The Kinetics and Stoicheiometry of Silver(III) Reduction by the Octacyano-complexes of Molybdenum(IV) and Tungsten(IV)

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The reactions of $[Ag(OH)_4]^-$ with $[Mo(CN)_8]^{4-}$ and $[W(CN)_8]^{4-}$ involve an initial one-electron reduction of Ag^{III} to Ag^{II} with second-order rate constants of 80 and 2.9×10^4 dm^3 mol^{-1} s^{-1} (25 °C, $I = 1.2$ mol dm^{-3}), respectively. The tungstate reaction is quantitative with a stoicheiometry of 1 : 1. The reaction with $[Mo(CN)_8]^{4-}$, however, does not go to completion. There is apparently an equilibrium of oxidation states. From the value of the equilibrium constant a formal potential of 0.87 V ($[OH^-] = 1.2$ mol dm^{-3}, 25 °C) is estimated for the reduction of $[Ag(OH)_4]^-$ to dimeric Ag^{II}. The rate of the initial one-electron redox step is strongly correlated with E_{M/M^+} for the series of reductants $[Fe(CN)_6]^{4-}$, MnO_4^{2-}, $[W(CN)_8]^{4-}$, and $[Mo(CN)_8]^{4-}$. The results are interpreted in terms of a general mechanism which involves silver(II) polymerisation following the initial redox step.

The ion $[Ag(OH)_4]^-$ is the simplest form of Ag^{III} that can be stabilised in aqueous media. It can be conveniently prepared by electrochemical oxidation of a silver anode in strong base.[1,2] Its stability decreases with decreasing hydroxide-ion concentration[1,3] and has a half-life for reduction to AgO by the solvent of about 1.5 h in 1.2 mol dm^{-3} NaOH at room temperature.

It is a low-spin d^8 square-planar complex. Thus, having vacant co-ordination sites it can undergo inner-sphere electron-transfer reactions in a five-co-ordinate intermediate or following substitution of bound hydroxide. Previous work involving the two-electron reductions of Ag^{III} by ethylenediamine (en),[4] HO_2^-,[5] arsenite,[6] N_3^-,[7] and $S_2O_3^{2-}$ [8] has provided evidence that either type of behaviour is possible. Indeed, in the reductions with N_3^-,[7] en,[4] and $S_2O_3^{2-}$ [8] parallel paths involving both mechanistic possibilities have been observed. Among these reductants, only HO_2^- [5] reacts by sequential one-electron transfers involving a silver(II) intermediate.

In order to focus attention on the stepwise reduction of silver(III), we have undertaken a study of reactions of $[Ag(OH)_4]^-$ with a series of substitutionally inert, one-electron reducing agents. Recently we published kinetic and stoicheiometric results for the reduction of Ag^{III} by manganate and ferrocyanide ions and preliminary results for the reduction by octacyanomolybdate(IV).[9] The present work completes the molybdenum(IV) study and extends the series to include $[W(CN)_8]^{4-}$.

Outer-sphere electron transfer appears to be characteristic in reactions of cyanometalates with other substitutionally inert species. This has been observed in the reduction of permanganate by $[Fe(CN)_6]^{4-}$ [10] and $[Mo(CN)_8]^{4-}$,[11] and in the oxidations of MnO_4^{2-} [12] and SO_3^{2-} [13,14] by $[Fe(CN)_6]^{3-}$, $[Mo(CN)_8]^{3-}$, and $[W(CN)_8]^{3-}$.

In contrast, the oxidations of a variety of iron(II) cyano-complexes occur by an inner-sphere process[15–19] as evidenced by the formation of binuclear complexes and the failure of Marcus theory. Parallel paths involving both types of behaviour appear to be operative in the reduction of V^V by $[Mo(CN)_8]^{4-}$.[20]

In the two $[M(CN)_8]^{4-}$ (M = Mo or W) systems presently under consideration, the initial step involves a one-electron reduction of Ag^{III} to Ag^{II}. With tungsten this reaction is rapid and complete. The reaction with $[Mo(CN)_8]^{4-}$, on the other hand, does not go to completion but appears to involve an equilibrium mixture of $Mo^{IV,V}$ and $Ag^{III,II}$. The results of this study in conjunction with those of previous work provide rate data for a series of one-electron reductions with a wide range of free energies. This allows an examination of the variation of electron-transfer rate with redox potential.

Experimental

All solutions were prepared using doubly distilled water. All chemicals were reagent grade. The ion $[Ag(OH)_4]^-$ was prepared by electrolysis of silver foil in 1.2 mol dm^{-3} NaOH as described previously.[1,2] The salts $K_4[Mo(CN)_8]\cdot 2H_2O$,[21] $K_4[W(CN)_8]\cdot 2H_2O$,[22a] and $Cs_3[W(CN)_8]\cdot 2H_2O$[22b] were prepared as described previously.

Solutions for kinetic and stoicheiometric experiments were prepared just prior to use with NaOH and sufficient $NaClO_4$ to give a total ionic strength, *I*, of 1.2 mol dm^{-3}. Since both cyanometalates are extremely light sensitive[23] all solutions were prepared by weight without aerial dilution under conditions of reduced light. When solutions were prepared in this manner, an initial rapid reaction previously observed in the molybdenum(IV) system[9] did not occur.

Ultraviolet–visible spectra were recorded on a Varian Cary 210 or Beckman DU-7 spectrophotometer, e.s.r. spectra on a Bruker ER-200 spectrometer at room temperature and 150 K.

Kinetic experiments were carried out with an Aminco-Morrow stopped-flow apparatus.[2] Silver(III) concentrations were in the range 1×10^{-6} to 4×10^{-4} mol dm^{-3}. Reductant concentrations were generally in at least a ten-fold excess. The monitoring wavelengths were as follows: (*i*) $[W(CN)_8]^{4-}$ reaction : decrease in silver(III) absorbance at 300 nm ($\varepsilon = 5.8 \times 10^3$ dm^3 mol^{-1} cm^{-1}),[9] increase in $[W(CN)_8]^{3-}$ absorbance at 357 nm ($\lambda_{max.}$), $\varepsilon = 1\,790$ dm^3 mol^{-1} cm^{-1};[24] (*ii*) $[Mo(CN)_8]^{4-}$ reaction : decrease in silver(III) absorbance at 267 nm ($\lambda_{max.}$), $\varepsilon = 1.17 \times 10^4$ dm^3 mol^{-1} cm^{-1}[1,2] and 300 nm, increase in $[Mo(CN)_8]^{3-}$ absorbance at 388 nm ($\lambda_{max.}$), $\varepsilon = 1\,360$ dm^3 mol^{-1} cm^{-1}.[24] U.v.–visible and e.s.r. spectra of reaction mixtures were used to identify $[W(CN)_8]^{3-}$ and $[Mo(CN)_8]^{3-}$ as products.

For tungsten the reaction is rapid and results in quantitative reduction of $[Ag(OH)_4]^-$. Consumption ratios were determined as $\Delta[W^{IV}]/\Delta[Ag(OH)_4^-]$ from the change in absorbance of W^{IV} at 435 nm (ε = 111 dm^3 mol^{-1} cm^{-1}).[24]

For the reaction with Mo^{IV}, which does not go to completion, consumption ratios were determined as $\Delta[Mo]/\Delta[Ag(OH)_4^-]$ from the changes in absorbance at 267 nm compared to that at 241 nm ($\lambda_{max.}$ for Mo^{IV}), ε = 15 540 dm^3 mol^{-1} cm^{-1},[24] or 388 nm, depending on where the relative absorbance change was largest. The major absorbing species are $[Ag(OH)_4]^-$, $[Mo(CN)_8]^{4-}$, and $[Mo(CN)_8]^{3-}$, respectively. In most kinetic experiments, the excess of Mo^{IV} was kept very high to obtain accurate rate data uncomplicated by spontaneous decomposition of reactants and products.

After standing for several minutes, the absorbances of both $[Ag(OH)_4]^-$ and $[Mo(CN)_8]^{3-}$ decreased and regeneration of $[Mo(CN)_8]^{4-}$ was observed. A suspension of a dark solid accompanied these changes. Filtration and dissolution of this solid in acidic bipyridyl indicated that little or no Ag^{II} was present.[7] This precipitate is most probably the result of the slow reduction of Mo^V and $Ag^{II,III}$ by the solvent.[9] No precipitate was found for the tungstate system even at long times.

Solutions of Ag^{2+} for comparison with the $[Ag(OH)_4]^-$ reactions were prepared by electrolysis at a platinum anode of a solution containing 0.1 mol dm^{-3} Ag^+, 1.0 mol dm^{-3} $HClO_4$, and 2.9 mol dm^{-3} $NaClO_4$.[25]

Results

Stoicheiometry.—Consumption ratios for the reaction of $[Ag(OH)_4]^-$ with $[W(CN)_8]^{4-}$ are given in Table 1.* Absorbance changes of reaction mixtures in the visible region correspond very well to those expected for the quantitative one-electron reduction of Ag^{III}. Thus, the stoicheiometry of the redox reaction is 1:1. At lower wavelengths, absorbances due to reduced silver are observed (see below).[9]

For molybdenum, u.v.–visible spectra of reaction mixtures indicated the presence of Mo^{IV}, Mo^V, and Ag^{III} at the end of the reaction. Both u.v.–visible and e.s.r. spectra indicated that, even for a constant initial $[Ag^{III}]$, the amount of Mo^V produced was dependent on the initial molybdenum(IV) concentration. Furthermore, when additional Mo^{IV} was added to a reaction mixture, additional Mo^V was formed and further Ag^{III} was lost. When reaction mixtures were added to an excess of alkaline KIO_4 solution more than 90% of the Ag^{III} initially present was recovered as the bis(periodato)silver(III) complex.[1] Under the same conditions, e.s.r. spectra confirmed the loss of all resonances due to Mo^V. This was observed even for a large excess of Mo^{IV} where the reaction was forced virtually to completion.

Experimental consumption ratios for the reaction of $[Ag(OH)_4]^-$ with $[Mo(CN)_8]^{4-}$ are given in Table 2. Although subject to rather large errors due to background absorbances, light sensitivity, and spontaneous reduction of silver(III), silver(II), and Mo^V, these data confirm that, over a 36-fold change in the ratio of initial concentrations, the stoicheiometry is close to 1:1 and the reaction involves an equilibrium mixture of oxidised and reduced silver and molybdenum species.

A number of attempts were made to fit the data in Table 2 by use of a consistent equilibrium expression. A reasonable correlation was obtained assuming an equilibrium between $[Ag(OH)_4]^-$, $[Mo(CN)_8]^{4-}$, $[Mo(CN)_8]^{3-}$, and dimeric silver(II). Although higher-order polymers may form and may add to the complexity of the equilibria, monomeric Ag^{II} should not be present in these solutions.[9,26] The last column in Table 2 contains values of the calculated equilibrium constant from the expression $K = [Mo(CN)_8{}^{4-}][\text{‘}(Ag^{II})_2\text{’}]^{\frac{1}{2}}/[Mo(CN)_8{}^{4-}][Ag(OH)_4{}^-]$ where ‘$(Ag^{II})_2$’ is of undetermined formula. Its concentration was calculated as half the change in $[Ag(OH)_4]^-$ absorbance at 267 nm assuming a stoicheiometry of 1:1 and no contribution from reduced silver.

Table 1. Stoicheiometry of the reaction of $[Ag(OH)_4]^-$ with $[W(CN)_8]^{4-}$ (I = 1.2 mol dm^{-3}, 25 °C)

$10^4[Ag^{III}]_0$/mol dm^{-3}	$10^4[W^{IV}]_0$/mol dm^{-3}	$\Delta[W^{IV}]/\Delta[Ag^{III}]$
1.8	4.5	0.89
0.92	6.7	0.91
0.50	8.2	1.08
		Av. = 0.96

Kinetics.—Reaction of $[Ag(OH)_4]^-$ *with* $[W(CN)_8]^{4-}$. Stopped-flow traces at 300 and 357 nm showed two distinct phases, although the relative change at 357 nm for the second portion was, for all experiments, very small (<5%). Both reactions obeyed pseudo-first-order kinetics with observed rate constants which are dependent on $[W(CN)_8{}^{4-}]$ and independent of $[OH^-]$. Kinetic data are given in Table 3. Figure 1 demonstrates the first-order dependence on $[W^{IV}]$ with a zero intercept for both reactions. While the first reaction ($k_a{}^W = 2.90 \times 10^4$ dm^3 mol^{-1} s^{-1}) can be attributed to the initial one-electron redox reaction, the second step ($k_b{}^W = 1.3 \times 10^3$ dm^3 mol^{-1} s^{-1}) does not involve a significant change from the apparent 1:1 redox stoicheiometry.

Reaction of $[Ag(OH)_4]^-$ *with* $[Mo(CN)_8]^{4-}$. This reaction obeys simple pseudo-first-order kinetics at all three monitoring wavelengths. Values of the observed rate constants are in Table 4. A plot of $k_{obs.}$ *vs.* $[Mo(CN)_8{}^{4-}]$ is linear with essentially zero intercept. The reaction has no $[OH^-]$ dependence. We attribute this reaction to the forward one-electron Ag^{III}–Mo^{IV} redox step (k_1 = 80 dm^3 mol^{-1} s^{-1}). Although we have shown that this reaction involves an equilibrium (see above), addition of Mo^V has no detectable effect on the rate. This is most likely due to the presence of subsequent, rapid reactions of silver(II) with itself.[9,26] Deviations from first-order kinetics which might occur towards the end of the kinetic traces because of such reactions could not be detected under our experimental conditions.

Reaction of silver(II) *with cyanometalates.* In an earlier paper[9] we postulated that stoicheiometries in excess of 1:1 occur in the alkaline oxidation of $[Fe(CN)_6]^{4-}$ and $MnO_4{}^{2-}$ by $[Ag(OH)_4]^-$ because reaction of these reductants with initially formed, *monomeric*, silver(II) is rapid enough to compete with dimerization of Ag^{II}. Concentration-independent conversion ratios near unity, for $[Mo(CN)_8]^{4-}$ and $[W(CN)_8]^{4-}$, on the other hand, are an indication that subsequent redox reactions are unimportant for these systems (Tables 1 and 2). We, thus, decided to compare the reactivities of the three cyanometalates directly with monomeric Ag^{II} which is stable in acidic solution when Ag^+ is in large excess.[27]

Stopped-flow mixing experiments were carried out using (2—5) × 10^{-4} mol dm^{-3} of Ag^{II} and similar concentrations of $[Fe(CN)_6]^{4-}$, $[W(CN)_8]^{4-}$, and $[Mo(CN)_8]^{4-}$. All three reducing agents form insoluble silver(I) salts and, because of the high $[Ag^+]$ required to stabilise Ag^{II}, precipitate formation was noticeable within a few seconds. For the $[Fe(CN)_6]^{4-}$ reaction, a rapid increase in absorbance at 420 nm occurred within the *ca.* 2 ms dead time of the apparatus, which we attribute to the oxidation of iron(II) to $[Fe(CN)_6]^{3-}$. No analogous oxidation reaction was observed for the other two systems within the time before interference by precipitation.

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* Cyanometalates, including both oxidation states of the two reducing agents used here, form ion pairs with alkali metals.[13] All silver(III) experiments were carried out at $[Na^+] = I$ = 1.2 mol dm^{-3}. Hence, the actual reacting species exhibit a high, but constant, degree of ion pairing.

Table 2. Stoicheiometric and equilibrium data for the reaction of $[Ag(OH)_4]^-$ with $[Mo(CN)_8]^{4-}$ at I = $[OH^-]$ = 1.2 mol dm^{-3}, 25 °C[a]

$10^4[Mo^{IV}]_0$	$10^4[Ag^{III}]_0$	$10^4\Delta[Mo^{IV}]$	$10^4\Delta[Ag^{III}]$	$10^4\Delta[Mo^{V}]$	Percentage conversion[b]	$\frac{\Delta[Mo]}{\Delta[Ag^{III}]}$	K^c/dm$^{\frac{3}{2}}$ mol$^{-\frac{1}{2}}$
		mol dm^{-3}					
0.991	2.91		0.447	0.484	48	1.1	15.8
1.39	2.72		0.600	0.550	40	0.92	19.8
4.63	1.13	0.667	0.677		59	0.98	22.6
5.20	0.850	0.546	0.522		64	1.0	17.4
5.50	0.680	0.529	0.465	0.579	81	1.2	21.3
5.78	0.567	0.454	0.387	0.506	85	1.2	17.7
5.95	0.490	0.390	0.340	0.460	87	1.2	16.7
						Av. =	18.7 ± 2.5

[a] Final absorbance measurements were made at λ = 240, 267, and 388 nm. Concentrations listed are those for the molybdenum species whose absorbance change is least affected by background absorbances (see text). Where entries are found in both columns 3 and 5, an average of the two was used to determine ΔMo. Absorbances due to reduced silver were assumed negligible. [b] $\Delta Mo/[Ag(OH)_4{}^-]_0$ or $\Delta[Ag(OH)_4{}^-]/[Mo^{IV}]_0$ depending on the initial concentration ratio. [c] Based on initial concentrations, absorbance changes at 267 nm, and assuming $\Delta[Mo]/\Delta[Ag^{III}]$ = 1.0.

Table 3. Kinetic data for the reaction of $[Ag(OH)_4]^-$ with $[W(CN)_8]^{4-}$ at 25 °C and I = 1.2 mol dm^{-3}

$[OH^-]$	$10^4[W^{IV}]$	$k_{obs.}$/s^{-1}	
mol dm^{-3}		*a*	*b*
1.2	1.05	2.60	
	3.51	9.43	
	5.13	17.1	
	7.02	21.0	
	10.00	28.1	
0.60	1.00	2.77, 2.67	0.115
	2.80	8.98, 8.92	0.393
	5.00	16.9	0.656
	7.00	21.6, 22.6	0.904
	10.00	27.4, 27.5	1.28
0.12	1.00	2.86	0.118
	2.81	8.22, 8.42	
	3.30		0.449
	5.00	16.4, 15.7	0.672
	7.02	20.3, 22.1	
	7.77		1.00
	10.00	28.3	1.27

[a] First value is for $k_{obs.}$ monitored at 357 nm, second is for observation at 300 nm. [b] Second stage was monitored at 300 nm.

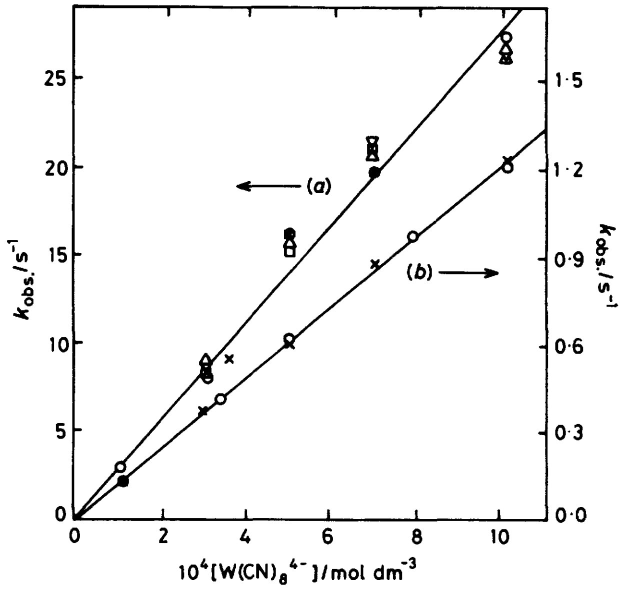

Figure 1. Plots of pseudo-first-order rate constants $k_{obs.}{}^W$ *vs.* $[W(CN)_8{}^{4-}]$ at 25 °C and I = 1.2 mol dm^{-3} at various $[OH^-]$ and wavelengths. (*a*) First stage: (×) $[OH^-]$ = 1.2, λ = 357; (△) 0.6, 357; (▽) 0.6, 300; (○) 0.12, 357; and (□) 0.12 mol dm^{-3}, 300 nm. (*b*) Second stage: (×) $[OH^-]$ 0.6, λ = 300; (○) 0.12 mol dm^{-3}, 300 nm

Discussion

The reactions of $[Ag(OH)_4]^-$ with $[W(CN)_8]^{4-}$ and $[Mo(CN)_8]^{4-}$ are multi-step processes, for which the initial step is the one-electron reduction of Ag^{III} to Ag^{II}. Similar results have been obtained for reactions of Ag^{III} with other one-electron reductants. However, unlike the reductions by $[Fe(CN)_6]^{4-}$ and $MnO_4{}^{2-}$,[9] these reactions do not proceed beyond a 1:1 stoicheiometry even for high excesses of $[M(CN)_8]^{4-}$. Thus, these ions seem to be very unreactive towards the silver(II) species produced. In the reactions of $[Ag(OH)_4]^-$ with $[Fe(CN)_6]^{4-}$ and $MnO_4{}^{2-}$, changes in conversion ratios[9] with concentration could be related to competition between redox and rapid polymerisation of silver(II).

Although Mo^V and W^V were clearly detected in e.s.r. spectra of reaction mixtures, no silver(II) resonance was apparent. An adduct involving spin coupling between silver(II) and molybdenum(V) products cannot explain this observation since loss of the molybdenum(V) resonance would also be expected. Since the measured stoicheiometries rule out complete reduction to diamagnetic Ag^I, the absence of a silver(II) (d^9) signal is an indication that the reduction products are spin-paired silver(II) species or Ag^I–Ag^{III} association complexes which are precursors to diamagnetic AgO.

From our analysis of the kinetic, stoicheiometric, and e.s.r. results, we conclude that the two reductions under consideration share many of the features, and are generally consistent with, the mechanism [equations (1)—(6)] proposed previously,[9] where

$$Ag^{III} + M^n \longrightarrow Ag^{II} + M^{n+1} \quad (1)$$

$$Ag^{II} + M^n \longrightarrow Ag^{I} + M^{n+1} \quad (2)$$

$$2Ag^{II} \longrightarrow I_s\,[= (Ag^{II})_2] \quad (3)$$

$$I_s + M^n \longrightarrow P + M^{n+1} \quad (4)$$

$$xI_s + (0 \text{ or } 1)\,M^n \longrightarrow I_s' + (0 \text{ or } 1)\,M^n \quad (5)$$

$$I_s' + (1 \text{ or } 2)\,M^n \longrightarrow P' + (1 \text{ or } 2)\,M^{n+1} \quad (6)$$

Table 4. Kinetic data for the reaction of $[Ag(OH)_4]^-$ with $[Mo(CN)_8]^{4-}$ at 25 °C and I = 1.2 mol dm^{-3}

$[OH^-]$/mol dm^{-3}	$10^3[Mo^{IV}]$/mol dm^{-3}	$k_{obs.}$[a]/s^{-1}
1.2	5.0	0.405
	3.5	0.273, 0.260[b]
	2.0	0.151
	1.0	0.066[c]
0.60	5.0	0.391, 0.441[d]
	3.5	0.288, 0.304[d]
	1.5	0.116, 0.115[c]
	0.5	0.048
0.12	5.0	0.432
	3.5	0.381, 0.312[d]
	1.5	0.119, 0.129[c]
	0.5	0.050, 0.047[c]

[a] Unless otherwise specified, reactions were monitored at 388 nm. [b] 3.5 × 10^{-3} mol dm^{-3} $[Mo(CN)_8]^{3-}$ added. [c] λ = 267 nm. [d] λ = 300 nm.

Table 5. Rate data for the reactions of $[Ag(OH)_4]^-$ with one-electron reducing agents (25 °C, I = 1.2 mol dm^{-3})[a]

Reaction	$[Fe(CN)_6]^{4-}$	$[W(CN)_8]^{4-}$	MnO_4^{2-}	$[Mo(CN)_8]^{4-}$
(1)	1.1×10^5	2.9×10^4	1.3×10^4	80
(2)	10^5	n.o.	10^4	n.o.
(3)	*ca.* 10^9		$>10^8$	
(4)	4×10^3		6×10^3	
(5)	4 s^{-1} [b]	1.3×10^3 [c]		
(6)	*d*		*d*	
k_{red}	3×10^4 [e]	4×10^4 [f]	7×10^3 [g]	3×10^4 [f]
$E_{M^+/M}$/V	0.46[h]	0.54[f]	0.56[h]	0.80[f]

[a] Values are in dm^3 mol^{-1} s^{-1}; unless otherwise stated n.o. = not observed. [b] $k_{obs.}$ for $[Fe(CN)_6{}^{4-}]$ = 1 × 10^{-3} mol dm^{-3}. [c] First order in $[W^{IV}]$; may involve complex formation. [d] Observed but not resolved for both systems. Dependence on $[Fe^{II}]$ between first and second order. [e] Ref. 41. [f] Ref. 38. [g] O. E. Myers and J. C. Shepard, *J. Am. Chem. Soc.*, 1961, **83**, 4739. [h] Ref. 12.

M^n and M^{n+1} are the two forms of the reductant, P and P′ contain at least one atom of Ag^I, and $I_s{}'$ may be or may become colloidal AgO. Rate constants are summarised in Table 5.

Of the four systems studied, $[Fe(CN)_6]^{4-}$, $MnO_4{}^{2-}$, $[W(CN)_8]^{4-}$, and $[Mo(CN)_8]^{4-}$, only the first two give clear evidence for the reduction of any of the silver(II) products. Although the degree of hydrolysis is different, the large distinction in rates for reaction (2) holds also in acidic solution. The second phase of the $[W(CN)_8]^{4-}$ reaction (see Figure 1) seems to involve a catalytic conversion of one silver(II) intermediate into another [equation (5)], perhaps accompanied by a small (< 5%) contribution from reaction (4) and/or (6).

The interconversion reaction [equation (5)] was also observed in the $[Fe(CN)_6]^{4-}$ system, but in that reaction the various stages were more highly coupled and were separable only in a limited concentration range. Thus, it was not possible to determine the iron dependence during this stage. If a common, metal-ion independent, conversion were possible for both systems [*i.e.* coefficients of zero in equation (5)], we would expect an intercept of 4 s^{-1} in Figure 1(*b*). The fact that this plot has a zero intercept suggests that either equation (5) is catalytic for both Fe^{II} and W^{IV} (k_5 = 4 × 10^3 and 1.3 × 10^3 dm^3 mol^{-1} s^{-1}, respectively) or that W^{IV} inhibits the I_s to $I_s{}'$ conversion (compared to $[Fe^{II}]$), *e.g.* by formation of a complex.

With reference to the possibility that W^{IV} forms a complex with one of the reduced silver species, we note the following: (*i*) the absorption coefficient at 300 nm at the end of the first phase of the tungsten(IV) reaction (*ca.* 600 cm^{-1} per mol of reduced silver) does not seem to agree well with determinations made for $[Fe(CN)_6]^{4-}$ (1 820 cm^{-1}) or $MnO_4{}^{2-}$ (2 200 cm^{-1}); (*ii*) no precipitate is formed in the final tungstate reaction mixtures. In the reactions of $[Co(edta)]^{2-}$ (edta = ethylenediaminetetra-acetate) with $[Fe(CN)_6]^{3-}$ [16] and of $[Cr(H_2O)_6]^{3+}$ with $NpO_2{}^+$ [28] where binuclear complexes are formed, the spectra of the adducts are essentially composites of the individual reactants. Thus, it is certainly possible that undetected complexes may be present which give rise to different kinetic behaviour among the different reductants.

Although slow polymerisation and precipitation does occur when Ag^{II} is produced in alkaline media, equation (5) may involve rearrangement of a silver(II) dimer, such as loss of water from a $H_3O_2{}^-$ bridge to form a μ-hydroxy dimer.[29,30]

The complexities of these reactions and the absence of speciation data for silver(II) in alkaline media result in the uncertainties inherent in the foregoing analysis of the secondary reactions. However, it seems clear that the assignment of the rate constants for reaction (1) is, indeed, correct.

Marcus and others[31–36] have developed a theory by which rates of outer-sphere electron transfers can be predicted. One of the most widely used results of this work is the Marcus cross-relationship (7) where k is the rate constant of the reaction

$$k = (k_{ox}k_{red}Kf)^{\frac{1}{2}} \qquad (7)$$

under consideration, k_{ox} and k_{red} are the rate constants for the self-exchange reactions, for the oxidant and reductant respectively, K is the equilibrium constant for the cross-reaction, $\log f = (\log K)^2/[4\log (k_{ox}k_{red}/Z^2)]$, and Z is the collision frequency normally taken as 10^{11} dm^3 mol^{-1} s^{-1}.

For a wide variety of cross-reactions where k_{ox}, k_{red}, and K are known equation (7) has been able to predict the rate to within about an order of magnitude.[11,12,37–39] In the present system, however, neither the reduction potential nor the self-exchange rate of $[Ag(OH)_4]^-$–$[Ag(OH)_4]^{2-}$ is known. Thus, a rigorous treatment is precluded. Recasting equation (7) in the form shown in (8) allows a test of the linear free-energy relationship implied by equation (7).

$$\log k = 0.5\,[\log(k_{ox}k_{red}f)] + 8.46\,(E_{ox} - E_{red}) \qquad (8)$$

Recently, Leipoldt, *et al.*[12] investigated the oxidation of $MnO_4{}^{2-}$ by $[Mo(CN)_8]^{3-}$, $[W(CN)_8]^{3-}$, and $[Fe(CN)_6]^{3-}$. Since the three oxidants and the reductant are all substitutionally inert in this series, these reactions are almost certainly outer-sphere. In fact, their values of $k_{obs.}$ and $k_{calc.}$ are in reasonable agreement, consistent with an outer-sphere process. Furthermore, since the k_{red} values for these three cyanometalates are similar, a plot of log k *vs.* E_{ox} was linear with a slope close to the expected value of 8.46 V^{-1}.* On the other hand, Arselli *et al.*[42] found a lack of consistency with equation (7) for the reduction of Ag^{2+} by a series of metal cations. This demonstrates the absence of a simple common outer-sphere mechanism for that series.

Figure 2 shows plots of log k_1 and log $(k_1/k_{red}{}^{\frac{1}{2}})$ *vs.* E_{M/M^+} using rate constants for reaction (1), self-exchange data, and electrode potentials ($E_{M/M^+} = -E_{red}$) listed in Table 5. Both

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* The value of k_{red} for Fe (300 dm^3 mol^{-1} s^{-1}) used by these authors was that determined at 0.1 °C and 0.01 mol dm^{-3} KOH.[40] Using the value corrected[41] for their conditions [25 °C and I = 0.2 mol dm^{-3} (KCl)], 1.6 × 10^4 dm^3 mol^{-1} s^{-1}, gives a somewhat better correlation of the calculated values.

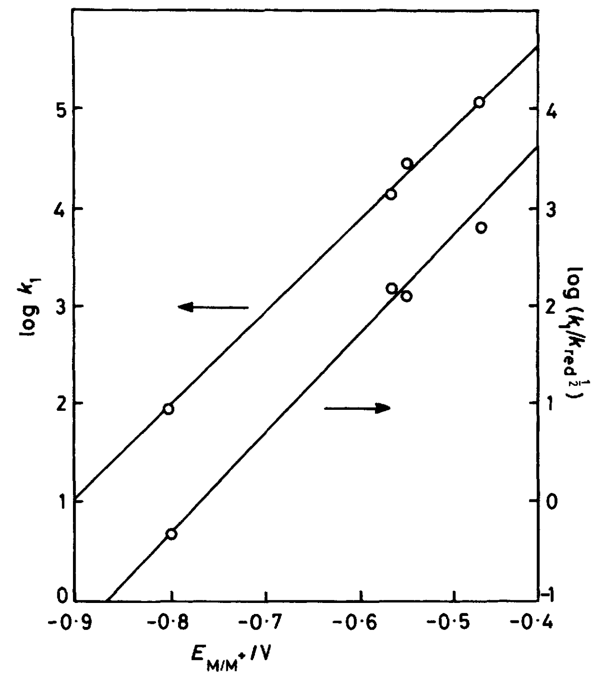

Figure 2. Plots of log k_1 and log(k_1/$k_{red}^{\frac{1}{2}}$) *vs.* E_{M/M^+} (M = Fe, W, Mn, or Mo)

plots are linear with slopes (8.9 and 9.6 V^{-1}) close to that predicted by equation (8). While this is consistent with an outer-sphere process, the lack of values for k_{ox} and E_{ox} for the $[Ag(OH)_4]^-$–$[Ag(OH)_4]^{2-}$ couple prevents us from ruling out an inner-sphere mechanism for reaction (1). Gould[37] has pointed out the dangers in assigning an outer-sphere mechanism based solely on the linearity of relative rate correlations. Ratner and Levine[43] have shown that 'independent activation' of the reactants is sufficient for adherence to equation (7). Indeed, there are a number of examples of inner-sphere reactions for which plots such as in Figure 2 are linear.[29,32,37,44]

Recently, Anast and Margerum[19] proposed that reduction of a series of copper(III) peptides by ferrocyanide proceed by an inner-sphere path involving a cyanide bridge. Nevertheless, for most of these oxidants a plot of log ($k/f^{\frac{1}{2}}$) *vs.* log K was linear with a slope close to 0.5 as predicted by equation (7). However, the experimental rate constants were one to two orders of magnitude greater than predicted from independently determined exchange rates. The rates were in good agreement with predictions only in cases where bulky groups blocked the axial positions of the copper(III) peptide complexes. Similarly, the reductions[44] of copper(III) peptides by $IrCl_6^{3-}$ and the oxidation of copper(II) peptides by $IrCl_6^{2-}$ gave self-exchange rates for $Cu^{III,II}$ of about three orders of magnitude greater than determined independently even though in these cases a Marcus correlation was also obtained.

These results for copper–peptide reactions are particularly germane to the present work, since both Ag^{III} and Cu^{III} are square-planar, d^8 systems for which axial attack on the metal centre can be expected. Furthermore, cyanometalates have been shown to react in many cases *via* cyanide bridges and binuclear adducts (see introduction).

Conclusions

The one-electron redox reactions for the reduction of $[Ag(OH)_4]^-$ by $[Fe(CN)_6]^{4-}$, $[W(CN)_8]^{4-}$, MnO_4^{2-}, and $[Mo(CN)_8]^{4-}$ have rates which indicate a common mechanism, but, without independently measured values of the silver redox potential and self-exchange rate, we cannot distinguish between outer- and inner-sphere behaviour.

From the value of $K = 19$ dm$^{\frac{3}{2}}$ mol$^{-\frac{1}{2}}$ estimated for the equilibrium in the molybdate system, we obtain a value of 0.07 V for the potential of reaction (9) at 25 °C and $I = [OH^-] = 1.2$ mol dm^{-3}. Using the value of 0.80 V for the $Mo^{IV,V}$ couple[38] gives $E = 0.87$ V at 25 °C and $I = [OH^-] = 1.2$ mol dm^{-3} for reaction (10).

$$[Mo(CN)_8]^{4-} + [Ag(OH)_4]^- \rightleftharpoons [Mo(CN)_8]^{4-} + \tfrac{1}{2}\text{‘}(Ag^{II})_2\text{’} \quad (9)$$

$$[Ag(OH)_4]^- + e^- \longrightarrow \tfrac{1}{2}\text{‘}(Ag^{II})_2\text{’} \quad (10)$$

Since the observed equilibrium (9) is a composite of at least two equilibria, an exact determination of the $[Ag(OH)_4]^-$–$[Ag(OH)_4]^{2-}$ potential is not possible. However, since no e.s.r. resonance for Ag^{II} is observed, we may presume that there is no monomeric Ag^{II}. Assuming that (*i*) the $[Ag(OH)_4]^{-/2-}$ potential is at least 0.1 V greater than that of $MnO_4^{-/2-}$ and (*ii*) the dimerisation reaction has an overall equilibrium constant $>10^3$, we obtain a rough estimate of 0.7 V for the $[Ag(OH)_4]^{-/2-}$ redox potential. If the rate constants plotted in Figure 2 are, indeed, those for an outer-sphere process, the self-exchange rate for $[Ag(OH)_4]^{-/2-}$ should be of the order of 10—10^2 dm^3 mol^{-1} s^{-1}. We hope to be able to gain further insight into the intimate mechanism of one-electron reductions of $[Ag(OH)_4]^-$ through further studies with other reductants, including some {*e.g.* cobalt(II) sepulchrate (1,3,6,8,10,13,16,19-octa-azabicyclo[6.6.6]icosane) and $[Ru(NH_3)_6]^{2+}$} which can react only by an outer-sphere mechanism.

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