

Cation-Independent Electron Transfer between Ferricyanide and Ferrocyanide Ions in Aqueous Solution

Achim Zahl,[†] Rudi van Eldik,[†] and Thomas W. Swaddle*[‡]

Institut für Anorganische Chemie, Universität Erlangen-Nürnberg, Egerlandstrasse 1, 91058 Erlangen, Germany, and Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4

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Electron transfer between $\text{Fe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$ in homogeneous aqueous solution with K^+ as the counterion normally proceeds almost exclusively by a K^+ -catalyzed pathway, but this can be suppressed, and the direct $\text{Fe}(\text{CN})_6^{3-}$ – $\text{Fe}(\text{CN})_6^{4-}$ electron transfer path exposed, by complexing the K^+ with crypt-2.2.2 or 18-crown-6. $\text{Fe}(\text{CN})_6^{4-}$ -NMR line broadening measurements using either crypt-2.2.2 or (with extrapolation to zero uncomplexed $[\text{K}^+]$) 18-crown-6 gave consistent values for the rate constant and activation volume ($k_0 = (2.4 \pm 0.1) \times 10^2 \text{ L mol}^{-1} \text{ s}^{-1}$ and $\Delta V_0^\ddagger = -11.3 \pm 0.3 \text{ cm}^3 \text{ mol}^{-1}$, respectively, at 25 °C and ionic strength $I = 0.2 \text{ mol L}^{-1}$) for the uncatalyzed electron transfer path. These values conform well to predictions based on Marcus theory. When $[\text{K}^+]$ was controlled with 18-crown-6, the observed rate constant k_{ex} was a linear function of uncomplexed $[\text{K}^+]$, giving $k_{\text{K}} = (4.3 \pm 0.1) \times 10^4 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$ at 25 °C and $I = 0.26 \text{ mol L}^{-1}$ for the K^+ -catalyzed pathway. When no complexing agent was present, k_{ex} was roughly proportional to $[\text{K}^+]_{\text{total}}$, but the corresponding rate constant k_{K}' ($=k_{\text{ex}}/[\text{K}^+]_{\text{total}}$) was about 60% larger than k_{K} , evidently because ion pairing by hydrated K^+ lowered the anion–anion repulsions. Ionic strength as such had only a small effect on k_0 , k_{K} , and k_{K}' . The rate constants commonly cited in the literature for the $\text{Fe}(\text{CN})_6^{3-/4-}$ self-exchange reaction are in fact $k_{\text{K}}'[\text{K}^+]_{\text{total}}$ values for typical experimental $[\text{K}^+]_{\text{total}}$ levels.

Introduction

Rate constants k for outer-sphere electron transfer (OSET) between cations in aqueous solution are generally not significantly affected by the nature or concentration of the counterions (anions); even in cases such as the $\text{Co}(\text{phen})_3^{3+/2+}$ self-exchange¹ where the nature of the anion does influence the rate constant noticeably,² the effect can be accommodated acceptably within the Brønsted–Bjerrum–Christiansen adaptation of Debye–Hückel theory:³

$$\ln k^I = \ln k^{I=0} + 2z_1z_2A'I^{1/2}/(1 + BaI^{1/2}) \quad (1)$$

where z_1 and z_2 are the charge numbers of the reacting ions,

* Author to whom correspondence should be addressed. Tel.: (403) 220-5358. Fax: (403) 284-1372. E-mail: swaddle@ucalgary.ca.

[†] Universität Erlangen-Nürnberg.

[‡] University of Calgary.

(1) Abbreviations: phen, 1,10-phenanthroline; crypt-2.2.2 (C222), 4,7-, 13,16,21,24-hexaoxa-1,10-diazabicyclo[8.8.8]hexacosane; 18-crown-6 (18C6), 1,4,7,10,13,16-hexaoxacyclooctadecane; EDTA, ethylenedinitrilotetraacetate.

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A and B are the calculable Debye–Hückel parameters, a is a parameter identified with the anion–cation close-contact distance (but best regarded as adjustable), and I is the ionic strength. In organic solvents, anion–cation pairing is expected to be significant over and above ionic strength effects, but seems to lead only to a retardation of cation–cation electron transfer.⁴

In sharp contrast, electron transfer (ET) between aqueous anions shows strong cation-dependent accelerations that cannot be ascribed solely to medium effects. For the $\text{MnO}_4^{2-/1-}$ self-exchange reaction in aqueous alkali at constant ionic strength, the observed rate constant k_{ex} can be resolved into terms with zero- and first-order dependence on the concentration of the alkali-metal cation M^+ :⁵

$$k_{\text{ex}} = k_0 + k_{\text{M}}[\text{M}^+] \quad (2)$$

Thus, the k_{M} term represents *catalysis* of electron transfer

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by M^+ . The volumes of activation ΔV_M^\ddagger ($\Delta V^\ddagger = -RT(\partial \ln k/\partial P)_T$) for the M^+ -catalyzed pathways are about $15 \text{ cm}^3 \text{ mol}^{-1}$ more positive⁶ than that for the uncatalyzed path (ΔV_0^\ddagger), and this has been ascribed to partial deaquation of $M^+(\text{aq})$ when it participates in the reaction.⁵

For the aqueous cyanometalate couples $\text{Fe}(\text{CN})_6^{3-/4-}$, $\text{Os}(\text{CN})_6^{3-/4-}$, $\text{Mo}(\text{CN})_8^{3-/4-}$, and $\text{W}(\text{CN})_8^{3-/4-}$, cation-catalyzed paths have been found to overwhelm k_0 completely at reactant concentrations high enough for the measurement of k_{ex} by ^{13}C - or ^{14}N -NMR line broadening.^{7–12} Added M^+ salts showed a linear dependence of k_{ex} on the additional $[M^+]$, but extrapolation to a hypothetical “zero cation” concentration was not feasible because of the uncertain effects of anion–cation pairing and the very small relative magnitude of k_0 . Wahl et al.,¹³ however, used a radioiron tracer method to measure k_{ex} for the aqueous $\text{Fe}(\text{CN})_6^{3-/4-}$ couple at low reactant concentrations and with large tetralkylammonium counterions R_4N^+ (which had a relatively small catalytic effect), and by extrapolation to zero cation concentration obtained $k_0 = 6.0 \text{ L mol}^{-1} \text{ s}^{-1}$ at $0.1 \text{ }^\circ\text{C}$ ($I = 0$). This is 4 orders of magnitude smaller than the values commonly cited for the $\text{Fe}(\text{CN})_6^{3-/4-}$ exchange rate constant (e.g., $1.9 \times 10^4 \text{ L mol}^{-1} \text{ s}^{-1}$ at $25 \text{ }^\circ\text{C}$ and $I = 0.1 \text{ mol L}^{-1}$), but such values are conditional (i.e., are valid only at a particular concentration of a particular cation) and their use in, say, applications of the Marcus cross-relation is of questionable value.

The primary objective of the present study was to attempt to obtain kinetic parameters for the cation-independent $\text{Fe}(\text{CN})_6^{3-/4-}$ self-exchange reaction at practical ionic strengths by sequestering the cation (K^+) with macrocyclic ligands having special affinity for K^+ .^{14–21} As it was necessary to distinguish between the true cation-independent path and a possible one catalyzed by the sequestered K^+ ion, two quite different macrocycles, crypt-2.2.2 (Kryptofix 222)^{14–18} and 18-crown-6,^{1,14,19–21} were used. Concentration dependence studies were also important in this respect, but it was necessary to distinguish between catalysis by the cations and acceleration of the self-exchange reaction by increasing ionic strength (eq 1).

Apparent volumes of activation $\Delta V_{\text{ex}}^\ddagger$ for the various cyanometalate self-exchange reactions have been reported to be strikingly positive with alkali-metal cations but negative with R_4N^+ ,^{11,12} and these observations are consistent with complete dominance of a cation-catalyzed electron transfer pathway involving deaquation of the alkali-metal cation (R_4N^+ are not aquated), as well as with the results of parallel high-pressure studies^{22,23} of the corresponding electrode reactions. The early high-pressure observations on the K^+ -catalyzed $\text{Fe}(\text{CN})_6^{3-/4-}$ self-exchange reaction, however, were compromised by experimental difficulties reported at the time,¹¹ and a re-examination of this system with improved equipment has therefore been undertaken. Moreover, it has not been clear to what extent the apparent $\Delta V_{\text{ex}}^\ddagger$ in the presence of alkali-metal cations includes contributions from ion-pairing, which is known to be extensive in the K^+ – $\text{Fe}(\text{CN})_6^{3-/4-}$ system.^{11,13} The present study allows for the measurement of $\Delta V_{\text{ex}}^\ddagger$ under conditions in which ion-pairing is insignificant but catalysis by K^+ is still important.

Experimental Section

Materials. Carbon-13-enriched $\text{K}_4\text{Fe}(^{13}\text{CN})_6 \cdot 3\text{H}_2\text{O}$ was made by mixing 0.80 g of $\text{FeCl}_2 \cdot 4\text{H}_2\text{O}$ (Aldrich, 99.995%) in 10 mL of water under Ar with a solution of 0.39 g of K^{13}CN (Cambridge Isotope Laboratories; 98+% KCN, 99% ^{13}C) in 7 mL of water, warming the mixture to form a clear yellow solution, adding ethanol to the point of incipient precipitation, and cooling the mixture to $5 \text{ }^\circ\text{C}$ overnight (cf. Thompson²⁴). The pale yellow crystals were redissolved at $60\text{--}70 \text{ }^\circ\text{C}$ in water containing a few milligrams of K^{13}CN , the solution was filtered, and $\text{K}_4\text{Fe}(^{13}\text{CN})_6 \cdot 3\text{H}_2\text{O}$ was recrystallized with ethanol as before. The identity of the product (particularly the degree of hydration) was established by CHN microanalysis. $\text{K}_3\text{Fe}(\text{CN})_6$ (Merck, p.a., natural ^{13}C abundance), unenriched $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$ (Merck, p.a.), crypt-2.2.2 (Aldrich, 98%), and 18-crown-6 (Aldrich, 99.5%) were used as received. Deuterium oxide (Aldrich, 99.9% D isotopic purity) and/or Millipore purified water were used for preparation of all solutions.

NMR Measurements. Solutions were prepared by weight. Concentrations were converted to the molar scale (as at $22 \text{ }^\circ\text{C}$ and 0.1 MPa for all temperatures and pressures) with adequate accuracy using density measurements made by averaging the weights of multiple 0.200 mL aliquots of the solutions, with calibration against pure water. For aqueous solutions of 18-crown-6 alone, more precise density data are available.²⁵

Carbon-13-NMR and ^1H -NMR line width measurements at ambient pressure were made on a Bruker AVANCE DPX-300 spectrometer (7.05 T) equipped with a BOSS I shim system. Samples were contained in a 5 mm o.d. tube spinning at 20 Hz in a QNP probehead, thermostated with a calibrated B-VT 3300 digital temperature control unit ($\pm 0.5 \text{ }^\circ\text{C}$). Carbon-13 inversion recovery measurements on a solution of $\text{K}_4\text{Fe}(^{13}\text{CN})_6$ (0.084 mol (kg of D_2O)⁻¹) gave a longitudinal relaxation time T_1 of 5.8 s. Delay times for ^{13}C line broadening measurements on solutions containing $\text{K}_4\text{Fe}(^{13}\text{CN})_6$, $\text{K}_3\text{Fe}(\text{CN})_6$, and macrocycle (where required) were therefore set at 30 s ($\sim 5T_1$). For shimming purposes, the solvent was either pure D_2O or $\sim 5\%/95\% \text{ D}_2\text{O}/\text{H}_2\text{O}$. Variable temperature measurements were made at 25.0, 35.0, 45.0, and 55.0 $^\circ\text{C}$.

- (6) Average value over a 180 MPa pressure range; ΔV_0^\ddagger was pressure-dependent.
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For high-pressure line broadening measurements, a Bruker AVANCE DRX-400 spectrometer with a wide-bore magnet was used. Solution samples containing H_2O at natural H isotope abundance were enclosed in a static cut-down 5 mm o.d. commercial NMR tube with a floating MACOR or Kel-F piston sealed with two neoprene O-rings, and placed in a homemade high-pressure NMR probehead (described elsewhere²⁶) resonating at 100.13 MHz for ^{13}C nuclei. The temperature was kept constant (± 0.5 °C) with a circulating water–ethylene glycol mixture and monitored with a NiCrNi thermocouple. Pressures of up to 180 MPa were applied in 30 MPa steps with Hoshinert 130 fluorocarbon fluid (Hoechst). The initial measurement was made at 2 MPa rather than at atmospheric pressure to remove any small bubbles and ensure settlement of the pressure vessel contents. Magnetic field homogeneity better than 6×10^{-9} was achieved by shimming with a BOSS I shim system on the ^1H -FID at each pressure. The ^{13}C 90° pulse width was 30 μs , the sweep width was 2000 Hz, and the irradiation frequency was 100.63 MHz.

Results

As shown previously,^{11,13} the ^{13}C -NMR line broadening due to $\text{Fe}(\text{CN})_6^{3-/4-}$ self-exchange under the conditions of our experiments lies in the “slow exchange” region on the NMR time scale and the exchange reaction rate is first-order with respect to both $[\text{Fe}(\text{CN})_6^{3-}]$ and $[\text{Fe}(\text{CN})_6^{4-}]$, so that the conditional exchange rate constant k_{ex} is given by

$$k_{\text{ex}} = \pi(\Delta\delta\nu_{1/2} - \Delta\delta\nu_{1/2}^0)/[\text{Fe}(\text{CN})_6^{3-}] \quad (3)$$

where $\Delta\delta\nu_{1/2}$ and $\Delta\delta\nu_{1/2}^0$ are the line widths of the $\text{Fe}(\text{CN})_6^{4-}$ resonance in the presence and in the absence of $\text{Fe}(\text{CN})_6^{3-}$, respectively. For the variable-temperature experiments in the QNP probehead, $\Delta\delta\nu_{1/2}^0$ was found to be 0.31 ± 0.02 Hz, independent of temperature (25–55 °C). For the high-pressure probehead, $\Delta\delta\nu_{1/2}^0$ was 0.87 ± 0.06 Hz, independent of pressure (0–150 MPa). Values of $\Delta\delta\nu_{1/2}^0$ were unaffected by the presence of crypt-2.2.2 or 18-crown-6.

In variable temperature or pressure experiments, the initial measurements were normally rechecked at the end of the cycle to ensure that solute decomposition or instrumental response drift had not occurred. Examples of experiments that failed this test were $\text{Fe}(\text{CN})_6^{3-/4-}$ exchange reactions in the presence of K_4EDTA with KOH as advocated by Wahl et al.¹³ to suppress possible catalysis by trace metal ions. So far from improving the reproducibility of the kinetic measurements (as Wahl et al.¹³ found), in our hands EDTA reduced a substantial fraction of the $\text{Fe}(\text{CN})_6^{3-}$ over the time span of the pressure or temperature cycle. The experiments of Wahl et al.¹³ involved lower temperatures and evidently much shorter working times than those reported here, so that the extent of reduction of $\text{Fe}(\text{CN})_6^{3-}$ in their studies may not have been significant. Conversely, because Wahl et al.¹³ worked with very low concentrations of the hexacyanoferrates, their experiments may have been more vulnerable than ours to the effects of trace metal ion contaminants. We found

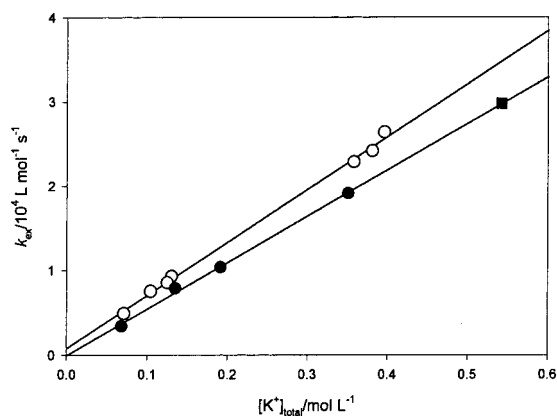


Figure 1. Dependence of the $\text{Fe}(\text{CN})_6^{3-/4-}$ exchange rate constant k_{ex} on the total $[\text{K}^+]_{\text{total}}$ at 25.0 °C in the absence of added solutes. Hollow symbols: solvent 5%/95% $\text{D}_2\text{O}/\text{H}_2\text{O}$. Filled symbols: solvent 100% D_2O . Filled square: from ref 11, converted to molar scale.

no significant effect of KOH on k_{ex} other than that of the additional K^+ .

The range of usable hexacyanoferrate concentrations was rather narrow, being limited at the lower end by the need for enough ^{13}C (≥ 0.2 mg in 0.8 mL) for accurate NMR line width measurements, and at the upper end by the perturbation of solvent properties by the large quantities of crypt-2.2.2 and particularly 18-crown-6 needed to complex the K^+ ions adequately.

Self-Exchange Kinetics without Sequestration of K^+ .

Figure 1 shows that, for solutions of $\text{K}_4\text{Fe}(\text{CN})_6$ and $\text{K}_3\text{Fe}(\text{CN})_6$ without complexing agents, k_{ex} is effectively proportional to the total K^+ concentration $[\text{K}^+]_{\text{total}}$; the small intercepts on the k_{ex} axis are negligible, given the experimental uncertainties. The averaged specific rate constant k_{ex}' ($=k_{\text{ex}}/[\text{K}^+]_{\text{total}}$, listed in the Supporting Information, Table S1) at 25.0 °C for four runs with solutions containing only $\text{K}_4\text{Fe}(\text{CN})_6$ and $\text{K}_3\text{Fe}(\text{CN})_6$ in 5%/95% or 10%/90% $\text{D}_2\text{O}/\text{H}_2\text{O}$, $[\text{K}^+]_{\text{total}} = 0.07$ – 0.13 mol L^{-1} , was $(7.0 \pm 0.2) \times 10^4$ $\text{L}^2 \text{mol}^{-2} \text{s}^{-1}$, with $\Delta H_{\text{ex}}^{\ddagger} = 22.9 \pm 0.7$ kJ mol^{-1} and $\Delta S_{\text{ex}}^{\ddagger} = -75 \pm 2$ J $\text{K}^{-1} \text{mol}^{-1}$ (25–55 °C; error limits are standard deviations). A small but significant secondary hydrogen isotope effect is evident in Figure 1, with $k_{\text{ex}}' = (5.3 \pm 0.4) \times 10^4$ $\text{L}^2 \text{mol}^{-2} \text{s}^{-1}$ at 25.0 °C for 100% D_2O . Dilute (4–10%) D_2O was therefore used as solvent for locking and shimming samples in definitive ambient-pressure studies, to allow comparison with the high-pressure experiments for which 100% H_2O was the solvent. Furthermore, the required stability constants K_{crypt} and K_{crown} for the formation of the complexes $\text{K}(\text{crypt-2.2.2})^+$ and $\text{K}(\text{18-crown-6})^+$, respectively, are available only for H_2O solutions.^{15–21} Good agreement between the extrapolated new k_{ex}' data for 100% D_2O and those reported previously¹¹ is evident in Figure 1.

Effect of 18-Crown-6. Addition of 18-crown-6 lowered the $\text{Fe}(\text{CN})_6^{3-/4-}$ exchange rate dramatically as K^+ was complexed (Figure 2), but the asymptotic limit of k_{ex} at large excesses of 18-crown-6 was greater than zero, implying the existence of a slow $\text{K}^+(\text{aq})$ -independent path. For dilute D_2O solutions, “best” values of K_{crown} (117.0, 83.3, 60.5, and 44.9 L mol^{-1} at 25.0, 35.0, 45.0, and 55.0 °C, respectively) were estimated from the literature^{19–21} and used to calculate the

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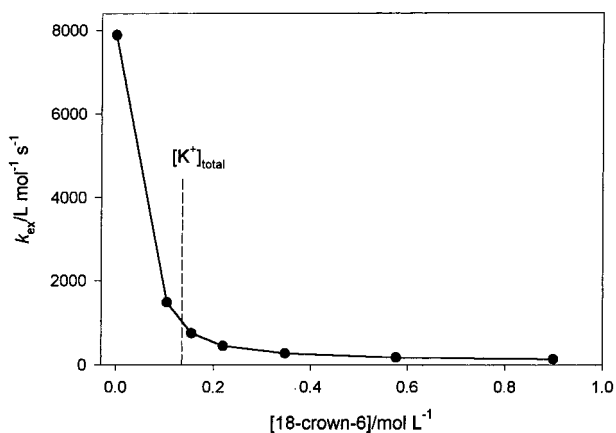


Figure 2. Effect of adding 18-crown-6 on k_{ex} for $\text{Fe}(\text{CN})_6^{3-/4-}$ in 100% D_2O at 25.0 °C. Broken vertical line represents $[\text{K}^+]_{\text{total}}$.

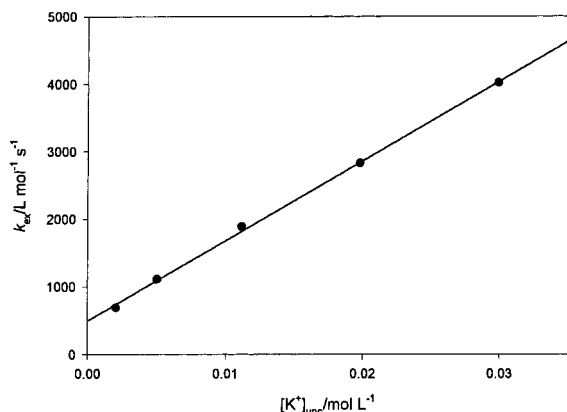


Figure 3. Dependence of k_{ex} for $\text{Fe}(\text{CN})_6^{3-/4-}$ on $[\text{K}^+]_{\text{unc}}$ in 10% $\text{D}_2\text{O}/\text{H}_2\text{O}$ at 55 °C; $[\text{K}^+]_{\text{total}} = 0.125 \text{ mol L}^{-1}$.

concentrations of uncomplexed K^+ remaining ($[\text{K}^+]_{\text{unc}}$). When the total 18-crown-6 concentration approached or exceeded $[\text{K}^+]_{\text{total}}$ —that is, when ion-pairing between K^+ (aq) and $\text{Fe}(\text{CN})_6^{3-}$ or $\text{Fe}(\text{CN})_6^{4-}$ would be much reduced— k_{ex} was found to be a linear function of $[\text{K}^+]_{\text{unc}}$ with a definite intercept k_{ex}° at $[\text{K}^+] = 0$, as shown in Figure 3 for the least favorable case (high ligand concentrations, and highest temperature leading to the smallest K_{crown} ; see Supporting Information, Figures S1–S4, for other conditions):

$$k_{\text{ex}} = k_{\text{ex}}^\circ + k_{\text{K}}[\text{K}^+]_{\text{unc}} \quad (4)$$

Equation 4 is obviously analogous to eq 2, suggesting (but not proving) that k_{ex}° may be identified with the direct $\text{Fe}(\text{CN})_6^{3-/4-}$ exchange rate constant k_0 (see below). Values of k_{ex}° are listed in Table 1.

When 18-crown-6 was deficient or absent, k_{ex} values were somewhat higher than predicted by eq 4. Thus, for an $\text{Fe}(\text{CN})_6^{3-/4-}/18\text{-crown-6}$ solution with $[\text{K}^+]_{\text{total}} = 0.125 \text{ mol L}^{-1}$ ($I = 0.26 \text{ mol L}^{-1}$), $k_{\text{K}} = (4.34 \pm 0.06) \times 10^4 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$ at 25.0 °C ($\Delta H_{\text{K}}^\ddagger = 24.5 \pm 0.6 \text{ kJ mol}^{-1}$ and $\Delta S_{\text{K}}^\ddagger = -74.2 \pm 1.9 \text{ J K}^{-1} \text{ mol}^{-1}$, 25–55 °C), whereas for the same solution without 18-crown-6 k_{ex}' was $6.86 \times 10^4 \text{ L}^2 \text{ mol}^{-2} \text{ s}^{-1}$.

Effect of Crypt-2.2.2. Because K_{crypt} is relatively large even at elevated temperatures ($3.80 \times 10^5 \text{ L mol}^{-1}$ at 25

Table 1. Kinetic Parameters for the Cation-Independent Pathway of $\text{Fe}(\text{CN})_6^{3-/4-}$ Self-Exchange with K^+ Concentration Control by Crypt-2.2.2 or 18-Crown-6

$[\text{K}^+]_{\text{total}}/$ mol L^{-1}	$I/$ mol L^{-1}	$[\text{ligand}]/$ mol L^{-1}	$k_{\text{ex}}^\circ/$ $\text{L mol}^{-1} \text{ s}^{-1}$	$\Delta H_{\text{ex}}^{\circ\ddagger}/$ kJ mol^{-1}	$\Delta S_{\text{ex}}^{\circ\ddagger}/$ $\text{J K}^{-1} \text{ mol}^{-1}$
0.067 ^a	0.154	0.445 (18C6) ^b	228 ± 17	20.8 ± 2.1	-130 ± 7
0.101 ^a	0.231	0.127 (C222)	231 ± 2	19.8 ± 0.4	-133 ± 1
0.102 ^a	0.233	0.108 (C222)	239 ± 2	21.0 ± 0.5	-129 ± 2
0.125 ^c	0.264	1.07 (18C6) ^b	264 ± 11	14.5 ± 1.0	-150 ± 3
0.130 ^a	0.291	0.264 (C222) ^b	256 ± 5	22.6 ± 2.1	-123 ± 7
0.198 ^d	0.449	0.277 (C222)	290 ± 7		
0.255 ^d	0.580	0.320 (C222)	336 ± 6		
0.350 ^d	0.800	0.461 (C222)	333 ± 5		

^a 5%/95% $\text{D}_2\text{O}/\text{H}_2\text{O}$. ^b Maximum concentration in the series. ^c 10%/90% $\text{D}_2\text{O}/\text{H}_2\text{O}$. ^d Variable pressure run, 100% H_2O .

Table 2. Effect of Added Crypt-2.2.2 on the $\text{K}_4\text{Fe}(\text{CN})_6\text{--K}_3\text{Fe}(\text{CN})_6$ Electron Transfer Rate Constant^a

$[\text{crypt-2.2.2}]_{\text{total}}/$ mol L^{-1}	$[\text{K}^+]_{\text{unc}}/$ mol L^{-1}	$k_{\text{ex}}/$ $\text{L mol}^{-1} \text{ s}^{-1}$
0	0.130	9308
0.080	0.048	1885
0.140	2.3×10^{-5}	253
0.185	5.4×10^{-6}	247
0.204	4.0×10^{-6}	244
0.264	2.2×10^{-6}	212

^a 25.0 °C, 5%/95% $\text{D}_2\text{O}/\text{H}_2\text{O}$.

°C, $6.96 \times 10^4 \text{ L mol}^{-1}$ at 55 °C),¹⁸ addition of crypt-2.2.2 in even a small excess over $[\text{K}^+]_{\text{total}}$ lowered $[\text{K}^+]_{\text{unc}}$ to $\leq 3 \times 10^{-5} \text{ mol L}^{-1}$ and so reduced the contribution to k_{ex} from the K^+ -catalyzed pathway to $< 2 \text{ L mol}^{-1} \text{ s}^{-1}$ at 25 °C, i.e., $< 1\%$ of k_{ex}° . Thus, we have a direct measure of k_{ex}° . Increasing the excess of crypt-2.2.2 resulted in a slight downward trend in k_{ex}° (Table 2), presumably because the excess ligand (molar mass 376.5) begins to constitute a significant fraction of the medium, with unknown implications for solvent properties such as the dielectric constant. Accordingly, in one series of temperature-dependence experiments with crypt-2.2.2 in variable excess (Table 2, and fifth entry in Table 1), k_{ex}° values were extrapolated back to exact equivalence between $[\text{crypt-2.2.2}]_{\text{total}}$ and $[\text{K}^+]_{\text{total}}$ to obtain values of k_{ex}° and the corresponding enthalpy and entropy of activation, $\Delta H_{\text{ex}}^{\circ\ddagger}$ and $\Delta S_{\text{ex}}^{\circ\ddagger}$, respectively. However, Table 1, which combines the k_{ex}° data for both crypt-2.2.2 and 18-crown-6 as K^+ scavengers, shows that good consistency in $\Delta H_{\text{ex}}^{\circ\ddagger}$ and $\Delta S_{\text{ex}}^{\circ\ddagger}$ can be obtained without such precautions.

If k_{ex}° truly represents the rate constant k_0 for cation-independent $\text{Fe}(\text{CN})_6^{3-/4-}$ electron transfer rather than for pathways catalyzed feebly by $\text{K}(\text{crypt-2.2.2})^+$ and $\text{K}(18\text{-crown-6})^+$, k_{ex}° must be demonstrably the same for the crypt-2.2.2 and 18-crown-6 systems at comparable ionic strength I (which, by definition, is independent of complexation of the K^+ by uncharged ligands) and temperature T . Table 1 shows that this is the case; for either system, we can take as representative values $k_0 = k_{\text{ex}}^\circ = 238 \pm 10 \text{ L mol}^{-1} \text{ s}^{-1}$ at 25.0 °C, $\Delta H_0^\ddagger = 21.0 \pm 1.0 \text{ kJ mol}^{-1}$, and $\Delta S_0^\ddagger = -129 \pm 3 \text{ J K}^{-1} \text{ mol}^{-1}$ for $I \sim 0.2 \text{ mol L}^{-1}$ ($\Delta H_{\text{ex}}^{\circ\ddagger}$ and $\Delta S_{\text{ex}}^{\circ\ddagger}$ values for the case where $[18\text{-crown-6}]$ ranged up to 1.07 mol L^{-1} are of doubtful significance because the high concentration of free ligand may have perturbed solvent properties

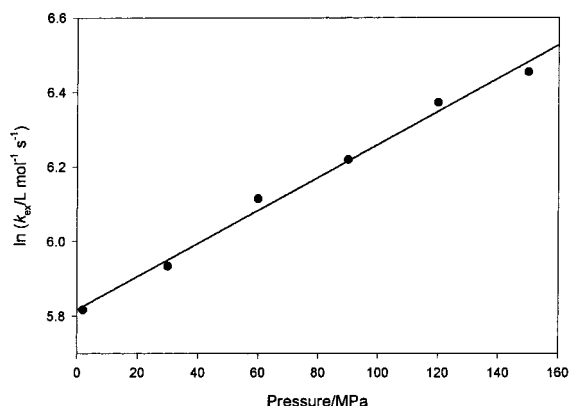


Figure 4. Pressure dependence of k_{ex} for $\text{Fe}(\text{CN})_6^{3-/4-}$ in H_2O at $25.0\text{ }^\circ\text{C}$ with $[\text{K}^+]_{\text{total}} = 0.247\text{ mol L}^{-1}$ and $[\text{crypt-2.2.2}] = 0.320\text{ mol L}^{-1}$.

substantially). In addition, k_{ex}° must not be proportional to the concentration of complexed K^+ , but this criterion could be compromised by the expected acceleration of the $\text{Fe}(\text{CN})_6^{3-/4-}$ exchange by increasing ionic strength according to eq 1. It turns out, however, that k_{ex}° varies quite slowly with I because the parameter a in eq 1 is large: a least-squares fit of the k_{ex}° values of Table 1 to eq 1 gave $a = 2.6\text{ nm}$ and $k_0^{I=0} = 10.2\text{ L mol}^{-1}\text{ s}^{-1}$ at $25.0\text{ }^\circ\text{C}$. If we assume that ΔH_0^\ddagger is still $\sim 21\text{ kJ mol}^{-1}$ at infinite dilution, we can estimate $k_0^{I=0} \sim 4.3\text{ L mol}^{-1}\text{ s}^{-1}$ at $0.1\text{ }^\circ\text{C}$, which, in view of the large extrapolation inherent in eq 1, is in reasonable agreement with the value of $6.0\text{ L mol}^{-1}\text{ s}^{-1}$ found at $0.1\text{ }^\circ\text{C}$ by Wahl and co-workers.¹³

Effects of Pressure. For five solutions in H_2O made up with only $\text{K}_3\text{Fe}(\text{CN})_6$ and $\text{K}_4\text{Fe}^{13}\text{CN}_6$, or these solutes plus KCl or KOH , $\ln k_{\text{ex}}$ was a linear function of pressure (see, e.g., Figure S5 in the Supporting Information)

$$\ln k_{\text{ex}} = \ln k_{\text{ex}}^\circ - P\Delta V_{\text{ex}}^\ddagger/RT \quad (5)$$

giving consistent values of $\Delta V_{\text{ex}}^\ddagger$ ($\Delta V_{\text{K}}^\ddagger$ in Table S2 in the Supporting Information) with an average of $-2.1 \pm 0.3\text{ cm}^3\text{ mol}^{-1}$. These experiments were carried out with three independent preparations of $\text{K}_4\text{Fe}^{13}\text{CN}_6$. In one further case, $\text{K}_3\text{Fe}(\text{CN})_6$ and $\text{K}_4\text{Fe}(\text{CN})_6$ with natural abundance of ^{13}C were used with a necessarily high concentration of the latter, giving $\Delta V_{\text{K}}^\ddagger$ about $1\text{ cm}^3\text{ mol}^{-1}$ more positive. Values of the extrapolated zero-pressure specific rate constant k_{K}' ($=k_{\text{ex}}^\circ/[\text{K}^+]_{\text{total}}$) were in satisfactory agreement with those measured directly in the variable-temperature experiments. When the solvent was 95% D_2O (with 5% H_2O for shimming), $\Delta V_{\text{K}}^\ddagger$ was $-0.8 \pm 0.3\text{ cm}^3\text{ mol}^{-1}$, again indicating the existence of a small but not negligible solvent isotope effect.

For solutions in H_2O containing an excess of crypt-2.2.2 over $[\text{K}^+]_{\text{total}}$, the measured $\ln k_{\text{ex}}$ was a linear function of pressure within the experimental uncertainty, as exemplified by Figure 4 (and Figure S6 in the Supporting Information), for a range of solution compositions and different preparations of $\text{K}_4\text{Fe}^{13}\text{CN}_6$ (first three entries in Table S3 in the Supporting Information). In these experiments, $[\text{K}^+]_{\text{unc}} \leq 1.0 \times 10^{-5}\text{ mol L}^{-1}$, so that at least 99.7% of the exchange reaction proceeded by the K^+ -independent pathway. The

weighted average of $\Delta V_{\text{ex}}^\ddagger$ is $-11.3 \pm 0.3\text{ cm}^3\text{ mol}^{-1}$ in H_2O at $25.0\text{ }^\circ\text{C}$. For 95% D_2O as solvent, a slight curvature of the $\ln k_{\text{ex}}$ vs P plot is perceptible (Supporting Information, Figure S7) and could be represented as a quadratic function of P :

$$\ln k_{\text{ex}} = \ln k_{\text{ex}}^\circ - P\Delta V_{\text{ex}}^\ddagger/RT + \Delta\beta_{\text{ex}}^\ddagger P^2/2RT \quad (6)$$

Theory predicts that a plot of $\ln k_{\text{ex}}$ vs P for OSET should be slightly curved, although curvature is seldom evident.²⁷ In the present case, the nonlinearity is not great enough to warrant invoking a significant compressibility coefficient of activation $\Delta\beta_{\text{ex}}^\ddagger$ (included as footnotes to Table S3). Instead, for purposes of comparison of all the data, and of the data with theoretical predictions, $\ln k_{\text{ex}}$ will be taken here as a linear function of P , and $\Delta V_{\text{ex}}^\ddagger$ so derived may be considered as an average value valid at the midpoint of the pressure range (75 MPa).

For solutions in H_2O containing $\text{K}_3\text{Fe}(\text{CN})_6$, $\text{K}_4\text{Fe}^{13}\text{CN}_6$, and 18-crown-6, the $\text{K}^+(\text{aq})$ -dependent pathway always contributed a significant fraction of the measured rate constant k_{ex} , so that a four-parameter equation must be solved:

$$k_{\text{ex}} = k_0 \exp(-P\Delta V_0^\ddagger/RT) + k_{\text{K}}[\text{K}^+]_{\text{unc}} \exp(-P\Delta V_{\text{K}}^\ddagger/RT) \quad (7)$$

Furthermore, the value of $[\text{K}^+]_{\text{unc}}$ must first be calculated from $[\text{K}^+]_{\text{total}}$ for each pressure using the volume change ΔV_{crown} of aqueous $\text{K}(18\text{-crown-6})^+$ complex formation ($13\text{ cm}^3\text{ mol}^{-1}$ at $25.0\text{ }^\circ\text{C}$)²⁸ together with the atmospheric-pressure value of K_{crown} (117.0 L mol^{-1}):^{19,21}

$$K_{\text{crown}}^P = 117.0 \exp(-P\Delta V_{\text{crown}}/RT) \quad (8)$$

Fortunately, k_0 (Table 1) and k_{K} (eq 4) are accurately known from the variable-temperature study, and we may assume for the moment that ΔV_0^\ddagger is the same as $\Delta V_{\text{ex}}^\ddagger$ for the case where crypt-2.2.2 effectively extinguished the K^+ dependent pathway (Table S3). Then, the k_{ex} data of Table S4 in the Supporting Information give $\Delta V_{\text{K}}^\ddagger = -2.1 \pm 0.9\text{ cm}^3\text{ mol}^{-1}$ at $25.0\text{ }^\circ\text{C}$, which is identical with the average value of $\Delta V_{\text{K}}^\ddagger$ of Table S2. Thus, although the rate constants k_{K} and k_{K}' for the $\text{K}_3\text{Fe}(\text{CN})_6$ – $\text{K}_4\text{Fe}(\text{CN})_6$ exchange in the presence and absence, respectively, of 18-crown-6 are not quite the same, the respective volumes of activation are identical. Conversely, then, $k_{\text{K}}[\text{K}^+]_{\text{unc}}$ in eq 7 can be calculated for each pressure with $\Delta V_{\text{K}}^\ddagger$ fixed at $-2.1\text{ cm}^3\text{ mol}^{-1}$ (Table S4), whereupon the linear plot of $\ln(k_{\text{ex}} - k_{\text{K}}[\text{K}^+]_{\text{unc}})$ vs P confirms that the volume of activation for the $\text{K}^+(\text{aq})$ -independent path is $-11.1 \pm 0.9\text{ cm}^3\text{ mol}^{-1}$. Thus, not only the rate constants but also the volumes of activation for the $\text{K}^+(\text{aq})$ -independent pathways of the $\text{Fe}(\text{CN})_6^{3-/4-}$ exchange are the same whether 18-crown-6 or crypt-2.2.2 is used to sequester K^+ .

Discussion

Characterization of the Cation-Independent $\text{Fe}(\text{CN})_6^{3-/4-}$ Exchange Pathway. The identity of the rate constants and

(27) Swaddle, T. W. *Can. J. Chem.* **1996**, *74*, 631.

(28) Høiland, H.; Ringseth, J. A.; Brun, T. S. *J. Solution Chem.* **1979**, *8*, 779.

also the volumes of activation for the “zero free K^+ ” pathways of the $K_3Fe(CN)_6-K_4Fe(CN)_6$ self-exchange reaction in the cases of $[K^+]$ control by crypt-2.2.2 and 18-crown-6 demonstrate that they refer to the true, cation-independent $Fe(CN)_6^{3-/4-}$ pathway k_0 , and not to paths weakly catalyzed by $K(18\text{-crown-6})^+$ or $K(\text{crypt-2.2.2})^+$. This conclusion is reinforced by the absence of dependence of k_0 so measured on the total cation concentration, beyond the weak trend that is accounted for by medium effects (eq 1). The adjustable parameter a in eq 1 calculated for the crypt-2.2.2- $K_3Fe(CN)_6-K_4Fe(CN)_6$ self-exchange is very large (2.6 nm) relative to any physically reasonable anion-cation contact distances, even given the large size of $K(\text{crypt-2.2.2})^+$, but empirically it accounts for the remarkably slight dependence of k_0 on the ionic strength.

We conclude that, for typical working ionic strengths on the order of 0.2 mol L^{-1} , the cation-independent pathway for the $Fe(CN)_6^{3-/4-}$ exchange in H_2O at $25.0 \text{ }^\circ\text{C}$ is characterized by the parameters $k_0 = 2.4 \times 10^2 \text{ L mol}^{-1} \text{ s}^{-1}$, $\Delta H_0^\ddagger = 21.0 \text{ kJ mol}^{-1}$, $\Delta S_0^\ddagger = -129 \text{ J K}^{-1} \text{ mol}^{-1}$, and $\Delta V_0^\ddagger = -11.3 \text{ cm}^3 \text{ mol}^{-1}$. The free energy of activation ΔG_0^\ddagger is thus 59.5 kJ mol^{-1} , which corresponds closely to that calculated from Marcus theory by Cannon²⁹ (60 kJ mol^{-1}) for comparable conditions.

For simple adiabatic OSET, ΔV_0^\ddagger can be predicted by an extension of Marcus theory²⁷ in terms of contributions ΔV_{IR}^\ddagger from inner-sphere reorganization (usually taken to mean metal-ligand bond length readjustment), ΔV_{SR}^\ddagger from solvent reorganization, ΔV_{DH}^\ddagger representing the pressure dependence of ionic activity coefficients according to extended Debye-Hückel theory (eq 1), and $(\Delta V_{Coul}^\ddagger + \Delta V_{prec}^\ddagger)$ from the pressure dependences of the Coulombic work and pre-exponential parts of the formation constant for the $\{Fe(CN)_6^{3-}, Fe(CN)_6^{4-}\}$ precursor complex:

$$\Delta V_0^\ddagger = \Delta V_{IR}^\ddagger + \Delta V_{SR}^\ddagger + \Delta V_{DH}^\ddagger + (\Delta V_{Coul}^\ddagger + \Delta V_{prec}^\ddagger) \quad (9)$$

Because metal-ligand bond lengths in the reduced species usually contract and those in the oxidized partner usually expand by a similar amount as the reactants move to a common configuration in the transition state, ΔV_{IR}^\ddagger is normally small and represents mainly differences in compressibility between the reactants. Stranks³⁰ estimated $\Delta V_{IR}^\ddagger \sim +0.6 \text{ cm}^3 \text{ mol}^{-1}$ for typical cationic couples, but the $Fe(CN)_6^{3-/4-}$ couple may be anomalous in that the effective radius of the hexacyanoferrate(III) ion in solids appears to be similar to or, for the same counterion, larger than that of the hexacyanoferrate(II) (445 and 433 pm, respectively, in M^{2+} salts),³¹ presumably because of strong π back-bonding by the cyanide ligands. We may therefore expect ΔV_{IR}^\ddagger to be in the range 0 to $-1 \text{ cm}^3 \text{ mol}^{-1}$ for $Fe(CN)_6^{3-/4-}$. The remaining terms on the right-hand side of eq 9 can be calculated as described previously,²⁷ taking the separation of the Fe centers when electron transfer occurs to be

approximately the sum of the radii of the reactants (but variable and therefore pressure-dependent) and the anion-cation close-approach parameter a to be 2.6 nm, determined as described above by fitting the experimental k_0 data to eq 1. For the midrange pressure of 75 MPa, ΔV_{SR}^\ddagger and ΔV_{prec}^\ddagger are -7.2 and $+0.9 \text{ cm}^3 \text{ mol}^{-1}$, respectively.³² For typical cation-cation OSET reactions at practical ionic strengths, the terms ΔV_{Coul}^\ddagger and ΔV_{DH}^\ddagger tend to cancel each other,²⁷ but for the $Fe(CN)_6^{3-/4-}$ couple ΔV_{DH}^\ddagger is numerically smaller ($+2.9 \text{ cm}^3 \text{ mol}^{-1}$) than ΔV_{Coul}^\ddagger ($-6.8 \text{ cm}^3 \text{ mol}^{-1}$) because of the large value of a , resulting in a total predicted ΔV_0^\ddagger of -10.2 to $-11.2 \text{ cm}^3 \text{ mol}^{-1}$ (depending on the value assigned to ΔV_{IR}^\ddagger). This value is rather more negative than predicted for most OSET reactions, but agreement with the experimental value of $-11.3 \pm 0.3 \text{ cm}^3 \text{ mol}^{-1}$ for $Fe(CN)_6^{3-/4-}$ is excellent, vindicating the theoretical treatment and, conversely, confirming that the measured k_0 represents the direct adiabatic anion-anion OSET process.

Cation Catalysis. The ionic strength dependence of the $K^+(\text{aq})$ -catalyzed rate constant k_K from the 18-crown-6 studies was not measured, but it is evidently very small (i.e., a is again large) at the ionic strengths used here because the rate constant k_K' for the $K_3Fe(CN)_6-K_4Fe(CN)_6$ self-exchange in absence of sequestering agents is effectively directly proportional to $[K^+]_{\text{total}}$ (Figure 1), which is quite surprising for reactions involving highly charged species. The fact that k_K' is some 60% larger than k_K at $25 \text{ }^\circ\text{C}$ is almost certainly a consequence of ion-pair formation by $K^+(\text{aq})$ in the absence of 18-crown-6, since the very large $K(18\text{-crown-6})^+$ ions can be expected to have very little tendency to pair with the hexacyanometalate anions.

Ion pairing by $K^+(\text{aq})$ is expected to accelerate OSET by reducing electrostatic repulsions between the hexacyanoferrate ions, but its calculated influence on the Coulombic work terms is too small to account for all of the catalytic effect of $K^+(\text{aq})$. For example, if we take the radii of the $Fe(CN)_6^{3-}$ and $Fe(CN)_6^{4-}$ to be 445 and 433 pm, respectively,³¹ and make the extreme assumptions that ion-pairing of both reactants is complete and has the sole effect of reducing the charge on each reactant by one unit, k_K'/k_0 is calculated to be about 32 for our reaction conditions (or ~ 12 , if one or more deaquated K^+ is placed between the reactants), whereas k_K' is found experimentally to be about $300k_0$. Khoshtariya et al., in their recent review of thermal, electrochemical, and optical electron transfer dynamics in cyanometalate couples,³³ also conclude that the catalytic effect of cations must be distinguished from equilibrium anion-cation association phenomena.

Kharkats and Chonishvili³⁴ showed that the effect of interposing a cation between two anions undergoing electron transfer would be a reduction of the Marcus solvent reorganizational part ΔG_{SR}^\ddagger of the free energy of activation ΔG^\ddagger ,

(29) Cannon, R. D. *Electron Transfer Reactions*; Butterworth: London, 1980; p 219.

(30) Stranks, D. R. *Pure Appl. Chem.* **1974**, *38*, 303.

(31) Brown, D. B.; Shriver, D. F. *Inorg. Chem.* **1969**, *8*, 37.

(32) If the Fe-Fe separation at the moment of electron transfer is taken to be pressure-independent, i.e., if hard-sphere contact of the reactants is assumed, ΔV_{prec}^\ddagger is eliminated but a concomitant positive change in ΔV_{SR}^\ddagger offsets it closely.

(33) Khoshtariya, D. E.; Dolidze, T. D.; Neubrand, A.; van Eldik, R. J. *Mol. Liq.* **2000**, *89*, 127.

(34) Kharkats, Y. I.; Chonishvili, G. M. *Sov. Electrochem.* **1975**, *11*, 164.

the reduction approaching 50% asymptotically as the cation:anion radius ratio increases beyond about 0.3, where the effect is minimal ($\sim 12\%$). For the $\text{Fe}(\text{CN})_6^{3-/4-}/\text{K}^+$ case, $\Delta G_{\text{SR}}^\ddagger$ may be calculated to be about 22 kJ mol^{-1} for the k_0 pathway and the cation:anion radius ratio is ~ 0.3 , so $\Delta G_{\text{SR}}^\ddagger$ should be reduced by about 2.6 kJ mol^{-1} , which means an acceleration of less than 3-fold due to K^+ bridging. This is much too small, even when combined with the most optimistic estimates of the effect of ion-pairing. Furthermore, the Kharkats–Chonishvili approach predicts only a small variation in k_M' for typical cyanometalate self-exchange reactions, probably in the order $\text{M} = \text{Li} \geq \text{Na} \geq \text{K} \leq \text{Rb} < \text{Cs}$ (because the ion radius ratios bracket the extremum in Figure 4 of ref 34), whereas in fact the observed sequence is $\text{Li} < \text{Na} < \text{K} < \text{Rb} < \text{Cs}$ and the span in k_M' across this series can exceed 100-fold.¹² Besides, the effect of cation size on the R_4N^+ -catalyzed $\text{Fe}(\text{CN})_6^{3-/4-}$ exchange rate is *opposite* to that predicted by the Kharkats–Chonishvili theory: the larger R_4N^+ , the slower the exchange rate.¹³ Thus, cation catalysis of cyanometalate self-exchange reactions must be due in large part to factors other than the electrostatic effects of ion-pairing or the Kharkats–Chonishvili effect on $\Delta G_{\text{SR}}^\ddagger$. It is tempting to try to relate the relative efficacies of alkali-metal ions in catalyzing the $\text{Fe}(\text{CN})_6^{3-/4-}$ exchange reaction to the trend in their polarizabilities, but Cannon³⁵ points out that this apparent correlation is irrelevant because other cations of low polarizability such as $\text{Co}(\text{NH}_3)_6^{3+}$ and $(\text{CH}_3)_4\text{N}^+$ can be very effective catalysts for cyanometalate OSET reactions.

A quantitative explanation of the catalytic effect of cations on anion–anion ET kinetics is still not available, but it seems that a cation can assist transfer of the negatively charged electron by providing a path of positive potential between the reacting anions,¹² which explains why anion catalysis of cation–cation ET is much less effective. In other words, the cation-catalyzed pathway has some of the attributes of an inner-sphere ET mechanism and is therefore faster than cation-independent OSET regardless of the evident adiabaticity of the latter. Catalysis of anion–anion ET will be most effective if the electron transfer path provided by a bridging cation is as short as possible; thus, the efficiency of R_4N^+ ions falls with increasing size of R ,¹³ but rises with increasing ionic radius for alkali-metal ions because they form much shorter bridges if they are at least partially deaquated, and the energy needed to deaquate them falls as the ionic radius increases. The fact that $\text{K}(\text{crypt-2.2.2})^+$ and $\text{K}(\text{18-crown-6})^+$ are not catalysts supports the view that alkali-metal cations must be at least partially stripped of coordinated ligands to catalyze ET. Tetraalkylammonium ions are not actively solvated in water,³⁶ and presumably the catalytic power of the relatively large $(\text{CH}_3)_4\text{N}^+$ compares with that of the heavier alkali-metal ions only because of the extra energy input required for deaquation of the latter. This model explains why volumes of activation for self-exchange of cyanometalates are negative with R_4N^+ counterions but much more positive with alkali-metal cations, since deaquation of

metal ions in water results in a positive volume change for the system.¹² Furthermore, the k_{ex} data of Campion et al.¹³ for the R_4N^+ -catalyzed $\text{Fe}(\text{CN})_6^{3-/4-}$ self-exchange reaction, converted according to $k_{\text{ex}}' = k_{\text{ex}}/[\text{R}_4\text{N}^+]$, give $\Delta S_{\text{ex}}^{\ddagger} = -151$ and $-160 \text{ J K}^{-1} \text{ mol}^{-1}$, with $\Delta H_{\text{ex}}^{\ddagger} = -1.2$ and 0.0 kJ mol^{-1} , for the Me_4N^+ - and Et_4N^+ -catalyzed pathways, respectively, whereas for the K^+ -catalyzed path we find $\Delta S_{\text{ex}}^{\ddagger} = -75 \text{ J K}^{-1} \text{ mol}^{-1}$ and $\Delta H_{\text{ex}}^{\ddagger} = 22.9 \text{ kJ mol}^{-1}$. The contrast in these data is again consistent with some degree of deaquation of K^+ (requiring an input of enthalpy but increasing the entropy of the system through release of bound water molecules) but not R_4N^+ . Khoshtariya et al.³³ pursue the question of alkali-metal vs tetraalkylammonium ion catalysis at length.

For the $\text{Fe}(\text{CN})_6^{3-/4-}$ self-exchange, values of $\Delta V_{\text{K}}^\ddagger$ (or equivalently $\Delta V_{\text{K}^{\ddagger}}$) for the K^+ -catalyzed path are $-2 \text{ cm}^3 \text{ mol}^{-1}$ in H_2O and $-1 \text{ cm}^3 \text{ mol}^{-1}$ in D_2O , which are 9–10 $\text{cm}^3 \text{ mol}^{-1}$ more positive than ΔV_0^\ddagger for the cation-independent path and are reminiscent of the corresponding results for K^+ and Na^+ catalysis of the MnO_4^{2-} exchange,⁵ the one other anion–anion exchange for which both cation-catalyzed and uncatalyzed pathways have been characterized. The foregoing deaquation argument is appropriate in both cases.^{5,12} Unfortunately, the value found for $\Delta V_{\text{K}}^\ddagger$ in this study disagrees sharply with the previous estimate ($22 \pm 2 \text{ cm}^3 \text{ mol}^{-1}$ in D_2O),¹¹ yet was highly reproducible with different sources of reagents, various concentrations, addition of KCl , the presence or absence of ^{13}C enrichment, and neutral or alkaline pH. Only when EDTA^{4-} was present (as recommended by Wahl et al.¹³) was an apparent retardation by rising pressure seen, but this turned out to be due to slow reduction of the $\text{Fe}(\text{CN})_6^{3-}$ by the EDTA^{4-} as the experiment progressed. The earlier study suffered from a necessarily small pressure range and other instrumental difficulties noted at the time,¹¹ but these were specifically allowed for; the only explanation for the discrepancy seems to be contamination of samples in the earlier study by some reducing agent, probably introduced by slight leakage of pressurizing fluid into the sample tube, resulting in slow reduction of the $\text{Fe}(\text{CN})_6^{3-}$ much as in our present experience with added EDTA^{4-} . This underscores the importance of ensuring that data obtained by any technique on the up-pressure and down-pressure legs of a pressure cycle are consistent within the experimental uncertainty; this crucial check was omitted in the previous study¹¹ because of instrumental difficulties. In the pressure studies of self-exchange reactions of the Os, Mo, and W cyanometalates,¹² this check was always carried out, and the published volumes of activation are considered reliable.

Conclusions. Sequestration of the counterion (K^+) by the K^+ -selective macrocycles crypt-2.2.2 and 18-crown-6 can expose the cation-independent pathway for $\text{Fe}(\text{CN})_6^{3-/4-}$ exchange, the rate constant for which ($k_0 = 2.4 \times 10^2 \text{ L mol}^{-1} \text{ s}^{-1}$ at 25°C and ionic strength 0.2 mol L^{-1}) is 100-fold lower than the values usually cited in the literature, which refer to the K^+ -catalyzed pathway. Both k_0 and the corresponding ΔV_0^\ddagger ($-11.3 \text{ cm}^3 \text{ mol}^{-1}$) are independent of the choice of ligand and of the concentration of complexed K^+ , so that the pathway observed is truly the direct anion–

(35) Reference 29, p 226.

(36) Symons, M. C. R. *Phys. Chem. Chem. Phys.* **1999**, *1*, 113.

anion exchange and not a pathway catalyzed by $\text{K}(\text{crypt-2.2.2})^+$ or $\text{K}(\text{18-crown-6})^+$. The magnitudes of k_0 and ΔV_0^\ddagger are accounted for very satisfactorily by Marcus-type theory,^{27,29} which implies that the uncatalyzed OSET pathway is adiabatic.

In the absence of sequestering agents, the K^+ -catalyzed pathway overwhelms k_0 , and its rate is essentially proportional to the total $[\text{K}^+]$ even though there is a minor contribution from ion-pairing in addition to the catalytic component. Neither the direct nor the K^+ -catalyzed pathways show any marked dependence on ionic strength as such for practical values of I , so that the rate of the catalyzed exchange is counterintuitively proportional to $[\text{K}^+]$. The catalytic effect of K^+ (and other alkali metal ions) is much greater than can be accounted for solely by reduction of the Coulombic work terms by ion-pairing, or by the electrostatic effect of a bridging K^+ on the solvent reorganizational component of the free energy as suggested by Kharkats and Chonishvili.³⁴

Catalysis by $\text{K}^+(\text{aq})$ appears to involve its partial deaquation, which is reflected in a volume of activation $9\text{--}10\text{ cm}^3\text{ mol}^{-1}$ more positive than that for the uncatalyzed pathway.

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Supporting Information Available: Representative data sets displayed as Tables S1–S4 and Figures S1–S7. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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