

Kinetics of the Oxidation of Ascorbic Acid and Substituted 1,2- and 1,4-Dihydroxybenzenes by the Hexacyanoruthenate(III) Ion in Acidic Perchlorate Media

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The kinetics of oxidation of ascorbic acid and a series of substituted 1,2- and 1,4-dihydroxybenzene compounds (H_2Q) by $[Ru(CN)_6]^{3-}$ have been investigated in acidic perchlorate media. The inverse dependences of the rate constants on acid concentrations for 2,3-dicyano-1,4-dihydroxybenzene, 4,5-dihydroxybenzene-1,3-disulphonate, and ascorbic acid have been attributed to concurrent rate-determining pathways involving the one-electron oxidations of H_2Q or HQ^- by $[Ru(CN)_6]^{3-}$ to the corresponding semiquinone or ascorbate radical intermediate. The cross-reaction rate constants have been correlated with the semiquinone or ascorbate reduction potentials in terms of the Marcus relationship to yield a $[Ru(CN)_6]^{3-}$ - $[Ru(CN)_6]^{4-}$ electron self-exchange rate constant of $(1.0 \pm 0.8) \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. This is compared with those for other low-spin d^5 - d^6 transition-metal complex couples and discussed in terms of the inner-sphere and solvent reorganization energies.

There have been numerous investigations of electron-exchange and electron-transfer reactions involving the $[Fe(CN)_6]^{3-/4-}$ couple in aqueous solution,¹⁻⁶ and the chemical and electrochemical properties of this complex couple are well understood. Considerably less is known about the electron-transfer behaviour of the corresponding $[Ru(CN)_6]^{3-/4-}$ couple,⁷⁻¹⁴ likely the result of the higher reduction potential and greater instability of the $[Ru(CN)_6]^{3-}$ ion in solution.⁸ The limited investigations to date on this couple have been concerned with both thermal and photochemical reactions, employing the $[Ru(CN)_6]^{4-}$ ion as a reductant of the $[MnO_4]^-$ ion⁹ and OH^\bullet radical¹¹ and as a reductive quencher of excited-state $[*M(bipy)_3]^{n+}$ ($bipy = 2,2'$ -bipyridine) complexes^{10,12} and lanthanide ions.¹³ The $[Ru(CN)_6]^{3-}$ ion, generated by laser photoionization, has recently been used, along with $[Fe(CN)_6]^{3-}$ and $[Os(CN)_6]^{3-}$, in a kinetic study of the oxidation of ferrocyanochrome c.¹⁴ The differences in the reactivities of the iron, osmium, and ruthenium hexacyanides were attributed to their relative reduction potentials, with the electron self-exchange rate constants for the three couples taken to be very similar. The self-exchange rate constant for the $[Ru(CN)_6]^{3-/4-}$ couple has been estimated to be 2×10^2 and $1.2 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ by the application of the Marcus theory relationship to the rate constant for the oxidation of $[Ru(CN)_6]^{4-}$ by MnO_4^- ⁸ and $[*Ru(bipy)_3]^{2+}$,¹² respectively. As part of our current investigations of the reactions of cyanoruthenate complexes in aqueous solution,^{15,16} we have undertaken studies of the kinetics of electron-transfer reactions of the $[Ru(CN)_6]^{3-/4-}$ couple with inorganic and organic reactants.

The 1,2- and 1,4-dihydroxybenzenes and their substituted derivatives, along with ascorbic acid, are well characterized two-electron reductants ($H_2Q \rightarrow Q + 2H^+ + 2e^-$) that have importance in biological electron-transport systems¹⁷. These compounds have been used in a number of electron-transfer studies involving transition-metal oxidants such as $[Co(H_2O)_6]^{3+}$,¹⁸ $[IrCl_6]^{2-}$,¹⁹⁻²¹ $[Rh_2(O_2CCH_3)_4(H_2O)_2]^+$,²² and tris(polypyridine)metal(III) complexes of iron, ruthenium, and osmium.^{20,23,24} The reaction process usually involves the rate-determining one-electron oxidation to a semiquinone radical (HQ^\bullet) followed by a second one-electron oxidation to the quinone, by either an inner-sphere or outer-sphere mechan-

ism, depending on the nature of the oxidant. The additions of various ring substituents to the parent species (H_2Q) allow for a systematic study of these reductants over a wide range of semiquinone reduction potentials.

In this paper the results of a kinetic and mechanistic study of the reduction of $[Ru(CN)_6]^{3-}$ by substituted 1,2- and 1,4-dihydroxybenzenes and ascorbic acid in aqueous perchlorate media are reported. The Marcus relationship^{25,26} has been utilized to correlate the cross-reaction rate constants with the semiquinone reduction potentials and to derive a rate constant for the $[Ru(CN)_6]^{3-/4-}$ self-exchange reaction. This exchange rate constant is compared the values determined previously for other small low-spin d^5 - d^6 iron and ruthenium couples, such as $[Fe(CN)_6]^{3-/4-}$ and $[Ru(NH_3)_6]^{3+/2+}$, and is discussed in terms of the contributions of inner- and outer-sphere reorganization barriers to electron exchange.

Experimental

Materials.—Potassium hexacyanoruthenate(II), $K_4[Ru(CN)_6] \cdot 3H_2O$, was used as received (Alfa) or synthesized from $RuCl_3 \cdot xH_2O$ (Aldrich) and KCN according to the procedure of Howe.²⁷ Solutions of the yellow hexacyanoruthenate(III) anion were prepared by oxidation with Ce^{IV} in acidic media, followed by passage down a cation-exchange column (BDH Amberlite resin IR-120, H^+ or Na^+) to remove the Ce^{3+} , Ce^{4+} , and K^+ . The concentrations of the $[Ru(CN)_6]^{3-}$ anion were determined by measurements on either a Perkin-Elmer 552 or a Hewlett-Packard 8452A spectrophotometer at λ_{max} ($\epsilon \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) = 460 (1 020), 356 (1 570), 328 (2 370), and 298 nm (2 150).⁸

The 3,5-(SO_3Na)₂ (Fisher), 3- CO_2H , 4- CO_2H , and 4- NO_2 (Aldrich) derivatives of 1,2-dihydroxybenzene, the 2- CO_2H and 2,5-(SO_3H)₂ (Aldrich) derivatives of 1,4-dihydroxybenzene, as well as the parent compounds, were used as received. 2,3-Dicyano-1,4-dihydroxybenzene (Aldrich) was recrystallized once from methanol. L-Ascorbic acid (Aldrich) was used as received. N-Methylpyrazinium iodide was prepared as described previously.¹⁵ Solutions of the reductants were prepared using nitrogen- or argon-saturated distilled water. The solutions were stable to oxidation in 0.1 mol dm^{-3} $HClO_4$ and

Table 1. Properties of the reductants employed in the cross-reactions with the $[\text{Ru}(\text{CN})_6]^{3-}$ ion

	Reductant	R	E^{0a}/V
(1)		H	1.12
(2)		4-NO ₂	1.46
(3)		3-CO ₂ H	1.36
(4)		4-CO ₂ H	1.38
(5)		3,5-(SO ₃ ⁻) ₂	1.47
(6)		3,5-(SO ₃ ⁻) ₂	0.89
(7)		2-CO ₂ H	1.23
(8)		2,3-(CN) ₂	1.42
(9)		2,5-(SO ₃ ⁻) ₂	1.34
(10)		2,3-(CN) ₂	0.97
(11)	Ascorbic acid		1.19 ^b
(12)	Ascorbate anion		0.723 ^c

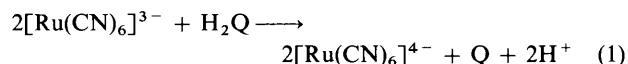
^a One-electron reduction potentials (*vs.* n.h.e.) for $\text{H}_2\text{Q}^{2+} + \text{e}^- \rightarrow \text{H}_2\text{Q}$ or $\text{HQ}^+ + \text{e}^- \rightarrow \text{HQ}^{\cdot-}$, from ref. 22. ^b Ref. 24. ^c Ref. 36.

were used within 24 h. Sodium perchlorate (BDH) was used as received and solutions were standardized by exchanging Na⁺ for H⁺ on a cation-exchange column (Amberlite IR-120) and titrating the effluent with standardized NaOH.

Kinetics.—The kinetic studies were performed using a TDI model IIA stopped-flow apparatus (Cantech Scientific), with transmittance data collected by a TDI 1024C transient recorder and processed on an interfaced Zenith ZF-151 microcomputer. All measurements were made under pseudo-first-order conditions of excess of reductant and plots of $\ln(A_t - A_\infty)$ against time were linear for at least three half-lives. The reported first-order rate constants represent the average of three to five replicate runs, monitored between 460 and 500 nm. The reactions were studied in aqueous perchlorate media with the ionic strength maintained at 0.10 mol dm⁻³ with added sodium perchlorate.

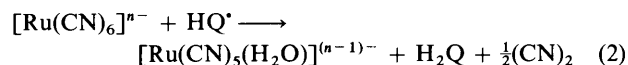
Results

The stoichiometries of the reduction of the $[\text{Ru}(\text{CN})_6]^{3-}$ ion by the substituted dihydroxybenzenes and ascorbic acid have been determined by spectrophotometric titrations. The anticipated 2:1 $[\text{Ru}(\text{CN})_6]^{3-}:\text{H}_2\text{Q}$ stoichiometry in equation (1),



as observed with a variety of one-electron transition-metal complex oxidants,^{18–24} was not seen in this system. Non-

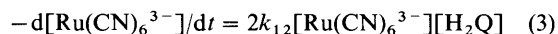
integer ratios larger than 2:1 were found and are attributed to slower secondary reactions involving the $[\text{Ru}(\text{CN})_6]^{4-}$ product. When the titrations were performed in the presence of an excess of the *N*-methylpyrazinium cation a band at 522 nm, due to the $[\text{Ru}(\text{CN})_5(\text{NC}_4\text{H}_4\text{NMe})]^{2-}$ complex,¹⁵ was observed. It is believed that this species results from aqua substitution on the $[\text{Ru}(\text{CN})_5(\text{H}_2\text{O})]^{3-}$ ion, which is generated from the reaction of the semiquinone radical $\text{HQ}^{\cdot-}$ with $[\text{Ru}(\text{CN})_6]^{4-}$ or $[\text{Ru}(\text{CN})_6]^{3-}$ (followed by reduction) [equation (2)]. Similar reactions of the $[\text{Ru}(\text{CN})_6]^{4-}$ and $[\text{Ru}(\text{CN})_6]^{3-}$



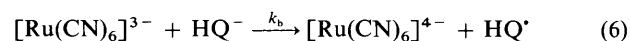
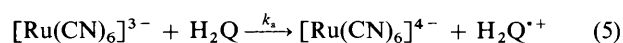
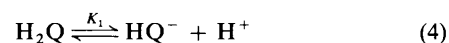
ions have been observed in the presence of Br₂¹⁵ and Hg²⁺.⁸ Under the reaction conditions for the kinetics experiments, $[\text{H}_2\text{Q}] \gg [\text{Ru}(\text{CN})_6]^{3-}$, it was found that less than 5% of the initial $[\text{Ru}(\text{CN})_6]^{3-}$ was converted into the redox-inactive substituted product.

Kinetics.—The $[\text{Ru}(\text{CN})_6]^{3-}$ ion is a moderately strong oxidant in aqueous solution, with a reduction potential [0.92 V *vs.* normal hydrogen electrode (n.h.e.)]¹⁶ that is about 0.5 V higher than that of the $[\text{Fe}(\text{CN})_6]^{3-}$ ion.¹ By analogy with the very acidic $[(\text{Fe}(\text{CN})_5(\text{CNH}))]^{2-}$ ion ($\text{p}K_a < 0$),²⁸ $[\text{Ru}(\text{CN})_6]^{3-}$ is considered to be unprotonated at pH > 0. The UV-visible spectrum of $[\text{Ru}(\text{CN})_6]^{3-}$ is independent of acid concentration, and the observed pH dependence of the reduction potential¹⁶ of the $[\text{Ru}(\text{CN})_6]^{3-/4-}$ couple is related to the acid-dissociation equilibria of the reduced form $[(\text{Ru}(\text{CN})_{6-n}(\text{CNH})_n)]^{(4-n)-}$.

The kinetics of the oxidation of a series of substituted 1,2- and 1,4-dihydroxybenzenes (Table 1) by $[\text{Ru}(\text{CN})_6]^{3-}$ were investigated in 0.10 mol dm⁻³ perchlorate (H⁺/Na⁺) media at several temperatures. At constant [H⁺] and with the reductants present in excess, the pseudo-first-order rate constants exhibited a first-order dependence on $[\text{H}_2\text{Q}]$, as shown in Figure 1. The rate law for the two-electron oxidation of H₂Q is given by equation (3).



The rate constants for 4,5-dihydroxybenzene-1,3-disulphonate ($\text{p}K_a = 7.62$),²⁹ 2,3-dicyano-1,4-dihydroxybenzene ($\text{p}K_a = 5.5$),³⁰ and ascorbic acid ($\text{p}K_a = 4.03$)³¹ were measured as a function of the solution acid concentration. For the dihydroxybenzene species the acidities of the hydroxyl groups are increased substantially from those of the parent species ($\text{p}K_a$ for 1,2- and 1,4-dihydroxybenzenes are 9.24²⁹ and 9.85,³² respectively). The oxidation rate constants displayed an inverse dependence on [H⁺] over the range 0.001–0.100 mol dm⁻³ $\{[\text{H}_2\text{Q}] = (0.5–5.0) \times 10^{-3} \text{ mol dm}^{-3}\}$ at an ionic strength of 0.10 mol dm⁻³ maintained with HClO₄/NaClO₄ mixtures. The inverse acid dependence is illustrated in Figure 2 and is consistent with the reaction scheme in equations (4)–(7),



in which the rate-determining one-electron oxidations of H₂Q or HQ⁻ are followed by a rapid second one-electron oxidation of the semiquinone radical HQ^{·-} [$\text{p}K_{r1}(\text{H}_2\text{Q}^{\cdot+}) < -1$ for the

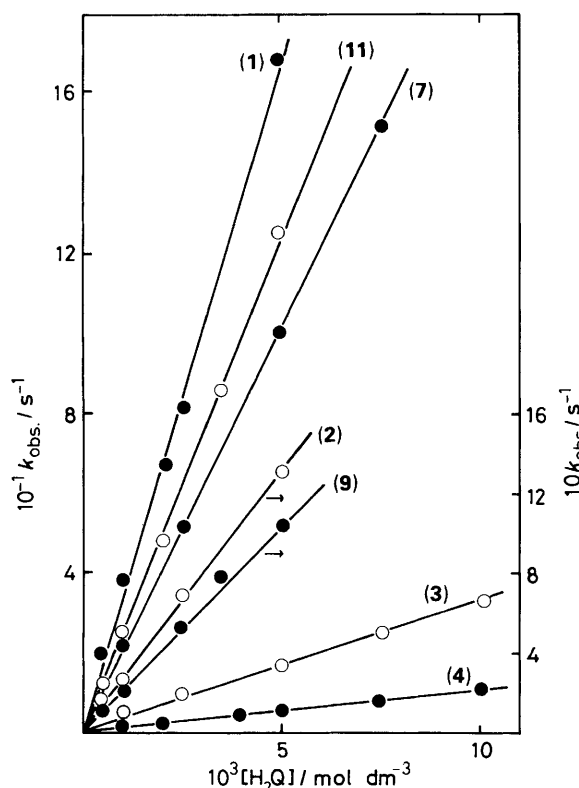


Figure 1. Plots of k_{obs} against $[\text{H}_2\text{Q}]$ for the reductions of the $[\text{Ru}(\text{CN})_6]^{3-}$ ion by ascorbic acid and substituted 1,2- and 1,4-dihydroxybenzenes. The reductants are numbered according to Tables 1 and 2

Table 2. Rate and activation parameters for the reduction of the $[\text{Ru}(\text{CN})_6]^{3-}$ ion by substituted 1,2- and 1,4-dihydroxybenzenes and ascorbic acid in aqueous perchlorate media

Reductant	$k_{12}^a / \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$	$\Delta H^{\ddagger a} / \text{kJ mol}^{-1}$	$\Delta S^{\ddagger a} / \text{J K}^{-1} \text{mol}^{-1}$
(1)	$(1.74 \pm 0.14) \times 10^4$	8.3 ± 1.1	-138 ± 3
(2)	$(1.30 \pm 0.10) \times 10^2$	15.9 ± 2.0	-150 ± 6
(3)	$(1.66 \pm 0.08) \times 10^3$	18.7 ± 0.7	-120 ± 2
(4)	$(5.16 \pm 0.13) \times 10^2$	10.5 ± 0.8	-157 ± 2
(5)	$(2.29 \pm 0.23) \times 10^{1b}$	10.7 ± 0.9^b	-183 ± 3^b
(6)	$(5.8 \pm 0.4) \times 10^{5d}$		
(7)	$(1.01 \pm 0.03) \times 10^4$	8.6 ± 1.4	-139 ± 4
(8)	$(1.75 \pm 0.02) \times 10^2$	11.8 ± 2.1	-162 ± 6
(9)	$(1.05 \pm 0.03) \times 10^{2b}$	8.0 ± 1.4^b	-179 ± 4^b
(10)	$(1.8 \pm 0.3) \times 10^{6d}$		
(11)	$(1.21 \pm 0.03) \times 10^4$		
(12)	$(4.4 \pm 0.2) \times 10^{6d}$		

^aAt 25.0 °C, $[\text{H}^+] = 0.10 \text{ mol dm}^{-3}$ (unless otherwise indicated), $I = 0.10 \text{ mol dm}^{-3}$. ^b $[\text{H}^+] = 0.085 \text{ mol dm}^{-3}$; $I = 0.10 \text{ mol dm}^{-3}$ (NaClO_4). ^cValue of k_a , determined as described in the text. ^dValue of k_b , determined as described in the text.

dihydroxybenzenes³³] or $\text{Q}^{\cdot-}$ in the case of ascorbic acid ($\text{p}K_{r1} \approx -4$, $\text{p}K_{r2} = -0.45$ ²⁴). At acidities where $[\text{H}^+] \gg K_1$, the second-order rate constant k_{H} may be related to k_a and k_b and the acid-dissociation constant K_1 by equation (8).

$$k_{\text{H}} = k_a + k_b K_1 [\text{H}^+]^{-1} \quad (8)$$

The rate constants k_a and k_b were calculated from the

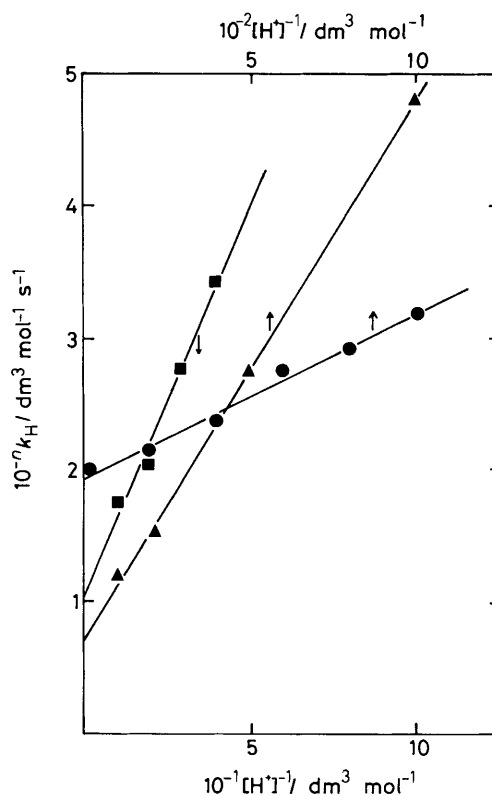


Figure 2. Plots of $10^{-n}k_{\text{H}}$ against $[\text{H}^+]^{-1}$ for the reductions of the $[\text{Ru}(\text{CN})_6]^{3-}$ ion by ascorbic acid ($n = 4$, \blacktriangle), 2,3-dicyano-1,4-dihydroxybenzene ($n = 2$, \blacksquare), and 4,5-dihydroxybenzene-1,3-disulphonate ($n = 1$, \bullet) at 25.0 °C [$I = 0.10 \text{ mol dm}^{-3}$ ($\text{HClO}_4/\text{NaClO}_4$)]

intercepts and slopes, respectively, of the plots of k_{H} against $[\text{H}^+]^{-1}$ in Figure 2. The rate constants, k_b , for the conjugate base reductants HQ^- are about 10^3 – 10^4 times greater than the values (k_a) for the corresponding H_2Q species. The increased reactivity of HQ^- compared with H_2Q is the result of a much lower semiquinone reduction potential (Table 1). For the more basic dihydroxybenzene reductants ($\text{p}K_a > 8$)²² in this study inverse acid rate dependences would be very much less pronounced at low pH, such that the values of k_{H} (and the corresponding activation parameters) at $[\text{H}^+] = 0.1 \text{ mol dm}^{-3}$ are dominated by k_a . The second-order rate constants k_{12} and the corresponding enthalpies and entropies of activation for the reactions are presented in Table 2. The kinetics of the oxidation of 1,4-dihydroxybenzene [$E^0(\text{H}_2\text{Q}^{\cdot+} - \text{H}_2\text{Q}) = 1.09 \text{ V}$] by $[\text{Ru}(\text{CN})_6]^{3-}$ were too rapid to follow. The enthalpies and entropies of activation for the oxidations of the dihydroxybenzenes fall in the ranges of 8–19 kJ mol^{-1} and -180 to $-115 \text{ J K}^{-1} \text{mol}^{-1}$, respectively. Similar activation parameters have been reported for the oxidation of these species by $[\text{IrCl}_6]^{2-}$ in $1.0 \text{ mol dm}^{-3} \text{ HClO}_4$ ($E^0 = 0.957 \text{ V}$).¹⁹

The dependence of k_{12} on the semiquinone reduction potential has been observed previously for the oxidation of these dihydroxybenzene compounds by a number of metal oxidants.^{18,19,22,23} The rate constants for the $[\text{Ru}(\text{CN})_6]^{3-}$ cross-reactions are consistently lower than those for $[\text{Rh}_2(\text{O}_2\text{CCH}_2)_4(\text{H}_2\text{O})_2]^{+}$ ($E^0 = 1.22 \text{ V}$)²² and substituted tris(1,10-phenanthroline)iron(III) complexes ($E^0 = 0.97$ – 1.25 V)²³ as the thermodynamic driving forces and metal complex self-exchange rate constants are higher in these reactions. The values for the oxidation by $[\text{IrCl}_6]^{2-}$ are slightly smaller than the corresponding rate constants for $[\text{Ru}(\text{CN})_6]^{3-}$, despite a somewhat larger $\text{Ir}^{\text{IV}} - \text{Ir}^{\text{III}}$ reduction potential, which may result from the use of a medium of higher ionic strength (1.0 mol dm^{-3}).

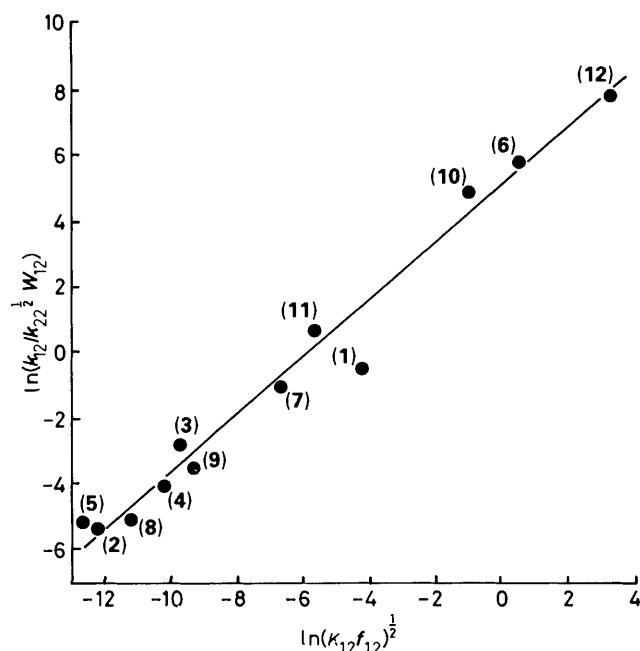


Figure 3. Plot of $\ln(k_{12}/k_{22}^{1/2} W_{12})$ against $\ln(K_{12} f_{12})^{1/2}$ for the oxidations of substituted 1,2- and 1,4-dihydroxybenzenes and ascorbic acid by $[\text{Ru}(\text{CN})_6]^{3-}$ at 25°C. The points correspond to the reductants in Tables 1 and 2

Discussion

The cross-reaction kinetic data from this study may be correlated in terms of the Marcus equation,²⁴ which relates the rate constant for a cross-reaction, k_{12} , to the rate constant for the component self-exchange reactions, k_{11} and k_{22} , and the equilibrium constant for the cross reaction, K_{12} , equations (9)–(12).²

$$k_{12} = (k_{11} k_{22} K_{12} f_{12})^{1/2} W_{12} \quad (9)$$

$$\ln f_{12} = \frac{[\ln K_{12} + (w_{12} - w_{21})/RT]^2}{4 \left[\ln \left(\frac{k_{11} k_{22}}{A_{11} A_{22}} \right) + \frac{w_{11} + w_{22}}{RT} \right]} \quad (10)$$

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

$$w_{ij} = \frac{z_i z_j e^2}{D_s \sigma_{ij} (1 + \beta \sigma_{ij} l^{\ddagger})} \quad (12)$$

In the above 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 as equal to the sum of the radii of the ions), D_s is the static dielectric constant of the medium, $\beta = (8\pi N e^2 / 1000 D_s k T)^{1/2}$, and $A_{ii} = [4\pi N \sigma_{ii}^2 \nu_n(\delta r) / 1000]_{ii}$, where ν_n is the effective nuclear frequency and δr is the thickness of the reaction shell²⁶ (≈ 0.8 Å). For the reactions in this study $A_{11} A_{22}$ is taken to be $10^{25} \text{ dm}^6 \text{ mol}^{-2}$, while radii of 4.7 and 5.0 Å are used for the $[\text{Ru}(\text{CN})_6]^{3-}$ ion³⁴ and the reductants (5.5 Å for the disulphonate derivatives),²² respectively.

Using equation (9) the cross-reaction rate constants (from Table 2; k_a or k_{12} measured at $[\text{H}^+] = 0.1 \text{ mol dm}^{-3}$) were related to the thermodynamic driving forces of the reaction and a value for the electron self-exchange rate constant for the $[\text{Ru}(\text{CN})_6]^{3-/4-}$ couple may be determined. The self-exchange rate constants for the $\text{H}_2\text{Q}-\text{H}_2\text{Q}^{+}$ and $\text{HQ}^--\text{HQ}^{\cdot}$ couples have been estimated to be about $2 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ from direct measurements of the rate constants of several $\text{Q}^{2-}-\text{Q}^{\cdot-}$ exchange couples.³⁵ This value has been employed successfully

in several Marcus correlations with other transition-metal oxidants.²² Self-exchange rate constants of 1×10^5 and $1 \times 10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ have been calculated for the ascorbic acid couples, $\text{H}_2\text{A}-\text{H}_2\text{A}^{+}$ and $\text{HA}^--\text{HA}^{\cdot}$, respectively, from the application of Marcus relationship to a number of cross-reactions.^{24,36} The reduction potentials of the semiquinone and ascorbate radicals are listed in Table 1. The $[\text{Ru}(\text{CN})_6]^{3-/4-}$ self-exchange rate constants calculated from the cross-reactions using equation (9) fall in the range of 10^4 – $10^6 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ with a (geometric) mean value of $k_{11} = (1.0 \pm 0.8) \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$. The spread in the individual calculated k_{11} values may be due to some variations in the dihydroxybenzene-semiquinone self-exchange rate constants with the nature (charge and size) of the substituents. A correlation of the kinetic and thermodynamic parameters in the Marcus equation may be made by plotting $\ln(k_{12}/k_{22}^{1/2} W_{12})$ against $\ln(K_{12} f_{12})^{1/2}$ (Figure 3). The slope of this plot is found to be 0.87 ± 0.05 , reasonably close to the theoretical value of unity. The intercept, which corresponds to $\frac{1}{2} \ln k_{11}$, yields a value of $1.6 \times 10^4 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$, in agreement with the mean rate constant above, given the slope of less than unity in Figure 3.

The electron self-exchange rate constants for a number of organic and transition-metal complex couples have been predicted with reasonable success using the semi-classical model for electron transfer.^{26,37} The exchange rate constant k_{11} may be expressed as the product of a pre-equilibrium constant K_A , an effective nuclear frequency ν_n , an electronic factor κ_{el} , and a nuclear factor which contains terms for both inner-sphere (ΔG_{in}^{\ddagger}) and solvent reorganizations ($\Delta G_{out}^{\ddagger}$) as well as an inner-sphere nuclear tunnelling factor Γ_n [equation (13)].

$$k_{11} = K_A \nu_n \kappa_{el} \Gamma_n \exp[-(\Delta G_{in}^{\ddagger} + \Delta G_{out}^{\ddagger})/RT] \quad (13)$$

The inner-sphere term corresponds to the reorganization of bond distances and angles required prior to electron transfer and the outer-sphere term is the energy needed to change the orientations of the solvent molecules surrounding the reactants. The inner-sphere reorganization energy may be calculated with a knowledge of the bond distances and angles and vibrational frequencies and force constants for the two redox partners [equation (14)].

$$\Delta G_{in} = \frac{1}{2} \sum f_i [(\Delta d_0)_i / 2]^2 \quad (14)$$

While the Ru–C distance is known for the $[\text{Ru}(\text{CN})_6]^{4-}$ ion {2.082 Å in $\text{Mn}_2[\text{Ru}(\text{CN})_6] \cdot 8\text{H}_2\text{O}$ },³⁸ the instability of $[\text{Ru}(\text{CN})_6]^{3-}$ has precluded measurements of the Ru–C distance in this complex. An estimate of the change in the Ru–C bond distance upon intervalence electron transfer in the $[(\text{NC})_5\text{Ru}-\text{CN}-\text{Ru}(\text{NH}_3)_5]^-$ ion has recently been reported by the use of post-resonance-enhanced Raman scattering techniques.³⁹ For the terminal Ru–C bonds Δd_0 was calculated to be $\pm(0.035 \pm 0.007)$ Å from the Ru–C stretching frequency. The reduced Ru–C stretching force constant is taken to be 285 N m^{-1} {for the $[\text{Ru}(\text{CN})_6]^{4-}$ ion $f(\text{Ru}-\text{C})$ is 279 N m^{-1} ,^{40,41} from Raman data}. The inner-sphere reorganization barrier is calculated [equation (11)] to be $3.2 \pm 1.2 \text{ kJ mol}^{-1}$. The outer-sphere solvent reorganization barrier, $\Delta G_{out}^{\ddagger}$, may be calculated using a constant-volume ellipsoidal model^{34,42} [equation (15)]

$$\Delta G_{out}^{\ddagger} = \frac{(\Delta e)^2 \sigma^2}{8 r_a^2 r_b} \left(\frac{1}{D_{op}} - \frac{1}{D_s} \right) S(\lambda_0) \quad (15)$$

where σ is the distance between the metal centres and r_a and r_b ($= r_a + \sigma/2$) are the lengths of the minor and major semiaxes, respectively, of the ellipsoid, D_{op} and D_s are the optical and static dielectric constants of the solvent, and $S(\lambda_0)$ is a shape

Table 3. Parameters for electron-exchange reactions of low-spin d^5 - d^6 iron and ruthenium couples

Couple ^a	Δd_0 ^b /Å	σ /Å	I /mol dm ⁻³	k_{11} ^c /dm ³ mol ⁻¹ s ⁻¹	Ref.
[Ru(CN) ₆] ^{3-/4-}	0.035(7) ^d	9.4	0.10 (K ⁺)	2.1×10^4	16
[Fe(CN) ₆] ^{3-/4-}	0.026(10) ^e	9.0	0.10 (K ⁺)	1.6×10^4	45, f
[Ru(H ₂ O) ₆] ^{3+/2+}	0.09(2) ^g	6.5	5.0	2.0×10^1	46
[Ru(NH ₃) ₆] ^{3+/2+}	0.040(8) ^h	6.7	0.75	2.2×10^4	47
[Ru(en) ₃] ^{3+/2+}	0.022(20) ⁱ	8.4	0.75	3.1×10^4	48
[RuL ₂] ^{3+/2+}		8.6	0.10	5×10^4	49
[RuL ₂] ^{3+/2+}		9.0	0.10	1.2×10^5	50, j

^a L¹ = 1,4,7-triazacyclononane, L² = 3,6,10,13,16,19-hexa-azabicyclo[6.6.6]heicosane. ^b From X-ray structural data unless otherwise indicated (error limits in parentheses). ^c Directly measured self-exchange rate constants, unless otherwise indicated. ^d From Raman scattering measurements (ref. 39). ^e B. I. Swanson, S. I. Hamburg, and R. R. Ryan, *Inorg. Chem.*, 1974, **13**, 1685. ^f Extrapolated from data in refs. 4–6. ^g P. Bernhard, H.-B. Burgi, J. Hauser, H. Lehmann, and A. Ludi, *Inorg. Chem.*, 1982, **21**, 3936. ^h From data in H. C. Stynes and J. A. Ibers, *Inorg. Chem.*, 1971, **10**, 2304. ⁱ From data in P. J. Smolenaers, J. K. Beattie, and N. S. Hutchinson, *Inorg. Chem.*, 1981, **20**, 2202 and H. J. Peresie and J. A. Stanko, *Chem. Commun.*, 1970, 1674. ^j Self-exchange rate constant determined from Marcus cross-reaction correlations.

factor. Using $\sigma = 2r_a = 9.4$ Å, $S(\lambda_0) = 0.71$,^{26,42} the value of $\Delta G_{\text{out}}^\ddagger$ is calculated to be 28 kJ mol⁻¹. The nuclear frequency, $\nu_n = \{[(v_{\text{in}})^2 \Delta G_{\text{in}}^\ddagger + (v_{\text{out}})^2 \Delta G_{\text{out}}^\ddagger] / (\Delta G_{\text{in}}^\ddagger + \Delta G_{\text{out}}^\ddagger)\}^{1/2}$, is calculated to be 4.2×10^{12} s⁻¹ ($v_{\text{in}} = 427$ cm⁻¹,⁴⁰ $v_{\text{out}} = 30$ cm⁻¹), while K_A at an ionic strength of 0.10 mol dm⁻³ is 5.3×10^{-3} dm³ mol⁻¹. The nuclear tunnelling factor for this couple is calculated to be 1.2, close to unity as expected for transition-metal couples at room temperature in which reorganization involves low-frequency metal-ligand vibrations. A value of 0.2 has been estimated for the electronic factor, κ_e , for the [Ru(H₂O)₆]^{3+/2+}, [Ru(NH₃)₆]^{3+/2+}, and [Ru(en)₃]^{3+/2+}, (en = ethylenediamine) couples on the basis of electronic coupling energies of about 70 cm⁻¹,^{43,44} and will be used for the hexacyanoruthenate(II) and (III) couple. The predicted value of the electron-exchange rate constant for the [Ru(CN)₆]^{3-/4-} couple from the semi-classical model [equation (13)] is $(2 \pm 1) \times 10^4$ dm³ mol⁻¹ s⁻¹, in good agreement with the average of the rate constants determined from the application of the Marcus relationship to cross-reactions involving the couple. Recent direct measurements of the self-exchange rate constant in our laboratory, using ¹³C n.m.r. line-broadening measurements, $k_{11} = (8.3 \pm 0.4) \times 10^3$ dm³ mol⁻¹ s⁻¹, and further kinetic studies employing transition-metal cross-reactants ($k_{11} \approx 1 \times 10^4$ dm³ mol⁻¹ s⁻¹) have produced very similar values.¹⁶

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. The exchange rate constant for the [Fe(CN)₆]^{3-/4-} couple has been measured directly on several occasions⁴⁻⁶ and shows a marked dependence on the concentration and nature of the electrolyte cations in solution. Wherland and Gray⁴⁵ have extrapolated the reported data to yield $k_{11} = 1.5 \times 10^4$ dm³ mol⁻¹ s⁻¹ (25.0 °C) at $I = 0.10$ mol dm³ (K⁺). The self-exchange rate constants have been measured for a number of small ruthenium(II) and (III) aqua and amine couples⁴⁶⁻⁵⁰ and the values of k_{11} , along with Δd_0 and σ , are presented in Table 3. These ruthenium amine couples, along with [Ru(CN)₆]^{3-/4-}, feature small inner-sphere reorganization barriers associated with the transfer of an electron occupying a non-bonding t_{2g} orbital. The exchange rate constants increase with an increase in the value of σ (smaller $\Delta G_{\text{out}}^\ddagger$) and the value of k_{11} for the [Ru(CN)₆]^{3-/4-} couple is consistent with the other ruthenium systems of a similar size.

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