Cation Catalysis of Anion−Anion Electron Transfer in Aqueous Solution: Self-Exchange Reaction Kinetics of Some Hexa- and Octacyanometalate Couples at Variable Pressure

Peter D. Metelski and Thomas W. Swaddle*

Department of Chemistry, University of Calgary, Calgary, Alberta, Canada T2N 1N4

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Rate constants k_{ex} for the $Os(CN)_6{}^{3-/4-}$, $Mo(CN)_8{}^{3-/4-}$, and $W(CN)_8{}^{3-/4-}$ self-exchange reactions in aqueous solution have been measured by ^{13}C NMR as functions of pressure, temperature, and added electrolyte concentrations. Detailed interpretation of k_{ex} values in the absence of added electrolytes is complicated by anion−cation association, but k_{ex} is strongly influenced by the nature of added cations ($Li^+ < Na^+ < K^+ < Rb^+ < Et_4N^+ < Cs^+ \leq Me_4N^+$) and is linearly dependent on their concentrations. For K^+ as the counterion, $\Delta V_{ex}^\ddagger$ for $Os(CN)_6{}^{3-/4-}$, $Mo(CN)_8{}^{3-/4-}$, and $W(CN)_8{}^{3-/4-}$ is $+19.0 \pm 0.9$, $+14.7 \pm 0.6$, and $+22.5 \pm 1.1$ cm^3 mol^{-1}, respectively; these values are completely inconsistent with a simple two-sphere Marcus-type model of the electron-transfer process, which predicts $\Delta V_{ex}^\ddagger$ on the order of -6 cm^3 mol^{-1}. With Et_4N^+ as the counterion, however, $\Delta V_{ex}^\ddagger$ for $Mo(CN)_8{}^{3-/4-}$ is -8.2 ± 0.6 cm^3 mol^{-1}, and for $W(CN)_8{}^{3-/4-}$ with Me_4N^+ $\Delta V_{ex}^\ddagger$ is -7.4 ± 0.5 cm^3 mol^{-1}. The results are interpreted in terms of a mechanism which is outer-sphere as far as the cyanometalate ions are concerned but in which a partially desolvated cation bridges the reacting anions. In the case of alkali metal cations, removal of some (probably two) of the coordinated water molecules precedes electron transfer, whereas the tetraalkylammonium ions have no coordinated water. Anion−anion electron transfer is much more sensitive to cation catalysis than cation−cation exchange is to anion effects, probably because a positively charged bridge provides a much more favorable tunneling path for the negatively charged electron than would an anionic mediator.

Introduction

Electron transfer between pairs of *anionic* metal complexes in solution has been much less intensively explored than cation−cation redox processes.[1] It appears, however, that catalysis of electron transfer by the counterions is much more marked for anion−anion[2−14] than for cation−cation[15−19] couples. In particular, electron transfer between ferricyanide and ferrocyanide ions in homogeneous aqueous solution with potassium as the counterion has been said to involve three K^+ in the transition state.[8,9,11] Furthermore, the $Fe(CN)_6{}^{3-/4-}$ self-exchange reaction with K^+ as counterion has a highly anomalous *positive* volume of activation $\Delta V_{ex}^\ddagger$ of $+22 \pm 2$ cm^3 mol^{-1},[11] whereas for uncatalyzed self-exchange reactions in water $\Delta V_{ex}^\ddagger$ is invariably *negative*, as predicted by an adaptation of Marcus theory that forecasts $\Delta V_{ex}^\ddagger = -6 \pm 2$ cm^3 mol^{-1} for the $Fe(CN)_6{}^{3-/4-}$ couple even after allowance for the electrostatic effects of ion association.[20,21] Pressure effects on the kinetics of the *heterogeneous* $Fe(CN)_6{}^{3-/4-}$ self-exchange reaction at a Pt electrode in various aqueous KCl media give $\Delta V_{el}^\ddagger = +11 \pm 1$ cm^3 mol^{-1}, so that the surprisingly positive reported value of $\Delta V_{ex}^\ddagger$ is vindicated by the "fifty percent rule," according to which $\Delta V_{el}^\ddagger$ is expected to be $^1/_2\Delta V_{ex}^\ddagger$.[22,23]

The main objective of the present study was to determine whether the $Fe(CN)_6{}^{3-/4-}$ results were peculiar to that couple, or whether marked cation catalysis accompanied by strongly positive $\Delta V_{ex}^\ddagger$ values is characteristic of other anion−anion electron-transfer reactions. The obvious candidates for investigation are the other hexacyanometalate(III/II) couples of group 8 and the octacyanometalate(V/IV) couples of group 6. Although Hoddenbagh and Macartney[12] were able to complete a series of self-exchange rate measurements on the aqueous $Ru(CN)_6{}^{3-/4-}$ couple at ambient pressure, this couple is insufficiently stable[24] on the time scale of a cycle of NMR or electrochemical kinetic measurements at high pressure (several hours). Aqueous solutions of the hexacyanoosmate complexes, however, are more

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* Corresponding author. Telephone: (403) 220-5358. Fax: (403)284-1372. E-mail: swaddle@chem.ucalgary.ca.

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stable than those of the Ru analogues, and in our experience are not significantly affected by air or room lighting over about a week. We have therefore focused our attention on the kinetics of the aqueous $Os(CN)_6^{3-/4-}$, $Mo(CN)_8^{3-/4-}$, and $W(CN)_8^{3-/4-}$ self-exchange reactions.

Redox reactions of the octacyanomolybdates and -tungstates have been extensively studied,[6,14,25−31] notably by Leipoldt's school,[7] but cross-reactions involving the hexacyanoosmates(III) and -(II) have received scant attention.[32−36] Macartney's detailed study[13] of the $Os(CN)_6^{3-/4-}$ self-exchange reaction using ^{13}C NMR provided a starting-point for our work. Macartney,[13] with D. Kerr, also made preliminary studies of the $Mo(CN)_8^{3-/4-}$ and $W(CN)_8^{3-/4-}$ exchange kinetics by the ^{13}C NMR method (cf. Campion et al.[6]), and we have endeavored to extend those studies in addition to measuring the pressure effects on the kinetics of the self-exchange reactions.

Experimental Section

Materials. Distilled water was further purified by passage through a Barnstead NANOpure train. $K_4Os(CN)_6 \cdot H_2O$ was made from K_2OsCl_6 (Strem).[37] Its purity was verified by CHN microanalysis and by its aqueous ^{13}C NMR spectrum, which showed only a single peak at 142.5 ppm (vs internal acetone at 29.9 ppm). Following Macartney,[13] the aqueous $Os(CN)_6^{3-}$ ion was prepared *in situ* by oxidation of $Os(CN)_6^{4-}$ with the stoichiometric amount of $IrCl_6^{2-}$ (Strem).

As the octacyano complexes of Mo and W are light-sensitive to various degrees,[38] these compounds and their solutions were handled using a red safelight, and otherwise kept in the dark. The method of Leipoldt et al.[39] was used to make $K_4Mo(CN)_8 \cdot 2H_2O$ and its ^{13}C-labeled form (from $K^{13}CN$: Sigma, 99.9 at. % ^{13}C). $K_3Mo(CN)_8$ was made via $Ag_3Mo(CN)_8$ by oxidation of $K_4Mo(CN)_8 \cdot 2H_2O$ with $KMnO_4$ solution.[40] The purity of the samples was verified by CHN analyses, UV−visible spectroscopy,[41] and (for the Mo^{IV} compounds in aqueous solution) the ^{13}C NMR spectrum, which showed only a single peak at 153 ppm. Tetramethylammonium (TMA) and tetraethylammonium (TEA) octacyanomolybdate(IV) were prepared by sonicating a suspension of 3.0 g (4.1 mmol) solid $Ag_4Mo(CN)_8$ and 14.5 mmol TMACl or TEACl (Eastman) in 50 mL water for 10 min, then filtering the solution to remove AgCl and concentrating the filtrate by rotary evaporation. The solid products were recrystallized twice from ethanol/diethyl ether and dried under vacuum. The UV−visible spectra of the tetraalkylammonium salts in water were identical with that of $K_4Mo(CN)_8 \cdot 2H_2O$ of established purity. The TMA and TEA salts of $Mo(CN)_8^{3-}$ were similarly prepared, except that the AgCl was removed by centrifugation and the supernatant solutions were authenticated by UV−visible spectroscopy and used directly.

Yellow $K_4W(CN)_8 \cdot 2H_2O$ was made by the method of Leipoldt et al.[42] and purified by precipitation from aqueous solution as $Ag_4W(CN)_8$ followed by trituration of the precipitate with a deficiency of aqueous potassium chloride; the pure K salt was reprecipitated with ethanol. The purity of the product was verified by CHN analyses and the ^{13}C NMR spectrum of its solution in D_2O (a single resonance at 145.6 ppm plus one small satellite peak on either side, $J_{W-C} = 29$ Hz). The same procedure was carried out in a Schlenk tube with $K^{13}CN$ (Sigma) to make $K_4W(^{13}CN)_8 \cdot 2H_2O$. $K_3W(CN)_8$ was made by the same method as $K_3Mo(CN)_8$. Solid $Li_4W(CN)_8$, $Cs_4W(CN)_8$, and $(TMA)_4W(CN)_8$, and solutions of the corresponding W^V salts, were made from $Ag_4W(CN)_4$ and $Ag_3W(CN)_8$, respectively, in the manner of the Mo analogues; the Li salt of $Mo(CN)_8^{4-}$, a dihydrate, could not be recrystallized and was used as the solid residue from complete rotary evaporation of the solution. The purity of all these W products was confirmed by UV−visible spectroscopy.[41]

Dynamic NMR Measurements at Ambient Pressure. Carbon-13 NMR measurements were made at 75.42 MHz with a Bruker AMX2/300 wide-bore (89 mm) spectrometer on solutions in D_2O in spinning 10 mm sample tubes. The temperature readout was calibrated using the ^1H peak separation of either methanol (below 298 K) or 1,2-ethanediol (80% in DMSO-d_6, above 298 K).

The longitudinal relaxation times T_1 of ^{13}C for solutions of $Os(CN)_6^{4-}$, $Mo(CN)_8^{4-}$, and $W(CN)_8^{4-}$ in D_2O were found by a standard inversion−recovery pulse sequence to be 7.2, 13.4, and 1.7 s at 22 °C. Interpulse delays of $5T_1$ were applied in running NMR spectra. The line widths W_0 of the $Os(CN)_6^{4-}$ (0.65 Hz) and $Mo(CN)_8^{4-}$ (1.4 Hz) were not significantly dependent on temperature over the respective ranges 276−326 and 274−313 K. For $K_4W(CN)_8$ solutions, W_0 was given by $(0.00850T - 1.78)$ Hz for $T > 278$ K.

For the Os exchange experiments, weighed amounts of $K_4Os(CN)_6 \cdot H_2O$ and D_2O, and an aliquot of aqueous K_2IrCl_6 equivalent to the desired $[Os^{III}]$, were introduced successively into the NMR tube. For measurements of the temperature dependences of the $Mo(CN)_8^{3-/4-}$ and $W(CN)_8^{3-/4-}$ self-exchanges, solutions were made up from weighed amounts of the solid K^+ salts of the cyanometalate salts. For experiments intended to demonstrate the effect of added alkali metal cations M^+, weighed amounts of MCl were also added—in these cases, minor amounts of the counterion K^+ were present in addition to M^+. For studies of the very rapid reactions in the presence of tetraalkylammonium ions R_4N^+, however, small aliquots of solutions of $(R_4N)_3[Mo(CN)_8]$ or $(R_4N)_3[W(CN)_8]$ in H_2O were weighed into the NMR sample tube together with the requisite amounts of solid $(R_4N)_4[Mo(CN)_8]$ or $(R_4N)_4[W(CN)_8]$, respectively, R_4NCl, and D_2O. It was shown that the added MCl or R_4NCl had no effect on the ^{13}C line width of the diamagnetic cyanometalate alone (±0.2 Hz). Thus, line broadening in the presence of the paramagnetic partner was ascribable entirely to electron transfer dynamics rather than to any paramagnetic impurities introduced with the relatively high concentrations of added electrolyte (cf. Vallazza et al.[43]).

Dynamic NMR Measurements at Variable Pressure. The general design[44] of the high-pressure probe head for the wide-bore Bruker AMX2−300 spectrometer loosely resembles that described by Frey, Helm and Merbach,[45] a major difference being that all electrical and high pressure connections were made through the base of the pressure vessel so that the assembled device could be easily fed into the magnet bore from below (cf. van Eldik et al.[46]). Following the practice of Jonas and co-workers,[47,48] connections on the low-pressure side of the electrical feedthroughs were made with short (65 mm) lengths of copper−constantan thermocouple wire having a magnesium oxide

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dielectric and an Inconel sheath. Sample cavity temperature was measured with a calibrated internal 100 Ω Pt resistance thermometer, and the pressure dependence of its response was determined (<0.0001 Ω MPa^{-1}).[49]

The sample was contained in a standard 10 mm NMR tube, cut down to 54 mm length, fitted with a free Teflon piston to exclude the pressurizing fluid. Since the sample could not be spun, persistent inhomogeneities in the magnetic field inside the pressure vessel led to a rather wide ^{13}C line width for $Os(CN)_6^{4-}$, $Mo(CN)_8^{4-}$, and $W(CN)_8^{4-}$ in the absence of exchange ($W_0 = 50-52$ Hz), but fortunately the broadening due to chemical exchange was large, and the precision of the kinetic measurements was not compromised. Solutions were made up as described above for the variable temperature studies except that, because the pressurizable probe was relatively insensitive and had no provision for an internal deuterium lock, concentrations of the diamagnetic cyanometalate ions were much higher (≈0.1 mol L^{-1}) and the solvent was ^1H_2O.

Results

Electron-Transfer Kinetics of $Os(CN)_6^{3-/4-}$. Macartney[13] established that the $Os(CN)_6^{3-/4-}$ self-exchange rate lies in the "slow" region of the ^{13}C NMR time scale and is first order with respect to each of $[Os(CN)_6^{3-}]$ and $[Os(CN)_6^{4-}]$, independent of pH at pH > 4, but markedly dependent on the identity and concentration of added electrolytes (rate with $LiClO_4 < NaClO_4 < KCl < NH_4Cl$). Our measurements of the $Os(CN)_6^{3-/4-}$ self-exchange rate at ambient pressure were therefore conducted at near-neutral pH, with and without added electrolytes. The overall second-order rate constant k_{ex} for the $Os(CN)_6^{3-/4-}$ self-exchange was obtained from eq 1

$$k_{ex} = k_{obsd}[\text{oxidant}^{3-}]^{-1} = \pi(W_{1/2} - W_{1/2}{}^0)[\text{oxidant}^{3-}]^{-1} \tag{1}$$

in which k_{obsd} is the observed rate constant (first-order in $[Os(CN)_6^{4-}]$) and $W_{1/2}$ and $W_{1/2}{}^0$ are the line widths of the $Os(^{13}CN)_6^{4-}$ resonance in the presence and absence, respectively, of the oxidant $Os(CN)_6^{3-}$.

Figure 1 shows the effects on k_{ex} of adding various MCl to $K_4Os(CN)_6-K_3Os(CN)_6-K_3IrCl_6$ solutions. The accessible concentration ranges of added RbCl and CsCl were limited by solubility of the hexacyanoosmate salts. For each M$^+$, k_{ex} was a linear function of the stoichiometric [M$^+$], rising in the order M = Li < Na < K < Rb < Cs:

$$k_{ex} = k_{ex}{}^0 + k_M[M^+] \tag{2}$$

where $k_{ex}{}^0$ represents the rate constant when the counterion K$^+$ of the cyanometalates was the only cation present. Values of k_M are collected in Table 1. For 1.0 mol L^{-1} KCl at 25.0 °C, the calculated value of k_{ex} (1.38 × 10^5 L mol^{-1} s^{-1}) is in excellent agreement with that measured by Macartney.[13] Figure 1 also shows that the effects of added KNO_3 and KSO_3CF_3 were the same as that of KCl: thus, the effect of the added electrolyte on k_{ex} is specifically a property of the added cation.

The $Os(CN)_6^{3-/4-}$ self-exchange rate was subject to a small solvent hydrogen isotope effect. For comparable aqueous solutions containing 0.95 mol L^{-1} KCl, k_{ex} was 1.60 × 10^5, 1.32 × 10^5, and 1.05 × 10^5 L mol^{-1} s^{-1} at 25.0 °C for water containing respectively 0, 32, and 100% D_2O. An effect of similar magnitude ($Os(CN)_6^{3-/4-}$ self-exchange 31% slower in 100% D_2O than in H_2O) was found for solutions with $[K_4Os(CN)_6] = 0.030$ mol L^{-1} and $[K_3Os(CN)_6] \sim 3$ mmol L^{-1} but no added electrolyte.

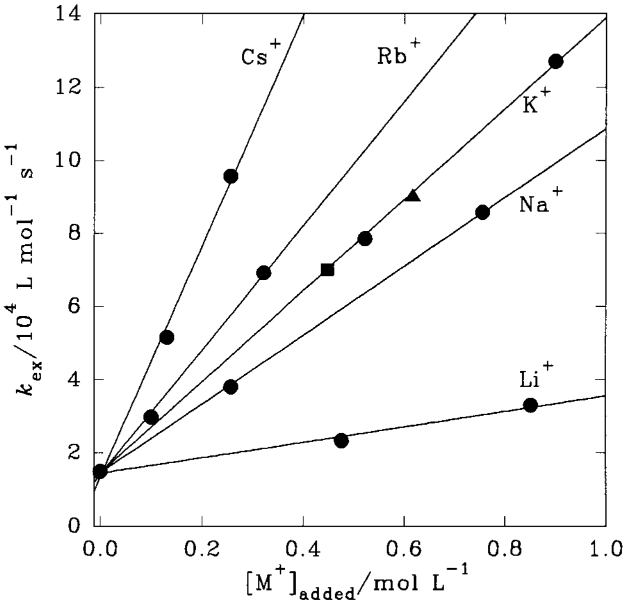

Figure 1. Effect of added salts of alkali metals M on k_{ex} for the homogeneous self-exchange of $K_4Os(CN)_6$ (0.0289 mol L^{-1}) and $K_3Os(CN)_6$ (0.00311 mol L^{-1}) in 68% H_2O/32% D_2O in the presence of K_3IrCl_6 (0.00311 mol L^{-1}) at 25.0 °C: (●) MCl; (▲) KNO_3; (■) KSO_3CF_3.

Table 1. Effect of Added Alkali-Metal Chlorides MCl on $Os(CN)_6^{3-/4-}$ Exchange Rate Constants According to Eq 2[a]

M	$k_{ex}{}^0/10^4$ L mol^{-1} s^{-1}	$k_M/10^4$ L^2 mol^{-2} s^{-1}
Li	1.44 ± 0.13	2.1 ± 0.2
Na	1.45 ± 0.06	9.4 ± 0.2
K	1.45 ± 0.19	12.6 ± 0.2
Rb	1.40 ± 0.13	17.0 ± 0.7
Cs	1.34 ± 0.34	31.5 ± 2.1

[a] 25.0 °C; $[K^+]_{counterion} = 0.134$ mol L^{-1} in all cases; solvent 68% H_2O/32% D_2O.

Relatively high concentrations of ^{13}C-enriched hexacyanoosmates were necessary for the high-pressure experiments because of the relative inefficiency and large natural ^{13}C line width of the pressurizable NMR probe. Line broadenings of 100 Hz at 0.1 MPa, decreasing to 24 Hz at 200 MPa, were obtained with $[K_4Os(CN)_6] = 0.189$ mol L^{-1} and $[K_3Os(CN)_6] = [K_3IrCl_6] = 0.0101$ mol L^{-1} in H_2O at 25.0 °C, and rate constants k_{ex} were calculated from eq 1. Values of k_{ex} (Fig. S3)[44] were accurately reproducible over the upward and downward legs of the pressure cycle, and ln k_{ex} was a linear function of pressure within the experimental uncertainty. Thus, $\Delta V_{ex}^{\ddagger} = -RT(\partial \ln k_{ex}/\partial P)_T = +18.5 \pm 0.8$ cm^3 mol^{-1} was effectively constant over the range 0−200 MPa, and $k_{ex}{}^{P=0}$ (the zero-pressure value of k_{ex}) was (3.33 ± 0.13) × 10^4 L mol^{-1} s^{-1}. A similar set of measurements was made in 1.0 mol L^{-1} KCl (Table S1),[44] giving $k_{ex}{}^{P=0} = 1.34 \times 10^5$ L mol^{-1} s^{-1} and $\Delta V_{ex}^{\ddagger} = +19.4 \pm 0.9$ cm^3 mol^{-1}. Thus, although k_{ex} is very sensitive to electrolyte effects, $\Delta V_{ex}^{\ddagger}$ was the same, within the experimental uncertainty, whether additional electrolytes were present. A value of $\Delta V_{ex}^{\ddagger} = +19.0 \pm 0.9$ cm^3 mol^{-1} was adopted for the $Os(CN)_6^{3-/4-}$ self-exchange reaction.

Electron-Transfer Kinetics of $Mo(CN)_8^{3-/4-}$ and $W(CN)_8^{3-/4-}$. Carbon-13 line broadening measurements at 25.0 °C on $K_4Mo(CN)_8/K_3Mo(CN)_8$ solutions in 0.87 mol L^{-1} KCl ($[K^+]_{total} = 0.91$ mol L^{-1}, Table S2)[44] and on $K_4W(CN)_8/K_3W(CN)_8$ solutions in 1.00 mol L^{-1} KCl ($[K^+]_{total} = 1.2$ mol L^{-1},

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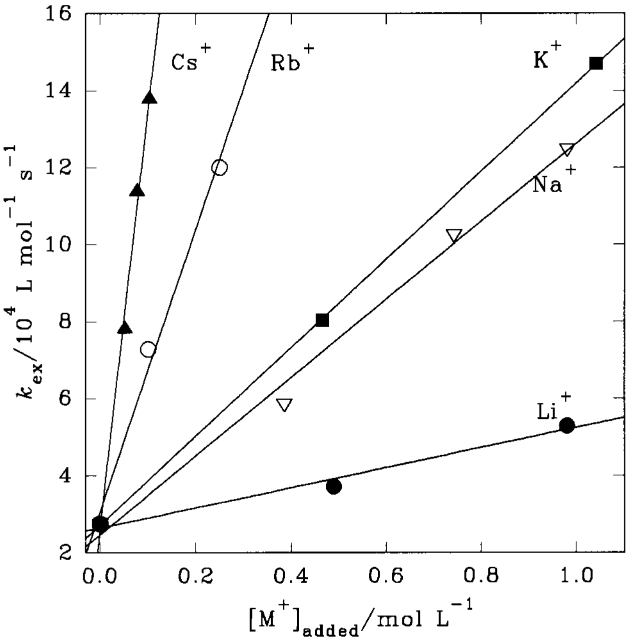

Figure 2. Effect of added alkali metal chlorides MCl on k_{ex} for the homogeneous self-exchange of $K_4Mo(CN)_8$ (0.0313 mol L^{-1}) and $K_3Mo(CN)_8$ (0.00211 mol L^{-1}) in 50% D_2O/H_2O at 25.0 °C.

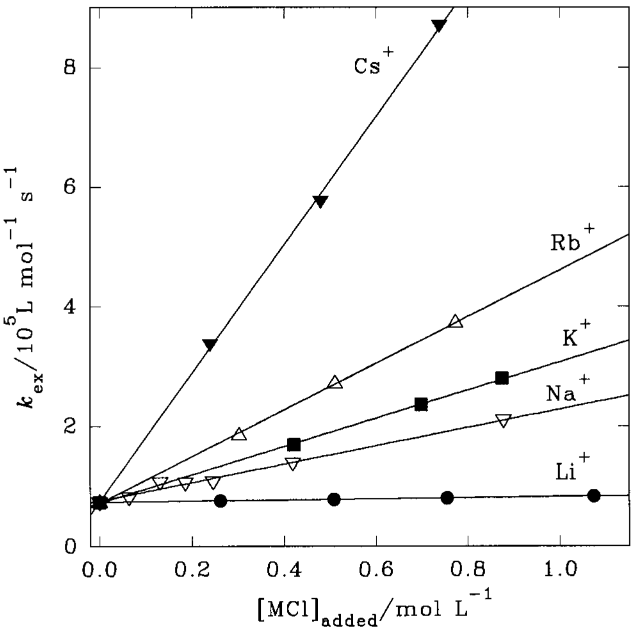

Figure 3. Effect of added alkali metal chlorides MCl on k_{ex} for the homogeneous self-exchange of $K_4W(CN)_8$ (0.0314 mol L^{-1}) and $K_3W(CN)_8$ (0.719 mmol L^{-1}) in D_2O at 25.0 °C.

Table 2. Effect of Added Electrolytes on k_{ex} for the $Mo(CN)_8^{3-/4-}$ Couple at 25 °C According to eq 2

counterion	added electrolyte	$k_{ex}^0/10^4$ L mol^{-1} s^{-1}	$k_M/10^4$ L^2 mol^{-2} s^{-1}
$K^{+\,a}$	LiCl	2.7 ± 0.2	2.6 ± 0.4
	NaCl	2.5 ± 0.4	10.2 ± 0.6
	KCl	2.7 ± 0.1	11.5 ± 0.1
	RbCl	3.1 ± 0.6	37 ± 4
	CsCl	2.6 ± 0.4	108 ± 6
$Me_4N^{+\,b}$	Me_4NCl	–	150 ± 12
$Et_4N^{+\,c}$	Et_4NCl	–	53 ± 3

[a] $[Mo^{IV}]$ = 0.0313 mol L^{-1}; $[Mo^{V}]$ = 0.00211 mol L^{-1}; 50% H_2O/50% D_2O; k_{ex}^0 represents the exchange rate constant (average (2.7 ± 0.2) × 10^4 L mol^{-1} s^{-1}) with the counterion K^+ as the only cation present. [b] $[Mo^{IV}]$ = 0.0394 mol L^{-1}; $[Mo^{V}]$ = 0.17 mmol L^{-1}; 20% H_2O/80% D_2O. [c] $[Mo^{IV}]$ = 0.0345 mol L^{-1}; $[Mo^{V}]$ = 0.622 mmol L^{-1}; 40% H_2O/60% D_2O.

Table 3. Effect of Added Electrolytes on k_{ex} for the $W(CN)_8^{3-/4-}$ Couple at 25 °C According to eq 2

counterion	added electrolyte	$k_{ex}^0/10^4$ L mol^{-1} s^{-1}	$k_M/10^4$ L^2 mol^{-2} s^{-1}
$K^{+\,a}$	LiCl	7.4 ± 0.1	0.89 ± 0.02
	NaCl	7.6 ± 0.4	15.2 ± 0.8
	KCl	7.2 ± 0.2	23.5 ± 0.4
	RbCl	7.2 ± 0.3	38.9 ± 0.6
	CsCl	7.4 ± 0.4	107 ± 2
$Me_4N^{+\,b}$	Me_4NCl	–	107 ± 9

[a] $[W^{IV}]$ = 0.0314 mol L^{-1}; $[W^{V}]$ = 0.719 mmol L^{-1}; D_2O solvent; k_{ex}^0 represents the exchange rate constant (average (7.4 ± 0.2) × 10^4 L mol^{-1} s^{-1}) with the counterion K^+ as the only cation present. [b] $[W^{IV}]$ = 0.0307 mol L^{-1}; $[W^{V}]$ = 1.04 μmol L^{-1}; 21% H_2O/79% D_2O.

Table S4)[44] showed that the pseudo-first-order rate constants k_{obsd} were accurately proportional to $[X(CN)_8^{3-}]$, giving k_{ex} = (1.46 ± 0.03) × 10^5 L mol^{-1} s^{-1} for X = Mo and (1.52 ± 0.02) × 10^5 L mol^{-1} s^{-1} for X = W at these concentrations of K^+. For X = Mo, k_{ex} varied only slightly over wide ranges in $[K_4Mo(CN)_8]$, in the absence of additional electrolytes, which, given that k_{ex} is sensitive to added K^+, implies that ion association buffers the concentration of free K^+ in the absence of added electrolyte. For the $K_4W(CN)_8/K_3W(CN)_8$ exchange in the absence of added electrolyte, k_{ex} for the does vary somewhat with $[K_4W(CN)_8]$ at the lowest concentrations (Table S5). Solvent hydrogen isotope effects on the electron-transfer rate of the aqueous $Mo(CN)_8^{3-/4-}$ couple are small (rates are ≤10% slower in D_2O than in H_2O; Table S3[44]), but for $W(CN)_8^{3-/4-}$ no significant hydrogen isotope effect was discernible. For both the Mo and W exchanges, the temperature dependence of the ^{13}C NMR line width in the absence of added electrolyte confirmed that electron transfer was occurring in the "slow exchange" region. Fits to the Eyring equation (Figures S4 and S7)[44] yielded $\Delta H_{ex}^{\ddagger}$ = 16.8 ± 1.3 kJ mol^{-1}, $\Delta S_{ex}^{\ddagger}$ = −104 ± 4 J K^{-1} mol^{-1}, and k_{ex}^{298} = 2.6 × 10^4 L mol^{-1} s^{-1} for $K_4Mo(CN)_8$ (0.0413 mol L^{-1}) with $K_3Mo(CN)_8$ (2.85 mmol L^{-1}) in D_2O, and $\Delta H_{ex}^{\ddagger}$ = 17.6 ± 1.1 kJ mol^{-1}, $\Delta S_{ex}^{\ddagger}$ = −88 ± 3 J K^{-1} mol^{-1}, and k_{ex}^{298} = 1.3 × 10^5 L mol^{-1} s^{-1} for $K_4W(CN)_8$ (0.20 mol L^{-1}) with $K_3W(CN)_8$ (0.25 mmol L^{-1}) in 50% H_2O/D_2O.

Added alkali metal chlorides accelerated the $K_3Mo(CN)_8/K_4Mo(CN)_8$ and $K_3W(CN)_8/K_4W(CN)_8$ exchanges linearly (Figures 2 and 3), in much the same way as for the $Os(CN)_6^{3-/4-}$ couple (Figure 1). The $Mo(CN)_8^{3-/4-}$ exchange with TMA^+ or TEA^+ as the sole cation and $W(CN)_8^{3-/4-}$ with TMA^+ were similarly linearly accelerated by addition of TMACl or TEACl. The data fitted eq 2, within the experimental uncertainty (which was smaller for the more tractable W system), giving the parameters of Tables 2 and 3. The relatively slight effect of added LiCl on the $W(CN)_8^{3-/4-}$ exchange is noteworthy, and the ^{13}C line width was therefore measured for a solution of $Li_4W(CN)_8$ (0.348 mol L^{-1}) in D_2O at 25 °C with and without $Li_3W(CN)_8$ (2.81 mmol L^{-1}; no other electrolytes present), giving k_{ex} = 4.5 × 10^4 L mol^{-1} s^{-1}. This is about 30% of the value of k_{ex} expected if K^+ had been the only cation present, for roughly comparable concentrations. On the other hand, the variation in k_{ex} with the identity and stoichiometric concentration of the counterion in the absence of added electrolyte (Table S5)[44] is much less than expected from the marked accelerations due to *added* cations (Figure 3). The implication is that the counterions are largely associated with the cyanometalate ions, but the extent of this association is not readily quantifiable.

A preliminary pressure experiment on the $Mo(CN)_8^{3-/4-}$ exchange in H_2O with $[K_4Mo(CN)_8] = 0.178$ mol L^{-1} and $[K_3Mo(CN)_8] = 0.00284$ mol L^{-1} showed that ln k_{ex} decreased linearly with increasing pressure, giving $\Delta V_{ex}^{\ddagger} = +14.7 \pm 1.5$ cm^3 mol^{-1}. A definitive study with $[K_4Mo(CN)_8] = 0.0785$ mol L^{-1}, $[K_3Mo(CN)_8] = 0.0485$ mol L^{-1} and no added electrolyte gave $\Delta V_{ex}^{\ddagger} = +14.7 \pm 0.6$ cm^3 mol^{-1} with $k_{ex}^0 = (3.01 \pm 0.07) \times 10^4$ L mol^{-1} s^{-1} (Figure S5).[44] In sharp contrast, when the only cation present was TEA^+, ln k_{ex} for the $Mo(CN)_8^{3-/4-}$ exchange in H_2O *increased* linearly with increasing pressure (Figure S6),[44] giving $\Delta V_{ex}^{\ddagger} = -8.2 \pm 0.6$ cm^3 mol^{-1} and $k_{ex}^{P=0} = (6.1 \pm 0.2) \times 10^4$ L mol^{-1} s^{-1} when $[(TEA)_4Mo(CN)_8] = 0.0688$ mol L^{-1} and $[(TEA)_3Mo(CN)_8] = 6.72$ mmol L^{-1}. Thus, not only the magnitude but also the *sign* of $\Delta V_{ex}^{\ddagger}$ is dependent on the identity of the cation present.

For the $W(CN)_8^{3-/4-}$ exchange in H_2O, a preliminary pressure study with K^+ as the counterion showed a linear decrease in ln k_{ex} with rising P, giving $\Delta V_{ex}^{\ddagger} = +21 \pm 2$ cm^3 mol^{-1}. Definitive measurements with $[K_4W(CN)_8] = 0.226$ mol L^{-1} and $[K_3W(CN)_8] = 0.0139$ mol L^{-1} (Figure S8)[44] gave $\Delta V_{ex}^{\ddagger} = +22.5 \pm 1.1$ cm^3 mol^{-1}. When CsCl (0.25 mol L^{-1}) was present in a solution of $K_4W(CN)_8$ (0.114 mol L^{-1}) and $K_3W(CN)_8$ (0.22 mmol L^{-1}) in H_2O, such that over 80% of the exchange rate was carried by the Cs^+-dependent path, the pressure-induced retardation was a little smaller but still striking (Table S6),[44] giving an apparent $\Delta V_{ex}^{\ddagger}$ of $+16 \pm 2$ cm^3 mol^{-1}. In contrast, the $W(CN)_8^{3-/4-}$ exchange was markedly *accelerated* by increasing pressure when the only cation present was TMA^+ (Figure S9),[44] giving $\Delta V_{ex}^{\ddagger} = -7.4 \pm 0.5$ cm^3 mol^{-1} for $[(TMA)_4W(CN)_8] = 0.156$ mol L^{-1} and $[(TMA)_3W(CN)_8] = 5.94$ μmol L^{-1} at 25.0 °C.

Discussion

The octacyanometalates considered in this study are inert toward thermal ligand substitution[50-52] on the time scales of the self-exchange reactions, so that the mechanisms of electron transfer are of the obligate outer-sphere type. For such reactions, if they are adiabatic, the simplest form of Marcus theory[53] gives

$$k_{ex} = Z \exp(-\Delta G^*/RT) \tag{3}$$

where

$$\Delta G^* = \Delta G_{IR}^* + \Delta G_{SR}^* + \Delta G_{COUL}^* + \Delta G_{BBC}^* \tag{4}$$

in which the frequency factor $Z \sim 1 \times 10^{11}$ L mol^{-1} s^{-1} and ΔG^* is the free energy of activation comprising contributions ΔG_{IR}^* from internal reorganization (usually attributed to metal–ligand bond length changes) of the reactants, ΔG_{SR}^* from solvent reorganization, ΔG_{COUL}^* from the Coulombic work of bringing the charged reactants together, and ΔG_{BBC}^* from the influence of ionic strength I according to the Brønsted–Bjerrum–Christiansen (BBC) equation:

$$\ln (k_{ex}/k_{ex}^{I=0}) = 2Az_1z_2I^{1/2}/(1 + BaI^{1/2}) \tag{5}$$

$$\Delta G_{BBC}^* = -2RTAz_1z_2I^{1/2}/(1 + BaI^{1/2}) \tag{6}$$

In eqs 5 and 6, z_1 and z_2 are the ionic charge numbers of the reactants (here, −3 and −4), A and B are the Debye–Hückel parameters, and a is the anion–cation closest-approach distance. For all three couples studied here, the change Δd_0 in the metal–carbon bond lengths d_0 accompanying oxidation or reduction is small. For $Mo(CN)_8^{4-}$ and $Mo(CN)_8^{3-}$, d_0 is 216[54] and 212 pm,[55] respectively, while the corresponding bond lengths for the W analogues are 217–218 and 214 pm,[56,57] and Macartney[13] estimates that Δd_0 is no more than 5 pm for the $Os(CN)_6^{3-/4-}$ couple. Consequently, the contribution of ΔG_{IR}^* in the couples studied here must be small, so that ΔG^* at infinite dilution and 298 K is dominated by ΔG_{SR}^* (~ 21 kJ mol^{-1}) and ΔG_{COUL}^* (~ 23 kJ mol^{-1}), and would be essentially the same for all three couples (cf. similar estimates by Campion et al.[8] for the $Fe(CN)_6^{3-/4-}$ exchange reaction). Thus, if ΔG_{IR}^* is neglected entirely, eqs 3–6 suggest a rate constant k_{ex} of about 2×10^3 L mol^{-1} s^{-1} at 298 K for all three couples at zero ionic strength and $k_{ex} \sim 10^5$–10^6 L mol^{-1} s^{-1} at practical values of I. At first sight, these predictions might seem to be consistent with our experimental results and to explain the observed accelerations (represented by k_M) induced by added electrolytes.

Quantitative consideration of the results, however, shows that such a simple explanation cannot be correct. First, the order in k_M values anticipated from the trend in a on the basis of the ionic radii of M^+ would be M = Cs < Rb < K < Na < Li, unless ill-defined *hydrated* cation radii are used (see below). Second, the surprisingly accurate linearity of the dependence of k_{ex} on $[M^+]$ seen in Figures 1–3 is inconsistent with eq 5, which predicts an exponential dependence of k_{ex} on a function of $\sqrt{I}$. Third, as explained below, the large, positive values of $\Delta V_{ex}^{\ddagger}$ for the self-exchange reactions in the presence of alkali metal cations cannot be understood on the basis of a simple two-sphere Marcus model. Fourth, although data on anion–cation association for the cyanometalates considered here are sparse,[58,59] there have been several quantitative studies of ion pairing for the analogous $Fe(CN)_6^{3-}$ [60,61] and $Fe(CN)_6^{4-}$ [58,62-65] anions, and it is clear that the formation of ion pairs and probably higher ion aggregates must be extensive at the high cyanometalate concentrations necessary for our experiments (particularly the high-pressure NMR studies).

Role of Ion Association. Cation–cyanometalate ion pair formation constants[58-65] are themselves quite strongly concentration-dependent, so it is virtually impossible to adjust measured k_{ex} values for the combined effects of ion pairing and BBC medium dependence, or even to know approximately what the concentrations of *free* M^+ were when k_{ex} was measured. It is therefore difficult to compare k_{ex} values obtained under different concentrations. Nevertheless, our rate constants are in satisfactory agreement with those of Macartney[13] and with the estimates of Campion et al.[6] insofar as comparison is possible.

Ion pair formation constants K_{IP} for the aqueous cyanometalates at 298 K generally increase down Group 1 from Li^+ to

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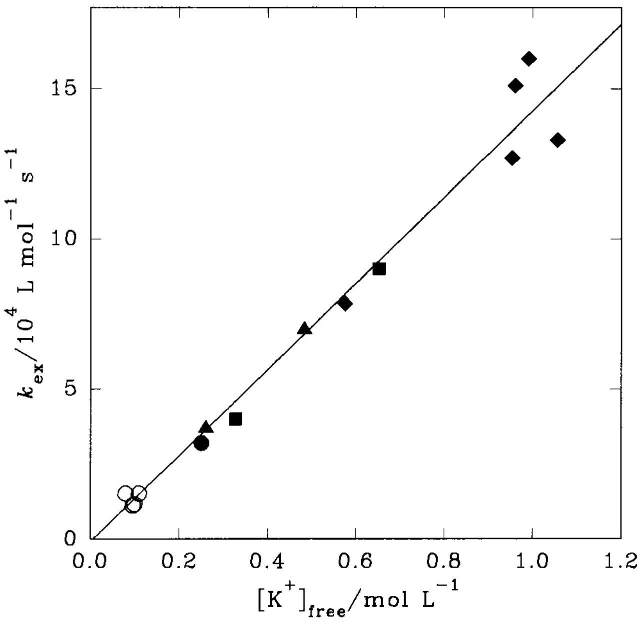

Figure 4. Correlation of k_{ex} for the hexacyanoosmate(II)/(III) exchange with free K^+ concentration calculated on the basis of $\{K_3,Os(CN)_6\}^-$ as the principal Os species in the more concentrated solutions (filled symbols) and $\{K,Os(CN)_6\}^{3-}$ as the main Os species in the most dilute solutions (open symbols): (○ and ●) no added K salts; (◆) KCl added; (▲) KSO_3CF_3 added; (■) KNO_3 added. Values of k_{ex} from D_2O solutions are normalized to H_2O as solvent.

Cs^+, and decrease with increasing electrolyte concentration. Nichugovskii and Shvedov[65] studied the effects of added MCl on the $Fe(CN)_6^{3-/4-}$ potential and obtained K_{IP} = 83, 83, 133, 244, and 395 L mol^{-1} for pairing of $Fe(CN)_6^{4-}$ (0.4 mmol L^{-1}) with M = Li, Na, K, Rb, and Cs, respectively, with salt concentrations of 0.05 mol L^{-1}; K_{IP} increased with increasing dilution. Rutkovskii and Mironov[61] found $K_{IP} \sim 0.5$, 2.0, and 3.3 L mol^{-1} for $Fe(CN)_6^{3-}$ with $M^+ = Na^+, K^+$, and Cs^+, respectively, using $LiNO_3$ to maintain ionic strength constant at 3.0 mol L^{-1}. Lemire and Lister[59] used molar conductances to obtain K_{IP} = 12, 23, 37, and 51 L mol^{-1} at infinite dilution for the pairing of $W(CN)_8^{3-}$ with M^+ where M = Na, K, Rb, and Cs, respectively. It should be noted that tetraalkylammonium ions (R_4N^+) engage in ion pairing with cyanometalates to about the same extent as, say, K^+.[58,60]

Ion pairing of the highly charged anions with the available M^+ can therefore be expected to be close to saturated in the solutions used in the present study. The ion association studies in the literature involved low concentrations of the cyanometalates, and further association to form triple or quadruple ion clusters was generally not considered. In the present work, however, the dominant species in the more concentrated solutions (i.e., those with high concentrations of the cyanometalate salts, as in the pressure studies, or with added M^+) may well have been the higher aggregates such as $\{M_3,Os(CN)_6\}^-$, although association probably did not extend beyond pairing in the most dilute solutions. A particularly troubling case was the $K_3Os(CN)_6/K_4Os(CN)_6$ high pressure study without added KCl, for which the stoichiometric $[K^+]$ was 0.82 mol L^{-1} but $k_{ex}^{P=0}$ suggested a free K^+ concentration of around 0.2 mol L^{-1}. Figure 4 shows an attempt to bring all k_{ex} values for the $K_3Os(CN)_6/K_4Os(CN)_6$ exchange, with or without added K^+ salts, together on a common footing by assuming the dominant Os species to be $\{M_3,Os(CN)_6\}^-$ in all cases except very dilute solutions without added electrolyte (for which $\{M,Os(CN)_6\}^{3-}$ was taken to be dominant), and correcting the concentration of *free* K^+ ions accordingly. Figure 4 is clearly linear with zero intercept, implying that there is only one significant electron-transfer pathway and that it is mediated by the free K^+.

Table 4. Volumes of Activation for Self-Exchange of Aqueous Cyanometalate Couples at 25.0 °C[a]

couple	counterion	$\Delta V_{ex}^{\ddagger}$/cm^3 mol^{-1}
$Fe(CN)_6^{3-/4-}$	K^+	+22 ± 2 [b]
$Os(CN)_6^{3-/4-}$	K^+	+18.5 ± 0.8
	K^+ [c]	+19.4 ± 0.9
$Mo(CN)_8^{3-/4-}$	K^+	+14.7 ± 0.6
	$(C_2H_5)_4N^+$	−8.2 ± 0.6
$W(CN)_8^{3-/4-}$	K^+	+22.5 ± 1.1
	K^+ [d]	+16 ± 2
	$(CH_3)_4N^+$	−7.4 ± 0.5

[a] See text for details of solution composition. [b] Reference 14. [c] 1.0 mol L^{-1} KCl present. [d] 0.25 mol L^{-1} CsCl present (>80% of reaction carried by Cs^+-mediated pathway).

The parameters k_M of eq 2 can therefore be regarded as rate constants for an M^+-catalyzed pathway over a range of I in which the dependences of the activity coefficients of the reactants and the transition state on I effectively cancel. This is reasonable, since (for example) the mean activity coefficients of aqueous NaCl and KCl vary only slightly with I for $I \sim 1$ mol L^{-1}. The slope of Figure 4 corresponds to a rate constant $k_M' = (1.44 \pm 0.06) \times 10^5$ L^2 mol^{-2} s^{-1}, about 14% higher than k_M for K^+ in Table 1 in which there is no allowance for ion association. Thus, the k_M values of Table 1 are not strongly affected by the neglect of ion pairing, and are at least empirically useful.

Figures 1 and 4 show that the effects of added KNO_3 and KSO_3CF_3 were the same as that of KCl, so confirming that the catalysis of electron transfer is specifically a property of the cation. For the $Fe(CN)_6^{3-/4-}$ self-exchange reaction, Campion et al.[8] could find no evidence that cations (alkali metal, quaternary ammonium and arsonium, and cobalticenium ions) participate in the actual electron-transfer step, and interpreted their results in terms of enhanced reactivity of ion pairs through reduction of Coulombic repulsions. Interestingly, as noted above, both k_M and K_{IP} for cyanometalates in water increase in the sequence $Li^+ \sim Na^+ < K^+ < Rb^+ < Cs^+ \approx R_4N^+$, but the ranges in K_{IP} are much smaller than the corresponding spread in k_M, so that k_M must reflect more than a mere propensity of M^+ for ion association. An indication of an electronic role for alkali metal ions in electron-transfer comes from studies by Khoshtariya and co-workers,[66-68] who have shown that association of aqueous $Fe(CN)_6^{3-}$ with $Fe(CN)_6^{4-}$ in the presence of K^+ is characterized by an absorption band in the near-infrared and have interpreted this as a direct observation of a "reactive associate" for electron transfer.[67] The spectroscopic feature, however, disappears when Me_4N^+ is the only cation present.[66] In fact, quaternary ammonium ions give some of the highest k_M values, similar to those for the heavier alkali metal ions (Tables 2 and 3; cf. the $Fe(CN)_6^{3-/4-}$ self-exchange reaction[8]), so the kinetic implications of the spectroscopic observations are not immediately apparent.

Volumes of Activation. The volumes of activation $\Delta V_{ex}^{\ddagger}$ for self-exchange in the cyanometalate couples with various counterions are collected in Table 4. Each of these $\Delta V_{ex}^{\ddagger}$ values has been independently verified, within the experimental uncertainty,

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by high-pressure electrode reaction kinetics through the "fifty percent rule".[22,23,69]

Theoretical calculations of $\Delta V_{ex}^{\ddagger}$ were carried out on the basis of a two-sphere model derived from Marcus theory, as described elsewhere.[20,21] With the cyanometalate ion radii assumed to be ~450 pm, $\Delta V_{ex}^{\ddagger}$ was calculated to be -6 ± 2 cm^3 mol^{-1}; simulations of the electrostatic effect of ion pairing on $\Delta V_{ex}^{\ddagger}$ did not change this result significantly, partly because the pressure dependence of BBC medium effects effectively cancels that of the Coulombic work terms in the experimental range of ionic strength.[70] In any event, whatever assumptions are made, the $\Delta V_{ex}^{\ddagger}$ values predicted for aqueous systems invariably turn out to be *negative*. A striking feature of Table 4, however, is that the experimental $\Delta V_{ex}^{\ddagger}$ is always *strongly positive* when the cation is an alkali metal, and essentially the same $\Delta V_{ex}^{\ddagger}$ is obtained whether swamping concentrations of salts of the same cation are added. This vindicates our previous finding for the $Fe(CN)_6^{3-/4-}/K^+$ system,[11] and adds emphasis to the foregoing observation that a pathway mediated by a cation carries essentially the whole self-exchange reaction rate, so that a simple two-sphere Marcus-type model of the outer-sphere electron transfer process is inappropriate. Furthermore, there is a dramatic difference between the strongly positive $\Delta V_{ex}^{\ddagger}$ for the exchanges mediated by alkali metal ions and the moderately *negative* $\Delta V_{ex}^{\ddagger}$ values for reactions in which the cation is a quaternary ammonium ion.

Reaction Mechanism. Since pressure affects intermolecular processes much more than internal molecular properties, volumes of activation are particularly sensitive to solvational changes,[70] and we therefore reiterate our previous suggestion[4] that the positive $\Delta V_{ex}^{\ddagger}$ values associated with alkali metal ion catalysis of anion−anion electron-transfer reflect removal of some coordinated water molecules from M^+(aq) in the activation process. Presumably, this deaquation could promote electron transfer by facilitating close contact of the reactant anions with a bridging M^+ ion. On the other hand, the tetraalkylammonium ions carry no coordinated water molecules, and $\Delta V_{ex}^{\ddagger}$ is on the order of that predicted. The difference in $\Delta V_{ex}^{\ddagger}$ between K^+ and R_4N^+ is 23−30 cm^3 mol^{-1}. It can be predicted[71] that complete removal of one coordinated water molecule from K^+(aq) should be accompanied by a volume change of about +13 cm^3 mol^{-1}, which suggests displacement of two water molecules from opposite sides of the K^+(aq) leaving an effective short bridge through K^+ for electron transfer between the reacting anions.

The partial-deaquation mechanism explains the catalytic efficacy sequence for M^+ ($M = Li < Na < K < Rb < Cs$), since this is the sequence of the enthalpies of hydration of M^+ (−515, −405, −321, −296, and −263 kJ mol^{-1}, respectively);[72] thus, Cs^+(aq) is the most readily deaquated and is the best catalyst of all the alkali metal ions, while Li^+ is difficult to deaquate and consequently shows very little catalytic power (Figures 1−3). Lemire and Lister[59] note that the ion pair formation constant sequence $M = Na < K < Rb < Cs$ for $W(CN)_8^{3-}$ could similarly be attributed to better anion−cation contact through partial dehydration of M^+. They also note, however, that infrared spectroscopic evidence[73] favors a "solvent separated" ion pair in the case of $\{K,Fe(CN)_6\}^{2-}$, so that extensive dehydration accompanying ion pairing would seem to be ruled out. A more likely explanation of the trend in K_{IP} is that ion pairing involves contact between essentially *fully hydrated* ions, and the strength of the pairing interaction therefore rises progressively from Li^+ to Cs^+ as the *hydrated* radii of M^+ *decrease*. Such a decrease in hydrated radii on descending Group 1 can been inferred from estimated Debye−Hückel ion contact distances[74] (which could, however, reflect partial dehydration of M^+) or from Stokes radii for M^+(aq) calculated from ion mobilities[75] (which do not). In other words, the partial deaquation proposed here as a prerequisite for M^+ catalysis of anion−anion electron transfer is probably not relevant to ion association as such.

As noted in the Introduction, cation−cation electron-transfer reactions are much less sensitive to counterion effects than are anion−anion redox processes. Significant anion effects on some cation−cation reactions have been noted, however, and may be explained as above. Thus, Clark and Hoffman[18,19] found that the rate constants for oxidative quenching of $^*Ru(bpy)_3^{2+}$ by the dipositive methyl viologen cation correlated with the free energy of hydration of the anion present—that is, rates were highest with the anions that held the water of hydration least firmly. The reason for the greater influence of cations on anion−anion electron-transfer rates may well be very simple: the particle being transferred is a *negatively* charged electron, so that provision of a bridge with *positive* charge will create a more electrostatically favorable route (lower barrier height) for electron tunneling between the reactants than would an anionic bridge for cation−cation exchange reactions.

Finally, it should be noted that strong cation catalysis very similar to that described here for self-exchange reactions has been reported, not only for asymmetric anion−anion reactions such as that of $Fe(CN)_6^{4-}$ with $IrCl_6^{2-}$ [3] or of $Mo(CN)_8^{4-}$ with $S_2O_8^{2-}$,[7,14] but also for reactions of anions with *neutral* molecules, such as the reduction of $Fe(CN)_6^{3-}$ by L-ascorbic acid in which the rate constant increases in the order $Li^+ < Na^+ < K^+ < Rb^+$ with linear dependence on the cation concentration.[76] Thus, the function of the cations in promoting anion−anion electron transfer is more a matter of facilitating electron tunneling than of assisting the approach of reactants of like charge.

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Supporting Information Available: Details of construction of the high-pressure NMR probehead; Figures S3−S9 and Tables S1−S6 as specified above (17 pages). Ordering information is given on any current masthead page.

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