Kinetics of the Reduction of a Tetra-μ-acetato-dirhodium Cation by Substituted 1,2- and 1,4-Dihydroxybenzene Compounds in Aqueous Perchlorate Media

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The kinetics of the reduction of the tetra-μ-acetato-dirhodium cation, $[Rh_2(O_2CCH_3)_4(OH_2)_2]^+$ ($[Rh_2]^+$), by substituted 1,2- and 1,4-dihydroxybenzene compounds (H_2Q) have been investigated in aqueous perchlorate media. The observed rate equation (below) is interpreted in terms of a rate-

$$-d[Rh_2^+]/dt = 2(k_1 + k_2K_1/[H^+])[Rh_2^+][H_2Q]$$

determining one-electron oxidation of H_2Q or HQ^- to a semiquinone radical intermediate. The rate constants for the cross-reactions are correlated with the semiquinone reduction potentials by means of the Marcus relationship. Self-exchange rate constants for the dihydroxybenzene/semiquinone and semiquinone/quinone couples are discussed in terms of the inner-sphere and solvent reorganization energies for electron exchange.

The chemistry of dimeric rhodium(II) complexes containing bridging carboxylate ligands has been the subject of considerable research during the last two decades.[1,2] In addition to investigations of their interesting structural and spectroscopic properties, these complexes have been employed as catalysts[3] and potential antitumour agents.[4] Dirhodium(II) carboxylate complexes, such as $[Rh_2(O_2CCH_3)_4(OH_2)_2]$ may be chemically or electrochemically oxidized to mixed-valence cations in which the unpaired electron is delocalized between the two rhodium atoms. In contrast to rather extensive electrochemical studies of $[Rh_2(O_2CR)_4L_2]^{0/+}$ couples (L = neutral ligand), which have characterized the dependence of the reduction potentials on the nature of the bridging RCO_2^- and axial L groups,[5,6] less attention has been paid to the chemical redox reactions of the dirhodium carboxylates.[7,8]

We have recently reported[7] the results of a kinetic investigation of a series of outer-sphere electron-transfer reactions involving the $[Rh_2(O_2CCH_3)_4(OH_2)_2]^{0/+}$ couple. An application of the Marcus relationship for electron-transfer processes to the cross-reaction data yielded a self-exchange rate constant of 1.5×10^5 dm^3 mol^{-1} s^{-1} for the $[Rh_2(O_2CCH_3)_4(OH_2)_2]^{0/+}$ couple. This moderately rapid rate of electron exchange could be rationalized in terms of small inner-sphere and solvent reorganization barriers to electron self-exchange. The $[Rh_2(O_2CCH_3)_4(OH_2)_2]^+$ cation, with relatively labile axial water ligands, has also been observed to undergo inner-sphere reductions with suitable reactants such as the Br^- ion.[8a]

The compounds 1,2- and 1,4-dihydroxybenzene, and their substituted derivatives (H_2Q), are well characterized two-electron reductants ($H_2Q \longrightarrow Q + 2H^+ + 2e^-$) which are important in biological electron-transport systems.[9] These compounds have frequently been employed in redox reactions with transition metal ions[10,11] and complexes,[12–15] undergoing two one-electron oxidations to the quinone *via* inner-sphere or outer-sphere electron-transfer mechanisms, depending on the nature of the oxidant. Derivatization of the parent species (H_2Q) with various ring substituents results in reducing agents covering a wide range of semiquinone ($Q^{\cdot-}$) reduction potentials.

In this paper the results of a study of the kinetics and mechanism of the reduction of the $[Rh_2(O_2CCH_3)_4(OH_2)_2]^+$ cation by substituted 1,2- and 1,4-dihydroxybenzenes in aqueous perchlorate media are presented. The Marcus relationship has been used to correlate the cross-reaction rate constants with the semiquinone reduction potentials. The derived self-exchange rate constants for the $H_2Q/H_2Q^{\cdot+}$ couples are discussed in terms of inner-sphere and solvent reorganization barriers to electron exchange.

Experimental

Materials.—Tetra-μ-acetato-dirhodium(II) $[Rh_2(O_2CCH_3)_4]$ (Aldrich), was used as received. Acidic perchlorate solutions of the pink $[Rh_2(O_2CCH_3)_4(OH_2)_2]^+$ cation were prepared by either electrochemical oxidation at a platinum electrode, or by oxidation using solid PbO_2, followed by filtration through a fine glass frit. The rhodium dimer concentrations were determined by measurements on a Perkin-Elmer 552 spectrophotometer: for $[Rh_2(O_2CCH_3)_4(OH_2)_2]$, $\lambda_{max.}$ = 585 nm (ε = 241 dm^3 mol^{-1} cm^{-1}); for $[Rh_2(O_2CCH_3)_4(OH_2)_2]^+$, $\lambda_{max.}$ = 515 nm (ε = 308 dm^3 mol^{-1} cm^{-1}) and 758 nm (ε = 298 dm^3 mol^{-1} cm^{-1}).[16]

The 3-COOH, 4-COOH, 4-NO_2 (Aldrich), and 3,5-$(SO_3H)_2$ (Fisher) derivatives of 1,2-dihydroxybenzene, and the 2-COOH, 2-$COCH_3$, 2,5-$(SO_3K)_2$, and 2,3-$(CN)_2$ (Aldrich) derivatives of 1,4-dihydroxybenzene were used as received. Solutions of the reductants were prepared using nitrogen-saturated distilled water just prior to their use in kinetic experiments. Lithium perchlorate was prepared by the neutralization of perchloric acid with lithium carbonate followed by repeated recrystallizations from distilled water.

Kinetic Measurements.—The kinetic studies were made 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 Sinclair ZX81 microcomputer. All measurements were made under pseudo-first-order conditions of excess reductant concentrations 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 6—8 replicate experiments, monitored at 515 nm. The reactions were studied in aqueous acidic perchlorate media with the ionic strength maintained at 0.10 mol dm^{-3} or 1.00 mol dm^{-3} with added lithium perchlorate.

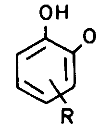
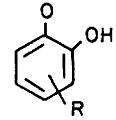
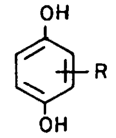
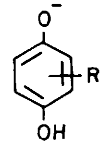
Results

The stoicheiometries of the reduction of the $[Rh_2(O_2CCH_3)_4(OH_2)_2]^+$ cation (abbreviated as $[Rh_2]^+$) by the substituted 1,2- and 1,4-dihydroxybenzene compounds (H_2Q) were determined by spectrophotometric titrations, monitored at 585 nm or 755 nm. For the majority of the reductants in this study (Table 1) the ratio of $[Rh_2]^+$ consumed to H_2Q added was (2.00 ± 0.05): 1.00 such that the overall reaction may be written as in equation (1), where Q is the corresponding 1,2- or 1,4-

$$2[Rh_2]^+ + H_2Q \longrightarrow 2[Rh_2]^0 + Q + 2H^+ \qquad (1)$$

benzoquinone and $[Rh_2]^0$ is the neutral complex. Exceptions to this stoicheiometric ratio were observed in the reactions of $[Rh_2(O_2CCH_3)_4(OH_2)_2]^+$ with the 2,3-, 2,5-, and 3,4-dihydroxybenzoic acids. With these reductants the two-electron oxidation product Q–COOH underwent a further two-electron oxidation as an overall 4:1 ratio of $[Rh_2]^+$ to H_2Q was observed. This stoicheiometry, along with spectroscopic studies of the products, are suggestive of an oxidative decarboxylation [equation (2)] occurring after the initial two-electron oxidation.

Table 1. Properties of the reductants employed in the reductions of the $[Rh_2(O_2CCH_3)_4(OH_2)_2]^+$ ion

	Reductant	R	pK[a]	E^0/V[b]
(1)		3-COOH	10.06 (0.1)	1.36
(2)		4-COOH	8.83 (0.1)	1.38
(3)		4-NO$_2$	6.69 (0.1)[c]	1.46
(4)		3,5-(SO$_3^-$)$_2$	7.62 (0.1)	1.47
(5)		3,5-(SO$_3^-$)$_2$	12.5 (0.1)	0.89
(6)		4-NO$_2$	10.85 (0.1)	0.94
(7)		2-COOH	10.0 (0.5)	1.23
(8)		2-COCH$_3$		1.32
(9)		2,5-(SO$_3^-$)$_2$		1.34
(10)		2,3-(CN)$_2$	5.5[d]	1.42
(11)		2,3-(CN)$_2$	8.0[d]	0.97

[a] A. E. Martell and R. M. Smith, 'Critical Stability Constants,' Plenum Press, New York, 1982, vol. 5, pp. 342—347. Ionic strength is given in parentheses. [b] One-electron reduction potentials (*vs.* n.h.e.) for $H_2Q^{\cdot+} + e^- \longrightarrow H_2Q$ or $HQ^{\cdot} + e^- \longrightarrow HQ^-$, calculated as described in the text. [c] $\Delta H^0 = 24.0$ kJ mol^{-1}, $\Delta S^0 = -48$ J K^{-1} mol^{-1}. [d] R. G. Brown and G. Porter, *J. Chem. Soc., Faraday Trans. 1*, 1977, 1281.

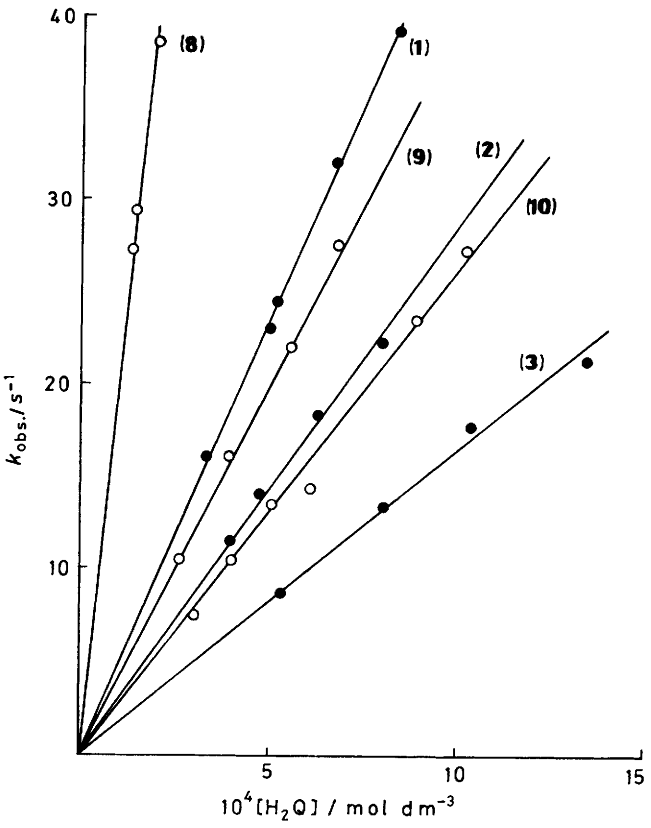


Figure 1. Dependences of $k_{obs.}$ on the dihydroxybenzene concentration for the reduction of $[Rh_2(O_2CCH_3)_4(OH_2)_2]^+$ in 1.00 mol dm^{-3} perchloric acid. The reductants are numbered as in Table 1

Table 2. Rate constants and activation parameters for the reductions of the $[Rh_2(O_2CCH_3)_4(OH_2)_2]^+$ ion by substituted 1,2- and 1,4-dihydroxybenzenes

Reductant[a]	$k_{12}^{obs.\,b}$/ dm^3 mol^{-1} s^{-1}	$\Delta H^{\ddagger\,c}$/ kJ mol^{-1}	$\Delta S^{\ddagger\,d}$/ J K^{-1} mol^{-1}	ln K_{12}	$k_{12}^{calc.\,e}$/ dm^3 mol^{-1} s^{-1}
(1)	2.36×10^4	43.8	−14	−5.45	3.2×10^4
(2)	1.45×10^4	38.6	−35	−6.23	2.1×10^4
(3)	8.20×10^3	46.6	−14	−9.34	3.6×10^3
	6.50×10^3 (0.10)	44.5	−23		
(4)	8.15×10^3	43.6	−24	−9.73	5.5×10^3
	1.37×10^4 (0.10)				
(5)	3.0×10^9 (0.10)			14.4	1.4×10^9
(6)	6.6×10^8 (0.10)	22.4	−1	12.5	1.9×10^8
(7)	1.34×10^5	33.9	−33	−0.39	4.5×10^5
(8)	9.93×10^4	46.9	+8	−3.89	7.4×10^4
(9)	2.05×10^4	42.8	−19	−4.67	6.6×10^4
(10)	1.32×10^4	46.9	−9	−7.79	8.7×10^3
	1.09×10^4 (0.10)				
(11)	2.2×10^8 (0.10)			11.3	1.1×10^8

[a] Numbered as in Table 1. [b] At 25.0 °C, I = 1.00 mol dm^{-3} unless otherwise indicated (in parentheses). [c] Uncertainty is ±2.0 kJ mol^{-1}. [d] Uncertainty is ±8 J K^{-1} mol^{-1}. [e] Calculated using $k_{11} = 2.0 \times 10^6$ dm^3 mol^{-1} s^{-1} for $H_2Q^{\cdot+}/H_2Q$ and $HQ^{\cdot}/HQ^-$, and $k_{22} = 1.5 \times 10^5$ dm^3 mol^{-1} s^{-1} for $[Rh_2(O_2CCH_3)_4(OH_2)_2]^{+/0}$ (see text).

$$2[Rh_2]^+ + Q\text{–}COOH \longrightarrow 2[Rh_2]^0 + Q\text{–}OH + CO_2 + 2H^+ \quad (2)$$

The kinetics and mechanism of this secondary process with $[Rh_2]^+$ and other metal oxidants are presently under investigation.

Kinetics.—The kinetics of the oxidation of a series of substituted 1,2- and 1,4-dihydroxybenzene compounds by $[Rh_2(O_2CCH_3)_4(OH_2)_2]^+$ were studied at several temperatures in 1.00 mol dm^{-3} perchloric acid. With the reductant present in excess the pseudo-first-order rate constants exhibited a first-order dependence on $[H_2Q]$, as shown in Figure 1. The rate law for the stoicheiometric two-electron oxidation of H_2Q is given by equation (3).

$$-d[Rh_2{}^+]/dt = 2k_{12}[Rh_2{}^+][H_2Q] \quad (3)$$

The rate constant k_{12} and the corresponding enthalpies and entropies of activation for the reactions are presented in Table 2. Similar values of $\Delta H^\ddagger$ (30—50 kJ mol^{-1}) and $\Delta S^\ddagger$ (-40 to $+10$ J K^{-1} mol^{-1}) have been reported for the oxidation of these compounds by cationic metal complexes.[10,12] The rate constants determined for the oxidation of the neutral reductants 1,2-dihydroxy-4-nitrobenzene and 1,2-dicyano-3,6-dihydroxybenzene change little between ionic strengths of 0.10 mol dm^{-3} and 1.00 mol dm^{-3} (Table 2) while for 4,5-dihydroxybenzene-1,3-disulphonate the expected decrease in rate constant with increasing ionic strength is observed. Attempts to study the kinetics of the oxidation of the parent 1,2- and 1,4-dihydroxybenzenes revealed that the reactions were too rapid ($k_{12} \geqslant 10^7$ dm^3 mol^{-1} s^{-1}) to be followed by the stopped-flow technique.

With electron-withdrawing substituents such as $-NO_2$, $-SO_3{}^-$, and –CN, the acidity of the reductants is increased substantially from that of the parent species (pK_1 = 9.24 and 9.85 for 1,2- and 1,4-dihydroxybenzene, respectively).[17,18] The rate constants for the oxidation of the deprotonated HQ^- anion species by $[Rh_2]^+$ were determined from a study of the dependence of the redox rate constants on $[H^+]$ in acidic perchlorate media. In the range $[H^+]$ = 0.0050—0.100 mol dm^{-3}, the second-order rate constants displayed an inverse dependence on the acid concentration. Figure 2 illustrates this dependence for the 4-NO_2 and 3,5-$(SO_3)_2$ derivatives of 1,2-dihydroxybenzene and for 1,2-dicyano-3,6-dihydroxybenzene at 25.0 °C and an ionic strength of 0.10 mol dm^{-3}. The results are consistent with the reaction scheme in equations (4)—(7), in

$$H_2Q \overset{K_1}{\rightleftharpoons} HQ^- + H^+ \quad (4)$$

$$[Rh_2]^+ + H_2Q \xrightarrow{k_a} Rh_2 + H_2Q^{\bullet +} \quad (5)$$

$$[Rh_2]^+ + HQ^- \xrightarrow{k_b} Rh_2 + HQ^\bullet \quad (6)$$

$$[Rh_2]^+ + HQ^\bullet \xrightarrow{\text{fast}} Rh_2 + Q + H^+ \quad (7)$$

which the rate-determining one-electron oxidations of H_2Q or HQ^- are followed by a rapid second one-electron oxidation of the semiquinone radical $HQ^\bullet$ (pK for $H_2Q^{\bullet +}$ is < -1).[12] Under steady-state conditions for $H_2Q^{\bullet +}$ and $HQ^\bullet$ and at acidities where $[H^+] \gg K_1$, the second-order rate constant k_{12} may be related to the specific rate constants k_a and k_b and the acid dissociation constant K_1 by equation (8).

$$k_{12} = k_a + k_bK_1/[H^+] \quad (8)$$

Table 2 includes the rate constants calculated from the plots of k_{12} against $[H^+]^{-1}$ in Figure 2. The rate constants for the HQ^- anions are 10^4—10^5 times greater than the values for the corresponding H_2Q species. The increased reactivity of HQ^- compared with H_2Q, the result of a much lower semiquinone reduction potential (Table 1), has been observed previously for the oxidation of dihydroxybenzene compounds by a number of metal oxidants.[10,14,15]

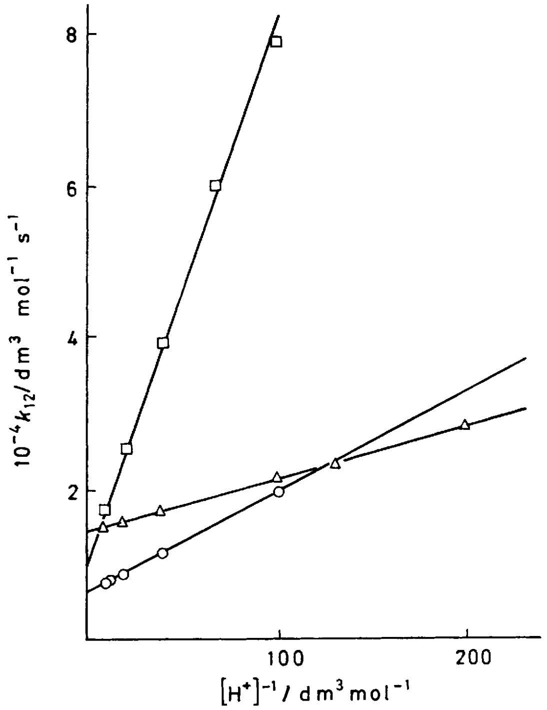


Figure 2. Inverse acid dependences of k_{12} for the reduction of $[Rh_2]^+$ by 1,2-dihydroxy-4-nitrobenzene (○), 4,5-dihydroxybenzene-1,3-disulphonate (△), and 1,2-dicyano-3,6-dihydroxybenzene (□)

Discussion

The $[Rh_2(O_2CCH_3)_4(OH_2)_2]^+$ cation is a moderately strong one-electron oxidant, with a reduction potential of 1.22 V [*vs.* normal hydrogen electrode (n.h.e.)] in 1.00 mol dm^{-3} $HClO_4$. While the substitution of the bridging acetate ligands is very slow, the axially co-ordinated water ligands are fairly labile, with an exchange rate estimated to be 10^3—10^4 s^{-1}.[8a] An inner-sphere mechanism has been proposed for the oxidation of Br^- by $[Rh_2(O_2CCH_3)_4(OH_2)_2]^+$, in which the intermediate $[Rh_2(O_2CCH_3)_4Br]$ was detected.[8a] In the reactions in the present study, however, no intermediate is observed and an outer-sphere mechanism appears to be operating. The redox rate constants k_{12} for the reduction of the substituted 1,2- and 1,4-dihydroxybenzenes fall in the range (0.65—13) × 10^4 dm^3 mol^{-1} s^{-1}, while k_{12} for the parent 1,2- and 1,4-dihydroxybenzene compounds are $\geqslant 10^7$ dm^3 mol^{-1} s^{-1}. The rate constants are observed to increase with a decrease in the one-electron reduction potential of the semiquinone radical. These observations suggest that the rate-determining step is an outer-sphere electron transfer rather than the formation of an inner-sphere intermediate.

The relationship between k_{12} and the semiquinone reduction potentials, along with the differences in rate constants for H_2Q and HQ^- may be rationalized in terms of the Marcus theory for outer-sphere electron-transfer reactions.[19,20] The rate constant for a cross-reaction, k_{12}, is related to the rate constants for the oxidant and reductant self-exchange reactions, k_{11} and k_{22}, and the equilibrium constant for the cross-reaction, K_{12}, is given by equation (9), where equations (10)—(12) apply. In these

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

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

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

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

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 a_i and a_j, the radii of ions i and j), $\beta = (8\pi Ne^2/1\,000D_skT)^{\frac{1}{2}}$, D_s is the static dielectric constant of the solvent and for the reactions in this study $A_{11}A_{22}$ is taken to be 10^{25} dm^6 mol^{-2} s^{-2}.[20] The radii of the $[Rh_2]^+$ and H_2Q species are estimated to be *ca.* 5 Å.

The reduction potentials of the $[Rh_2(O_2CCH_3)_4(OH_2)_2]^+$ cation are 1.26 and 1.22 V in 0.10 and 1.00 mol dm^{-3} $HClO_4$, respectively.[7] The one-electron reduction potentials of the semiquinone radicals, $H_2Q^{\bullet+}$ (E_1^0) and $HQ^{\bullet}$ (E_2^0), for the dihydroxybenzenes in this study may be calculated from the proton equilibrium constants [pK_1(H_2Q), pK_2(HQ^-), pK_{r1}($H_2Q^{\bullet+}$), and pK_{r2}($HQ^{\bullet}$)] and the $Q^{\bullet-}$ reduction potentials (E_3^0), using equations (13) and (14).[15]

$$E_1^0 = E_3^0 + 0.059(pK_1 + pK_2 - pK_{r1} - pK_{r2}) \quad (13)$$

$$E_2^0 = E_3^0 + 0.059(pK_2 - pK_{r2}) \quad (14)$$

The E_3^0 potentials and acid dissociation constants for the semiquinone radical species employed in equations (13) and (14) were determined experimentally or extrapolated from values of similar compounds (pK_{r1} = −1 and pK_{r2} = 4.1 for 1,4-dihydroxybenzene)[13] using a linear relationship between E^0 and pK.[12] The acid dissociation constants and potentials for the substituted dihydroxybenzenes are listed in Table 1.

An electron self-exchange rate constant of 1.5 × 10^5 dm^3 mol^{-1} s^{-1} has been derived for the $[Rh_2(O_2CCH_3)_4(OH_2)_2]^{0/+}$ couple from the application of the Marcus relationship to cross-reaction kinetic data.[7] Estimates of the self-exchange rate constants for the $H_2Q/H_2Q^{\bullet+}$, $HQ^-/HQ^{\bullet}$, and $Q^{2-}/Q^{\bullet-}$ couples have been determined from either direct exchange measurements or by use of the Marcus relationship. Steenken and Neta[21] have reported rate constants for the reactions of substituted dihydroxybenzenes Q^{2-} with semiquinone radicals $Q^{\bullet-}$, from which $Q^{2-}/Q^{\bullet-}$ self-exchange rate constants of 2 × 10^6 dm^3 mol^{-1} s^{-1} may be calculated. In kinetic studies prior to this report self-exchange rate constants of 5 × 10^7 dm^3 mol^{-1} s^{-1} were estimated for the $H_2Q/H_2Q^{\bullet+}$ couple from cross-reactions of substituted dihydroxybenzenes with $[IrCl_6]^{2-}$ and $[FeL_3]^{3+}$ (L = 2,2′-bipyridine or 1,10-phenanthroline) complexes.[12,13] A neglect of the work terms with the former oxidant and an underestimation of k_{11} for the $[FeL_3]^{2+/3+}$ couple in the latter systems has probably led to an overestimation of the $H_2Q/H_2Q^{\bullet+}$ self-exchange rate constant. In this work it will be assumed that the self-exchange rate constants for $H_2Q/H_2Q^{\bullet+}$, $HQ^-/HQ^{\bullet}$, and $Q^{2-}/Q^{\bullet-}$ couples are similar, and the directly measured value of 2 × 10^6 dm^3 mol^{-1} s^{-1} is employed in equation (9).

The calculated rate constants for the reduction of $[Rh_2(O_2CCH_3)_4(OH_2)_2]^+$ by the substituted dihydroxybenzenes are presented in Table 2. These values are in very good agreement with the experimental rate constants for both the neutral reductants and their anions. This agreement is also demonstrated by the correlation of $\ln[k_{12}/(k_{11}k_{22})^{\frac{1}{2}}W_{12}]$ with $\ln(K_{12}f_{12})^{\frac{1}{2}}$, shown in Figure 3. This relationship, a rearrangement of equation (9), will have a slope of unity and an intercept of zero when the systems are behaving according to the Marcus theory. A least-squares fit of the cross-reaction data yields a slope of 1.07 and an intercept of 0.45 for the plot in Figure 3. Slight deviations from the theoretical curve observed for some of the cross-reactants may be due to uncertainties in the semiquinone reduction potentials and self-exchange rate constants. It is likely that k_{22} for $H_2Q/H_2Q^{\bullet+}$ will vary slightly with the nature of the substituents on the dihydroxybenzenes. The kinetic data in this study indicate that 2 × 10^6 dm^3 mol^{-1} s^{-1} is a good estimate of the self-exchange rate constants for the dihydroxybenzene/semiquinone couples regardless of their extent of protonation. The increased reactivity of the anionic species HQ^- compared with the neutral reductant H_2Q is entirely due to the lowering of the redox potential upon deprotonation.

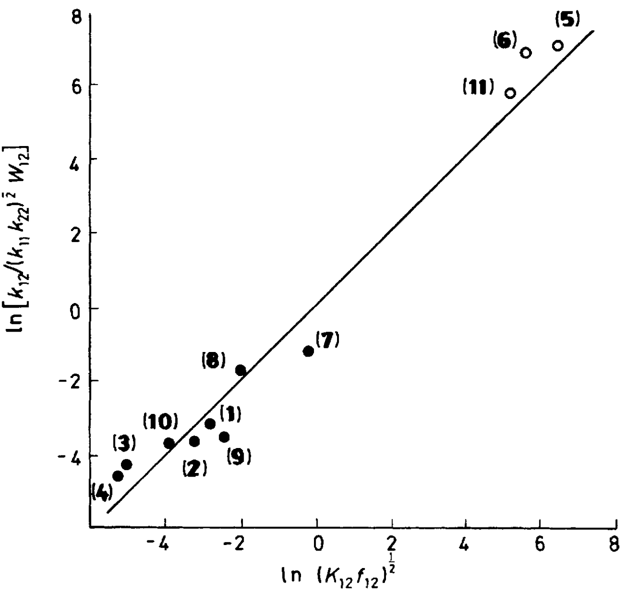


Figure 3. Plot of $\ln[k_{12}/(k_{11}k_{22})^{\frac{1}{2}}W_{12}]$ *versus* $\ln(K_{12}f_{12})^{\frac{1}{2}}$ for the reactions of $[Rh_2(O_2CCH_3)_4(OH_2)_2]^+$ with substituted 1,2- and 1,4-dihydroxybenzenes (●) and their anions (○). The reductants are numbered as in Table 1

The large range of electron self-exchange rate constants (10^{-6}—10^9 dm^3 mol^{-1} s^{-1}) that have been determined for organic and transition metal complexes can be rationalised with reasonable success in terms of a semi-classical model for electron transfer.[22] The dimolecular exchange rate constant k_{11} may be expressed as the product of a pre-equilibrium constant K_A, an effective nuclear frequency ν_n, and electronic and nuclear factors κ_{el} and κ_n, respectively, equation (15). The nuclear factor

$$k_{11} = K_A\nu_n\kappa_{el}\kappa_n \quad (15)$$

contains terms for both inner-sphere (ΔG^*_{in}) and solvent (ΔG^*_{out}) reorganizations, equation (16), where Γ_λ is the inner-

$$\kappa_n = \Gamma_\lambda \exp[-(\Delta G^*_{in} + \Delta G^*_{out})/RT] \quad (16)$$

sphere nuclear tunnelling factor. 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.[23]

The moderately rapid rate of electron exchange in the dirhodium tetra-acetate couple has been rationalized in terms of relatively small inner-sphere and solvent reorganization

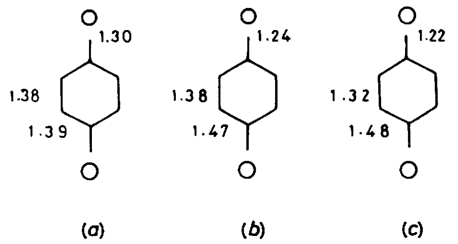


Figure 4. The C–C and C–O bond distances (Å) in the species (*a*) Q^{2-}, (*b*) $Q^{\bullet -}$, and (*c*) Q species (data from refs. 26—28)

barriers.[7] The exchange process involves the transfer of an electron from a weakly antibonding π^* orbital,[24] which results in only small changes in the Rh–Rh (0.069 Å) and Rh–O (0.088 Å for $Rh-OH_2$ and 0.025 Å for $Rh-O_2CCH_3$) bond distances. The rate constants for electron exchange between an organic radical and its parent species are generally very rapid (10^6—10^9 $dm^3\ mol^{-1}\ s^{-1}$). Self-exchange rate constants of 1×10^8 and 2×10^6 $dm^3\ mol^{-1}\ s^{-1}$ have been estimated for the semiquinone/quinone ($Q^{\bullet -}/Q$)[25] and dihydroxybenzene/semiquinone ($Q^{2-}/Q^{\bullet -}$)[21] couples, respectively, from kinetic measurements. Similar solvent reorganization energies would be expected for the two couples, suggesting that the difference in exchange rate constants lies in the relative magnitudes of the inner-sphere reorganization barriers.

The extent of reorganization of the bond distances in these couples may be estimated from the crystal structure data for 1,4-dihydroxybenzene[26] and the corresponding quinone,[27] and from the calculated molecular structure of the semiquinone radical.[28] The semiquinone radical resembles the quinone more than it does the dihydroxybenzene* (Figure 4), such that there are greater changes in the C–O and C–C bond distances for $Q^{2-}/Q^{\bullet -}$ than for the $Q^{\bullet -}/Q$ couple. The larger inner-sphere reorganization barrier for the $Q^{2-}/Q^{\bullet -}$ couple is consistent with its slower rate of exchange. With both couples the effects of inner-sphere tunnelling must be considered. The nuclear tunnelling factor is normally close to unity at room temperature for transition metal complexes[31] which involve reorganization *via* low-frequency metal–ligand vibrations. When $h\nu > kT$ the vibration modes which allow for nuclear reorganization are not fully populated by thermal excitation and the electron transfer occurs to some extent by nuclear tunnelling.[20,32] In the $Q^{2-}/Q^{\bullet -}$ and $Q^{\bullet -}/Q$ couples the involvement of C–C and C–O vibration modes of higher frequencies result in tunnelling factors calculated to be 110 and 8, respectively. Nuclear tunnelling has previously been found to be important in the NO_2^-/NO_2 couple ($\Gamma_\lambda = 79$),[33] which also involves high-frequency vibration modes.

In conclusion the Marcus theory relationship predicts, using self-exchange rate constants from direct or indirect measurements, $[Rh_2]^+/H_2Q$ and $[Rh_2]^+/HQ^-$ cross-reaction rate constants in good agreement with the experimental values. The self-exchange rate constants for the dihydroxybenzene/semiquinone and semiquinone/quinone couples may be rationalized in terms of a semi-classical model, with the inner-sphere nuclear tunnelling factor shown to be of importance in reducing the barrier to electron exchange.

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* While the structure of a complex containing the Q^{2-} ion has not been reported a shortening in the C–O bond distance of 0.08 Å upon deprotonation of 1,4-dihydroxybenzene[26] is suggested by the relative C–O bond distances in phenol[29] and the phenoxide ion.[30]