

Oxidation of cyanometalates by *trans*-cyclohexane-1,2-diamine-*N,N,N',N'*-tetraacetatomanganate(III): Kinetics and mechanism

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Abstract. The electron transfer reactions of $\text{Mo}(\text{CN})_8^{4-}$, $\text{W}(\text{CN})_8^{4-}$ and $\text{Fe}(\text{CN})_6^{4-}$ with the manganese(III) complex of *trans*-cyclohexane-1,2-diamine-*N,N,N',N'*-tetraacetic acid have been studied by stopped-flow spectrophotometry in the pH range 2.0–6.5. Analysis of kinetic data conforms to an outer-sphere process in each case. The validity of Marcus' cross-reaction relation to these reactions is fairly satisfactory.

Keywords. Electron transfer reactions; manganese(III); *trans*-cyclohexane-1,2-diamine-*N,N,N',N'*-tetraacetate; cyanometalates of W(IV), Mo(IV) and Fe(II).

1. Introduction

A number of papers (Gangopadhyay *et al* 1994) have appeared recently on the electron transfer activity of manganese(III) complex of *trans*-cyclohexane-1,2-diamine-*N,N,N',N'*-tetraacetic acid, $[\text{Mn}^{\text{III}}(\text{cdta})]^-$. The majority of these reactions are found to undergo inner-sphere process with relatively few of them following the outer-sphere route. On the other hand, cyanometalates, $\text{M}(\text{CN})_x^{4-}$ ($x = 8$ for Mo and W, and $x = 6$ for Fe) are reported (Jordan and Ewing 1962) to be outer-sphere cross-reactants. A kinetic investigation of $[\text{Mn}^{\text{III}}(\text{cdta})]^-$ with cyanometalates would be interesting since these are appropriate candidates for testing the validity of Marcus cross reaction relations.

2. Experimental

The potassium salt of *trans*-cyclohexane-1,2-diamine-*N,N,N',N'*-tetraacetatomanganate(III), $\text{K}[\text{Mn}(\text{cdta})]$, $2.5 \text{ H}_2\text{O}$ was prepared, characterised and standardised as reported earlier (Hamm and Suwyn 1967).

2.1 Preparation of cyanometalates and other reagents

The potassium salts of octacyanomolybdate and octacyanotungstate were prepared and standardised by literature methods (Furman and Miller 1950; Goodenow and

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Garner 1955). Potassium ferrocyanide was of reagent grade (E Merck, Germany). Ionic strength of the reaction medium was maintained with doubly recrystallised sodium perchlorate (Fluka, AG). The buffer components e.g., sodium acetate, acetic acid, sodium dihydrogen phosphate and sodium hydroxide were reagent grade. All solutions were prepared fresh prior to use. Distilled water, freshly redistilled in the presence of alkaline permanganate solution in an all-glass still was used to prepare solutions.

2.2 Kinetic measurements

The kinetics under various reaction conditions were monitored through the loss of oxidant measured spectrophotometrically by the stopped-flow technique. The Union RA-401 stopped-flow spectrophotometer (Otsuka Electronics, Japan) interfaced with a data processor RA-451 (Otsuka Electronics, Japan) comprising a CPU (Packard-Bell 286) was used for this purpose. The reaction temperature ($\pm 0.1^\circ\text{C}$) was controlled by a Hakke F3 thermostat by circulating water around the reservoir of the reaction solution. The pH measurements were carried out with a Systronics (model 335, India) pH-meter. The glass electrode of the pH-meter assembly was calibrated by using solutions of known $[\text{H}^+]$ at desired experimental conditions and the actual $[\text{H}^+]$ was evaluated in terms of $-\log[\text{H}^+]$ from the calibration curve.

2.3 Stoichiometry

Spectrophotometric titration with excess oxidant reveals a 1:1 stoichiometry and can be represented by



3. Results and discussion

The reactions were carried out in the range pH 2.0–6.5 at ionic strength 0.2 mol dm^{-3} at various temperatures as a function of reductant concentration. The kinetics were followed by monitoring the first-order change in $[\text{Mn}^{\text{III}}(\text{cdta})^-]$ at 510 nm (the absorption maximum of $\text{Mn}^{\text{III}}(\text{cdta})(\text{H}_2\text{O})^-$) under pseudo-first-order conditions of excess cyanometalates. The pseudo-first-order rate constants (k_{obs}) were evaluated by treating the kinetic curve of the average of 5–6 runs by the least-square curve-fit method. The pseudo-first-order rate constants thus evaluated varied within an error limit of $\pm 3\%$. A first-order dependence of k_{obs} on $[\text{M}(\text{CN})_x^{4-}]$ at different temperatures was ascertained for each system from the linearity of a plot of k_{obs} vs. $[\text{M}(\text{CN})_x^{4-}]$ with nearly zero intercepts (table 1). A general rate-law may be framed as

$$\begin{aligned} -d/dt[\text{Mn}^{\text{III}}(\text{cdta})^-] &= k[\text{Mn}^{\text{III}}(\text{cdta})^-][\text{M}(\text{CN})_x^{4-}] \\ &= k_{\text{obs}}[\text{Mn}^{\text{III}}(\text{cdta})^-]. \end{aligned} \quad (2)$$

The oxidation of $\text{Mo}(\text{CN})_8^{4-}$ and $\text{W}(\text{CN})_8^{4-}$ by $\text{Mn}^{\text{III}}(\text{cdta})^-$ showed no dependence of k_{obs} on pH (2.0–6.5) and the reactions could be expressed in a straightforward way:

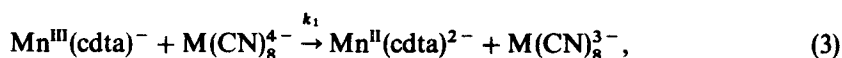


Table 1. Second-order rate constants, $k(\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})$, at different temperatures for the oxidation of cyanometalates by $\text{Mn}^{\text{III}}(\text{cdta})^-$ at $I = 0.20 \text{ mol dm}^{-3} (\text{NaClO}_4)$.

Reductant	$10^{-4} k(\text{dm}^3 \text{mol}^{-1} \text{s}^{-1})$ at temperature ($^{\circ}\text{C}$)			
	10	20	30	40
$\text{Mo}(\text{CN})_8^{-4a}$		0.512 ± 0.14	0.664 ± 0.23	0.773 ± 0.17
$\text{W}(\text{CN})_8^{-4b}$		5.71 ± 0.50	6.92 ± 0.20	8.66 ± 0.55
$\text{Fe}(\text{CN})_6^{-4c}$	21.70 ± 0.80	28.10 ± 1.0	31.89 ± 2.0	—

^a $-\log[\text{H}^+] = 3.94$, $[\text{Mn}^{\text{III}}(\text{cdta})^-] = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$; $\Delta H^\ddagger = (13.3 \pm 2.1) \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = (129.2 \pm 7.1) \text{ JK}^{-1} \text{ mol}^{-1}$

^b $-\log[\text{H}^+] = 3.94$, $[\text{Mn}^{\text{III}}(\text{cdta})^-] = 1.0 \times 10^{-4} \text{ mol dm}^{-3}$; $\Delta H^\ddagger = (13.4 \pm 0.8) \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = (108.3 \pm 3.0) \text{ JK}^{-1} \text{ mol}^{-1}$

^c $-\log[\text{H}^+] = 5.36$, $[\text{Mn}^{\text{III}}(\text{cdta})^-] = 5.0 \times 10^{-5} \text{ mol dm}^{-3}$; $\Delta H^\ddagger = (11.4 \pm 2.3) \text{ kJ mol}^{-1}$, $\Delta S^\ddagger = (179.4 \pm 8.4) \text{ JK}^{-1} \text{ mol}^{-1}$.

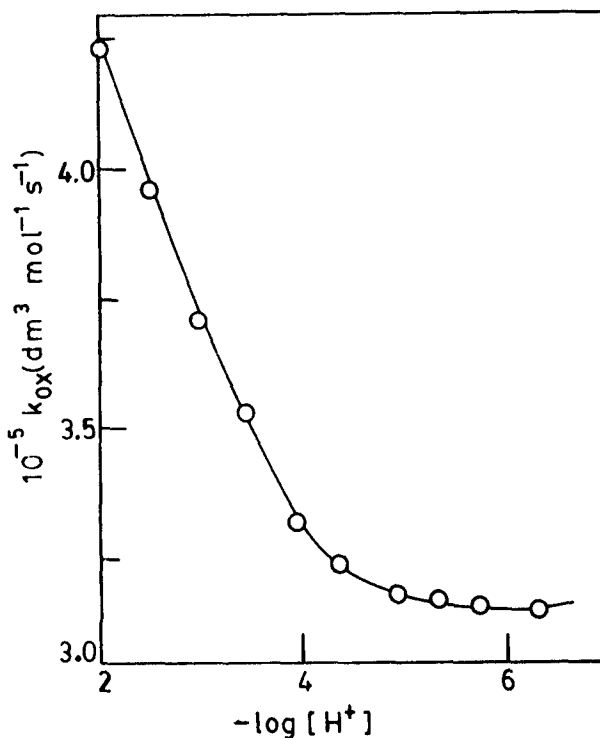
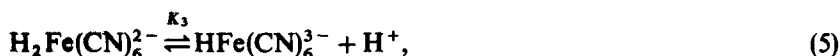


Figure 1. Plot of k_{ox} vs. $-\log[\text{H}^+]$ for the oxidation of ferrocyanide by $\text{Mn}^{\text{III}}(\text{cdta})^-$ with $[\text{Mn}(\text{cdta})^-] = 5.0 \times 10^{-5} \text{ mol dm}^{-3}$, $[\text{Fe}(\text{CN})_6^{4-}]_t = 4.0 \times 10^{-4} \text{ mol dm}^{-3}$, $I = 0.20 \text{ mol dm}^{-3} (\text{NaClO}_4)$, and temperature = 30°C . The curve has been drawn through calculated k_{ox} values and circles denote experimental points.

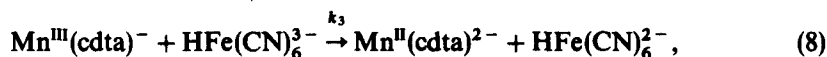
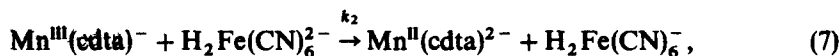
with

$$k_{\text{obs}} = k_1 [\text{M}(\text{CN})_6^{4-}], \quad (\text{M} = \text{Mo and W}). \quad (4)$$

The plot of k_{ox} ($k_{\text{ox}} = k_{\text{obs}}/[\text{M}(\text{CN})_6^{4-}]$) vs. $-\log [\text{H}^+]$ shows a decreasing curve with a limiting value at $\text{pH} \sim 5.0$ ($-\log [\text{H}^+] = 4.89$) (figure 1) for the oxidation of $\text{Fe}(\text{CN})_6^{4-}$ with $\text{Mn}^{\text{III}}(\text{cdta})^-$. This behaviour could be justified by considering the protic equilibria associated with the ferrocyanide ion represented by (5) and (6)



The values of K_3 and K_4 are reported to be $(6 \pm 2) \times 10^{-3} \text{ mol dm}^{-3}$ and $(6.7 \pm 0.03) \times 10^{-5} \text{ mol dm}^{-3}$, respectively (Jordan and Ewing 1962). In the experimental range of pH (2.0–6.5), the reacting ferrocyanide species would be $\text{H}_2\text{Fe}(\text{CN})_6^{2-}$, $\text{HFe}(\text{CN})_6^{3-}$ and $\text{Fe}(\text{CN})_6^{4-}$, and following reaction sequence would be relevant



and the rate law derived as

$$\begin{aligned} -\text{d}/\text{dt}[\text{Mn}^{\text{III}}(\text{cdta})^-] &= k_{\text{ox}}[\text{Mn}^{\text{III}}(\text{cdta})^-][\text{Fe}(\text{CN})_6^{4-}], \\ &= k_{\text{obs}}[\text{Mn}^{\text{III}}(\text{cdta})^-], \end{aligned} \quad (10)$$

$$[\text{Fe}(\text{CN})_6^{4-}]_t = [\text{H}_2\text{Fe}(\text{CN})_6^{2-}] + [\text{HFe}(\text{CN})_6^{3-}] + [\text{Fe}(\text{CN})_6^{4-}], \quad (11)$$

$$k_{\text{ox}} = \frac{k_2[\text{H}^+]^2 + k_3K_3[\text{H}^+] + k_4K_3K_4}{[\text{H}^+]^2 + K_3[\text{H}^+] + K_3K_4}, \quad (12)$$

$$k_{\text{ox}} = k_{\text{obs}}/[\text{Fe}(\text{CN})_6^{4-}]_t.$$

Experimental values of k_{ox} at different $[\text{H}^+]$ were fitted to (12) by means of Simplex Optimisation Program and the best fit of data thus achieved was then fitted to a nonlinear least-squares program to get the standard deviation of each parameter as: $k_2 = (4.58 \pm 0.02) \times 10^5$, $k_3 = (3.71 \pm 0.01) \times 10^5$ and $k_4 = (3.16 \pm 0.01) \times 10^5 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$; $K_3 = (6.46 \pm 0.30) \times 10^{-3}$ and $K_4 = (2.25 \pm 0.13) \times 10^{-4} \text{ mol dm}^{-3}$. A reasonable agreement between the experimental and calculated k_{ox} (figure 1), and also between the reported and calculated equilibrium constants (K_3 and K_4) is noted.

The lowering of rate with increase in pH is unexpected from the thermodynamic point of view. The couples $\text{H}_2\text{Fe}(\text{CN})_6^{-/2-}$, $\text{HFe}(\text{CN})_6^{2-/3-}$ and $\text{Fe}(\text{CN})_6^{3-/4-}$ have the formal potentials (E^0/V) 0.69, 0.416 and 0.34 respectively (Das-Sharma *et al* 1993) and that of $\text{Mn}(\text{cdta})^{-/2-}$ is 0.814 V (Hamm and Sawyn 1967). From these values it is reasonable to consider that $\text{Fe}(\text{CN})_6^{4-}$ is the most effective in transferring electrons

to $\text{Mn}^{\text{III}}(\text{cdta})^-$, and $\text{H}_2\text{Fe}(\text{CN})_6^{2-}$ is the least so. The observed anomaly in electron transfer activity could be explained from electrostatic considerations. When two reactants are negatively charged, the increase in negative charge on one of the reacting species would cause a greater electrostatic repulsion hindering their closest approach in the transition state and thereby the reaction rate decreases. These two opposing factors would act simultaneously slightly offsetting the latter, and an eventual decrease in rate with pH, though not in a drastic manner has been observed. The relevance of proton dependence of rate for the reduction of ferrocyanide may be due to the incomplete dissociation of ferrocyanic acid (third and fourth proton dissociation) whereas the proton independence of rate for cyanotungstate and cyanomolybdate may be due to their complete dissociation of fourth proton in $\text{HM}(\text{CN})_6^{3-}$ in aqueous solution (Kolthoff and Thomsicek 1935) and evidenced from the independence of their UV visible spectra on acidity of the medium (pH 2.0–6.0).

In the reactions studied, no spectral evidence could be gathered to support any inner-sphere association. We have attempted the validity of the Marcus cross-reaction relations (Marcus 1964) ((13)–(15)) without allowance for work terms

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

$$\log f_{12} = (\log K_{12})^2/4[\log(k_{11}k_{22}/Z^2)], \quad (14)$$

$$\log K_{12} = n\Delta E^0/0.06023 \text{ at } 30^\circ\text{C}, \quad (15)$$

where k_{11} , k_{22} , K_{12} , f_{12} and Z have their usual significance. With the help of (13)–(15) along with the reported values of k_{11} , k_{22} and the E^0 of the respective couples, the electron transfer rate constants for each reaction are calculated and listed in table 2. Due to wide variation of the formal reduction potential of $\text{Fe}(\text{CN})_6^{3-/4-}$ couple with acidity and ionic strength of the medium (Kolthoff and Thomsicek 1935) we have determined it under our experimental conditions by cyclic voltammetric measurements. Such determinations showed the formal potentials to be 0.52, 0.49 and 0.31 V (vs. SCE) respectively for $\text{H}_2\text{Fe}(\text{CN})_6^{2-}$, $\text{HFe}(\text{CN})_6^{2-/3-}$ and $\text{Fe}(\text{CN})_6^{3-/4-}$ at 0.2 mol dm^{-3} HClO_4 , pH 4.0 and 5.50 (acetate buffers) and ionic strength 0.2 mol dm^{-3} (NaClO_4). From a comparison of experimental and calculated k_{12} in table 2, it is apparent that a reasonable agreement holds and the electron transfer nearly follows an outer-sphere path. The slight deviation of calculated rate

Table 2. Second-order rate constants for the oxidation of cyanometalates by $[\text{Mn}^{\text{III}}(\text{cdta})]^-$ at 30°C .

Reductants	$E^0(\text{V})$	k_{22} ($\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$)	$k_{12}(\text{exp})$ ($\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$)	$k_{12}(\text{calcd})$ ($\text{mol}^{-1} \text{ dm}^3 \text{ s}^{-1}$)
$\text{Mo}(\text{CN})_6^{4-}$	0.80 ^a	3.0×10^{4a}	6.64×10^3	1.89×10^2
$\text{W}(\text{CN})_6^{4-}$	0.54 ^a	7.0×10^{4a}	6.92×10^4	2.95×10^4
$\text{H}_2\text{Fe}(\text{CN})_6^{2-}$	0.52 ^b	3.0×10^{4c}	4.62×10^5	2.71×10^4
$\text{HFe}(\text{CN})_6^{2-}$	0.49 ^b	1.0×10^{4a}	3.71×10^5	2.59×10^4
$\text{Fe}(\text{CN})_6^{4-}$	0.31 ^b	5.0×10^{3d}	3.15×10^5	3.03×10^5

^aCampion *et al* (1964); ^bcyclic voltammetrically determined; ^cDas-Sharma *et al* (1993); ^ddeMaine and Stanbury (1991); $k_{11}(\text{Mn}(\text{cdta})^{2-/1-}) = 0.70 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ (Macartney and Thompson 1989).

constants from those of experimental ones could arise from (i) formal potential values which would be at some variance with the true electrode potentials, and (ii) negligence of work terms. The present study involves reactions between two negatively charged species whereby alkali metal cation from the reaction medium (NaClO_4) may act as a bridge between them. As a consequence the observed values for electron transfer rate constant may not be truly intrinsic.

References

- Campion R J, Purdie N and Sutin N 1964 *Inorg. Chem.* **3** 1091
Das-Sharma M, Gangopadhyay S, Ali M and Banerjee P 1993 *J. Chem. Res. (S)* 122
deMaine M M and Stanbury D M 1991 *Inorg. Chem.* **30** 2104
Furman N H and Miller C O 1950 *Inorg. Syn.* **3** 160
Gangopadhyay S, Ali M and Banerjee P 1994 *Coord. Chem. Rev.* **133** (in press)
Goodenow E L and Garner C S 1955 *J. Am. Chem. Soc.* **77** 5268
Hamm R E and Suwyn M A 1967 *Inorg. Chem.* **6** 139
Jordon J and Ewing G J 1962 *Inorg. Chem.* **1** 587
Kolthoff M and Thomsicek W J 1935a *J. Phys. Chem.* **39** 945
Kolthoff M and Thomsicek W J 1935b *J. Phys. Chem.* **39** 955
Macartney D H and Thompson D W 1989 *Inorg. Chem.* **28** 2195
Marcus R A 1964 *Annu. Rev. Phys. Chem.* **15** 155