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The Aqueous Hexacyanoferrate(II/III) Self-Exchange Reaction at High Pressures

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Measurements of the rate of the $Fe(CN)_6^{3-/4-}$ self-exchange in aqueous $KCl/(C_6H_5)_4AsCl$ media at ionic strength 0.5 mol kg^{-1} are consistent with the dominance of a single pathway involving the ion aggregates $\{K^+,Fe(CN)_6^{3-}\}$ and $\{(K^+)_2,Fe(CN)_6^{4-}\}$, with rate constants 5×10^5 kg mol^{-1} s^{-1} at 25 °C if the stepwise formation constants of the two ion aggregates are taken to be the same ($\approx$1.1 mol kg^{-1}; data from the literature show that dissociation of $\{K^+,Fe(CN)_6^{4-}\}$ may be neglected). The pressure dependence of the homogeneous exchange reaction (0.1–100 MPa) is described by $\Delta V_{ex}^{\ddagger} = +22 \pm 2$ cm^3 mol^{-1}—a uniquely strongly positive volume of activation for reactions between ions of like charge and one which helps explain the strongly positive volumes of activation associated with the reduction of cationic complexes by $Fe(CN)_6^{4-}$. In contrast, the effect of pressure on the $Fe(CN)_6^{3-/4-}$ self-exchange kinetics at a Pt electrode, as measured by cyclic voltammetry, gives $\Delta V_{el}^{\ddagger} = +8 \pm 2$ cm^3 mol^{-1}. These widely–differing volumes of activation can be reconciled by an extension of Marcus' theory (*Electrochim. Acta* **1968**, *13*, 995 and works cited). Analogy with counterion effects on the $MnO_4^{-/2-}$ exchange kinetics (*Inorg. Chem.* **1987**, *26*, 2265) suggests specific involvement of the cation in electron transfer between anions, in addition to any charge-neutralization effects.

Introduction

The hexacyanoferrate(II/III) couple is commonly used in conventional electrochemistry[2,3] and redox studies in bioinorganic chemistry[4–7] and has been the subject of several kinetic investigations in its own right.[2,3,7–13] To date, two studies of the effects of pressure P on the kinetics of the aqueous hexacyanoferrate(III/II) *electrode* reaction (at gold[12] and platinum[13] surfaces) have been published, and others on the associated equilibria[14,15] and diffusion coefficients[16] at high P have appeared recently, while there are several reports of high-pressure kinetic studies on "cross"-reactions involving this couple in *homogeneous* solution.[6,11–21] These latter reports[17–21] are intriguing in that the volumes of activation $\Delta V^{\ddagger}$ found for the reduction of cationic Co^{III} complexes by $Fe(CN)_6^{4-}$ are, after allowance for ion association effects, strongly positive (e.g., +37 cm^3 mol^{-1} for $Co(NH_3)_5OH_2^{3+}$[20]), whereas moderately *negative* $\Delta V^{\ddagger}$ values are predicted[21] and found[22,23] for outer-sphere self-exchange electron-transfer reactions of typical metal complexes in water. In order to put these observations in perspective, as well as to enhance our understanding of an important redox couple, we have measured the effect of P on the kinetics of the $Fe(CN)_6^{3-/4-}$ reaction in *homogeneous* aqueous solution, using ^{13}C-NMR.[7,9]

To date, our ability to measure pressure effects on the kinetics of homogeneous self-exchange redox reactions has been confined to those paramagnetic/diamagnetic couples for which the rates lie in the NMR time frame[22,23] and to those slow enough to permit the use of tracer[24] or optical rotatory[23] techniques. Extension of the high-pressure methodology to include electrode reaction[12–14] rates would expand the range of systems accessible for study substantially. Rate constants for electrode processes are not directly comparable with those for homogeneous reactions, not least because the dimensions are different (cm s^{-1} vs L mol^{-1} s^{-1}), but Marcus[25] and Hush[26] among others[27] have presented theoretical frameworks for such comparisons. The theory of Marcus[25] is the most widely cited and is adapted below to encompass the effect of *pressure* on homogeneous and electrode electron-transfer rates—a simpler comparison, since dimensionally-compatible volumes of activation are obtained in either case. Thus, a further objective of the present research was to test the validity of this approach by comparing the pressure dependence of the kinetics of the $Fe(CN)_6^{3-/4-}$ reaction in homogeneous aqueous solution with analogous data for the same reaction at an electrode.[12–14]

There is, however, a major complication with redox reactions of $M(CN)_6^{3-/4-}$ (M = Fe, Ru, Os) in water in that these highly-

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charged reactants associate strongly with their counterions.[2,7-12,28-33] Since extensive ion association is unavoidable at the reactant concentrations necessary for ^{13}C-NMR studies, we have reexamined the homogeneous $Fe(CN)_6^{3-/4-}$ exchange kinetics at ambient pressure to refine the conclusions of previous workers[7-11] concerning the nature and extent of involvement of the cation—in this case, K^+.

Experimental Section

Potassium hexacyanoferrate(III) (BDH AnalaR) and -(II) (Fisher Certified reagent) were recrystallized twice from water. Carbon-13-enriched $K_4Fe(CN)_6$ was made from KCN (99% ^{13}C; Sigma Chemical Corp.) and aqueous iron(II) sulfate.[10a] Deuterium oxide (Aldrich) was used as received.

For kinetic studies at ambient pressure, ^{13}C-NMR line-width measurements were made on D_2O solutions of $K_3Fe(CN)_6$ and $K_4Fe(CN)_6$ of either natural or (for experiments at constant ionic strength, where low hexacyanoferrate concentrations were necessary) enriched ^{13}C abundance. Potassium chloride was added to adjust the K^+ concentration as desired. In experiments at constant ionic strength I, tetraphenylarsonium chloride was used to make up the electrolyte balance. Addition of $EDTA^{4-}$, used in some instances in the radioisotopic $Fe(CN)_6^{3-/4-}$ exchange study of Wahl et al.[9c] to eliminate the effects of adventitious metal ions, was found not to affect the line-width measurements and was deemed unnecessary. A Varian XL-200 spectrometer (4.7 T) with standard multinuclear probehead, calibrated temperature controller (±0.1 °C), and spinning 10-mm sample tube was used.

For the high-pressure study, ^{13}C-enriched $K_4Fe(CN)_6$ was used, and the solutions, contained in a static cut-down 10-mm commercial NMR tube with a floating Teflon piston sealed with two O-rings, were placed inside a Vespel support bearing the rf saddle coils; the whole fitted within a specially-constructed Berylco pressure vessel with exterior helical channels through which thermostating fluid (water) circulated. The temperature inside the pressure vessel was monitored with a Pt resistance probe and was constant to better than ±1 °C. The apparatus is roughly similar to that described by Merbach et al.[34] for a 5-mm sample tube in a higher-field (9.4 T) spectrometer. Our use of a 10-mm sample tube was dictated by the low sensitivity of the samples in ^{13}C-NMR on the XL-200 spectrometer, as the signal-to-noise ratio was unacceptable with the 5-mm tube for which the probehead was designed. With the 10-mm tube, however, the clearance between the saddle coils and the pressure vessel walls was minimal, so that capacitive rf signal losses were significant and, furthermore, rf retuning was necessary every time the pressure was changed. This problem was compounded by the tendency of the coil support to swell slightly with increasing pressure, apparently through reversible absorption of the pressurizing fluid, and this limited the pressure ceiling to about 100 MPa. The system was reshimmed on the ^{2}H-FID at each pressure, for maximum reliability. Typically, several thousand transients were accumulated to give reliable line-width measurements; since the longitudinal relaxation time of ^{13}C was about 5 s, overnight or longer runs were necessary.

Results

Rate Equation at Constant [K^+]. At constant [K^+], the broadening $\Delta\nu_{1/2}$ of the ^{13}C-NMR line width of $Fe(CN)_6^{4-}$ due to the presence of $Fe(CN)_6^{3-}$ was directly proportional to [$Fe(CN)_6^{3-}$], within the experimental uncertainty of ±5%. Thus, at 25.0 °C, [$Fe(CN)_6^{4-}$] = 0.100 mol kg^{-1}, and $[K^+]_{tot}$ = 0.49 mol kg^{-1},[35] the function $\pi\Delta\nu_{1/2}/[Fe(CN)_6^{3-}]$ was effectively constant at (3.30 ± 0.13) × 10^4 kg mol^{-1} s^{-1} over the range [$Fe(CN)_6^{3-}$] = 1.2–9.4 mmol kg^{-1} and may be identified with the rate constant k_{obsd} for the homogeneous exchange of $Fe(CN)_6^{3-}$ with $Fe(CN)_6^{4-}$ (first order with respect to the stoichiometric concentrations of each of these). In particular, the strong upward curvature noted by Kurland and Winkler in plots of $\Delta\nu_{1/2}(^{13}C)$ vs [$Fe(CN)_6^{3-}$] (Figure 1 of ref 7) was absent. Values of k_{obsd} so obtained were in satisfactory agreement with those measured by Loewenstein et al.[10] using ^{14}N-NMR and by Wahl et al.[9] using a radiochemical method, insofar as conditions were comparable.

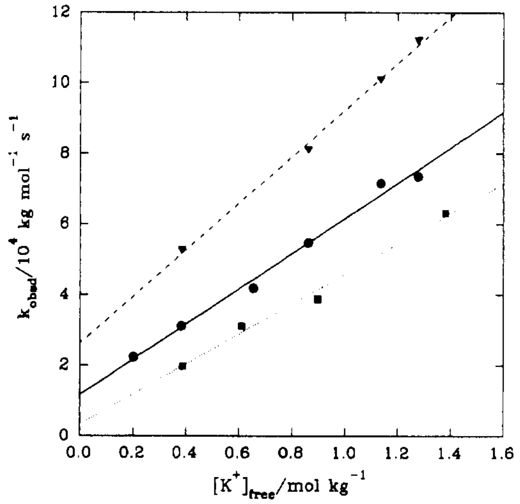

Figure 1. Rate constants k_{obsd} for the homogeneous $Fe(CN)_6^{3-/4-}$ exchange reaction in aqueous KCl as a function of the unassociated K^+ concentration at uncontrolled ionic strength. [$Fe(CN)_6^{4-}$] = 0.049–0.097 mol kg^{-1}; [$Fe(CN)_6^{3-}$] = 0.0016–0.0033 mol kg^{-1}. Squares and dotted line: 11.2 °C. Circles and solid line: 25.0 °C. Triangles and dashed line: 35.0 °C.

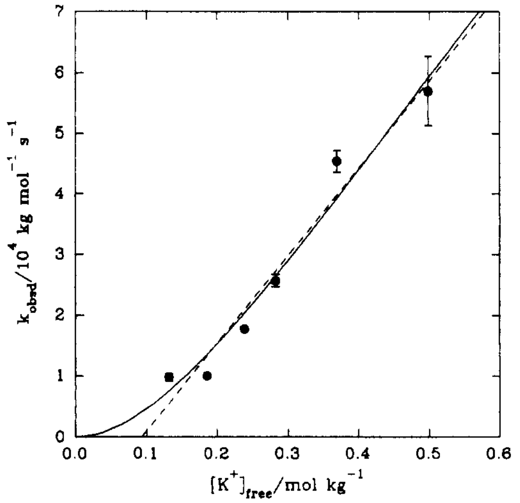

Figure 2. Rate constants k_{obsd} for the homogeneous $Fe(CN)_6^{3-/4-}$ exchange reaction in aqueous $KCl/(C_6H_5)_4AsCl$ at 25 °C as a function of the unassociated K^+ concentration at ionic strength 0.50 mol kg^{-1}. [$Fe(CN)_6^{4-}$] = 0.010 28 mol kg^{-1}; [$Fe(CN)_6^{3-}$] = 0.010 72 mol kg^{-1}. Dashed line: linear least-squares regression. Solid curve: eq 8 with K set to 1.1 kg mol^{-1} and k_3 = 4.8 × 10^5 kg mol^{-1} s^{-1}.

Dependence of the Homogeneous Self-Exchange Rate on [K^+]. The marked dependence of k_{obsd} upon [K^+] (Figures 1 and 2) or ionic strength I was more difficult to analyze. The formation constants of the ion pairs {K^+, $Fe(CN)_6^{4-}$} and {K^+,$Fe(CN)_6^{3-}$} have been estimated to be K_{II} = 31 and K_{III} = 7 L mol^{-1}, respectively, at 25 °C and I = 0.1 mol L^{-1}. In our experiments, I was higher than this, so that K_{II} and K_{III} would be expected to

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(35) The molal scale was used consistently in this work because the small solution samples were prepared by weight and because the scale is pressure- and temperature-independent (see: Hamann, S.; le Noble, W. J. *J. Chem. Educ.* **1984**, *61*, 658). For most of the solutions considered here, conversion to molar (mol L^{-1}) concentrations valid at 20 °C and 0.1 MPa can be effected approximately by multiplying the molality by 0.99 (more precisely, by 0.9894 for 0.5 mol kg^{-1} NaCl and by 0.9858 for 0.1 mol kg^{-1} $K_4Fe(CN)_6$).

be somewhat lower,[31] but since $[K^+]_{tot}$ ranged from 0.13 to 1.4 mol kg^{-1}, it may be assumed to a reasonable approximation that $Fe(CN)_6^{4-}$ was essentially all ion paired while ion pairing of $Fe(CN)_6^{3-}$ was extensive but incomplete. Some secondary ion association of $Fe(CN)_6^{4-}$ to give $\{(K^+)_2,Fe(CN)_6^{4-}\}$ (stepwise formation constant K_{II}') may also be anticipated. The extent of ion association, however, affects the free cation concentration and hence the ionic strength, which recursively influences the ion-pair formation constants[31] as well as the exchange rate constants k_i (i is the number of K^+ ions involved) for the various conceivable combinations of reactants:

$$Fe(CN)_6^{3-} + Fe(CN)_6^{4-} \rightarrow \quad k_0 \tag{1}$$

$$Fe(CN)_6^{3-} + \{K^+,Fe(CN)_6^{4-}\} \rightarrow \quad k_1 \tag{2}$$

$$\{K^+,Fe(CN)_6^{3-}\} + \{K^+,Fe(CN)_6^{4-}\} \rightarrow \quad k_2 \tag{3}$$

$$\{K^+,Fe(CN)_6^{3-}\} + \{(K^+)_2,Fe(CN)_6^{4-}\} \rightarrow \quad k_3 \tag{4}$$

$$\{(K^+)_2,Fe(CN)_6^{3-}\} + \{(K^+)_2,Fe(CN)_6^{4-}\} \rightarrow \quad k_4 \tag{5}$$

Thus, a definitive analysis of the kinetic phenomena would be virtually impossible, even with unlimited amounts of very precise data, and although in Figure 1 k_{obsd} appears to be a linear function of $[K^+]_{free}$ (=$[K^+]_{tot}$ corrected approximately for ion pairing on the assumption that 1:1 ion pairing is virtually complete), the slope and intercept have no particular significance because I varies widely. If, however, ^{13}C-enriched $Fe(CN)_6^{4-}$ is used, line-broadening data can be obtained with $[Fe^{II}] \approx [Fe^{III}] \approx 0.01$ mol kg^{-1} and $[K^+]$ can be varied while I is maintained at 0.5 mol kg^{-1} with tetraphenylarsonium chloride, which is known[9c] to have a much smaller effect on k_{obsd} than does KCl; the results of such a series of experiments are illustrated in Figure 2.

At first sight, Figure 2 suggests that k_{obsd} may be a linear function (broken line) of $[K^+]_{free}$, but the intercept on the k_{obsd} axis would then be *negative*, which defies any simple chemical interpretation. However, given that the predominant hexacyanoferrate species present can be confidently expected to be $\{K^+,Fe(CN)_6^{4-}\}$, $Fe(CN)_6^{3-}$, $\{K^+,Fe(CN)_6^{3-}\}$, and $\{(K^+)_2,Fe(CN)_2^{4-}\}$,[28-32] it may be anticipated that the predominant exchange pathways under our experimental conditions will be reactions 3 and 4. Indeed, computer analyses of the rate data based on bimolecular paths 1–5 and using literature values[28-32] of K_{II}, K_{III}, and K_{II}' (this last assumed to equal K_{III}) confirmed that paths 1, 2, and 5 can be disregarded. Thus, we have

$$k_{obsd} = (k_2 + k_3K_{II}'[K^+])K_{III}[K^+]/(1 + K_{II}'[K^+])(1 + K_{III}[K^+]) \tag{6}$$

where $[K^+]$ is the concentration of the free cation, estimated as explained above.

Nonlinear least-squares regression did not give definitive values for all four parameters in eq 6, since they are correlated, but it became clear that k_2 (pathway 3) was of negligible importance and that values of K_{II}' and K_{III} on the order of 1.0 and 1.3 kg mol^{-1}, respectively, and $k_3 \approx 4.8 \times 10^5$ kg mol^{-1} s^{-1} were consistent with the experimental data. The equation of Hanania et al.[31]

$$\log K_{III} = 1.46 - 3.06I^{1/2}/(1 + 1.5I^{1/2}) \tag{7}$$

implies $K_{III} \approx 2.5$ kg mol^{-1} at $I = 0.5$ mol kg^{-1} and 25 °C, so these values are reasonable. If k_2 is set to zero, then K_{II}' and K_{III} cannot be distinguished in computation; however, simple electrostatic considerations (as well as the foregoing) suggest that they can be conveniently set to a common value K of about 1 kg mol^{-1}, so that we have

$$k_{obsd} = k_3K^2[K^+]^2/(1 + K[K^+])^2 \tag{8}$$

The curve in Figure 2 represents eq 8 with K set to 1.1 kg mol^{-1} and $k_3 = 4.8 \times 10^5$ kg mol^{-1} s^{-1}. Other satisfactory fits of the data can be obtained with somewhat different combinations of K and k_3 (the latter is very sensitive to the choice of the former), but working values of $K_{III} \approx K_{II}' \approx 1$ kg mol^{-1} and $k_3 \approx 5 \times 10^5$ kg mol^{-1} s^{-1} at $I = 0.5$ mol kg^{-1} and 25 °C may be adopted so long as the various assumptions noted above are borne in mind.

These results explain at least qualitatively the dependence of k_{obsd} on $[K^+]$ at variable I as shown in Figure 1. As $[K^+]$ increases, so does I, and K therefore *decreases*. This decreasing trend in K apparently offsets any opposing effect on I on k_3; a quantitative analysis is impractical because the Brønsted–Bjerrum–Christiansen or other Debye–Hückel-based expressions for the dependence of k_3 on I cannot be expected to be accurate at the high I values of Figure 1. The key point, however, is that the data of Figure 1, like those of Figure 2, are consistent with the predominance of the single reaction pathway (4). The apparent linearity of the plots in Figure 1 is therefore illusory, and the slopes and intercepts of the linear regressions have no physical significance.

Effect of Other Alkali-Metal Cations. To obtain a general indication of the effect of the nature of the cation on the self-exchange rate constant, ^{13}C line widths were measured for solutions containing 2.3 ± 0.3 mmol kg^{-1} ^{13}C-enriched $K_4Fe(CN)_6$, 2.6 ± 0.2 mmol kg^{-1} $K_3Fe(CN)_6$, and 249 ± 5 mmol kg^{-1} MCl (M = Li, Na, K). The measured k_{obsd} values (10^4 kg mol^{-1} s^{-1}) were 1.27, 2.0, and 2.5 for added LiCl, NaCl, and KCl, respectively. This sequence parallels that found by Holzwarth et al.[11] for cation effects on the kinetics of the reaction of aqueous $Fe(CN)_6^{4-}$ with $IrCl_6^{2-}$.

Pressure Dependence of the Homogeneous Self-Exchange Rate. The pressure dependence of k_{obsd} at 25 °C was measured in three independent series of experiments using ^{13}C-enriched $K_4Fe(CN)_6$ (75–87 mmol kg^{-1}) and normal $K_3Fe(CN)_6$ (2.1–2.4 mmol kg^{-1}) with no added electrolyte. In the absence of added $Fe(CN)_6^{3-}$, the "natural" ^{13}C-NMR line width of $Fe(CN)_6^{4-}$ was unaffected by pressure. At 0.1 MPa, the "natural" $Fe(CN)_6^{4-}$ line width of 9 ± 1 Hz (which included field inhomogeneity contributions from the pressure vessel) broadened to 28 ± 1 Hz in the presence of $Fe(CN)_6^{3-}$, giving atmospheric-pressure k_{obsd} values ($(2.6 \pm 0.1) \times 10^4$ kg mol^{-1} s^{-1}) in good agreement with those obtained for comparable conditions in the commercial probehead. This line width, however, narrowed markedly as the pressure was increased (to ca. 16 Hz near 100 MPa), so that the experimental uncertainty in k_{obsd} increased even though the rate constant itself decreased. Furthermore, signal losses and tuning problems increased with the pressure, so that the pressure ceiling was about 100 MPa. Nevertheless, the effect of pressure on k_{obsd} was sufficiently large (Figure 3) to allow measurement of ΔV_{ex}^* ($=-RT(\partial \ln k_{obsd}/\partial P)_T$, assumed here to be independent of P) to ±10%. The combined data of Figure 3, which are normalized on a common value for 0.1 MPa, give $\Delta V_{ex}^* = +21.8 \pm 1.7$ cm^{-3} mol^{-1}.

Pressure Dependence of the Self-Exchange Reaction Rate at an Electrode. We recently published a study[14] of the pressure dependence of the electrode potential (on shiny Pt, vs $Ag^+/AgCl$) of the $Fe(CN)_6^{3-/4-}$ couple in aqueous KCl, as obtained from cyclic voltammograms (CVs). It is possible to extract values of the *heterogeneous* self-exchange rate constant k_{el} for $Fe(CN)_6^{3-/4-}$ from the peak-to-peak potential separation δE of the CVs (published as supplemental data to ref 14) via the kinetic parameter ψ:[36]

$$k_{el} = \psi(D\pi vnF/RT)^{1/2} \tag{9}$$

where D is the diffusion coefficient of $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$

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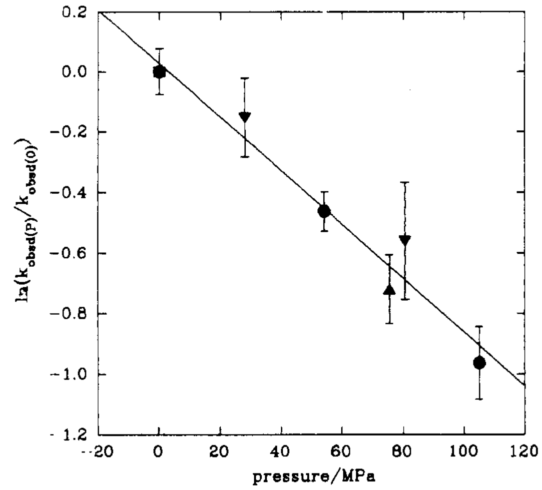

Figure 3. Pressure dependence of the rate constant k_{obsd} for the homogeneous $Fe(CN)_6^{3-/4-}$ exchange reaction in aqueous solution at 25 °C (counterion K^+; no additional electrolyte). Circles: $[Fe(CN)_6^{4-}]$ = 0.0751 mol kg^{-1}; $[Fe(CN)_6^{3-}]$ = 0.002 43 mol kg^{-1}. Triangles (two runs): $[Fe(CN)_6^{4-}]$ = 0.0869 mol kg^{-1}; $[Fe(CN)_6^{3-}]$ = 0.002 11 mol kg^{-1}.

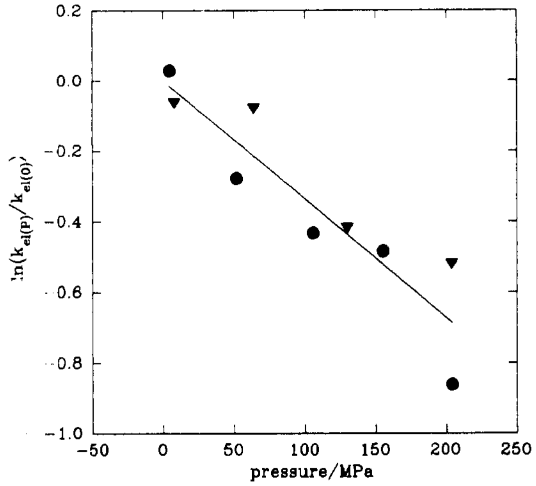

Figure 4. Pressure dependence of the relative rate constant for the heterogeneous $Fe(CN)_6^{3-/4-}$ exchange reaction at a Pt electrode in aqueous KCl solution at 25 °C, from cyclic voltammograms of $K_3Fe(CN)_6$. I = 0.51 mol kg^{-1}; [Fe] = 1.46 mmol kg^{-1}. Circles and triangles represent different experiments. Data are from supplementary material for ref 14.

(assumed to be the same for both), v is the scan rate, and the other symbols have their usual electrochemical meanings. Values of ψ can be obtained from δE by interpolation of the tabulated values given by Bard and Faulkner.[36] This procedure has not generally enjoyed much favor among electrochemists, since δE can be difficult to reproduce precisely from one experiment to another—as was the case here, even at atmospheric pressure—and accordingly we made no attempt heretofore[14] to determine values of k_{el} from our CV data. However, despite the unreliability of the *absolute* values of k_{el} so obtained, values of $k_{el(P)}$ at pressures P in aqueous KCl media *relative* to those measured at "zero" (i.e., atmospheric) pressure ($k_{el(0)}$) in the same pressure cycle do display consistent trends, as shown in Figures 4 and 5 for I = 0.5 and 1.0 mol kg^{-1}, respectively, at 25 °C. From eq 9, we have

$$k_{el(P)}/k_{el(0)} = (\psi_P/\psi_0)(D_P/D_0)^{1/2} \qquad (10)$$

for a fixed scan rate, whence, from Walden's rule

$$\ln (k_{el(P)}/k_{el(0)}) \approx \ln \psi_P - \ln \psi_0 - [\ln (\eta_P/\eta_0)]/2 \qquad (11)$$

where η_P is the viscosity of the solvent at pressure P (which we compute for water from the data of Sengers and Kamgar-Parsi[37]). Figures 4 and 5 show plots of the right-hand side of eq 11, normalized to $\ln \psi_0 = 0$, against P. Although these unedited data show considerable scatter, a moderate retarding effect of pressure is clear, and linear least-squares regression gives $\Delta V_{el}^{\ddagger}$ (assumed independent of P) = +8.3 ± 1.5 and +7.5 ± 1.7 cm^3 mol^{-1} at I = 0.5 and 1.0 mol kg^{-1}, respectively, at 25 °C. Similarly, our treatment of data obtained independently by Shalders and Tregloan[38] in high-pressure cyclic voltammetric studies of the $Fe(CN)_6^{3-/4-}$ couple in KNO_3 media at 25 °C gave $\Delta V_{el}^{\ddagger}$ = +10.5 ± 0.9, +9.7 ± 1.0, +5.9 ± 1.8, and ±6.4 ± 1.6 cm^3 mol^{-1} at I = 0.010, 0.033, 0.10, and 0.33 mol L^{-1}, respectively. Thus, if we disregard the dependence of $\Delta V_{el}^{\ddagger}$ on I, we may conclude that $\Delta V_{el}^{\ddagger}$ = +8 ± 2 cm^3 mol^{-1} for the $Fe(CN)_6^{3-/4-}$ exchange at a Pt electrode in K^+ media at 25 °C and moderate ionic strengths.

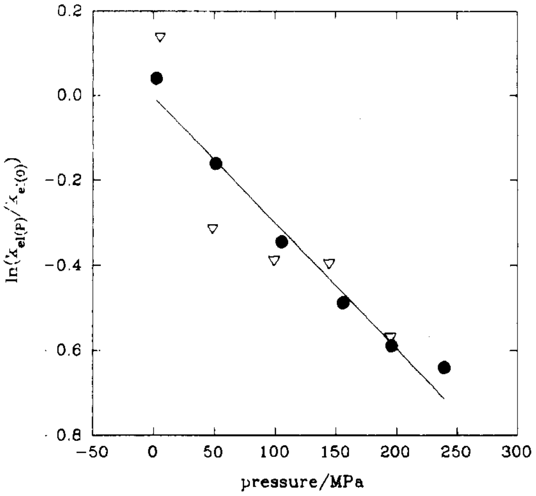

Figure 5. Pressure dependence of the relative rate constant for the heterogeneous $Fe(CN)_6^{3-/4-}$ exchange reaction at a Pt electrode in aqueous solution at 25 °C. Conditions are as for Figure 4, but [Fe] = 4.78 mmol kg^{-1} and I = 0.99 mol kg^{-1}.

Discussion

Mechanism of the Homogeneous Self-Exchange Reaction. In this work, an effort has been made to separate ionic strength effects from specific cation effects on the rate of the homogeneous $Fe(CN)_6^{3-/4-}$ exchange reaction in aqueous K^+ media with $(C_6H_5)_4As^+$ as support. Such separations are necessarily imperfect, since *all* cations, including $(C_6H_5)_4As^+$, seem to promote this exchange reaction to some degree, but the analysis presented above strongly implies that the only important path for electron transfer at practical electrolyte concentrations involves *three* K^+ ions. This was suggested long ago by Shporer et al.[10a] on the basis of a less detailed analysis, but as they and Wahl et al.[9] remark, there is no *direct* evidence that any of the K^+ ions is involved in the actual transmission of the electron. On the other hand, while cation effects on the $MnO_4^{-/2-}$ electron-transfer reaction are also very marked,[39] the rates of electron transfer reactions between *cationic* complexes in water are generally relatively insensitive to the effects of anions, so that the role of the cation in anion–anion reactions may involve more than mere reduction of Coulombic repulsions between the reactants.

Effect of Pressure on the Homogeneous Self-Exchange Reaction. The $Fe(CN)_6^{3-/4-}$ exchange is necessarily of the outer-sphere electron-transfer (OSET) type, since ligand substitution is many orders of magnitude slower than electron transfer[8] and is

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(37) Sengers, J. V.; Kamgar-Parsi, B. *J. Phys. Chem. Ref. Data* **1984**, *13*, 185.

(38) Shalders, R. D.; Tregloan, P. A. Unpublished results.

(39) Spiccia, L.; Swaddle, T. W. *Inorg. Chem.* **1987**, *26*, 2265 and references cited therein.

considered to be close to the adiabatic limit.[40] It is therefore amenable to predictions of $\Delta V_{ex}^{\ddagger}$ by an adaptation of Marcus–Hush theory, described elsewhere,[22] that has proved satisfactory for simple OSET between metal complex ions in water. If, for agrument's sake, we assume the reactants to be $\{K^+,Fe(CN)_6^{3-}\} + \{K^+,Fe(CN)_6^{4-}\}$ and treat the ion pairs as spheres of charges 2– and 3– while retaining the hexacyanoferrate radii of 445 and 433 pm, respectively,[41] $\Delta V_{ex}^{\ddagger}$ is predicted to be about –5 cm^3 mol^{-1} for the conditions of our experiments. The observed value is +22 cm^3 mol^{-1}, which is in itself remarkable in that almost all $\Delta V_{ex}^{\ddagger}$ values measured to date for self-exchange reactions in homogeneous solution (or, indeed, electron transfer between *any* species that are not of opposite charge—Anderson and Wherland[42] report an exception involving a nonaqueous system) are *negative*. The Na^+-catalyzed pathway for $MnO_4^{-/2-}$ exchange is the only other homogeneous self-exchange reaction reported to date to have a positive $\Delta V_{ex}^{\ddagger}$ (+3 cm^3 mol^{-1}); for the K^+-catalyzed analogue, $\Delta V_{ex}^{\ddagger} = -1$ cm^3 mol^{-1}, i.e., 22 cm^3 mol^{-1} more positive than for the uncatalyzed exchange (which is directly observable in the $MnO_4^{-/2-}$ case).[39]

According to the above analysis, the observed $\Delta V_{ex}^{\ddagger}$ for $Fe(CN)_6^{3-/4-}$ represents a pathway containing one more K^+ ion than this model. Thus, the third K^+ ion, which accelerates the electron transfer strongly, is involved in a transition state that is some 27 cm^3 mol^{-1} more voluminous than would be expected if the additional K^+ were absent. The parallel with the $MnO_4^{-/2-}$ case, despite the different charge type, is striking, and for that reason, as well as because of estimates based on the Fuoss equation,[43] it seems unlikely that the excess in $\Delta V_{ex}^{\ddagger}$ could be accommodated entirely in terms of the volume change of formation of the ion aggregates $\{K^+,Fe(CN)_6^{3-}\}$ and $\{(K^+)_2,Fe(CN)_6^{4-}\}$. As was pointed out in an analysis of the $MnO_4^{-/2-}$ case,[39] total desolvation of the additional alkali-metal ion is probably involved, but even this can account for only about half of the difference in $\Delta V_{ex}^{\ddagger}$ values between the paths with and without the additional cation. The balance probably represents the relaxation of the need for close approach (with possible ligand interpenetration) of the reacting anions to effect electron transfer;[39] instead, the naked cation is interposed between them and facilitates electron transfer directly. Thus, consideration of the large difference in $\Delta V_{ex}^{\ddagger}$ between the K^+-catalyzed and uncatalyzed pathways lends credence to the view that the cation has a specific *electronic*, as distinct from merely Coulombic, role to play in facilitating OSET between anions in water.

Furthermore, the unusually large, positive $\Delta V_{ex}^{\ddagger}$ observed for $Fe(CN)_6^{3-/4-}$ exchange in the presence of K^+ implies that the similarly large $\Delta V^{\ddagger}$ values noted for certain *net* reactions involving reduction by $Fe(CN)_6^{4-}$ [17–21] have their origin in the hexacyanoferrate side of the reaction. Following the approach of Marcus,[25,27] $\Delta V^{\ddagger}$ for a "cross"-reaction can be expected to reflect $\Delta V_{ex}^{\ddagger}$ for the two corresponding self-exchange reactions (as well as the thermodynamic volume change for the cross-reaction itself), and consequently any redox process involving hexacyanoferrates can be expected to have an anomalously positive $\Delta V^{\ddagger}$. It should be noted that we ascribe this effect to the involvement of the counterion—a factor that is generally overlooked by those who use the convenient $Fe(CN)_6^{3-/4-}$ couple in studies involving redox kinetics.

Effect of Pressure on the Kinetics of the Electrode Reaction. Although the volumes of activation reported here for both the homogeneous ($\Delta V_{ex}^{\ddagger} = +22 \pm 2$ cm^3 mol^{-1}) and the heterogeneous ($\Delta V_{el}^{\ddagger} = +8 \pm 2$ cm^3 mol^{-1}) $Fe(CN)_6^{3-/4-}$ self-exchange reactions are subject to fairly large errors, it is certain that both are markedly positive and that the former is some 2–3 times larger than the latter. Sato and Yamada[12] obtained $\Delta V_{el}^{\ddagger} \approx +13$ cm^3 mol^{-1} from measurements of the exchange current density for reduction for $Fe(CN)_6^{3-}$ in aqueous KCl (1.0 mol L^{-1}) at a Pt microdisk at ca. 0, 40, and 100 MPa, so the true ratio of $\Delta V_{ex}^{\ddagger}$ to $\Delta V_{el}^{\ddagger}$ may be nearer to 2. (The high-pressure ac impedance measurements of Conway and Currie[13] yield a different parameter.) In any event, it is clear that $\Delta V_{ex}^{\ddagger}$ and $\Delta V_{el}^{\ddagger}$ are very different, and the question arises as to whether a measured $\Delta V_{el}^{\ddagger}$ value can be used to predict its analogue $\Delta V_{ex}^{\ddagger}$ for the homogeneous exchange.

It is unclear whether the homogeneous and heterogeneous exchange reactions are mechanistically equivalent, i.e., whether both involve three K^+ ions in the respective transition states—this is difficult enough to verify in the homogeneous case (see above) and almost impossible for the heterogeneous reaction because of the poor reproducibility of k_{el} between different cyclic voltammetric experiments. If, however, it is assumed that the mechanisms are equivalent, Marcus' theory[25,27] can be invoked to predict that the homogeneous and heterogeneous rate constants, k_{ex} and k_{el}, respectively, should be related by

$$k_{ex}/Z_{ex} = (k_{el}/Z_{el})^2 \qquad (12)$$

in which Z_{ex} and Z_{el} are the respective frequency factors. If Z_{ex} and Z_{el} are pressure-independent (which will be at least approximately true if electron transfer is adiabatic, as seems to be the case), then differentiation of eq 12 with respect to pressure gives

$$\Delta V_{ex}^{\ddagger} \approx 2\Delta V_{el}^{\ddagger} \qquad (13)$$

which, given the experimental uncertainties, is in reasonable agreement with observation.

It might be concluded, then, that cyclic voltammetric measurements at high pressure could be used to give at least approximate values for $\Delta V_{ex}^{\ddagger}$ in cases where the homogeneous exchange rate cannot be measured under pressure (e.g., for couples in which both partners are paramagnetic and hence not amenable to the NMR method). Unfortunately, this approach is likely to be productive only with couples for which $\Delta V_{el}^{\ddagger}$ and hence $\Delta V_{ex}^{\ddagger}$ are *positive*, i.e., for which the peak separation *δE increases* with increasing pressure; where the reverse is true, δE diminishes toward the reversible value as the pressure rises, and (given that errors tend to become worse as the pressure increases) the experimental uncertainties quickly become unacceptable.

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Supplementary Material Available: Tables of NMR and kinetic data for the homogeneous title reaction (4 pages). Ordering information is given on any current masthead page.

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