of k caused by the kinetic variable being studied. To resolve this complication, the data were extrapolated to constant viscosity in the following way. Throughout this study k increases linearly with η and the data can be plotted as in Figure 3 by combining the data in Tables I and II. From a linear least-squares analysis it is possible to extrapolate the values of k as a function of temperature at constant viscosity, and the results are summarized in Table IV. In a similar way, the data in Table III were corrected for the change in viscosity with increasing pressure and the extrapolated data are summarized in Table V.

The data in Tables II–V clearly demonstrate the increase in k with increasing viscosity. The effect becomes larger at higher temperatures and pressures. It is accompanied by a moderate increase in $\Delta H^\ddagger$ and $\Delta S^\ddagger$, whereas $\Delta G^\ddagger$ and $\Delta V^\ddagger$ remain constant within the experimental error limits of the data. The slight decrease in $\Delta G^\ddagger$ accounts for the overall increase in k with increasing viscosity. In other words, the increase in $\Delta S^\ddagger$ is responsible for the observed viscosity dependence, from which we conclude that the electron-transfer processes is "entropy controlled". Outer-sphere electron-transfer processes in general depend strongly on collisional contributions toward the activation enthalpy resulting from collisional interactions of the reactant and solvent molecules. Such interactions are expected to be suppressed to some extent in more viscous media, with a resulting increase in $\Delta H^\ddagger$ required for electron transfer. On the other hand, charge neutralization in reaction 2 results in a decrease in electrostriction, which is accompanied by a significant increase in entropy. With increasing

Table IV. Calculated Values of k as a Function of Temperature at Constant Viscosity and Ambient Pressure

	10^2k, s^{-1}					
T, K	0[a]	1[a]	3[a]	5[a]	7[a]	10[a]
293.2	6.51	7.14	8.40	9.66	10.92	12.81
298.2	12.77	14.42	17.73	21.03	24.34	29.30
303.2	25.23	29.71	38.66	47.62	56.57	70.01
308.2	44.68	59.75	89.90	120.05	150.20	195.42
$\Delta G^\ddagger$(298.2 K), kJ mol^{-1}	78.1	77.8	76.8	76.8	76.4	76.0
$\Delta H^\ddagger$, kJ mol^{-1}	95 ± 2	104 ± 1	116 ± 4	123 ± 5	128 ± 6	133 ± 6
$\Delta S^\ddagger$, J K^{-1} mol^{-1}	55 ± 6	88 ± 4	130 ± 12	156 ± 16	174 ± 19	192 ± 21

[a] η value in cP.

Table V. Calculated Values of k as a Function of Pressure at Constant Viscosity and 303.2 K

	10^2k, s^{-1}					
p, MPa	0^a	1^a	3^a	5^a	7^a	10^a
0.1	23.6	28.7	38.9	49.1	59.3	74.6
5	21.7	27.0	37.6	48.2	58.9	74.8
25	15.1	19.7	28.9	38.2	47.4	61.3
50	12.3	15.8	22.7	29.6	36.5	46.9
75	9.8	12.1	16.8	21.4	26.0	33.0
100	7.6	9.3	12.9	16.4	20.0	25.3
$\Delta V^{\ddagger}$, cm^3 mol^{-1}	28 ± 2	28 ± 1	27.8 ± 0.4	27.8 ± 0.6	27.8 ± 0.8	28 ± 1

[a] η value in cP.

viscosity the dielectric constant, dipole moment, and ionic mobility of the medium decrease, with the result that a further decrease in electrostriction is expected under such conditions. This results in more positive $\Delta S^{\ddagger}$ values in a more viscous medium, indicating that the transition state is less structured under such conditions. It follows that solvent rearrangement is the driving force behind the electron-transfer process within the ion pair, resulting in an entropy-controlled reaction.

The volume of activation is also expected to reveal characteristic properties concerning the electron-transfer process.[2-4] The large positive values found in this study can be interpreted in terms of a significant decrease in electrostriction on going from a 3+,4− precursor ion pair to a 2+,3− successor ion pair during electron transfer. In our earlier study,[4] we presented arguments in favor of an interpretation based on the large increase in partial molar volume when $Fe(CN)_6^{4-}$ is oxidized to $Fe(CN)_6^{3-}$. Due to the higher dielectric constant of water compared to that of glycerol, it is reasonable to expect that the first solvation shell will mainly consist of water molecules and that its composition may in fact hardly change for the solvent mixtures used in this study. The decrease in electrostriction will therefore mainly be accompanied by release of the smaller water molecules, which could account for the very constant $\Delta V^{\ddagger}$ value reported in Table V. Contributions from the second and third solvation spheres are expected to mainly affect the values of $\Delta S^{\ddagger}$ and to account for the trend in the data in Table IV.

Further mechanistic information can be obtained by an analysis of the intimate nature of the transition state in terms of Kramers' stochastic model.[32,33] This has in general directed the discussion of OSET reactions toward the adiabaticity or nonadiabaticity of the process, a question that is in general currently unsettled.[34-37] In a recent study, Spiccia and Swaddle[38] performed theoretical calculations to account for the experimentally observed $\Delta V^{\ddagger}$ for OSET between MnO_4^- and MnO_4^{2-} in aqueous medium. They conclude that an adiabatic or slightly nonadiabatic ellipsoidal-cavity model explains the experimental data very well. The need to invoke a cavity model may be due to the smallness of the reactant ions and could be unnecessary for OSET reactions of larger ions.[38] The experimentally determined ET rate constant (k in this study) is related to the transition-state-theory (TST) rate constant, k_{TST}, by the expression (4), where κ is the transmission coefficient[33] and represents the electronic factor for internal electron transfer within the outer-sphere complex.

$$k = \kappa k_{TST} \tag{4}$$

In many studies κ is assumed to be unity, which corresponds to an adiabatic OSET process. However, calculations have demonstrated[36] that κ can be significantly smaller than unity (as small as 2.5×10^{-3} [37]) in the case where ET is nonadiabatic. This corresponds to a situation where not each vibration within the transition state with energy k_BT will result in the formation of products. The coupling of the reaction coordinate with the surrounding medium (solvent) brings about that at low friction κ is proportional and at high friction inversely proportional to the collision frequency, which in turn is proportional to the viscosity of the medium. At low viscosity, weak coupling with the medium occurs and the process is collision-controlled. At high viscosity, strong coupling with the medium occurs and the reaction is diffusion-controlled.[32,33] The increase in k with increasing viscosity observed in this study suggests that weak coupling with the medium is present and that the electron-transfer process must have some nonadiabatic character. This is in agreement with a collision-controlled process and our arguments in favor of significant contributions from solvent rearrangement.

In terms of the pressure dependence of k, eq 4 results in the relationship $\Delta V^{\ddagger}(k) = \Delta V^{\ddagger}_{coll} + \Delta V^{\ddagger}_{TST}$, where $\Delta V^{\ddagger}_{coll} = -RT(\partial \ln \kappa/\partial P)_T$. The latter term may change sign depending on whether the process is collision- or diffusion-controlled, whereas $\Delta V^{\ddagger}_{TST}$ should remain constant independent of the effect of the medium. A conservative estimate of the latter, based on overall volume calculations and various theoretical considerations,[6-8,39,40] results in a value of ca. 28 cm^3 mol^{-1}. This means that although $\Delta V^{\ddagger}_{coll}$ is expected to be negative for a collision-controlled process, since κ increases with increasing viscosity, its overall contribution is very small since $\Delta V^{\ddagger}_{TST}$ is the major component contributing toward $\Delta V^{\ddagger}(k)$. Under such conditions it is understandable that $\Delta V^{\ddagger}(k)$ is independent of viscosity. Furthermore, the small contribution of $\Delta V^{\ddagger}_{coll}$ lets us believe that we are close to the maximum of the κ versus viscosity plot[32,33] in the present system, i.e. close to the situation where κ shows only a minor viscosity dependence on the border between collision- and diffusion-controlled processes. That means the electron-transfer process itself can be considered as slightly nonadiabatic or almost adiabatic with a κ value not too far away from unity. This is in good agreement with recent arguments presented in the literature.[38] The adiabatic character of the electron-transfer process is further supported by the significant temperature dependence of k_{ET}.[14] It was recently suggested[41] that plots of $\Delta S^{\ddagger}$ versus $\Delta V^{\ddagger}$ can be used to distinguish between adiabatic and nonadiabatic processes.

Within the experimental error limits involved, the ion-pair formation constants in Table III exhibit an increase with increasing pressure, which will result in a negative value for $\Delta \bar{V}(K)$. This is exactly opposite to what one would expect for such ion-pair formation,[26] and we found similar discrepancies before.[3,4] At present we feel that the data are not accurate enough to emphasize this trend too much. We have pointed out before[3,4] that the large experimental errors in K arise from the combination of different sets of experimental data in order to be able to construct the double-inverse plots as a function of pressure. Since K is obtained from a combination of the intercept and slope of such a plot, it is understandable that the error limits will be significantly larger than for k. In our earlier study[3] we reported a $\Delta \bar{V}(K)$ value of −15 ± 8 or −15.5 ± 0.4 cm^3 mol^{-1}, for the $Co(NH_3)_5H_2O^{3+}/Fe(CN)_6^{4-}$ system in water, depending on the method used to fit the data. Recently Saito and co-workers[26] reported a $\Delta \bar{V}(K)$ value of +3.5 ± 0.6 cm^3 mol^{-1} for this system. However, their $\Delta V^{\ddagger}(k)$

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value of +37.6 ± 1.2 cm^3 mol^{-1} is not too far away from our value of +26.5 ± 2.4 cm^3 mol^{-1}, demonstrating that the apparent discrepancy in $\Delta\bar{V}(K)$ does not affect the mechanistic interpretation for the electron-transfer step itself. Furthermore, Saito and coworkers[42] also reported a $\Delta\bar{V}(K)$ value of +23 ± 3 cm^3 mol^{-1} for the $Co(NH_3)_5py^{3+}/Fe(CN)_6^{4-}$ system, and the large deviation from the data for the corresponding aquo system (see above) remains uncertain. These discrepancies encourage us to point out that the precursor formation step probably involves more than pure electrostatic interaction, and it is quite possible that solvent molecules may not be released to such an extent as expected for the neutralization of charges accompanied by a decrease in electrostriction. A partial overlap of the molecular orbitals of the reactants may counteract the volume increase due to charge neutralization and result in overall negative $\Delta\bar{V}(K)$ values. The data in Tables II and III seem to support a slight increase in K with increasing viscosity, indicating that the thermodynamic stability of the precursor (ion pair) is affected to some extent by the viscosity of the medium.

We conclude that the results of the present study once again underline the importance of solvent rearrangement and collision processes in controlling the dynamics of the electron-transfer reaction in outer-sphere processes. The results can be understood in a qualitative way by considering the limitations of the transition-state theory and taking the dynamic effect of the reaction medium into account.

Acknowledgment. We gratefully acknowledge financial support from the Max Buchner Forschungsstiftung, the Deutsche Forschungsgemeinschaft, and the Fonds der Chemischen Industrie.

Supplementary Material Available: Listings of k_{obsd} for the reduction of $Co(NH_3)_5H_2O^{3+}$ by $Fe(CN)_6^{4-}$ as a function of temperature and [Fe(II)] (Table A) and as a function of pressure and [Fe(II)] (Table B) (2 pages). Ordering information is given on any current masthead page.

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Equilibrium of 17-Electron and 19-Electron Organometallic Radicals Derived from Carbonylmanganese Anions and Cations

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Received August 26, 1988

The transient 17-electron carbonylmanganese(0) radical $Mn(CO)_5^{\bullet}$ produced from the oxidation of $Mn(CO)_5^-$ is detected with the reversible potential $E° = 0.085$ V vs SCE by fast-scan cyclic voltammetry using platinum microelectrodes. The persistence of the substituted carbonylmanganese(0) radicals is prolonged by increasing numbers of phosphine ligands (P) in $Mn(CO)_4P^{\bullet}$ and $Mn(CO)_3P_2^{\bullet}$ radicals. In contrast, the 19-electron counterpart $Mn(CO)_6^{\bullet}$ cannot be detected by the corresponding electroreduction of the carbonylmanganese(I) cation $Mn(CO)_6^+$ even at very high scan rates. Furthermore, extensive substitution of the carbonylmanganese cation with different types of ligands did not increase the lifetimes of $Mn(CO)_5L^{\bullet}$ (where L = nitriles, isonitriles, phosphites, and phosphines), with τ estimated to be less than 100 ns. Finally, the evidence for the existence of the fugitive 19-electron carbonylmanganese(0) radical is obtained indirectly by the use of the diphosphine $PPh_2CH_2CH_2PPh_2$ (DPPE) as a chelating ligand. Thus, the quantitative analysis of the cathodic reduction of *cis*-$Mn(CO)_2(DPPE)_2^+$ by digital simulation of the cyclic voltammograms, especially those generated upon repetitive cycling, reveals the presence of the reversible interchange between the 19e radical $Mn(CO)_2(\eta^2\text{-DPPE})_2^{\bullet}$ and the 17e radical $Mn(CO)_2(\eta^2\text{-DPPE})(\eta^1\text{-DPPE})^{\bullet}$. The tethered diphosphine ligand allows such an unprecedented equilibrium to be observed despite a formation constant of $K \cong 10^6$ that overwhelmingly favors the 17-electron radical.

Introduction

Electron transfer provides invaluable access to metastable and reactive intermediates produced upon the oxidation–reduction of organometallic compounds, among which are an abundant variety of stable, diamagnetic metal carbonyls.[1,2] Thus, the electron-rich anions are nucleophiles[3,4] and the electron-poor cations are electrophiles[5] that yield 17-electron and 19-electron carbonylmetal radicals, respectively, upon the electron loss from and the electron accession to their 18-electron precursors.[6] Since electron-transfer processes are becoming increasingly relevant to organometallic chemistry,[7-9] it is important to establish the temporal limits for the detection and characterization of transient 17e and 19e radicals. In this study we utilize a series of carbonylmanganese anions and cations to explore the utility of the microvoltammetric techniques[10,11] for the study of reversible electron transfer, e.g.

$$\underset{}{Mn(CO)_5^-} \overset{-e^-}{\rightleftharpoons} \underset{17e}{Mn(CO)_5^{\bullet}} \overset{CO}{\rightleftharpoons} \underset{19e}{Mn(CO)_6^{\bullet}} \overset{+e^-}{\rightleftharpoons} Mn(CO)_6^+ \qquad (1)$$

In addition, a variety of substituted phosphine (P) derivatives such as the anionic $Mn(CO)_4P^-$, $Mn(CO)_3P_2^-$, etc. and the cationic $Mn(CO)_5P^+$, $Mn(CO)_4P_2^+$, etc. are available to modulate the reversible redox potentials $E°$ as well as the stabilities of the

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