Kinetics of Reduction of $[Os(CN)_6]^{3-}$ Ion by Ascorbic Acid and Substituted 1,2- and 1,4-Dihydroxybenzenes in Acidic Media. Effects of β-Cyclodextrin Inclusion of the Reductant†

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The kinetics of reduction of the hexacyanoosmate(III) ion by ascorbic acid and several substituted 1,2- and 1,4-dihydroxybenzenes have been investigated in acidic aqueous media. A Marcus correlation between the cross-reaction rate constants and the semiquinone or ascorbate radical reduction potentials has been constructed, yielding a $[Os(CN)_6]^{4-/3-}$ self-exchange rate constant of 1.7×10^4 dm^3 mol^{-1} s^{-1}, in good agreement with the directly measured value. The effects of β-cyclodextrin (β-cd) inclusion of 1,2-dihydroxybenzene and 4-*tert*-butyl-1,2-dihydroxybenzene on the kinetics of electron transfer have been investigated. The rate constant for 4-*tert*-butyl-1,2-dihydroxybenzene ($K_{cd} = 2500 \pm 500$ dm^3 mol^{-1}) decreases from 150 to 72 dm^3 mol^{-1} s^{-1} upon β-cd inclusion. There is no observed change in the rate constant for the oxidation of 1,2-dihydroxybenzene (23 ± 1 dm^3 mol^{-1} s^{-1}) due to very weak inclusion ($K_{cd} = 14 \pm 3$ dm^3 mol^{-1}) in the β-cd cavity.

Kinetic and mechanistic studies of electron-transfer reactions of the $[M(CN)_6]^{4-/3-}$ couples of the iron triad have, until recently, been almost exclusively concerned with the M = Fe system.[1,2] The relatively few investigations involving the ruthenium and osmium couples include the oxidation of $[M(CN)_6]^{4-}$ by MnO_4^- [3,4] and the reduction of $[M(CN)_6]^{3-}$ by ferrocytochrome c,[5] as well as their use as reductive quenchers for excited-state tris(polypyridine)ruthenium species[6,7] and lanthanide-ion cryptates.[8] During the past several years, electron-transfer reactions involving the $[M(CN)_6]^{4-/3-}$ (M = Ru or Os) couples in aqueous media have been investigated in our laboratory.[9-11] The electron self-exchange rate constants for the ruthenium[9] and osmium[10] couples have been determined directly by means of ^{13}C NMR line-broadening techniques. The outer-sphere electron-transfer cross-reactions of $[Ru(CN)_6]^{4-/3-}$ with a variety of inorganic[9] and organic[11] species have been investigated and the kinetic data correlated in terms of the Marcus theory[12] relationship. Recently, we have undertaken similar kinetic studies on cross-reactions involving $[Os(CN)_6]^{4-/3-}$. The $[Os(CN)_6]^{3-}$ ion has a lower reduction potential (0.63 V) than that of $[Ru(CN)_6]^{3-}$ (0.92 V) and is more stable in acidic aqueous media. The lower potential allows for kinetic studies of $[Os(CN)_6]^{4-/3-}$ with a wider range of oxidants and reductants than was possible with the $[Ru(CN)_6]^{4-/3-}$ system.

Ascorbic acid and substituted 1,2- and 1,4-dihydroxybenzenes are well characterized two-electron reductants ($H_2Q \longrightarrow Q + 2H^+ + 2e^-$) which have been employed in a number of electron-transfer studies involving transition-metal oxidants[13-18] such as $[IrCl_6]^{2-}$,[13] $[Co(H_2O)_6]^{3+}$,[14] $[Rh_2(O_2CCH_3)_4(H_2O)_2]^+$,[15] and tris(polypyridine)metal(III) complexes of iron,[16,17] nickel,[17] copper,[18] ruthenium,[17] and osmium.[17] The rate-determining step in these reactions in acidic media is normally the one-electron oxidation to a semiquinone or ascorbate radical ($H_2Q^{\bullet+}$ or $HQ^{\bullet}$), followed by a second one-electron oxidation to the quinone or dehydroascorbic acid. Employing a series of the dihydroxybenzene reductants, bearing a variety of ring substituents, allows for the study of electron-transfer reactions over a wide range of thermodynamic driving forces. The kinetics of the electron-transfer reactions involving these reductants has also been measured previously as a function of pressure,[19] in mixed-solvent systems,[20] and in the presence of anionic and cationic micelles[21] and microemulsions.[22] Significant decreases in the rate constants from the value in water are observed in these non-aqueous and organized media.

In this paper we report the results of a kinetic and mechanistic study of the oxidation of ascorbic acid and several substituted 1,2- and 1,4-dihydroxybenzenes in acidic aqueous media. The Marcus theory relationship for outer-sphere electron-transfer reactions has been used to correlate the cross-reaction rate constants with the semiquinone and ascorbate radical reduction potentials. In addition, we have investigated the kinetic effects of the inclusion of two of the reductants, 1,2-dihydroxybenzene and 4-*tert*-butyl-1,2-dihydroxybenzene, in the cavity of β-cyclodextrin, a cyclic oligosaccharide[23] which is capable of including organic guest molecules,[24] *e.g.* dihydroxybenzenes,[25,26] in its toroidal hydrophobic cavity.

Experimental

Materials.—The hexacyanoosmate(II) salt, $K_4[Os(CN)_6]\cdot 3H_2O$, was prepared by the literature method.[27] Solutions of the hexacyanoosmate(III) anion were prepared by the oxidation of $[Os(CN)_6]^{4-}$ in 0.10 mol dm^{-3} $HClO_4$ by lead dioxide, followed by filtering off the excess of solid PbO_2. The concentrations of the $[Os(CN)_6]^{3-}$ solutions were determined spectrophotometrically at 328 ($\varepsilon = 1625$) and 400 nm ($\varepsilon = 1450$ dm^3 mol^{-1} cm^{-1})[4,28] using a Hewlett-Packard 8254A diode-array spectrophotometer. The substituted 1,2- and 1,4-dihydroxybenzenes and L-ascorbic acid (Aldrich, Fisher) were used as received. Solutions of the reductants, prepared in nitrogen-saturated 0.10 mol dm^{-3} $HClO_4$, were stable if used within 6 h. The β-cyclodextrin (Aldrich) was dried at 80 °C for at least 10 h prior to use.

Kinetics.—The kinetic studies were performed using a Cary 3 spectrophotometer for the slower reactions and a TDI

† *Supplementary data available* (SUP No. 56926, 8 pp.): first-order rate constants. See Instructions for Authors, *J. Chem. Soc., Dalton Trans.*, 1993, Issue 1, pp. xxiii–xxviii.

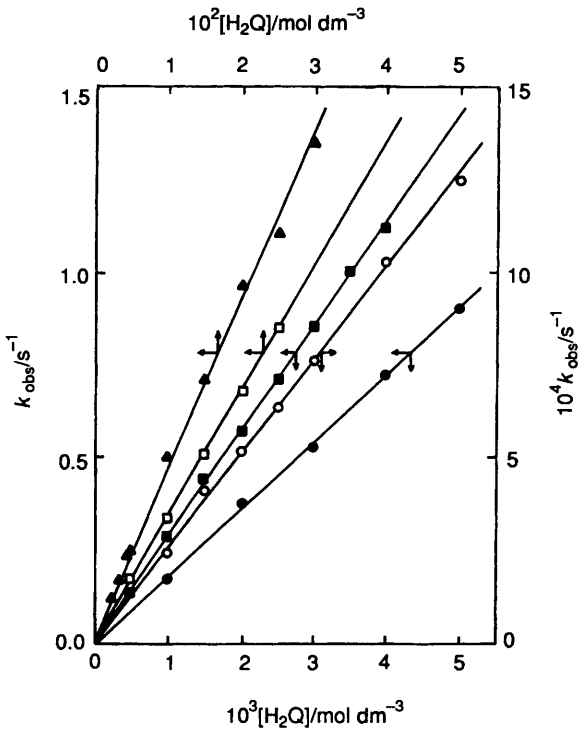

Fig. 1 Dependence of k_{obs} on the reductant concentration for the oxidation of ascorbic acid (●), 2,5-dihydroxybenzene-1,4-disulfonate (○), 4-*tert*-butyl-1,2-dihydroxybenzene (■), 2,5-dihydroxybenzoic acid (□) and 1,2-dihydroxybenzene (▲) by $[Os(CN)_6]^{3-}$ in 0.10 mol dm^{-3} $HClO_4$ at 25.0 °C

model IIA stopped-flow apparatus and data-acquisition system (Cantech Scientific) for the faster reactions. Reaction temperatures were controlled within 0.1 °C, over the range 10–40 °C, by means of external circulating baths. All measurements were made under pseudo-first-order conditions of an excess of the reductant, and plots of $\ln(A_t - A_\infty)$ (monitored at 412 nm) were linear for at least three half-lives. The reported first-order rate constants (SUP 56926) represent the average from four to six replicate runs. The acid-dependent reactions with ascorbic acid were studied in perchlorate media, with the ionic strength maintained at 0.10 mol dm^{-3} with added sodium perchlorate.

Stability Constant Calculations.—The stability constant K_{cd} and the estimated error for the β-cyclodextrin inclusion complex of 4-*tert*-butyl-1,2-dihydroxybenzene (H_2tbc) were determined from the electron-transfer kinetic measurements by the application of non-linear least squares and Simplex optimization programs to the expressions (1) and (12) for a 1 : 1 guest–host model.[29] The concentration of the inclusion complex [H_2tbc·cd] was determined from equation (1), in

$$[H_2tbc{\cdot}cd] = \tfrac{1}{2}\{B - (B^2 - 4[H_2tbc]_T[cd]_T)^{\frac{1}{2}}\} \quad (1)$$

which $B = ([H_2tbc]_T + [cd]_T + K_{cd}^{-1})$. The stability of the inclusion complexes of β-cd with 1,2-dihydroxybenzene and the quinone oxidation product tbc were calculated using equation (1) from ^{1}H NMR and UV/VIS titration measurements, respectively, as described previously.[29b]

Results

Kinetics.—The reduction of the $[Os(CN)_6]^{3-}$ ion by ascorbic acid and the substituted dihydroxybenzenes in 0.10 mol dm^{-3} $HClO_4$ results in the formation of the $[Os(CN)_6]^{4-}$ ion and dehydroascorbic acid or the appropriate quinone, respectively, according to the stoichiometry (2). With the reductants present

$$2[Os(CN)_6]^{3-} + H_2Q \longrightarrow 2[Os(CN)_6]^{4-} + Q + 2H^+ \quad (2)$$

in a pseudo-first-order excess [(0.5–50) × 10^{-3} mol dm^{-3}] over $[Os(CN)_6]^{3-}$ [(3–6) × 10^{-5} mol dm^{-3}], the observed first-order rate constants exhibited a first-order dependence on $[H_2Q]$, as shown in Fig. 1. The rate law for the two-electron oxidation of H_2Q is given by equation (3), where k_{12} is the second-order

$$-d[Os(CN)_6^{3-}]/dt = 2k_{12}[Os(CN)_6^{3-}][H_2Q] \quad (3)$$

rate constant for the rate-determining one-electron oxidation by the $[Os(CN)_6]^{3-}$ ion, equation (4). The semiquinone

$$[Os(CN)_6]^{3-} + H_2Q \xrightarrow{k_{12}} [Os(CN)_6]^{4-} + H_2Q^{\cdot+} \quad (4)$$

radical ($pK_r < -1$) is rapidly oxidized to the quinone by a second $[Os(CN)_6]^{3-}$ ion, equation (5). The second-order

$$[Os(CN)_6]^{3-} + HQ^{\cdot} \xrightarrow{fast} [Os(CN)_6]^{4-} + Q + H^+ \quad (5)$$

rate constants and activation parameters determined for 1,2-dihydroxybenzene, 4-*tert*-butyl-1,2-dihydroxybenzene, 2,5-dihydroxybenzoic acid, and the 2,5-dihydroxybenzene-1,4-disulfonate dianion are presented in Table 1.

The first acid dissociation constant for ascorbic acid (pK_1 = 4.03)[17] is considerably larger than the corresponding values for the deprotonation of the hydroxyl groups on the 1,2- and 1,4-dihydroxybenzenes employed in this study (pK_1 values range from 9 to 11).[13] Protonation of the oxidant $[Os(CN)_6]^{3-}$ does not occur at pH 1.[10] While the rate constants for the oxidation of the dihydroxybenzenes by transition-metal complexes are relatively independent of acid concentration below pH 2, the rate constant for the oxidation of ascorbic acid displays a significant inverse dependence on acid concentration, consistent with the reaction scheme in equations (6)–(8). The rate-

$$H^2A \rightleftharpoons HA^- + H^+ \quad (6)$$

$$[Os(CN)_6]^{3-} + H_2A \xrightarrow{k_a} [Os(CN)_6]^{4-} + H_2A^{\cdot+} \quad (7)$$

$$[Os(CN)_6]^{3-} + HA^- \xrightarrow{k_b} [Os(CN)_6]^{4-} + HA^{\cdot} \quad (8)$$

determining one-electron oxidations of H_2A or HA^- are followed by a rapid second one-electron oxidation of the ascorbate radical. Under conditions where $[H^+] \gg K_1$, the second-order rate constant k_H may be expressed in terms of k_a, k_b and K_1 by equation (9). The rate constants k_a and k_b were

$$k_H = k_a + k_bK_1[H^+]^{-1} \quad (9)$$

calculated from the intercepts and slopes, respectively, of the plots of k_H against $[H^+]^{-1}$ in Fig. 2. The acid dissociation constants for H_2A, 10^5K_1 = 0.62 (10.1), 0.77 (18.1), 0.93 (25.0), 1.1 (32.0) and 1.4 mol dm^{-3} (40.0 °C), were extrapolated from reported values for an ionic strength of 0.10 mol dm^{-3} maintained with sodium perchlorate.[13b] The rate constant for the conjugate-base reductant, k_b, is 700 times greater than the value of k_a for H_2A. This enhanced reactivity of ascorbate anion may be related to the lower reduction potential of the $HA^{\cdot}$–HA^- couple (0.72 V) compared to that of $H_2A^{\cdot+}$–H_2A (1.19 V).[17] The differences in the semiquinone radical reductions are also responsible for the trend in the rate constants (Table 1) determined for 1,2-dihydroxybenzene (1.12 V), 4-*tert*-butyl-1,2-dihydroxybenzene (1.09 V), 2,5-dihydroxybenzoic acid (1.23 V), and 2,5-dihydroxybenzene-1,4-disulfonate (1.34 V).[11,26] The

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

Reductant	k_{12}[a]/dm^3 mol^{-1} s^{-1}	$\Delta H^{\ddagger}$/kJ mol^{-1}	$\Delta S^{\ddagger}$/J K^{-1} mol^{-1}
Ascorbic acid	(5.8 ± 0.2) × 10[1b]	40.8 ± 6.5	−74 ± 19
Ascorbate anion	(3.6 ± 0.1) × 10[4b]	6.0 ± 2.0	−138 ± 6
1,2-Dihydroxybenzene	(2.28 ± 0.15) × 10	19.4 ± 2.5	−154 ± 7
4-*tert*-Butyl-1,2-dihydroxybenzene	(1.46 ± 0.05) × 10^2	19.3 ± 3.7	−138 ± 10
{H_2tbc·β-cd}	(0.72 ± 0.05) × 10^2	17.9 ± 3.2	−149 ± 9
2,5-Dihydroxybenzoic acid	(1.71 ± 0.02) × 10	30.0 ± 1.7	−121 ± 5
2,5-Dihydroxybenzene-1,4-disulfonate	(1.29 ± 0.05) × 10^{-2}	39.5 ± 5.9	−129 ± 18

[a] At 25.0 °C, $[H^+]$ = 0.10 mol dm^{-3}, except as noted. [b] Values of k_a and k_b calculated as described in the text.

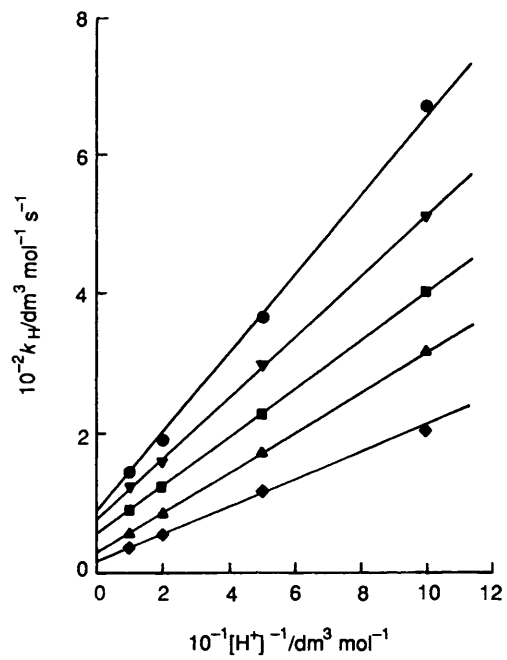

Fig. 2 Dependence of k_H on $[H^+]^{-1}$ for the oxidation of ascorbic acid by $[Os(CN)_6]^{3-}$ at 10.1 (◆), 18.1 (▲), 25.0 (■), 32.0 (▼) and 40.0 °C (●) [I = 0.10 mol dm^{-3} (H/Na)ClO_4]

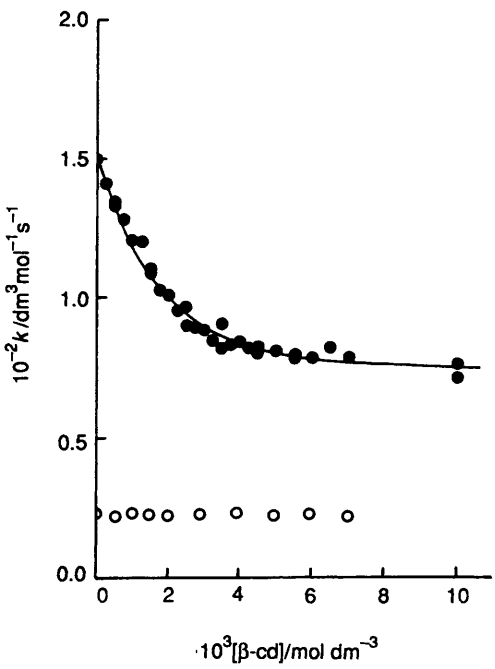

Fig. 3 Dependence of k on [β-cd] for the oxidations of 1,2-dihydroxybenzene (○) and 4-*tert*-butyl-1,2-dihydroxybenzene (●) by $[Os(CN)_6]^{3-}$ in 0.10 mol dm^{-3} $HClO_4$ at 25.0 °C

oxidations of the 1,2- and 1,4-dihydroxybenzenes and ascorbic acid display low enthalpies and moderately large negative entropies of activation (Table 1), in the same ranges as for the oxidation of these compounds by other outer-sphere oxidants, such as $[Ru(CN)_6]^{3-}$,[11] $[IrCl_6]^{2-}$,[13] and tris(polypyridine)-iron(III) complexes.[16]

Effects of Cyclodextrin Inclusion.—4-*tert*-Butyl-1,2-dihydroxybenzene (H_2tbc) forms an inclusion complex with β-cyclodextrin [equation (10)] in aqueous solution. The stability

$$H_2tbc + \beta\text{-cd} \overset{K_{cd}}{\rightleftharpoons} \{H_2tbc\cdot\beta\text{-cd}\} \quad (10)$$

constant K_{cd} had been determined previously in our laboratory to be (9.5 ± 2.1) × 10^3 dm^3 mol^{-1} (25 °C, 0.10 mol dm^{-3} $DClO_4$) by means of ^{1}H NMR chemical shift titrations of H_2tbc with β-cd and of β-cd with H_2tbc.[26] The parent 1,2-dihydroxybenzene binds much less strongly with a value of K_{cd} = 14 ± 3 dm^3 mol^{-1} determined by this method (monitoring the H^3 and H^5 protons of β-cyclodextrin) under the same conditions. A value of 109 ± 3 dm^3 mol^{-1} has been reported by Cai *et al.*[25] at 20 °C, with no added electrolytes, from ^{1}H NMR measurements. The lower value determined in this study is consistent with an expected decrease in binding constants with an increase in temperature[24] and the presence of perchlorate ions,[30] which inhibit the guest–host inclusion. The product of the oxidation of H_2tbc, the quinone tbc, binds much less strongly than the reduced form, with K_{cd} = 930 ± 100 dm^3 mol^{-1} from UV/VIS spectrophotometric titrations (420 nm, isosbestic point at 337 nm) in 0.10 mol dm^{-3} $HClO_4$ at 25.0 °C. With its lower binding constant and small concentration ($\leqslant \frac{1}{2}[Os(CN)_6^{3-}]_t$ during the course of the reaction) relative to the pseudo-first-order excesses of H_2tbc used, the binding of the oxidation product is expected to have a negligible effect on the binding of the reductant.

The rate constant for the oxidation of H_2tbc (2.0 × 10^{-3} mol dm^{-3}) by $[Os(CN)_6]^{3-}$ decreases with an increase in the concentration of β-cd (up to 1.0 × 10^{-2} mol dm^{-3}) in solution, as shown in Fig. 3. The rate constant for the oxidation of 1,2-dihydroxybenzene, however, is unaffected by the presence of β-cyclodextrin and remains constant at 23 ± 1 dm^3 mol^{-1} s^{-1}. The diminution of the rate constant for H_2tbc may be related to a second pathway involving the oxidation of a β-cyclodextrin-included reductant, equation (11). The observed second-order

$$[Os(CN)_6]^{3-} + \{H_2tbc\cdot\beta\text{-cd}\} \xrightarrow{k_2} [Os(CN)_6]^{4-} + \{H_2tbc\cdot\beta\text{-cd}\}^{\bullet+} \quad (11)$$

rate constant may be expressed in terms of the rate constants k_1 (in the absence of β-cd) and k_2, as given in equation (12).

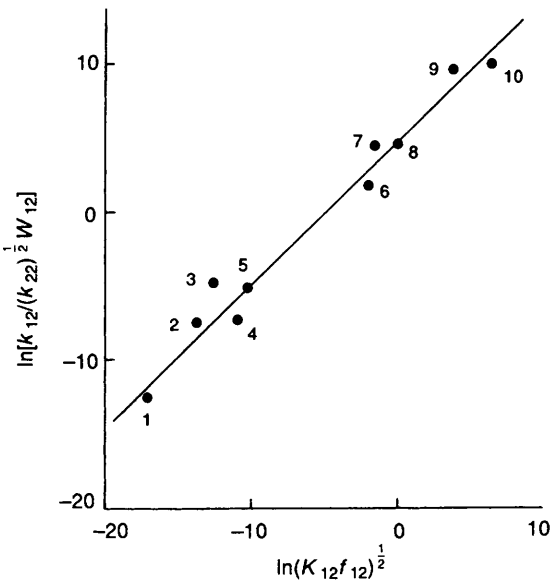

Fig. 4 Plot of $\ln[k_{12}/(k_{22})^{\frac{1}{2}}W_{12}]$ against $\ln(K_{12}f_{12})^{\frac{1}{2}}$ for the reduction of $[Os(CN)_6]^{3-}$ by 2,5-dihydroxybenzene-1,4-disulfonate (1), 2,5-dihydroxybenzoic acid (2), ascorbic acid (3), 1,2-dihydroxybenzene (4), 4-*tert*-butyl-1,2-dihydroxybenzene (5), ascorbate anion (6), $[Os(CN)_6]^{4-}$ (8) and ferrocytochrome c (10), and the oxidations of $[Os(CN)_6]^{4-}$ by $[MnO_4]^-$ (7) and $[*Ru(bipy)_3]^{2+}$ (9)

$$k = \frac{k_1[H_2tbc] + k_2[\{H_2tbc\cdot\beta\text{-cd}\}]}{[H_2tbc]_T} \quad (12)$$

A non-linear least-squares fit of the kinetic data by equations (1) and (12) yields rate constants of $k_1 = 150 \pm 6$ dm^3 mol^{-1} s^{-1} and $k_2 = 72 \pm 5$ dm^3 mol^{-1} s^{-1}, with $K_{cd} = (2.5 \pm 0.5) \times 10^3$ dm^3 mol^{-1}.

Discussion

The cross-reactant rate constants for the outer-sphere reductions of the $[Os(CN)_6]^{3-}$ ion by organic reductants in this study span a range of five orders of magnitude, owing to the differences in the semiquinone and ascorbate radical reduction potentials. The kinetic parameters determined for the reactions in the present study may be correlated in terms of the Marcus theory equation,[12] 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} [equations (13)–(16)].[31] In the above

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{\frac{1}{2}}W_{12} \quad (13)$$

$$\ln f_{12} = \frac{[\ln K_{12} + (w_{12} - w_{21})/RT]^2}{4\left[\ln\left(\frac{k_{11}k_{22}}{A_{11}A_{22}}\right) + \frac{w_{11} + w_{22}}{RT}\right]} \quad (14)$$

$$W_{12} = \exp[-(w_{12} + w_{21} - w_{11} - w_{22})/2RT] \quad (15)$$

$$w_{ij} = \frac{z_iz_je^2}{D_s\sigma_{ij}(1 + \beta\sigma_{ij}I^{\frac{1}{2}})} \quad (16)$$

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 relative permittivity of the medium, $\beta = (8\pi Ne^2/1000D_skT)^{\frac{1}{2}}$, 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 shell (≈ 0.8 Å). For the reactions in this study $A_{11}A_{22}$ is taken to be 10^{25} dm^6 mol^{-2}, while radii of 4.7 and 5.0 Å are used for the $[Os(CN)_6]^{3-}$ ion and the reductants (5.5 Å for the disulfonate derivative) respectively.

The electron self-exchange rate constants (k_{22}) for the H_2Q–$H_2Q^{\cdot+}$ and HQ^-–$HQ^{\cdot}$ couples (1,2- and 1,4-dihydroxybenzenes) have been estimated to be about 2×10^6 dm^3 mol^{-1} s^{-1} from direct measurements of the rate constants of several Q^{2-}–$Q^{\cdot-}$ exchange couples.[32] Self-exchange rate constants of 1×10^5 dm^3 mol^{-1} s^{-1} have been calculated for the ascorbic acid and ascorbate ion couples from the application of the Marcus theory relationship to a number of cross-reactions involving primarily metal complexes.[17,33]

In terms of the Marcus theory equation, the kinetic and thermodynamic parameters may be correlated by plotting $\ln[k_{12}/(k_{22})^{\frac{1}{2}}W_{12}]$ against $\ln(K_{12}f_{12})^{\frac{1}{2}}$, as shown in Fig. 4. Also included are points corresponding to the reduction of $[*Ru(bipy)_3]^{2+}$ (bipy = 2,2′-bipyridine) ($E^\circ = 0.84$ V, $k_{22} = 1 \times 10^8$ dm^3 mol^{-1} s^{-1})[34] by $[Os(CN)_6]^{4-}$ ($k_{12} = 3.0 \times 10^9$ dm^3 mol^{-1} s^{-1}, $I = 0.3$ mol dm^{-3}),[8] the oxidation of ferrocytochrome c ($E^\circ = 0.26$ V, $k_{22} = 1.2 \times 10^4$ dm^3 mol^{-1} s^{-1})[35] by $[Os(CN)_6]^{3-}$ ($k_{12} = 3.6 \times 10^8$ dm^3 mol^{-1} s^{-1}, $I = 0.11$ mol dm^{-3}),[5] the reduction of $[MnO_4]^-$ ($E^\circ = 0.56$ V, $k_{22} = 3.8 \times 10^3$ dm^3 mol^{-1} s^{-1})[36] by $[Os(CN)_6]^{4-}$ ($k_{12} = 7.0 \times 10^3$ dm^3 mol^{-1} s^{-1}, $I = 1.0$ mol dm^{-3}),[4] and the directly measured self-exchange reaction of the $[Os(CN)_6]^{4-/3-}$ couple [$k_{11} = 1.0 \times 10^4$ dm^3 mol^{-1} s^{-1}, $I = 0.1$ mol dm^{-3} (Na^+)].[10] A linear least-squares fit of the kinetic and equilibrium parameters for the cross-reactions, as presented in Fig. 4, yields a slope of 0.96 ± 0.06, close to the theoretical value of unity. From the intercept, equal to $\frac{1}{2}\ln(k_{11})$, a self-exchange rate constant of $k_{11} = 1.7 \times 10^4$ dm^3 mol^{-1} s^{-1} is calculated for the $[Os(CN)_6]^{4-/3-}$ couple, in good agreement with the directly measured value.

The electron-transfer kinetic measurements support the NMR observations that a very favourable inclusion of 4-*tert*-butyl-1,2-dihydroxybenzene in the cavity of β-cyclodextrin occurs in aqueous solution as a result of the hydrophobic 4-Bu^t substituent. The more hydrophilic 1,2-dihydroxybenzene guest is very weakly included, such that no change in the electron-transfer rate constant is observed up to [β-cd] = 7×10^{-3} mol dm^{-3} (only 9% of the reductant included at this concentration). The two most reasonable explanations for a decrease in the rate constant for the 4-*tert*-butyl-1,2-dihydroxybenzene upon inclusion of the reductant would be a change in the reduction potential for the $H_2tbc^{\cdot+}/H_2tbc$ couple and/or a reduction in the overlap of the donor and acceptor orbitals on the H_2tbc and $[Os(CN)_6]^{3-}$ species, respectively. The cyclic voltammographs of H_2tbc (0.10 mol dm^{-3} $HClO_4$) exhibit two-electron oxidation-reduction processes the peak potentials of which are independent of the concentration of β-cd.[26] The decrease in the rate constant therefore appears to result from the cyclodextrin host hindering the close approach of the $[Os(CN)_6]^{3-}$ ion to the reductant in the precursor complex. The electron transfer must take place over a longer distance, with poorer overlap between the π-donor orbitals on H_2tbc and the d_π acceptor orbitals on the oxidant. Decreases in the rate constants for the oxidation of substituted 1,2-dihydroxybenzenes by metal complexes have been observed in other organized media, such as micelles[21] and microemulsions,[22] as well as in aqueous–organic solvents.[20]

The inclusion stability constant determined for the $\{H_2tbc\cdot\beta\text{-cd}\}$ complex from the kinetic measurements in this study, $(2.5 \pm 0.5) \times 10^3$ dm^3 mol^{-1}, is smaller than the corresponding values of (8–10) $\times 10^3$ dm^3 mol^{-1}, calculated from ^{1}H NMR titrations and from the kinetics of the oxidations of H_2tbc by $[IrCl_6]^{2-}$, bis(1,4,7-triazacyclononane)nickel(III), and diaqua(1,4,8,11-tetraazacyclotetradecane)nickel(III).[26] The rate constants for the oxidations of H_2tbc by the iridium(IV) and nickel(III) complexes were also observed to decrease more substantially ($k_2/k_1 \approx 5$) than for $[Os(CN)_6]^{3-}$ ($k_2/k_1 \approx 2$) upon β-cd inclusion of the reductant. It is not clear why $[Os(CN)_6]^{3-}$ ion would be less affected by the inclusion of the reductant than these other oxidants. Possible sources of the

differences may lie in the thermodynamic driving forces for the redox reactions and in the nature of the donor–acceptor interactions and the preferred orientations of the reactants in the precursor complexes prior to electron transfer. Further kinetic investigations of the outer-sphere oxidation of dihydroxybenzenes and related reductants by other transition-metal complexes in the presence of α- and β-cyclodextrins, and *o*-methylated derivatives thereof, are in progress in our laboratory, to explore the relationships between the nature of the reactants and the effects of the cyclodextrin inclusions.

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