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Kinetics of Electron-Transfer Reactions Involving the $Ru(CN)_6^{4-/3-}$ Couple in Aqueous Media

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The kinetics and mechanisms of electron-transfer reactions involving the $Ru(CN)_6^{4-}$ and $Ru(CN)_6^{3-}$ ions in aqueous media have been investigated. The electron-self-exchange rate constant has been directly measured for the $Ru(CN)_6^{4-/3-}$ couple from ^{13}C NMR line-broadening experiments using ^{13}C-enriched complexes. At 25 °C and an ionic strength of 0.10 M ($NaClO_4$), $k_{11} = (8.3 \pm 0.4) \times 10^3$ $M^{-1}\ s^{-1}$ with $\Delta H^* = 40 \pm 5$ kJ mol^{-1} and $\Delta S^* = -36 \pm 15$ J $K^{-1}\ mol^{-1}$. The kinetics of the oxidation of the $Ru(CN)_6^{4-}$ ion by $IrCl_6^{2-}$ and $CoW_{12}O_{40}^{5-}$ and the reduction of the $Ru(CN)_6^{3-}$ ion by NO_2^-, I^-, $Ni([9]aneN_3)_2^{2+}$, and $IrCl_6^{3-}$ have been studied by using stopped-flow techniques. The cross-reaction data have been treated according to the Marcus relations and yield a self-exchange constant of $10^{4.0\pm0.8}$ $M^{-1}\ s^{-1}$ (25.0 °C, $I = 0.10$ M) for the $Ru(CN)_6^{4-/3-}$ couple. The directly and indirectly determined electron-exchange rate constants agree well with the value of $(2 \pm 1) \times 10^4$ $M^{-1}\ s^{-1}$, predicted by semiclassical model calculations. The rate constants are compared with the analogous values for a number of small, low-spin d^6/d^5 iron and ruthenium complex couples and are discussed in terms of the relative contributions of the inner- and solvent-sphere reorganization barriers to electron exchange.

Introduction

In contrast to the considerable attention devoted to kinetic data concerning the electron-exchange and electron-transfer reactions of the $Fe(CN)_6^{4-/3-}$ couple, relatively little attention has been paid to the corresponding reactions of the $Ru(CN)_6^{4-/3-}$ and $Os(CN)_6^{4-/3-}$ couples.[1] The higher redox potential ($E° = 0.92$ V vs NHE) and the instability and complex chemistry of the $Ru(CN)_6^{3-}$ ion in aqueous solution have undoubtedly contributed to its lesser development.[2,3] The $Ru(CN)_6^{4-}$ ion has been used recently as a reductant[4] and a reductive quencher[5-7] in several thermal and photochemical electron-transfer reactions. Intervalence and outer-sphere charge-transfer bands have been reported for several species of the types $(NH_3)_5RuLRu(CN)_5^{n-}$ (L = CN^- or a bridging N-donor) and $[Ru(CN)_6^{4-},(NH_3)_5RuL^{3+}]$ (L = a nitrogen heterocycle), respectively.[8-10] The $Ru(CN)_6^{3-}$ ion, generated by laser photoionization, has recently been employed, along with the $Fe(CN)_6^{3-}$ and $Os(CN)_6^{3-}$ ions, in a kinetic study of the oxidation of ferrocytochrome *c*.[11] The differences in reactivity of the iron, osmium, and ruthenium hexacyanides have largely been attributed to their relative reduction potentials, with the electron-self-exchange rate constants for the three couples taken to be very similar.

The reaction chemistry of the $Ru(CN)_6^{3-}$ ion in aqueous solution is rather complex, and its stability depends upon the pH of the solution and the concentration of $Ru(CN)_6^{4-}$ present. Crean and Schug[3] have reported that the $Ru(CN)_6^{3-}$ ion is relatively stable at neutral pH. Studies by Ismail et al.[5] indicate that in the presence of an excess of $Ru(CN)_6^{4-}$ a mixed-valence cyano-bridged dimer, $[(CN)_5Ru^{II}(CN)Ru^{III}(CN)_5]^{6-}$, is formed with a rate constant of 1×10^4 $M^{-1}\ s^{-1}$. Estimates of 2×10^2[4] and 1.2×10^4 $M^{-1}\ s^{-1}$[12] for the electron-self-exchange rate constant for the $Ru(CN)_6^{4-/3-}$ couple have been made from the application of the Marcus relationship to the rate constants for the reductions of MnO_4^- and $^*Ru(bpy)_3^{2+}$,[7] respectively, by the $Ru(CN)_6^{4-}$ ion. These values are similar in magnitude to the directly determined rate constant for the $Fe(CN)_6^{4-/3-}$ couple.[13-15] In the course of our investigations on the ligand-substitution[16a] and electron-transfer[16b] reactions of cyanoruthenate complexes in aqueous media, studies on the electron-transfer reactions of the $Ru(CN)_6^{4-/3-}$ couple were undertaken to improve upon the limited and conflicting data concerning this system.

In this paper we report the results of kinetic and electrochemical investigations of electron-transfer reactions involving the $Ru(CN)_6^{4-/3-}$ couple in aqueous solution. The self-exchange rate constant of the couple has been measured directly in aqueous solution from ^{13}C NMR line-broadening experiments, employing ^{13}CN labeled $Ru(CN)_6^{4-/3-}$ ions. The kinetics and mechanisms of a number of cross-reactions of the $Ru(CN)_6^{4-/3-}$ couple, employing well-characterized metal complexes and small inorganic anion couples, have been investigated. The Marcus relationship[17,18] has been applied to the outer-sphere cross-reaction data from this study and others[4,16b] to provide an estimate of the self-exchange rate constant for the $Ru(CN)_6^{4-/3-}$ couple. The directly and indirectly determined exchange rate constants are compared with a value predicted from a semiclassical electron-transfer model and with values for other small low-spin d^6/d^5 ruthenium and iron couples. The relative magnitudes of the electron-exchange rate constants are discussed in terms of the inner-sphere and solvent reorganization barriers.

Experimental Section

Materials. Potassium hexacyanoruthenate(II), $K_4Ru(CN)_6{\cdot}3H_2O$, was used as received (Alfa) or prepared by reported methods[10,19] using $RuCl_3{\cdot}xH_2O$ or Ru metal (Aldrich). The ^{13}CN-labeled $K_4Ru(CN)_6{\cdot}3H_2O$ complex (10–20% labeled) was prepared by the latter procedure using $K^{13}CN$ (Aldrich). Aqueous solutions ($<10^{-3}$ M) of the $Ru(CN)_6^{3-}$ ion were prepared by the method of Crean and Schug[3] using ceric sulfate as an oxidant followed by the exchange of Ce^{3+} and H^+ by Li^+, Na^+, or K^+ on a cation-exchange resin (BDH Amberlite IR-120). Concentrations of the Ru(III) solutions were determined spectrophotometrically [λ_{max}

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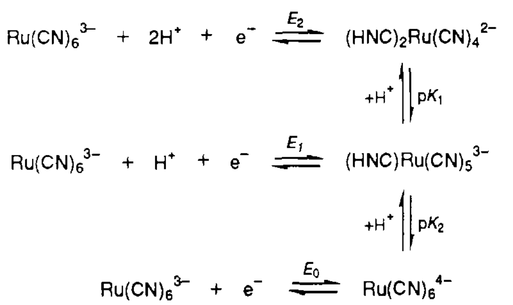
Scheme I



(ϵ, M^{-1} cm^{-1}): 298 (2150), 328 (2370), 356 (1570), and 460 nm (1020)],[3] and the solutions were used promptly after preparation. Iridium(IV) hexachloride, $Na_2IrCl_6 \cdot 6H_2O$ (Strem) and $Na_3IrCl_6 \cdot xH_2O$ (Johnson-Matthey) were used as received. The cobalt(II) heteropolytungstate complex, $K_6[CoW_{12}O_{40}] \cdot xH_2O$, was prepared by the method of Baker and McCutcheon.[21] Oxidation to the $CoW_{12}O_{40}^{5-}$ ion was accomplished in solution by using solid PbO_2. The $[Ni([9]aneN_3)_2](ClO_4)_2$ complex was prepared by the method of McAuley.[22] Sodium nitrite and sodium iodide (Fisher) were used as received.

Kinetic Measurements. The kinetic measurements were made by using a TDI Model IIA stopped-flow apparatus (Cantech Scientific) and data acquisition system interfaced to a Zenith ZF-151 PC. Pseudo-first-order conditions of excess reductant were employed, and plots of ln $(A_\infty - A_t)$ against time were linear for at least 3 half-lives. The first-order rate constants (given in the supplementary material) were determined from the average of four to six replicate experiments. The reaction temperature was maintained to within 0.1 °C over the range 5–35 °C by means of an external water bath. The pH's of the reaction solutions were controlled by using acetate and phosphate buffers or the appropriate amounts of $HClO_4$, while the ionic strengths were maintained by the addition of approporiate amounts of $LiClO_4$, $NaClO_4$, or $KClO_4$.

Physical Measurements. UV–visible spectra were recorded by using a Hewlett-Packard 8452A diode-array spectrophotometer. The cyclic voltammetric measurements were carried out in aqueous solution with a BAS CV-1B cyclic voltammograph (Bioanalytical Systems) attached to a Houston Instruments 100 X-Y recorder. The working (Pt button) and auxiliary (Pt wire) electrodes in the sample solution were separated from the reference electrode (Ag/AgCl) by a glass frit. The ^{13}C NMR spectra were recorded on a Bruker AM-400 instrument operating at 100.6 MHz. The aqueous samples were run in 10-mm tubes with a 5-mm tube of D_2O serving as an internal lock, and CH_3OH was employed as an external reference. The temperature of the probe was maintained to within 0.5 °C over the range 12–35 °C.

Results

Reduction Potential of the $Ru(CN)_6^{3-/4-}$ Couple. The electrochemical reduction potential of the $Ru(CN)_6^{3-/4-}$ couple has been variously reported to be 0.86 V (I = 0.2 M, KCl),[2] 0.902 V (I = 0.1 M, NaCl),[8] 0.94 V (I = 0.1 M, $NaClO_4$),[10] 0.947 V (I = 0.1 M, KCl),[23] and 0.98 V (I = 1.0 M, $NaClO_4$).[24] Cyclic voltammetry measurements on the $Ru(CN)_6^{3-/4-}$ reduction potential in this study were carried out in aqueous media as a function of pH (in the pH range 1–7, I = 0.10 M, $NaClO_4$). The observed increase in $E_{1/2}$ with increasing acidity (Figure 1) is attributed to three redox couples, involving the proton equilibria of the $Ru(CN)_6^{4-}$ ion, as shown in Scheme I. For a reversible electrode reaction involving protons

$$\text{oxidant} + mH^+ + ne^- \rightleftharpoons \text{reductant}$$

the Nernst equation (assuming similar diffusion coefficients of the reductant and oxidant and rapid diffusion of protons) may be written as

$$E_m = E_{1/2} + 0.059(m/n)\text{pH} \quad (1)$$

where E_m and $E_{1/2}$ are the formal electrode and half-wave potentials, respectively.[25] The dependence of $E_{1/2}$ on the pH for the Ru(III)/Ru(II) system is consistent with two-proton ($\Delta E_{1/2}/\Delta\text{pH}$ = 118 mV), one-proton ($\Delta E_{1/2}/\Delta\text{pH}$ = 59 mV), and zero-proton couples. From the cyclic voltammetry data (I = 0.10 M, $NaClO_4$), the pK_1 and pK_2 values are estimated to be 1.6 ± 0.2 and 3.2 ± 0.2, respectively, similar to those reported for the iron(II) complex at the same ionic strength (pK_1 = 1.22 ± 0.15 and pK_2 = 3.17 ± 0.03).[26] Values of pK_1 = 2.46 and pK_2 = 2.53 were calculated from a pH dependence of the rate of oxidation of $Ru(CN)_6^{4-}$ by MnO_4^- at an ionic strength of 1.02 M.[4] A much larger difference between the two pK values would be expected on statistical (ΔpK = 0.48) and electrostatic grounds. The values of E_2, E_1, and E_0 are calculated to be 1.19 ± 0.02 V, 1.10 ± 0.01 V, and 0.92 ± 0.01 V (vs. NHE), respectively. Shepherd[8] has reported similar values [1.15 V, 1.07 V, and 0.902 V, respectively, measured by differential-pulse polarography at 22 °C, I = 0.10 M (NaCl)] and gave a value of 1.27 V for the couple involving the $(HCN)_3Ru(CN)_3^-$ ion. The increase in potential upon protonation of the reduced species may be attributed to the withdrawal of electron density from the metal center. A similar increase in the ruthenicyanide potential has also been observed in the cyanide-bridged dimer couple *trans*-$[(CN)_5Ru(CN)Ru(NH_3)_4py]^{0/-}$ (py = pyridine), where a value of $E_{1/2}$ = 1.17 V was measured.[10]

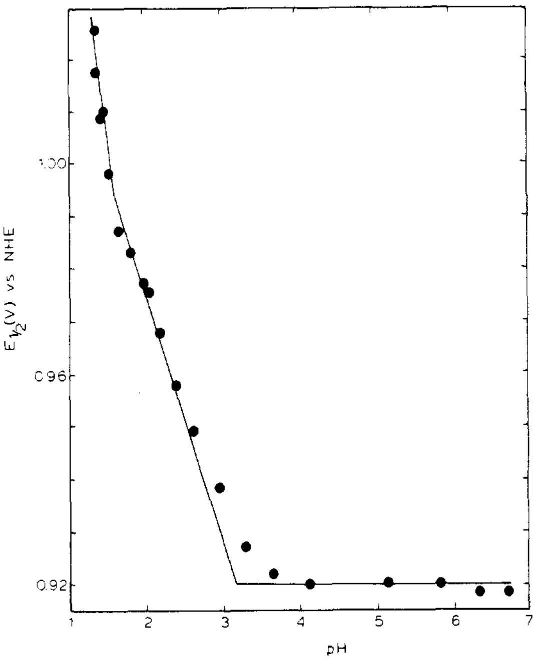


Figure 1. Dependence of $E_{1/2}$ (vs NHE) on pH for the reduction of $Ru(CN)_6^{3-}$ in aqueous solution at 25 °C and I = 0.10 M ($NaClO_4$).

Electron-Exchange Kinetic Studies. A direct measurement of the $Ru(CN)_6^{3-/4-}$ electron-self-exchange rate constant was accomplished from ^{13}CN NMR line-broadening experiments.

$$Ru(CN)_6^{4-} + {}^*Ru(CN)_6^{3-} \overset{k_{11}}{\rightleftharpoons} Ru(CN)_6^{3-} + {}^*Ru(CN)_6^{4-} \quad (2)$$

Samples of $K_4Ru(CN)_6 \cdot 3H_2O$ were prepared with 10–20% ^{13}CN enrichment to enhance the ^{13}CN signal at 162 ppm.[20] The diamagnetic signal has a line width (full width at half-maximum) of 3.0 Hz (W_D), which is broadened upon the addition of aliquots of the paramagnetic $Ru(CN)_6^{3-}$ ion. The lack of a change in the ^{13}C chemical shift upon broadening indicates that the exchange process is in the slow-exchange domain, $k_{11}[Ru(CN)_6^{3-}] \ll 2\pi(\delta\nu)$, and the exchange rate constant may be determined from the relationship between the extent of line broadening ($W_{DP} - W_D$) and the concentration of the paramagnetic species:[27]

$$\pi(W_{DP} - W_D) = k_{11}[Ru(CN)_6^{3-}] \quad (3)$$

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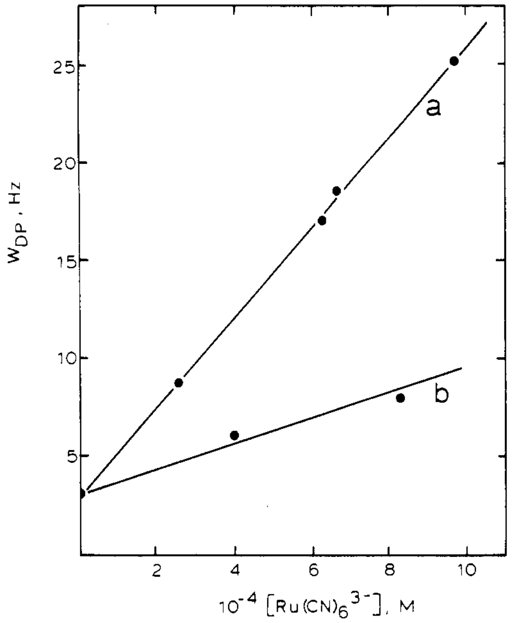

Figure 2. Dependence of the $Ru(CN)_6^{4-}$ ^{13}C NMR line width on the concentration of $Ru(CN)_6^{3-}$ in aqueous solution at (a) I = 0.50 M (KCl, 22 °C) and (b) I = 0.10 M ($KClO_4$, 25 °C).

Table I. Electron-Exchange Rate and Activation Parameters for the $Ru(CN)_6^{3-/4-}$ Couple from ^{13}C NMR Line-Broadening Studies

T, °C[a]	I, M (M^+)[b]	$10^{-3}k_{11}$,[c] M^{-1} s^{-1}
12.0	0.10 (Na^+)	3.3 ± 0.2
18.0	0.10 (Na^+)	4.9 ± 0.3
25.0	0.10 (Na^+)	8.3 ± 0.5
32.0	0.10 (Na^+)	10.3 ± 0.6
	$\Delta H^\ddagger$ = 40 ± 5 kJ mol^{-1}; $\Delta S^\ddagger$ = −36 ± 15 J K^{-1} mol^{-1}	
25.0	0.10 (K^+)	21 ± 4
22.0	0.40 (K^+)[d]	50 ± 3
22.0	0.50 (K^+)[d]	71 ± 3

[a] ±0.5 °C. [b] Ionic strength maintained with $KClO_4$ or $NaClO_4$ unless otherwise indicated. [c] Calculated by using eq 4. [d] Ionic strength maintained with KCl.

The linear dependences of $W_{DP} - W_D$ on [$Ru(CN)_6^{3-}$] at ionic strengths of 0.10 M ($KClO_4$, 25 °C) and 0.50 M (KCl, 22 °C) are shown in Figure 2. The values of k_{11} determined by using eq 4 are presented in Table I. The values of k_{11} at I = 0.10 M ($NaClO_4$) were measured at four temperatures between 12 and 32 °C, and activation parameters of $\Delta H^\ddagger$ = 40 ± 5 kJ mol^{-1} and $\Delta S^\ddagger$ = −36 ± 15 J K^{-1} mol^{-1} were determined. The ^{13}C NMR spectra of the $Ru(CN)_6^{3-/4-}$ mixtures were recorded immediately after preparation of the $Ru(CN)_6^{3-}$ solution. After 30 min the visible spectra of the mixtures began to display the appearance of a peak with a maximum at >900 nm, indicating the formation of the postulated cyano-bridged dimer, $(NC)_5Ru(CN)Ru(CN)_5^{6-}$ (λ_{max} = 1094 nm),[5] as observed by Schug and Crean[3] and Ismail et al.[5] In the latter report a rapid formation of this species ($k \approx 1 \times 10^4$ M^{-1} s^{-1}) was observed following the reductive quenching of $^*Ru(bpy)_3^{2+}$ in the presence of an excess of $Ru(CN)_6^{4-}$. No evidence for the formation of the bridged dimer on this time scale was observed on mixing $Ru(CN)_6^{3-}$ with an excess of $Ru(CN)_6^{4-}$ in our study.

Electron-Transfer Kinetic Studies. The kinetics of electron-transfer reactions of the $Ru(CN)_6^{3-}$ and $Ru(CN)_6^{4-}$ ions with a series of cross-reactants have been investigated in aqueous solution.

$$Ru(CN)_6^{3-} + Red \underset{}{\overset{k_{12}}{\rightleftharpoons}} Ru(CN)_6^{4-} + Ox \qquad (4)$$

The reactions were studied by following the disappearance of $Ru(CN)_6^{3-}$ for the forward reactions in eq 4 or the disappearance of the oxidant in the reverse reactions.

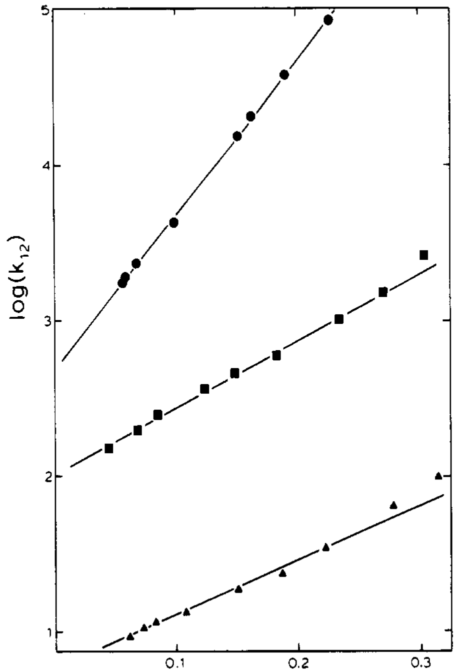

Figure 3. Dependences of log k_{12} on $I^{1/2}/(1 + \beta\sigma I^{1/2})$ for the oxidation of $Ru(CN)_6^{4-}$ by $IrCl_6^{2-}$ (●, σ = 9.0 Å) and the reductions of $Ru(CN)_6^{3-}$ by I^- (■, σ = 6.9 Å) and NO_2^- (▲, σ = 6.6 Å) at 25.0 °C, with the ionic strength maintained with $NaClO_4$.

Oxidations of I^- and NO_2^- by $Ru(CN)_6^{3-}$. The kinetics of the reduction of the $Ru(CN)_6^{3-}$ by the iodide ion ($E°(I^\bullet/I^-)$ = 1.33 V)[28a] were studied by using a pseudo-first-order excess of I^- at pH 6.5. The observed first-order rate constants for the rate-determining oxidation of I^- to $I^\bullet$ displayed a linear dependence on [I^-], and the second-order rate constants and activation parameters for the I^- oxidations are presented in Table II. The rate constants were observed to increase with an increase in ionic strength (0.0025–1.00 M ($NaClO_4$)), and the Debye–Hückel plot of log k_{12} against $I^{1/2}/(1 + \beta\sigma I^{1/2})$ in Figure 3, with β = 0.329 $M^{-1/2}$ $Å^{-1}$ and σ = 6.9 Å (from radii of 4.7 and 2.2 Å for $Ru(CN)_6^{3-}$ and I^-, respectively), yields a charge product of +4.1. At an ionic strength of 0.10 M, the cross-reaction rate constants are dependent on the nature of the cation in the $MClO_4$ electrolyte, with $k_H \gg k_K > k_{Na} \approx k_{Li}$ (Table II). A similar dependence of the rate constants on the nature of the alkali-metal cation was reported for the oxidation of I^- by $Fe(CN)_6^{3-}$.[29] Accelerations of the oxidation of I^- in acidic solution has been observed previously with $Fe(CN)_6^{3-}$ and Ni(III) tetraaza macrocycles.[30,31] The rate constants for the oxidation of I^- by $Ru(CN)_6^{3-}$ are similar to the parameters measured for the I^- oxidation by $IrCl_6^{2-}$ ($E°$ = 0.913 V[28b]): $k = 3.25 \times 10^2$ M^{-1} s^{-1} (I = 0.01 M ($NaClO_4$)), $\Delta H^\ddagger$ = 27.6 ± 0.8 kJ mol^{-1}, $\Delta S^\ddagger$ = −105 ± 8 J K^{-1} mol^{-1};[32] $k = 8.18 \times 10^2$ M^{-1} s^{-1} (I = 0.10 M ($NaClO_4$));[33] and $k = 1.38 \times 10^3$ M^{-1} s^{-1} (0.5 M H_2SO_4).[34]

The kinetics of the oxidation of the nitrite ion by $Ru(CN)_6^{3-}$ were investigated under conditions of pseudo-first-order excess NO_2^- concentrations (0.0025–0.040 M). In neutral (pH 6.8) aqueous solution ($pK_a(HNO_2)$ = 2.96),[35] linear dependences of k_{obs} on [NO_2^-], with small intercepts ((2–3) × 10^{-2} s^{-1}), were

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Table II. Rate and Activation Parameters for the Electron-Transfer Cross-Reactions Involving the $Ru(CN)_6^{4-/3-}$ Couple in Aqueous Solution

reductant	oxidant	pH	I, M (M^+)[a]	$10^{-3}k_{12}$,[b] $M^{-1}\ s^{-1}$	$\Delta H^{\ddagger}$, kJ mol^{-1}	$\Delta S^{\ddagger}$, J K^{-1} mol^{-1}
I^-	$Ru(CN)_6^{3-}$		0.10 (H^+)[c]	1.73 ± 0.20		
		6.5	0.10 (Li^+)	0.583 ± 0.016		
		6.5	0.10 (Na^+)	0.578 ± 0.005	9.2 ± 1.3	−163 ± 5
		6.5	0.10 (K^+)	0.829 ± 0.013		
NO_2^-	$Ru(CN)_6^{3-}$	1.0	0.10 (H^+)	0.0498 ± 0.0040[d]		
		1.31	0.10 (Na^+)	0.0395 ± 0.0003[d]		
		1.51	0.10 (Na^+)	0.0329 ± 0.0003[d]		
		2.03	0.10 (Na^+)	0.0251 ± 0.0004[d]		
		2.51	0.10 (Na^+)	0.0292 ± 0.0006[d]		
		2.84	0.10 (Na^+)	0.0278 ± 0.0004[d]		
		3.01	0.10 (Na^+)	0.0250 ± 0.0006[d]		
		6.8	0.10 (Na^+)	0.0236 ± 0.0009[d]	27.6 ± 1.5	−125 ± 5
$Ni([9]aneN_3)_2^{2+}$	$Ru(CN)_6^{3-}$	6.5	1.00 (Na^+)	220 ± 10		
$Ru(CN)_6^{4-}$	$CoW_{12}O_{40}^{5-}$	6.3	0.10 (Na^+)	3.53 ± 0.23	13.4 ± 1.3	−134 ± 5
$Ru(CN)_6^{4-}$	$IrCl_6^{2-}$	6.7	0.10 (Li^+)	20.3 ± 0.4		
		6.7	0.10 (Na^+)	20.6 ± 1.1		
		6.7	0.10 (K^+)	65.8 ± 2.3	19.2 ± 1.7	−88 ± 6
$IrCl_6^{3-}$	$Ru(CN)_6^{4-}$	6.7	0.10 (Li^+)	25.4 ± 1.9		

[a] Ionic strength maintained with $MClO_4$ as indicated (M^+). [b] At 25.0 °C. [c] $[H^+] = 0.09$ M. [d] Values of k_{12} over the pH range 1–3 are calculated from $k_{12} = k_{obs}[HNO_2]^2$ (Figure 4), while for pH 6.8 they are calculated from $k_{12} = k_{obs}/[NO_2^-]$.

observed. The kinetic behavior and a measured $Ru(CN)_6^{3-}$:NO_2^- stoichiometry of (1.95 ± 0.05):1 from spectrophotometric titrations suggest the mechanism

$$HNO_2 \overset{K_a}{\rightleftharpoons} H^+ + NO_2^- \qquad (5)$$

$$Ru(CN)_6^{3-} + NO_2^- \xrightarrow{k_{12}} Ru(CN)_6^{4-} + NO_2 \qquad (6)$$

$$2NO_2 + H_2O \xrightarrow{\text{fast}} HNO_2 + NO_3^- + H^+ \qquad (7)$$

The disproportionation reaction of NO_2 is a fast, thermodynamically favorable process, for which a rate constant of 1.2×10^7 $M^{-1}\ s^{-1}$ may be calculated from the equilibrium constant of 4.6×10^8 M for eq 7 and the rate constant for the reverse process, $k_{-7} = 2.7 \times 10^{-2}\ M^{-2}\ s^{-1}$.[35] The second-order rate constants for the reduction of $Ru(CN)_6^{3-}$ by NO_2^- are listed in Table II, along with the activation parameters determined at pH 6.8 and an ionic strength of 0.10 M. A plot of log k_{12} against $I^{1/2}/(1 + \beta\sigma I^{1/2})$ for this reaction ($\sigma = 6.6$ Å, for a radius of 1.9 Å for NO_2^-) in aqueous $NaClO_4$ media (Figure 3) yields a charge product of +3.4. Similar rate constants have been reported for the oxidation of NO_2^- by $IrCl_6^{2-}$ at 25.0 °C: $k = 19.6\ M^{-1}\ s^{-1}$ ($I = 0.10$ M);[32] $k = 26.9\ M^{-1}\ s^{-1}$ ($I = 1.0$ M).[36]

Previous studies of the electron-transfer reactions of the $IrCl_6^{2-/3-}$ ($E° = 0.913$ V)[28b] and $Fe(3,4,7,8\text{-}(CH_3)_4phen)_3^{3+/2+}$ ($E° = 0.84$ V)[35] couples in nitrous acid indicated fairly complex redox behavior in solution, as it is able to act both as an oxidant and as a reductant. In the present system a change in the order of the reaction with respect to both $[Ru(CN)_6^{3-}]$ and $[HNO_2]$ ($K_a(HNO_2) = 1.1 \times 10^{-3}$ M)[35] was observed in acidic solution (pH <3). The rate of disappearance of $Ru(CN)_6^{3-}$ becomes zero order in $[Ru(CN)_6^{3-}]$ and second order in $[HNO_2]$, with a slight dependence of the second-order rate constant (Table II) on acid concentration as illustrated in Figure 4. The second-order rate constant increases from 25.0 $M^{-1}\ s^{-1}$ at pH 3 to a value of 49.8 $M^{-1}\ s^{-1}$ at pH 1, which is very similar to the rate constant determined for the disproportionation of HNO_2 (42.7 $M^{-1}\ s^{-1}$).[35]

$$2HNO_2 \overset{k_d}{\rightleftharpoons} NO + NO_2 + H_2O \qquad (8)$$

The rate-determining disproportion process may be followed by the oxidation of NO by $Ru(CN)_6^{3-}$ to regenerate HNO_2.

$$Ru(CN)_6^{3-} + NO + H_2O \rightarrow Ru(CN)_6^{4-} + HNO_2 + H^+ \qquad (9)$$

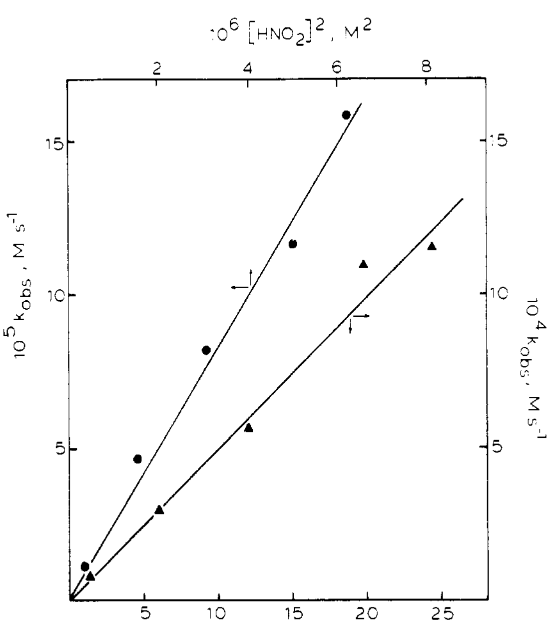

Figure 4. Dependences of the zero-order rate constants on $[HNO_2]$ for the reduction of $Ru(CN)_6^{3-}$ by HNO_2 at 25.0 °C, $I = 0.10$ M ($NaClO_4$), and pH 1.0 (▲) or 3.0 (●).

The reduction of $Fe(3,4,7,8\text{-}(CH_3)_4phen)_3^{3+}$ by NO ($E° = 0.875$ V for the HNO_2/NO couple) was found to be about 20 times faster than the reduction by NO_2^- ($E° = 1.04$ V for the NO_2/NO_2^- couple[28a]),[35] while, for the reduction of $IrCl_6^{2-}$, the NO pathway is about 5×10^4 times as fast as the reduction by NO_2^-.[36]

Reactions of $Ru(CN)_6^{4-/3-}$ with Metal Complexes. The kinetics of the reduction of the $Ru(CN)_6^{3-}$ ion by $Ni([9]aneN_3)_2^{2+}$ ($E° = 0.95$ V)[22] and the oxidation of $Ru(CN)_6^{4-}$ by $CoW_{12}O_{40}^{5-}$ ($E° = 1.00$ V)[37] were investigated under pseudo-first-order conditions of excess Ni(II) and Ru(II) concentrations, respectively. From the plot of k_{obs} against [Ni(II)] for the reduction of $Ru(CN)_6^{3-}$ by $Ni([9]aneN_3)_2^{2+}$, a second-order rate constant of $(2.2 \pm 0.1) \times 10^5\ M^{-1}\ s^{-1}$ was determined at 25.0 °C and an ionic strength of 1.0 M ($NaClO_4$). For the oxidation by $CoW_{12}O_{40}^{5-}$ a linear dependence of k_{obs} on [Ru(II)] ($(1–4) \times 10^{-3}$ M) was observed at pH 6.3 and an ionic strength of 0.10 M ($NaClO_4$). The rate and activation parameters for this cross-reaction are presented in Table II.

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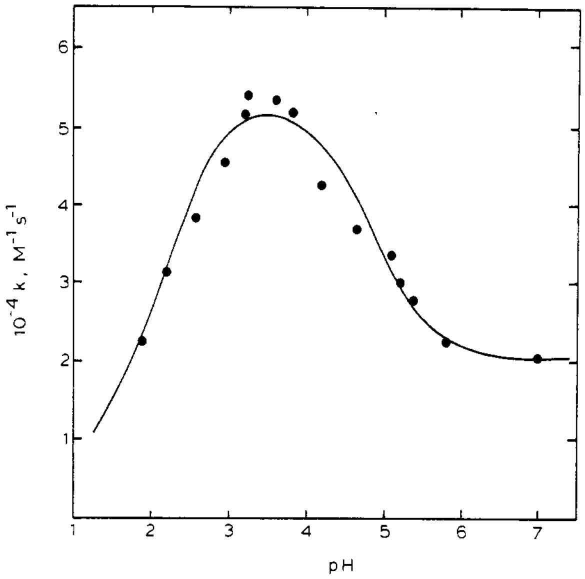

Figure 5. pH dependence of the rate constant for the reduction of $IrCl_6^{2-}$ by $Ru(CN)_6^{4-}$ at 25.0 °C and I = 0.10 M ($LiClO_4$). The curve represents the fit of the data to eq 11.

The kinetics of the electron-transfer reactions between the $Ru(CN)_6^{3-/4-}$ ($E°$ = 0.92 V) and $IrCl_6^{2-/3-}$ ($E°$ = 0.91 V) couples have been investigated in both directions.

$$Ru(CN)_6^{4-} + IrCl_6^{2-} \rightleftharpoons Ru(CN)_6^{3-} + IrCl_6^{3-} \qquad (10)$$

The rate constants for the oxidation of $Ru(CN)_6^{4-}$ by $IrCl_6^{2-}$ were determined at pH 6.8 under pseudo-first-order conditions of excess $Ru(CN)_6^{4-}$. Linear dependences of k_{obs} on $[Ru(CN)_6^{4-}]$ were observed, yielding the second-order rate constants presented in Table II along with the activation parameters measured at I = 0.10 M ($KClO_4$). The plot of the log k_{12} against $I^{1/2}/(1 + \beta\sigma I^{1/2})$, with σ = 9.0 Å, for the $Ru(CN)_6^{4-}/IrCl_6^{2-}$ reaction in $NaClO_4$ (Figure 3) media yields a charge product of +9.6.

The dependences of the rate constants for the oxidation of $Ru(CN)_6^{4-}$ by $IrCl_6^{2-}$ on pH have been investigated in both $LiClO_4$ and $KClO_4$ media. With the ionic strength maintained at 0.10 M by the former electrolyte, the rate constants increased with increasing pH in the range of 1.0–3.5 and then decreased above this pH, reaching a constant value at pH 7 (Figure 5). A similar pH rate dependence has been observed by Hicks[4] for the oxidation of $Ru(CN)_6^{4-}$ by MnO_4^- at ionic strengths of 1.1 M, maintained with $LiClO_4$ or $NaClO_4$. The bell-shaped curves were attributed to different specific rate constants (k_n) for the various $(HNC)_nRu(CN)_{6-n}^{(4-n)-}$ species, with $k_1 \gg k_2, k_0$. The pH dependence of the observed second-order rate constant for the $Ru(CN)_6^{4-}/IrCl_6^{2-}$ reaction may be expressed in terms of these specific rate constants and the proton equilibrium constants K_1 and K_2 from Scheme I:

$$k = \frac{k_2 + k_1K_1/[H^+] + k_0K_1K_2/[H^+]^2}{1 + K_1/[H^+] + K_1K_2/[H^+]^2} \qquad (11)$$

A fit of the data in Figure 5 to eq 11 yields $k_2 \leq 1 \times 10^3$ M^{-1} s^{-1}, $k_1 = 5.6 \times 10^4$ M^{-1} s^{-1}, and $k_0 = 2.0 \times 10^4$ M^{-1} s^{-1} with pK_1 = 2.1 and pK_2 = 4.7. The pK_n values derived in this fit are both larger than the corresponding values determined from the pH dependence of the reduction potential in $NaClO_4$ media and may reflect the change in the nature of the electrolyte cation. In $KClO_4$ media, at an ionic strength of 0.10 M, the rate constants for the $Ru(CN)_6^{4-}/IrCl_6^{2-}$ reaction increase with increasing pH before leveling off above pH 3.5. This behavior is similar to the pH rate dependence observed[38] for the oxidation of $Fe(CN)_6^{4-}$ by $IrCl_6^{2-}$ at an ionic strength of 0.93 M, maintained with $NaClO_4$. The ion-pair association constant for $K^+Ru(CN)_6^{4-}$ has been measured to be 300 M^{-1},[39] indicating that K^+ is likely to be important in the precursor complex of the redox process with the $IrCl_6^{2-}$ ion.

An increase in the electron-transfer rate constant with increasing pH would be anticipated for these reactions as the $Ru(CN)_6^{3-}$ reduction potential decreases with deprotonation of the Ru(II) species at higher pH, while the reduction potential of $IrCl_6^{2-}$ is pH independent above pH 1.[38] The decreases in the rate constants for the oxidations of $Ru(CN)_6^{4-}$ by $IrCl_6^{2-}$ and MnO_4^- in the presence of $LiClO_4$ are not expected on the basis of the thermodynamic driving forces of the reactions. Bruhn et al.[38] have concluded from their investigations of the kinetics of the $Fe(CN)_6^{4-}/IrCl_6^{2-}$ reaction and other electron-transfer reactions between anionic metal complexes that added cations can have a catalytic influence on both the solvent and metal–ligand bond reorganizations as well as promoting the coupling of the redox orbitals. The dependences of the rate constants on the nature and concentration of cations in solution, either H^+ or Li^+, Na^+, and K^+, may represent a composite of two opposing trends. An increase in cation concentration will accelerate the rate by increasing the electrostatic shielding of the repulsive negative charges on the reactants (H^+ (?) > K^+ > Na^+ > Li^+), while decreasing the rate through a decrease in the thermodynamic driving force of the reaction (specifically H^+). For the $Ru(CN)_6^{4-}/IrCl_6^{2-}$ reaction it appears that K^+ and H^+ are much more effective in promoting the redox process than either Na^+ or Li^+. For this reason, the rate constants measured in 0.10 M Li^+ or Na^+ media for the anion/anion cross-reactions in this study will be employed in the Marcus theory calculations below.

The kinetics of the reverse reaction in eq 10 were studied at 25.0 °C and an ionic strength of 0.10 M ($LiClO_4$, pH 6.7). The observed pseudo-first-order rate constants displayed a first-order dependence on the concentration of the excess $IrCl_6^{3-}$ and yielded a second-order rate constant of (2.54 ± 0.19) × 10^4 M^{-1} s^{-1}. The equilibrium constant for the reaction in eq 10 has been determined independently from (a) the differences in the reduction potentials of $IrCl_6^{2-}$ and $Ru(CN)_6^{3-}$ ($\Delta E°$ = –0.01 V), giving K_{10} = 0.7, (b) the ratio of the forward and reverse rate constants, giving K_{10} = 0.8, and (c) a spectrophotometric titration at 434 and 488 nm, giving K_{10} = 0.7 ± 0.1, in excellent agreement with each other.

Discussion

The electron-exchange rate constant for a transition-metal complex couple may be obtained directly from kinetics studies, employing techniques such as isotopic labeling or NMR line-shape analysis, from semiclassical model calculations, or from the application of the Marcus relationship to kinetic and thermodynamic data from a series of cross-reactions involving the couple. The directly measured rate constants for the $Ru(CN)_6^{4-/3-}$ couple at an ionic strength of 0.10 M, k_{11} = (8.3 ± 0.4) × 10^3 M^{-1} s^{-1} (Na^+) and (2.1 ± 0.4) × 10^4 M^{-1} s^{-1} (K^+), may be compared with the directly determined exchange parameters for the $Fe(CN)_6^{3-/4-}$ couple. The electron-exchange rate constant for the iron couple has been measured directly at high ionic strength by Shporer et al.[13] using ^{14}N NMR line-broadening experiments, k_{11} = (9.2 ± 1.3) × 10^4 M^{-1} s^{-1} ($I \approx 3.2$ M (K^+) at 32 °C), and by Kurland and Winkler[15] using ^{13}C NMR line-broadening experiments, k_{11} = 1.6 × 10^4 M^{-1} s^{-1} ($I \approx 1.0$ M ($K_4Fe(CN)_6$) at 25 °C). Campion et al.[14] determined the self-exchange rate constant using isotopic labeling at low ionic strength, k_{11} = (2.26 ± 0.03) × 10^2 M^{-1} s^{-1} ($I \approx 0.015$ M (K^+) at 0.1 °C). Wherland and Gray[40] have extrapolated the latter data to an ionic strength of 0.10 M (K^+) and 25.0 °C and give a value of 1.5 × 10^4 M^{-1} s^{-1}, very similar to the rate constant measured in this study for the $Ru(CN)_6^{4-/3-}$ couple. The $Ru(CN)_6^{4-/3-}$ exchange rate constants are observed to be dependent on the ionic strength of the medium and on nature of the cation ($k_K > k_{Na}$) of the added electrolyte. These phenomena were also observed in the reactions of the $Ru(CN)_6^{3-/4-}$ ions with anionic cross-reactants in this study and have been

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Table III. Electron-Transfer Rate Constants for the Cross-Reactions Involving the $Ru(CN)_6^{4-/3-}$ Couple in Aqueous Solution

oxidant	reductant	k_{12}, $M^{-1}\ s^{-1}$	$\Delta E°$, V	k_{22}, $M^{-1}\ s^{-1}$	k_{11},[a] $M^{-1}\ s^{-1}$
$Ru(CN)_6^{3-}$	I^-	5.8×10^2	−0.41	$2 \times 10^{8\,b}$	8×10^3
$Ru(CN)_6^{3-}$	NO_2^-	2.4×10	−0.12	$2 \times 10^{-2\,c}$	2×10^5
$Ru(CN)_6^{3-}$	$Ni([9]aneN_3)_2^{2+}$	2.2×10^5	−0.03	$6 \times 10^{3\,d}$	4×10^3
$Ru(CN)_6^{3-}$	$IrCl_6^{3-}$	2.5×10^4	0.01	$2.3 \times 10^{5\,e}$	1.6×10^3
$IrCl_6^{2-}$	$Ru(CN)_6^{4-}$	2.0×10^4	−0.01	$2.3 \times 10^{5\,e}$	1.8×10^3
$CoW_{12}O_{40}^{5-}$	$Ru(CN)_6^{4-}$	3.5×10^3	0.08	1.7^f	7.6×10^4
MnO_4^-	$Ru(CN)_6^{4-}$	$9.3 \times 10^{-1\,g}$	−0.36	$3.8 \times 10^{3\,h}$	1.0×10^3
$*Ru(bpy)_3^{2+}$	$Ru(CN)_6^{4-}$	$1 \times 10^{7\,i}$	−0.08	$1 \times 10^{8\,j}$	8×10^3

[a] The self-exchange rate constant for the $Ru(CN)_6^{4-/3-}$ couple, calculated from eq 12. [b] References 28b and 31. [c] References 35 and 41. [d] Reference 22; $I = 1.0$ M. [e] Reference 42. [f] Reference 43a; extrapolated from data in ref 43b. [g] Reference 4. [h] Reference 44; $I = 1.1$ M. [i] Reference 7. [j] Rybak, K.; Haim, A.; Netzel, T. L.; Sutin, N. *J. Phys. Chem.* **1981**, *85*, 2856.

previously reported for the electron-transfer reactions of the $Fe(CN)_6^{4-/3-}$ couple.[38] Additional kinetics studies on the cross-reactions of the $Ru(CN)_6^{3-/4-}$ couple with other anionic reactants are in progress to further elucidate the roles of specific cations.

The cross-reaction kinetic data from this study may be correlated in terms of a recent modification of the Marcus relationship,[17] which relates the rate constant for a cross-reaction k_{12} to the rate constants for the component self-exchange reactions k_{11} and k_{22} and the equilibrium constant for the cross reaction K_{12} by [18]

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{1/2}W_{12} \qquad (12)$$

where

$$\ln f_{12} = \frac{[\ln K_{12} + (w_{12} - w_{21})/RT]^2}{4\left[\ln\left(\dfrac{k_{11}k_{22}}{A_{11}A_{22}}\right) + \dfrac{w_{11} + w_{22}}{RT}\right]} \qquad (13)$$

$$W_{12} = \exp[-(w_{12} + w_{21} - w_{11} - w_{22})/2RT] \qquad (14)$$

$$w_{ij} = \frac{z_i z_j e^2}{D_s\sigma_{ij}(1 + \beta\sigma_{ij}I^{1/2})} \qquad (15)$$

In the preceding expressions w_{ij} is the work required to bring ions i and j (charges z_i and z_j) to the separation distance σ_{ij} (taken equal to the sum of the radii of the ions), D_s is the static dielectric constant of the medium, $\beta = (8\pi Ne^2/1000D_skT)^{1/2}$, and $A_{ii} = (4\pi N\sigma^2\nu_n(\delta r)/1000)_{ii}$, where δr is the thickness of the reaction shell (≈0.8 Å[18]). The self-exchange rate constants ($I = 0.1$ M) for the cross-reactants used in this study have been determined from direct measurements or by the employment of the Marcus cross-reactionship to several reactions involving the reactants (Table III). The following complex radii were used in the Marcus calculations: $Ru(CN)_6^{4-/3-}$, 4.7 Å; $IrCl_6^{4-}$, 4.4 Å; MnO_4^-, 2.8 Å; $CoW_{12}O_{40}^{5-}$, 5.0 Å; I^-, 2.2 Å; NO_2^-, 1.9 Å. The $Ru(CN)_6^{4-/3-}$ self-exchange rate constants derived from the cross-reactions in this study are presented in Table III, and yield a geometric mean of $k_{11} = 1.1 \times 10^4\ M^{-1}\ s^{-1}$. The range of values of k_{11} is consistent with the inherent uncertainties (e.g. ionic strength extrapolations) in the cross-reactant self-exchange rate constants and reduction potentials.[28a] The rate constants for the cross-reactions involving the $Ru(CN)_6^{4-/3-}$ couple have been correlated in terms of the Marcus relationship (eq 12), and a plot of ln $(k_{12}/(k_{22})^{1/2}W_{12})$ against ln $(K_{12}f_{12})^{1/2}$ is displayed in Figure 6. The plot also includes data for the oxidations of several organic reductants[16b] by $Ru(CN)_6^{3-}$ and for the oxidation of $Ru(CN)_6^{4-}$ by MnO_4^- ($E°$ = 0.56 V)[4] and $*Ru(bpy)_3^{2+}$ ($E°$ = 0.84 V).[7] A least-squares fit of the 13 points in the plot yields a slope of 0.95 ± 0.06, in excellent agreement with the theoretical value of unity. The calculated intercept of 4.6 ± 0.3 corresponds to ln $k_{11}^{1/2}$ and gives a self-exchange rate constant of $(1.0 \pm 0.7) \times 10^4\ M^{-1}\ s^{-1}$ for the $Ru(CN)_6^{4-/3-}$ couple at $I = 0.10$ M, in very good agreement with the directly measured value.

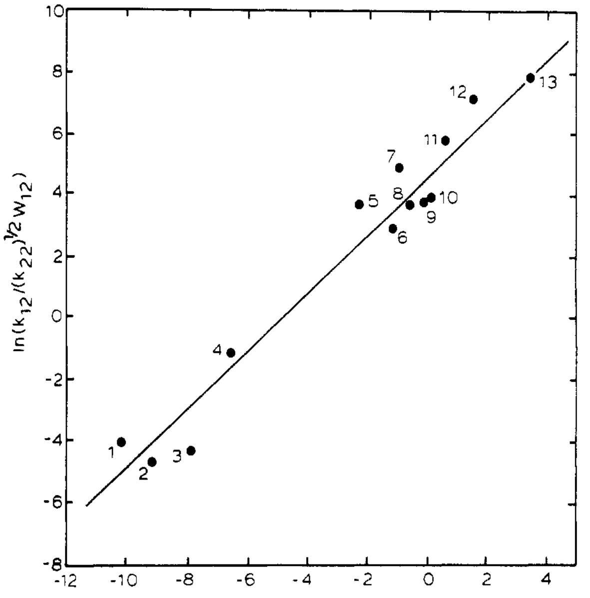

Figure 6. Plot of ln $(k_{12}/k_{22}^{1/2}W_{12})$ against ln $(K_{12}f_{12})^{1/2}$ for the cross-reactions of the $Ru(CN)_6^{4-/3-}$ couple with (1) 3,4-dihydroxybenzoic acid,[16b] (2) I^-, (3) MnO_4^-,[4] (4) 2,5-dihydroxybenzoic acid,[16b] (5) NO_2^-, (6) $*Ru(bpy)_3^{2+}$, (7) 2,3-dicyano-1,4-dihydroxybenzenate anion,[16b] (8) $Ni([9]aneN_3)_2^{2+}$, (9) $IrCl_6^{2-}$, (10) $IrCl_6^{3-}$, (11) 4,5-dihydroxybenzene-1,3-disulfonate anion,[16b] (12) $CoW_{12}O_{40}^{5-}$, and (13) ascorbate anion.[16b]

The electron-self-exchange rate constants for a number of organic and transition-metal complex couples have been predicted with reasonable success by using the semiclassical model for bimolecular electron exchange.[45] The rate constant k_{11} may be expressed as the product of a preequilibrium constant K_A, an effective nuclear frequency ν_n, an electronic factor κ_{el}, and a nuclear factor that contains terms for both inner-sphere (ΔG^*_{in}) and solvent reorganizations (ΔG^*_{out}) as well as an inner-sphere nuclear tunneling factor Γ_n:

$$k_{11} = K_A\nu_n\kappa_{el}\Gamma_n \exp[-(\Delta G^*_{in} + \Delta G^*_{out})/RT] \qquad (16)$$

The inner-sphere term, ΔG^*_{in}, corresponds to the reorganization of bond distances and angles required prior to electron transfer, and the outer-sphere term, ΔG^*_{out}, is the energy needed to change the orientations of the solvent molecules surrounding the reactants. The reorganization energies may be calculated with a knowledge of the bond distances and angles and vibrational frequencies and force constants for the two redox partners:

$$\Delta G^*_{in} = \tfrac{1}{2}\textstyle\sum f_i[(\Delta d_0)_i/2]^2 \qquad (17)$$

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(41) (a) A directly determined self-exchange rate constant of 580 $M^{-1}\ s^{-1}$ for the NO_2/NO_2^- couple has recently been reported,[41b] substantially larger than the value of $2 \times 10^{-2}\ M^{-1}\ s^{-1}$ derived from an application of the Marcus theory to kinetic data for cross-reactions of NO_2^- with metal oxidants.[35] The authors suggest[41b] that the direct exchange pathway is more efficient, involving strong overlap. (b) Stanbury, D. M.; deMaine, M. M.; Goodloe, G. *J. Am. Chem. Soc.* **1989**, *111*, 5496.

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While the Ru–C distance is known for the $[Ru(CN)_6]^{4-}$ ion (2.082 Å in $Mn_2[Ru(CN)_6]\cdot 8H_2O$),[46] the instability of the $[Ru(CN)_6]^{3-}$ ion has precluded measurements of the Ru–C distance in this complex. The change in the Fe–C bond distance for the $[Fe(CN)_6]^{4-/3-}$ couple has been determined to be −0.026 ± 0.010 Å from X-ray diffraction studies[47] and 0.00 ± 0.01 Å from EXAFS measurements.[45] An estimate of the change in the Ru–C bond distance upon intervalence electron transfer in the $[(NC)_5Ru\text{–}CN\text{–}Ru(NH_3)_5]^-$ ion has recently been reported by the use of postresonance-enhanced Raman scattering techniques.[48] For the terminal Ru–C bonds Δd_0 was calculated to be ±0.035 ± 0.007 Å from the Ru–C stretching band. The change in the $Ru\text{–}NH_3$ distance calculated by using this technique, 0.039 ± 0.008 Å, is in excellent agreement the crystallographic value of 0.040 ± 0.008 Å[49] (0.03 ± 0.01 Å from EXAFS measurements[45]). A force constant of 279 N m^{-1} has been reported for the Ru–C stretch in the $Ru(CN)_6^{4-}$ ion.[50,51] On the basis of the similarities in the Fe–C force constants for the $Fe(CN)_6^{4-}$ (230 N m^{-1}) and $Fe(CN)_6^{3-}$ (240 N m^{-1}) ions,[1] the reduced Ru–C force constant is taken to be 285 N m^{-1}. The inner-sphere reorganization barrier is calculated (eq 17) to be 3.2 ± 1.2 kJ mol^{-1}.

The outer-sphere solvent reorganization barrier, ΔG^*_{out}, is frequently calculated by using either two-sphere or ellipsoidal cavity dielectric continuum models.[17] The more realistic model for the precursor complex places the reactants in an ellipsoidal cavity.[52,53] The expression for ΔG^*_{out} in the constant-volume ellipsoidal model is given by

$$\Delta G^*_{out} = \frac{(\Delta e)^2\sigma^2}{8r_a^2 r_b}\left[\frac{1}{D_{op}} - \frac{1}{D_s}\right]S(\lambda_0) \qquad (18)$$

where Δe is the charge transferred, r_a and r_b are the lengths of the minor and major semiaxes, respectively, D_{op} and D_s are the optical and static dielectric constants of the medium, respectively, and $S(\lambda_0)$ is a shape factor. If r_b is taken to be $r_a + \sigma/2$ (the volume of the ellipsoid is equal to the sum of the volumes of the reactants at $\sigma = 2r_a$, and $S(\lambda_0) = 0.705$), with $r_a = 4.7$ A, the value of ΔG^*_{out} is calculated to be 28 kJ mol^{-1}.

The nuclear frequency, $\nu_n = \{[(\nu_{in})^2\Delta G^*_{in} + (\nu_{out})^2\Delta G^*_{out}]/(\Delta G^*_{in} + \Delta G^*_{out})\}^{1/2}$, is calculated to be $(4.2 \pm 1.5) \times 10^{12}\ s^{-1}$ ($\bar{\nu}_{in} = 427\ cm^{-1}$,[51] $\bar{\nu}_{out} = 30\ cm^{-1}$ [45]), while K_A at an ionic strength of 0.10 M is $5.3 \times 10^{-3}\ M^{-1}$. The nuclear tunneling factor for low-frequency modes at room temperature is normally close to unity, and a value of 1.2 is calculated for the $Ru(CN)_6^{4-/3-}$ couple.[17,54] A value of 0.2 has been estimated for the electronic factor, κ_{el}, for the $[Ru(H_2O)_6]^{2+/3+}$, $[Ru(NH_3)_6]^{2+/3+}$, and $[Ru(en)_3]^{2+/3+}$ couples on the basis of electronic coupling energies (H_{AB}) of about 70 cm^{-1}.[54] These exchanges are regarded as being marginally adiabatic (as opposed to nonadiabatic behavior as in the $Fe(H_2O)_6^{2+/3+}$ couple, $\kappa_{el} \approx 10^{-2}$)[55] because of the radial extension of the 4d orbitals and the involvement of the ligands in the electronic coupling. For the $Ru(CN)_6^{4-/3-}$ couple it would be anticipated the κ_{el} would be ≥0.2 because of the possible coupling contribution of the cyanide ligands through $Ru(t_{2g})\text{–}L(\pi^*)$ interactions. The predicted value of the electron-exchange rate constant for the $[Ru(CN)_6]^{4-/3-}$ couple from the semiclassical model is $(2 \pm 1) \times 10^4\ M^{-1}\ s^{-1}$ on the basis of the constant-volume ellipsoidal model. The latter value is in excellent agreement with the directly measured value and with the average of the rate constants determined from the application of the Marcus relationship to cross-reactions involving the couple.

Table IV. Parameters for Electron-Exchange Reactions of Low-Spin d^6/d^5 Iron and Ruthenium Couples

couple[a]	Δd_0, Å[b]	σ, Å	I, M	k_{11}, $M^{-1}\ s^{-1}$	ref
$Ru(CN)_6^{4-/3-}$	0.035 (7)[c]	9.4	0.10 (K^+)	2.1×10^4	*d*
$Fe(CN)_6^{4-/3-}$	0.026 (10)[d] (0.00 (1))[e]	9.0	0.10 (K^+)	1.5×10^4	40
$Ru(H_2O)_6^{2+/3+}$	0.09 (2)[f] (0.08 (3))[e]	6.5	5.0	2.0×10	56
$Ru(NH_3)_6^{2+/3+}$	0.040 (8)[g]	6.7	0.75	2.2×10^4	58
	(0.03 (1))[e]		0.013	8.2×10^2	59
$Ru(en)_3^{2+/3+}$	0.022 (20)[h]	8.4	0.75	3.1×10^4	60
$Ru([9]aneN_3)_2^{2+/3+}$		8.6	0.10	5×10^4	61
$Ru(sar)^{2+/3+}$	0.008 (18)[i]	9.0	0.10	1.2×10^5	62

[a] en = 1,2-diaminoethane, $[9]aneN_3$ = 1,4,7-triazacyclononane, and sar = 3,6,10,13,16,19-hexaazabicyclo[6.6.6]eicosane. [b] From X-ray structural data unless otherwise indicated (error limits in parentheses). [c] From Raman scattering measurements.[48] [d] This work. [e] From EXAFS measurements.[45] [f] Reference 57. [g] From data in ref 48. [h] From data in: Smolenaers, P. J.; Beattie, J. K.; Hutchinson, N. S. *Inorg. Chem.* **1981**, *20*, 2202. Peresie, H. J.; Stanko, J. A. *J. Chem. Soc., Chem. Commun.* **1970**, 1674. [i] Reference 63; for Ru(II), the Ru–N bond length in $Ru(1\text{-}Mesar)^{2+}$ was used.

The self-exchange rate constant for the $[Ru(CN)_6]^{3-/4-}$ couple is expected to be similar to the values determined for other small, low-spin d^5/d^6 complex couples of ruthenium and iron, in which exchange involves an electron occupying a nonbonding t_{2g} orbital. The self-exchange rate constants, along with the Δd_0 and σ values of several Ru(II)/Ru(III) couples[56–63] and the $Fe(CN)_6^{4-/3-}$ couple are listed in Table IV. The rate constant and structural parameters for the $Ru(CN)_6^{4-/3-}$ couple are very consistent with the other Ru(II)/Ru(III) amine couples of similar size. The trend of increasing self-exchange rate constants with an increase in the complex radii has been extended for the Ru(II)/Ru(III) couple series up to the very rapid exchange within the large $Ru(bpy)_3^{2+/3+}$ couple.[61,64]

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Supplementary Material Available: Tables of observed first-order and calculated second-order rate constants (8 pages). Ordering information is given on any current masthead page.

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