Electron-transfer Reactions and the Self-exchange Rate of the Perruthenate(VII)–Ruthenate(VI) Couple

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The kinetics of the reduction of perruthenate(VII) by $[Fe(CN)_6]^{4-}$ and $[W(CN)_8]^{4-}$ and the oxidation of ruthenate(VI) by $[Mo(CN)_8]^{3-}$ and $[Ru(CN)_6]^{3-}$ have been studied in aqueous alkaline solutions using stopped-flow techniques. The cross-reaction data have been treated according to the Marcus relations and yield a self-exchange rate constant of 10 ± 5 dm^3 mol^{-1} s^{-1} (25.0 °C, I = 1.0 mol dm^{-3}) for the perruthenate(VII)–ruthenate(VI) couple. This rather slow self-exchange rate is discussed in terms of possible structural differences between perruthenate(VII) and ruthenate(VI) in alkaline solution.

Although the anions perruthenate(VII) and ruthenate(VI) have been known for a long time,[1] there have been few studies on their redox reactions. The kinetics of the reduction of RuO_4^- by OH^- and MnO_4^{2-} have been reported.[2,3] The electron exchange between perruthenate and ruthenate was found to be too rapid to be followed by isotopic labelling techniques and a lower limit of 10^4 dm^3 mol^{-1} s^{-1} was estimated for the second-order rate constant.[4] We report here redox kinetic studies of the perruthenate(VII)–ruthenate(VI) couple with cyano complexes of Fe, Ru, Mo and W. Our goal is to estimate the self-exchange rate of this couple in aqueous solution from the rates of one-electron cross-reactions involving these complexes. {For simplicity, the formula of ruthenate(VI) in alkaline solution is often written as RuO_4^{2-} in this paper, although the correct formula[1,5] is more likely to be $[RuO_3(OH)_2]^{2-}$.}

Experimental

Materials.—The salt $K[RuO_4]$ was prepared by a literature method.[6] Solutions of RuO_4^{2-} were freshly prepared *in situ* by reduction of $K[RuO_4]$ in NaOH solution. The progress of the reduction was monitored by UV/VIS spectrophotometry [λ_{max}(ε/dm^3 mol^{-1} cm^{-1}) of RuO_4^{2-}: 460 nm (1820) and 385 (1030)].[7] The salts $K_4[W(CN)_8]\cdot 2H_2O$,[8] $Cs_3[Mo(CN)_8]$[9] and $K_4[Ru(CN)_6]$[10] were prepared by literature methods. Solutions of $[Ru(CN)_6]^{3-}$ were generated *in situ* from $[Ru(CN)_6]^{4-}$ according to the method of Crean and Schug.[11] All other chemicals were of reagent grade. Ionic strength was maintained with sodium trifluoroacetate, which was made by neutralization of standard trifluoroacetic acid solutions with sodium hydroxide. Double-distilled water was used for kinetic experiments.

Kinetics.—Kinetic experiments were performed under pseudo-first-order conditions using an Applied Photophysics DX-17MV stopped-flow spectrophotometer. The progress of the reaction was monitored by measuring absorbance changes at either 385 nm (λ_{max} of RuO_4^-) or 460 nm (λ_{max} of RuO_4^{2-}).[7] Pseudo-first-order rate constants, k_{obs}, were obtained by non-linear least-squares fits of A_t to time t according to the equation $A_t = A_\infty + (A_0 - A_\infty)\exp(-k_{obs}t)$, where A_0 and A_∞ are the initial and final absorbances, respectively.

Results

Although RuO_4^- is reduced by water to RuO_4^{2-} at high pH,[2] its solution in neutral water is stable for at least several hours at room temperature. On the other hand, RuO_4^{2-} is relatively stable in strong alkaline medium, but disproportionates to RuO_4^- and $RuO_2\cdot xH_2O$ in neutral or acidic solutions.[7] Accordingly the kinetics of the reduction of RuO_4^- by $[Fe(CN)_6]^{4-}$ and $[W(CN)_8]^{4-}$ were carried out by mixing a solution of the perruthenate in distilled water with a solution of the cyanide complex in alkaline solution (typically 0.2 mol dm^{-3} NaOH, with ionic strength adjusted to 2.0 mol dm^{-3} with CF_3CO_2Na). On the other hand, the kinetics of the oxidation of RuO_4^{2-} by $[Mo(CN)_8]^{3-}$ and $[Ru(CN)_6]^{3-}$ were carried out by mixing a solution of RuO_4^{2-} in 0.2 mol dm^{-3} NaOH (I = 2.0 mol dm^{-3}) with a solution of the cyanide complex in distilled water.

Kinetics of the Reduction of RuO_4^- *by* $[Fe(CN)_6]^{4-}$ *and* $[W(CN)_8]^{4-}$.—Preliminary experiments involved mixing a 1×10^{-4} mol dm^{-3} solution of RuO_4^- with 2×10^{-4} mol dm^{-3} of the cyanide complex in the stopped-flow spectrophotometer followed by repetitive scanning using the point-by-point method. The spectral changes showed a decrease in absorbance around 386 nm due to RuO_4^- and an increase in absorbance around 460 nm due to RuO_4^{2-} with isosbestic points at 400 nm for the reaction with $[Fe(CN)_6]^{4-}$ (Fig. 1) and at 295 and 345 nm for the reaction with $[W(CN)_8]^{4-}$. In each case the final spectrum indicated quantitative formation of

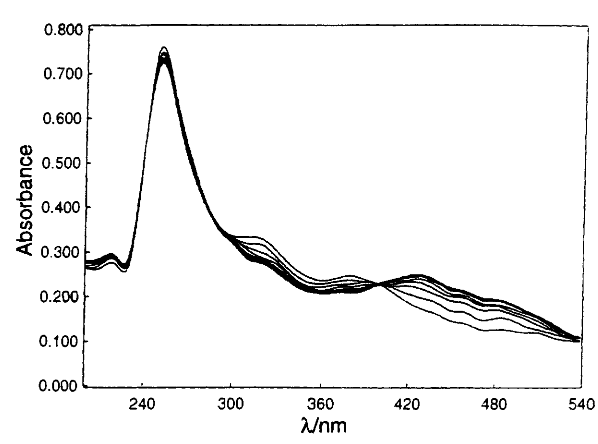

Fig. 1 Spectral changes during the reaction of RuO_4^- (1×10^{-4} mol dm^{-3}) with $[Fe(CN)_6]^{4-}$ (2×10^{-4} mol dm^{-3}) in 0.1 mol dm^{-3} NaOH (I = 1.0 mol dm^{-3}) at 25 °C. Total time is 5 s

RuO_4^{2-}. The reactions can be represented by equations (1) and (2).

$$RuO_4^- + [Fe(CN)_6]^{4-} \longrightarrow RuO_4^{2-} + [Fe(CN)_6]^{3-} \quad (1)$$

$$RuO_4^- + [W(CN)_8]^{4-} \longrightarrow RuO_4^{2-} + [W(CN)_8]^{3-} \quad (2)$$

The kinetics were carried out under pseudo-first-order conditions with the cyanide complexes in at least ten-fold excess; $[RuO_4^-] = 1\text{–}3 \times 10^{-4}$ mol dm^{-3} and [MCN] = 1–5 $\times 10^{-3}$ mol dm^{-3} {MCN = $[Fe(CN)_6]^{4-}$ or $[W(CN)_8]^{4-}$}. The reactions followed pseudo-first-order kinetics for over three half-lives. Plots of the pseudo-first-order rate constants against concentrations of the cyanide complexes were linear, so that the rate law is: rate = $k_2[RuO_4^-][MCN]$. Values of k_2 are given in Table 1. The rate constants are independent of $[OH^-]$ from 0.01 to 1.0 mol dm^{-3}. The rate constant k_2 for the reaction with $[Fe(CN)_6]^{4-}$ increases with ionic strength, in accordance with the reactants being of the same charge. Activation parameters were obtained from plots of $\ln(k/T)$ *versus* $1/T$ according to the Eyring equation: $\Delta H^\ddagger = 37.0 \pm 3.1$ kJ mol^{-1} and $\Delta S^\ddagger = -54 \pm 6$ J K^{-1} mol^{-1} for reduction by $[Fe(CN)_6]^{4-}$, with $\Delta H^\ddagger = 42.8 \pm 3.2$ kJ mol^{-1} and $\Delta S^\ddagger = -36 \pm 4$ J K^{-1} mol^{-1} for reduction by $[W(CN)_8]^{4-}$.

Kinetics of the Oxidation of RuO_4^{2-} *by* $[Mo(CN)_8]^{3-}$ *and* $[Ru(CN)_6]^{3-}$.—Preliminary repetitive scanning of solutions of RuO_4^{2-} with solutions of the cyanide complexes indicated isosbestic points at 251, 295 and 345 nm for $[Mo(CN)_8]^{3-}$ and at 371 and 406 nm for $[Ru(CN)_6]^{3-}$. Analysis of the final spectra indicated the reactions occurred according to equations (3) and (4).

$$RuO_4^{2-} + [Mo(CN)_8]^{3-} \longrightarrow RuO_4^- + [Mo(CN)_8]^{4-} \quad (3)$$

$$RuO_4^{2-} + [Ru(CN)_6]^{3-} \longrightarrow RuO_4^- + [Ru(CN)_6]^{4-} \quad (4)$$

The kinetics of oxidation by $[Mo(CN)_8]^{3-}$ was studied using excess of the molybdenum complex; $[RuO_4^{2-}] = 0.5\text{–}1.0 \times 10^{-4}$ mol dm^{-3} and $[Mo(CN)_8{}^{3-}] = 1.0\text{–}3.0 \times 10^{-3}$ mol dm^{-3}. The kinetics of oxidation by $[Ru(CN)_6]^{3-}$ was studied using an excess of RuO_4^{2-}; $[Ru(CN)_6{}^{3-}] = 1\text{–}3 \times 10^{-5}$ mol dm^{-3} and $[RuO_4^{2-}] = 0.2\text{–}1 \times 10^{-3}$ mol dm^{-3}. In both reactions pseudo-first-order kinetics were obeyed for over three half-lives and plots of the pseudo-first-order rate constants with concentrations of the excess reagent were linear, indicating the following rate law: rate = $k_2[RuO_4^{2-}][MCN]$ {MCN = $[Mo(CN)_8]^{3-}$ or $[Ru(CN)_6]^{3-}$}. Values of k_2 are given in Table 1. The oxidation by the molybdenum complex has $\Delta H^\ddagger = 23.9 \pm 1.8$ kJ mol^{-1} and $\Delta S^\ddagger = -87 \pm 8$ J K^{-1} mol^{-1}

Table 1 Rate constants for electron-transfer reactions of RuO_4^- and RuO_4^{2-}

Reactants	T/K	I/mol dm^{-3}	$[OH^-]$/mol dm^{-3}	$10^{-3}k_2$/dm^3 mol^{-1} s^{-1}
RuO_4^- + $[Fe(CN)_6]^{4-}$	298	1.0	1.0	3.15 ± 0.09
	298	1.0	0.10	3.20 ± 0.10
	298	1.0	0.01	3.10 ± 0.10
	298	0.50	0.10	2.35 ± 0.07
	298	0.10	0.10	1.26 ± 0.04
	290	1.0	0.10	2.02 ± 0.06
	305	1.0	0.10	4.56 ± 0.08
	313	1.0	0.10	6.72 ± 0.20
RuO_4^- + $[W(CN)_8]^{4-}$	298	1.0	1.0	2.17 ± 0.08
	298	1.0	0.20	2.75 ± 0.20
	298	1.0	0.10	2.75 ± 0.20
	290	1.0	0.10	1.63 ± 0.05
	305	1.0	0.10	4.10 ± 0.29
	313	1.0	0.10	6.49 ± 0.36
$[Mo(CN)_8]^{3-}$ + RuO_4^{2-}	298	1.0	0.10	12.10 ± 0.17
	290	1.0	0.10	9.65 ± 0.26
	305	1.0	0.10	16.95 ± 0.15
	313	1.0	0.10	20.95 ± 0.89
$[Ru(CN)_6]^{3-}$ + RuO_4^{2-}	298	1.0	0.1	0.02 ± 0.0006

Discussion

Table 2 shows the rate parameters for cross-reactions involving the RuO_4^-–RuO_4^{2-} couple. Data for the reaction involving MnO_4^{2-} were obtained from the work of Luoma and Brubaker.[3] If these redox reactions are outer-sphere, then the cross-reaction rate constant k_{12} is related to the component self-exchange reactions k_{11} and k_{22} and the equilibrium constant for the cross-reaction K_{12} by the Marcus cross equation (5),[18] where the individual terms are defined by equations (6)–(8).

$$k_{12} = (k_{11}k_{22}K_{12}f_{12})^{\frac{1}{2}}W_{12} \quad (5)$$

$$\ln f_{12} = \frac{[\ln K_{12} + (w_{12} - w_{21})/RT]^2}{4\left[\ln\left(\frac{k_{11}k_{22}}{A_{11}A_{22}}\right) + \frac{w_{11} + w_{22}}{RT}\right]} \quad (6)$$

$$W_{12} = \exp[-(w_{12} + w_{21} - w_{11} - w_{22})/2RT] \quad (7)$$

$$w_{ij} = \frac{z_iz_je^2}{D_s\sigma_{ij}(1 + \beta\sigma_{ij}I^{\frac{1}{2}})} \quad (8)$$

In the above equations, w_{ij} is the work required to bring ions i and j (charges z_i and z_j) to separation distance σ_{ij}, D_s is the static dielectric constant of the medium, $\beta = (8\pi Ne^2/1000D_skT)^{\frac{1}{2}}$, and $A_{ii} = (4\pi N\sigma^2\nu(\delta r)/1000)_{ii}$, where δr is the thickness of the reaction shell. The following values of σ_{ii} were used in the Marcus calculations: $[Fe(CN)_6]^{3-}$–$[Fe(CN)_6]^{4-}$, 9.0 Å; $[Ru(CN)_6]^{3-}$–$[Ru(CN)_6]^{4-}$, 9.4 Å; $[Mo(CN)_8]^{3-}$–$[Mo(CN)_8]^{4-}$, 9.6 Å; $[W(CN)_8]^{3-}$–$[W(CN)_8]^{4-}$, 9.6 Å; MnO_4^-–MnO_4^{2-}, 5.6 Å; RuO_4^-–RuO_4^{2-}, 6.0 Å. A plot of $\ln[k_{12}/(k_{22})^{\frac{1}{2}}W_{12}]$ against $\ln(K_{12}f_{12})^{\frac{1}{2}}$ (Fig. 2) gives a straight line with a least-squares slope of 0.91 ± 0.05, which is in reasonable agreement with the theoretical value of unity. The intercept of 1.1 ± 0.2 corresponds to $\ln k_{11}^{\frac{1}{2}}$ and gives a self-exchange rate constant of 10 ± 5 mol dm^{-3} for the RuO_4^-–RuO_4^{2-} couple at I = 1.0 mol dm^{-3}. This rather small value indicates that appreciable inner-sphere reorganisation is required for the couple. The structure of the perruthenate(VII) ion in $K[RuO_4]$ is close to tetrahedral with a Ru=O bond distance of 1.79 Å.[19] On the other hand, the barium salt of ruthenate(VI), which was previously assumed to be $Ba[RuO_4]\cdot H_2O$, actually has the molecular structure $Ba[RuO_3(OH)_2]$.

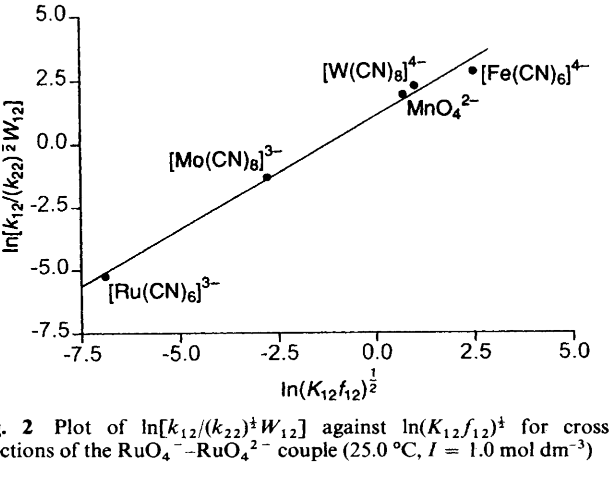

Fig. 2 Plot of $\ln[k_{12}/(k_{22})^{\frac{1}{2}}W_{12}]$ against $\ln(K_{12}f_{12})^{\frac{1}{2}}$ for cross reactions of the RuO_4^-–RuO_4^{2-} couple (25.0 °C, I = 1.0 mol dm^{-3})

Table 2 Rate parameters for cross-reactions involving the RuO_4^-–RuO_4^{2-} couple at 25.0 °C[a]

Oxidant	Reductant	$E°$/V	k_{12}/dm^3 mol^{-1} s^{-1}	K_{12}[b]	k_{22}/dm^3 mol^{-1} s^{-1}
RuO_4^-	$[Fe(CN)_6]^{4-}$	0.46[c]	3.2×10^3	1.8×10^2	1.9×10^4[d]
RuO_4^-	$[W(CN)_8]^{4-}$	0.54[c]	2.8×10^3	7.9	4.0×10^4[e]
RuO_4^-	MnO_4^{2-}	0.56[f]	1.1×10^2[g]	4.4	3.6×10^3[h]
$[Mo(CN)_8]^{3-}$	RuO_4^{2-}	0.73[c]	1.2×10^4	2.1×10^2	3.0×10^4[e]
$[Ru(CN)_6]^{3-}$	RuO_4^{2-}	0.92[i]	2.0×10^5	3.4×10^5	8.3×10^3[i]

[a] $E°$ refers to the reduction potential of the cross-reaction partner. [b] Calculated by using $E° = 0.59$ V for the RuO_4^-–RuO_4^{2-} couple (ref. 7). [c] Ref. 12. [d] Ref. 13. [e] Ref. 14. [f] Ref. 15. [g] Ref. 3. [h] Ref. 16. [i] Ref. 17.

The anion is trigonal bipyramidal with three equatorial oxo ligands (Ru=O 1.755 Å) and two axial hydroxo ligands (Ru–OH 2.02 Å).[1,5] If the solid-state structures of these ions persist in alkaline solution, then the rather large structural differences between the perruthenate(VII) ion and the ruthenate(VI) ion would account for the relatively slow self-exchange rate. Unfortunately we have not been able to find any means of distinguishing in solution between $RuO_4^{2-}\cdot H_2O$ and $[RuO_3(OH)_2]^{2-}$, which differ only in the distribution of protons within the ions. Luoma and Brubaker,[4] however, obtained a much higher value of $\geqslant 10^4$ dm^3 mol^{-1} s^{-1} for direct electron exchange between perruthenate(VII) and ruthenate(VI) in alkaline solution using tracer techniques. Presumably in this case electron exchange occurs through an inner-sphere process, possibly involving a hydroxo-bridged intermediate. The direct electron exchange between VO^{2+}(aq) and VO_2^+(aq), which again involves large structural changes, has also been found to be a rapid inner-sphere process.[20]

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