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Kinetics of the Oxidation of the Manganate Ion by Complex Cyanides of Mo(V), W(V) and Fe(III) in Alkaline Solution

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Introduction

The hexacyanoferrate(III) ion, octacyanomolybdate(V) ion, octacyanotungstate(V) ion and the manganate ion are kinetically inert complexes; neither of these complexes readily exchanges its ligands with the solvent or other ligands. It is thus to be expected that the redox reactions between these ions will be of the outer-sphere type and thus suitable for theoretical calculations, using the theory of Marcus [1]. Although more information concerning the mechanistic behaviour of MnO_4^- oxidations of organic compounds are available, studies of the MnO_4^- oxidations of various transition metal complexes have shown an outer-sphere electron transfer reaction mechanism [2–7].

Experimental

K_2MnO_4 was prepared as described by Brauer [8] while $Cs_3Mo(CN)_8 \cdot 2H_2O$ and $Cs_3W(CN)_8 \cdot 2H_2O$ were prepared as described by Leipoldt *et al.* [9–11]. All other reagents were of analytical grade. Redistilled water was used throughout. All the determinations were done under pseudo-first-order conditions using a large excess of the cyano complex. The reaction progress was monitored by measuring either the increase in the permanganate ion concentration at 528 nm or the decrease in the manganate ion concentration at 610 nm using a Durrum-D110 stopped flow spectrophotometer.

Results and Discussion

The pseudo-first-order plots of $\log[MnO_4^{2-}]$ against time were linear for at least two half-lives. The kinetic results show the rate law to be of the form:

$$R = k[MnO_4^{2-}][M(CN)_n^{3-}] \quad (1)$$

The hydroxide ion concentration had no significant effect on the reaction rate. The second-order rate constants were obtained from a plot of k_{obs} *versus* the cyano complex concentration. The second-order rate constants for the oxidation of MnO_4^{2-} by the various cyano complexes are given in Table I.

The experimental value of the second-order rate constants were tested on the basis of the Marcus theory which compares the rate of the redox reactions take place via an outer-sphere mechanism, with the rate of the electron exchange of the reaction components and the resultant driving force of the reaction. The Marcus cross-relation is given by

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

where

$$\ln f = (\ln K_{12})^2/4\ln(k_{11}k_{22}/z^2)$$

k_{12} = rate constant for the redox reaction

k_{11} = electron exchange rate constant for the couple MnO_4^{2-}–MnO_4^-

k_{22} = electron exchange rate constant for the couple $M(CN)_n^{3-}$–$M(CN)_n^{4-}$

K_{12} = equilibrium constant for the redox reaction

TABLE I. Calculated and Observed Rate Constants for the Reaction between MnO_4^{2-} and $M(CN)_n^{3-}$ Ions. k_{11} (MnO_4^{2-}/MnO_4^-) = 3×10^3 [12]; E° (MnO_4^-/MnO_4^{2-}) = 0.56 volt [13]; μ = 0.2 mol dm^{-3} (KCl); T = 25 °C.

$[M(CN)_n^{3-}]$	k_{22} M^{-1} s^{-1}	E° (volt)	K_{12}	k_{12} (calc) M^{-1} s^{-1}	k_{12} (obs) M^{-1} s^{-1}
$[Fe(CN)_6^{3-}]$	3×10^2 [3, 4]	0.46 [15]	0.02	1.3×10^2	3.8×10^2
$[W(CN)_8^{3-}]$	4×10^4 [14]	0.54 [15]	0.46	7.4×10^3	3.0×10^3
$[Mo(CN)_8^{3-}]$	3×10^4 [14]	0.73 [15]	752	21.9×10^4	8.5×10^4

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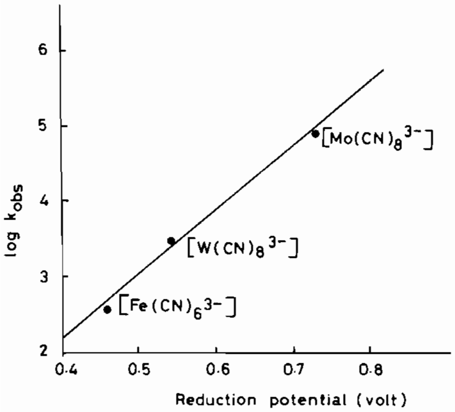

Fig. 1. Plot of log k_{obs} against reduction potential of the cyano complex. T = 25 °C; $\mu = 0.2$ mol dm^{-3}.

Z = collision frequency for charged species = 10^{11} M^{-1} s^{-1}

The various electron exchange rate constants, k_{11} and k_{22}, the reduction potentials, the calculated values of K_{12} as well as the values of the calculated reaction rate constants (by means of eqn. 2) are given in Table I. The value of the calculated reaction rate constants, k_{12}, are in agreement with the observed experimental rate constants.

The Marcus cross-relation may be written as

$$\log k_{12} = 0.5(\log k_{11} + \log k_{22} + \log f) + 8.46\, n(\Delta E^\circ) \tag{3}$$

The Marcus equation thus predicts a linear relationship between log k_{12} and the reduction potentials of the cyano complexes with a slope of 8.46 $volt^{-1}$. The plot of log k_{obs} for the oxidation of MnO_4^{2-} by $Fe(CN)_6^{3-}$, $W(CN)_8^{3-}$ and $Mo(CN)_8^{3-}$ against the E° values of the cyano complexes is shown in Fig. 1. The slope is 8.6 $volt^{-1}$ which is in good agreement with the theoretical value.

This result as well as the correlation between the observed experimental rate constants and the calculated rate constants, see Table I, is a strong indication that these reactions proceed via an outer-sphere reaction mechanism.

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