Tetrahedron. Vol. 28, pp. 5567 to 5571. Pergamon Press 1972. Printed in Great Britain

KINETICS AND MECHANISM OF Os(VIII) CATALYSED OXIDATION OF MALATE ION BY ALKALINE HEXACYANOFERRATE (III)

G. C. SONI and G. D. MENGHANI

Department of Chemistry, University of Jodhpur, Jodhpur, India

(*Received in the UK* 29 *July* 1972; *Accepted for publication* 14 *August* 1972)

Abstract— In the reaction between alkaline hexacyanoferrate(III) and malic acid catalysed by Os(VIII), the rate of hexacyanoferrate (III) disappearance was found to be proportional to the concentrations of malate ion, hydroxyl ion and Os(VIII), but independent of the concentration of hexacyanoferrate(III). The reaction was studied at different temperatures, various thermodynamic parameters ΔE, pZ, ΔS^* etc were evaluated.

KINETIC studies on the oxidation of a variety of substances both organic and inorganic by hexacyanoferrate(III) have that unless a catalyst is employed these reactions are either extremely slow or do not proceed. The most widely investigated catalyst is Os(VIII).

Although the kinetics of oxidation of several compounds has been investigated,[1-5] a review of literature shows that oxidation of α-hydroxy acids by alkaline hexacyanoferrate(III) has not received much attention. The present report deals with the oxidation of malic acid by alkaline hexacyanoferrate(III) catalysed by Os(VIII).

RESULTS

Since the rate laws are not affected by the presence or absence of oxygen, no attempt was made to remove oxygen from the mixture, [Substrate] $\gg$ $[Fe(CN)_6]^{-3}$ so as to prevent the secondary oxidation of products. In order to eliminate possible errors due to intervention of products, zero order rate constants (k_0S) were evaluated by graphical method, using the slope of the line obtained by plotting [Hexacyanoferrate] against time. The values of k_0/[malate] (Table 2) and k_0/[Os(VIII)] (Table 3) were found to be fairly constant. This shows first order dependence of the rate on malate and Os(VIII) ions. At low hydroxyl ion concentration the rate follows first order with respect to $[OH^-]$. However it becomes zero order at $[OH^-] > 0{\cdot}25$ M (Table 4). It is observed that change in ionic strength as a result of addition of either K_2SO_4 or KNO_3 affects the rate constants showing the positive salt effect to be operative.

TABLE 1. VARIATION OF REACTION RATE WITH CONCENTRATION OF HEXACYANOFERRATE(III)

[Malate] = $4{\cdot}69 \times 10^{-3}$ M, $[OsO_4] = 2{\cdot}76 \times 10^{-5}$ M,
[NaOH] = 0·14 M, Temp. 35°

$[Fe(CN)_6]^{-3} \times 10^4$ M	2·35	3·52	4·69	5·86
$k_0 \times 10^5$ mole l^{-1} min^{-1}	1·80	1·84	1·92	1·76

TABLE 2. VARIATION OF REACTION RATE WITH CONCENTRATION OF REDUCTANT

[Hexacyanoferrate(III)] = $4{\cdot}69 \times 10^{-4}$ M, [OsO_4] = $2{\cdot}76 \times 10^{-5}$ M,
[NaOH] = 0·14 M, Temp 35°C

[Malate] $\times 10^3$ M	4·69	3·52	2·35	1·17	0·58
$k_0 \times 10^5$ mole l^{-1} min^{-1}	1·95	1·33	0·79	0·38	0·19
$\frac{k_0 \times 10^2}{[\text{Malate}]}$ min^{-1}	0·39	0·38	0·33	0·33	0·33

TABLE 3. VARIATION OF REACTION RATE WITH CONCENTRATION OF CATALYST

[Hexacyanoferrate(III)] = $4{\cdot}69 \times 10^{-4}$ M, [Malate] = $4{\cdot}69 \times 10^{-3}$ M,
[NaOH] = 0·14 M, Temp 35°C

[OsO_4] $\times 10^5$ M	1·38	2·07	2·76	3·45	4·15
$k_0 = 10^5$ mole l^{-1} min^{-1}	1·19	1·36	1·84	1·97	2·16
$\frac{k_0}{[OsO_4]}$ min^{-1}	0·65	0·66	0·67	0·57	0·52

TABLE 4. VARIATION OF REACTION RATE WITH CONCENTRATION OF ALKALI

[Hexacyanoferrate(III)] = $4{\cdot}69 \times 10^{-4}$ M, [Malate] = $4{\cdot}69 \times 10^{-3}$ M.
[OsO_4] = $2{\cdot}76 \times 10^{-5}$ M, Temp 35°

[NaOH] $\times 10^2$ M	7·04	10·56	14·08	17·60	21·12	24·64	28·16	31·69
$k_0 \times 10^5$ mole l^{-1} min^{-1}	1·04	1·44	1·84	2·14	2·55	2·64	2·65	2·64

TABLE 5. EFFECT OF IONIC STRENGTH ON REACTION RATE

[Hexacyanoferrate(III)] = $4{\cdot}69 \times 10^{-4}$ M, [Malate] = $4{\cdot}69 \times 10^{-3}$ M,
[OsO_4] = $2{\cdot}76 \times 10^{-5}$ M, [NaOH] = 0·14 M, Temp. 35°C

µm	$k_0 \times 10^5$ mole l^{-1} min^{-1}	
	KNO_3	K_2SO_4
1·77	—	2·46
1·67	—	2·34
1·56	—	2·12
1·49	2·01	—
1·46	1·75	1·67
1·42	1·64	—
1·41	—	1·31
1·39	1·10	—
1·37	0·69	—

TABLE 6. EFFECT OF TEMPERATURE ON REACTION RATE

[Hexacyanoferrate(III)] = $4{\cdot}69 \times 10^{-4}$ M, [Malate] = $4{\cdot}69 \times 10^{-3}$ M, $[\text{OsO}_4] = 2{\cdot}76 \times 10^{-5}$ M, [NaOH] = 0·14 M

Temp. A	303°	308°	313°	318°	323°
$k_0 \times 10^5$ mole l^{-1} min^{-1}	1·53	1·84	2·12	2·46	3·00

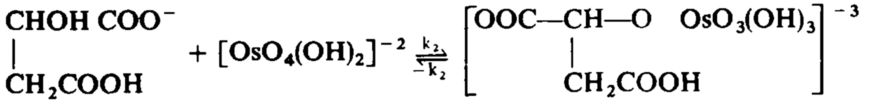
DISCUSSION

On the basis of experimental results oxidation of malic acid by hexacyanoferrate(III) in absence of Os(VIII) does not proceed at all even at high alkali concentration. The fact that hexacyanoferrate(III) is consumed, but does not take part in the rate law, suggests that hexacyanoferrate(III) does not react directly until after the rate determining step.

Since a one electron transfer is involved in the systen the possible existence of free radical intermediate in the oxidation of organic compounds by alkaline hexacyanoferrate(III) is expected, but experimental evidence does not indicate presence of free radicals.

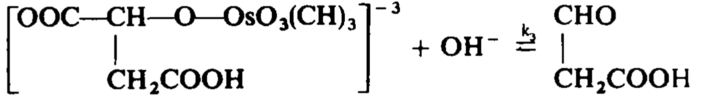
The alkali dependence of the reaction indicates that acid anions are the entities oxidized. The apparent increase in the solubility of OsO_4 in presence of malic acid and disappearance of yellow brown colour of alkaline OsO_4 on addition of malic acid, suggest that reaction takes place between substrate and OsO_4 with the formation of soluble complex.[5] The mechanism proposed involves formation of a complex between acid anion and osmate (VIII) ion furnished by action of OsO_4 and KOH. This complex then rapidly dissociates to give aldehyde and osmate (VI) ion, subsequently osmate (VIII) ion is regenerated by oxidation of osmate (VI) ion by hexacyanoferrate (III). This observation is in full agreement with that of Mayell[6] that hexacyanoferrate (III) is effective in oxidizing Os (VI) to Os (VIII). In view of the above facts, following mechanistic steps are suggested

$$\text{OsO}_4 + 2\,[\text{OH}^-] \overset{k_1}{\rightleftharpoons} [\text{OsO}_4(\text{OH})_2]^{-2} \tag{1}$$



$$\begin{array}{l}\text{CHOH COO}^- \\ | \\ \text{CH}_2\text{COOH}\end{array} + [\text{OsO}_4(\text{OH})_2]^{-2} \underset{-k_2}{\overset{k_2}{\rightleftharpoons}} \left[\begin{array}{l}\text{OOC—CH—O}\quad \text{OsO}_3(\text{OH})_3 \\ \qquad\quad | \\ \qquad\ \ \text{CH}_2\text{COOH}\end{array}\right]^{-3}$$

Slow (2)



$$\left[\begin{array}{l}\text{OOC—CH—O—OsO}_3(\text{CH})_3 \\ \qquad\quad | \\ \qquad\ \ \text{CH}_2\text{COOH}\end{array}\right]^{-3} + \text{OH}^- \overset{k_3}{\rightleftharpoons} \begin{array}{l}\text{CHO} \\ | \\ \text{CH}_2\text{COOH}\end{array} + \text{CO}_2 + [\text{OsO}_3(\text{OH})_4]^{-4} \tag{3}$$

$$[\text{OsO}_3(\text{OH})_4]^{-4} + 2\text{Fe(CN)}_6^{-3} \overset{k_4}{\rightleftharpoons} [\text{OsO}_4(\text{OH})_2]^{-2} + 2\text{Fe(CN)}_6^{-4} + \text{H}_2\text{O} \tag{4}$$

Applying steady state approximation, the rate law comes out to be

$$R = -\frac{\text{d}}{\text{d}t}[\text{Fe(CN)}_6]^{-3} = \frac{k_2k_3[\text{Malate}][\text{Os (VIII)}][\text{OH}^-]}{k_{-2} + k_3[\text{OH}^-]} \tag{5}$$

or

$$\frac{1}{R} = \frac{k_{-2}}{k_2k_3[\text{Malate}][\text{Os (VIII)}][\text{OH}^-]} + \frac{1}{k_2[\text{Malate}][\text{Os (VIII)}]} \tag{6}$$

At high alkali concentration it might be assumed that $k_3[\mathrm{OH}^-] \gg k_{-2}$ and the rate law then reduces to

$$R = k_2[\mathrm{Malate}][\mathrm{Os\,(VIII)}] \tag{7}$$

or

$$\frac{1}{R} = \frac{1}{k_2[\mathrm{Malate}][\mathrm{Os\,(VIII)}]} \tag{8}$$

On plotting $1/R$ against $1/[\mathrm{OH}^-]$ a curve composed of two straight lines intersecting at a point ($[\mathrm{OH}^-] = 0{\cdot}25$ M) was obtained (Fig 1). The first part of the curve (a straight line parallel to abscissa) proves zero order dependence and the second part of the curve (also a straight line) proves first order dependence of the rate on hydroxyl ion concentration. This is in good agreement with the Eqs 6 and 8.

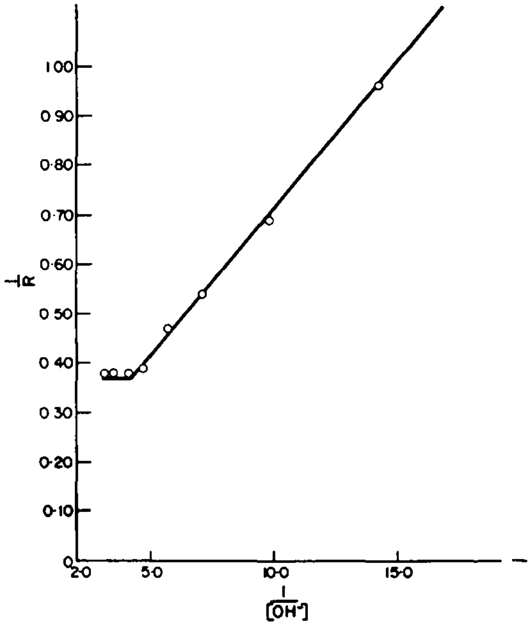


Fig 1

The thermodynamic parameters ΔE, pZ and ΔS^* were evaluated and found to be 6·5 Kcals mole^{-1}, $2{\cdot}9 \times 10^4$ min^{-1} (at 40°) and $-$ 38·9 EU respectively. More -ve value of ΔS^* than expected lends support to the rate determining step Eq 2. Where two anions coordinate to give a bigger complex ion resulting thereby in the loss of freedom of motion, positive salt effect suggests probably reaction between two similarly charged ions as shown in step (2) of the mechanism.

EXPERIMENTAL

Hexacyanoferrate(III) was of B.D.H. (AnalaR) grade sample. The standard soln of malic acid was prepared just before starting the reaction. The malic acid and the NaOH used were of Riedel and E. Merck grade.

The soln of catalyst was obtained by dissolving a known weight of OsO_4 in KOH aq [0·05 M].

A mixture containing the requisite quantities of malic acid, OsO_4, NaOH was prepared and together with the hexacyanoferrate (III) soln was thermostated for about 20 min to attain experimental temp of 35°. A known volume of hexacyanoferrate(III) was then transferred to the mixture and aliquots were removed from time to time and analysed for unconsumed hexacyanoferrate(III) with a Klett-Sumersons Photoelectric Colorimeter within the wave length range of 400–450 mμ. Variations of concentration of hexacyanoferrate(III) were well within the range of Beer's law ($1{\cdot}6 \times 10^{-3}$ M – $5{\cdot}0 \times 10^{-3}$ M). No absorption was evident due to other species.

Acknowledgement—One of us (G. C. Soni) is thankful to the Tu.G.C., India, for an award of a Junior Research Fellowship and a grant, we also thank Professor R. C. Kapoor for his encouragement and interest.

REFERENCES

[1] F. Solymoni, *Magyar Kem Fotyoirate* **63**, 294 (1957)
[2] E. J. Mechan, I. M. Kolthoff and H. Kakinchi, *J. Phys. Chem.* **66**, 1238 (1962)
[3] M. C. Agarwal and S. P. Mushram, *Ibid.* **72**, 1497 (1968)
[4] P. C. Pandey and V. N. Singh, *Ind. J. Chem.* **9**, 430 (1971)
[5] N. P. Singh and V. N. Singh, *Aust. J. Chem.* **21**, 2913 (1968)
[6] J. S. Mayell, *Ind. Eng. Chem.* **7**, 129 (1968)