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Kinetics of Oxidation of L-Malic Acid by Mn(III) Pyrophosphate

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The oxidation of L-malic acid by Mn(III) pyrophosphate in sulphuric acid medium has been found to be first order with respect to Mn(III). The oxidation rate has been found to increase with [malic acid], $[H^+]$ decreases inversely with [pyrophosphate] free. Thermodynamic parameters have been evaluated and a suitable mechanism involving complex formation and free radicals is proposed.

INTRODUCTION

The oxidation of L-malic acid by V(V),[1, 2] peroxydisulphate[3] and Ce(IV), and Cr has already been reported.[4] Some conflicting views have appeared regarding the products and the number of equivalent oxidant per mole of the acid in the oxidation reactions. To confirm and reconcile the conflicting views, present studies have been carried out.

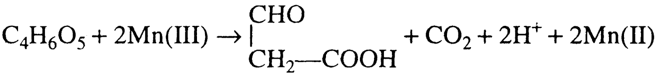
EXPERIMENTAL

Mn(III) pyrophosphate was prepared by the method of Linguange and Karplus[5]. L-malic acid (Reidel) was used, other reagents like H_2SO_4, $MnSO_4$, $KMnO_4$, $Na_4P_2O_7$, Mohr's salt and ceric sulphate etc. were of AR/BDH grade.

Reactions were followed by quenching aliquots withdrawn at regular intervals in slight excess of ferrous ammonium sulphate solution and estimating unreacted Fe(II) with Ce(IV) using N-phenyl anthranilic acid as an indicator.

RESULTS AND DISCUSSION

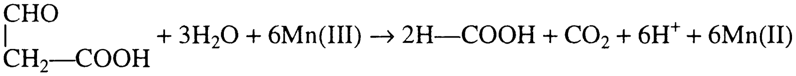
It was observed that one mole of L-malic acid required 2 moles of Mn(III) for oxidation. The equation is



$$C_4H_6O_5 + 2Mn(III) \rightarrow \begin{array}{l} CHO \\ | \\ CH_2\text{—}COOH \end{array} + CO_2 + 2H^+ + 2Mn(II)$$

Formyl acetic acid.

It was observed that 6 moles of Mn(III) were required per mole of formyl acetic acid for subsequent stage of reaction (very slow). Hence the reaction of this stage of oxidation is:



$$\begin{array}{l} CHO \\ | \\ CH_2\text{—}COOH \end{array} + 3H_2O + 6Mn(III) \rightarrow 2H\text{—}COOH + CO_2 + 6H^+ + 6Mn(II)$$

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The oxidation of L-malic acid is a fast reaction and formyl acetic acid formation has been confirmed in the reaction even after nearly 1 h. The latter stage of oxidation (*i.e.*, formation of H—COOH) is a very slow reaction. The formation of H—COOH (by $HgCl_2$ test) was confirmed only after a week. The formyl acetic acid is an unstable compound which is known to exist in solution only.

Thus it is evident from stoichiometric studies that the reaction product is formyl acetic acid and not formic acid. The formation of the formyl acetic acid (unstable) was confirmed by the test of —CHO and COOH groups in the test samples. The presence of free radicals was also confirmed during the reaction by the induced polymerisation reaction with acrylonitrile.

First order kinetics were found by the fading of Mn(III) when [L-malic acid] and $[H_2SO_4]$ were in large excess. The pseudo first order rate constants K_1 found to increase with [Mn(III)], [L-malic acid] and decrease with $[Na_4P_2O_7]$ (Table-1).

TABLE-1
EFFECT OF Mn(III), L-MALIC ACID AND $Na_4P_2O_7$ CONCENTRATIONS

$[H^+] = 1.5$ M Temp. 40°C

$[Mn(III)] \times 10^{-3}$ M	[Malic acid] $\times 10^{-3}$ M	$[Na_4P_2O_7] \times 10^{-2}$ M	$K_1 \times 10^4$ sec^{-1}
1.0	2.5	2.0	16.86
1.0	2.0	2.0	11.74
1.0	1.5	2.0	8.88
1.0	1.0	2.0	6.83
1.0	1.0	1.0	9.52
1.0	1.0	3.0	4.43
1.0	1.0	4.0	3.12
1.5	1.0	2.0	6.45
2.0	1.0	2.0	6.76
2.5	1.0	2.0	7.03

The rate has been found to increase with the first power of $[H^+]$ in runs (Table-2) where ionic strength was maintained by $NaHSO_4$ addition.

TABLE-2
EFFECT OF H^+ CONCENTRATION

$[Mn(III)] = 1.0 \times 10^{-3}$ M, [L-Malic acid] $= 1.0 \times 10^{-2}$ M
$[Na_4P_2O_7] = 2.0 \times 10^{-2}$ M, $[\mu] = 2.5$ M Temp. = 40°C

$[H^+]$	0.50	1 .00	1.50	2.00	2.50
$K_1 \times 10^4$ sec^{-1}	2.14	4.13	6.03	8.23	10.36

The linear Bunnett plot was obtained having slope value 10.21

The oxidation raction was studied at five different temperatures (Table-3). The various thermodynamic parameters evaluated have been also given in Table 3.

TABLE-3
EFFECT OF TEMPERATURE

$[\text{Mn(III)}] = 1.0 \times 10^{-3}$ M, $[\text{L-Malic acid}] = 1.0 \times 10^{-2}$ M
$[\text{H}^{+}] = 1.50$M $[\text{Na}_4\text{P}_2\text{O}_7] = 2.0 \times 10^{-2}$ M,

Temp. °C	$K_1 \times 10^4$ sec.$^{-1}$	ΔE kJ mol^{-1}	ΔS* JK^{-1} mol^{-1}	ΔG* kJ mol^{-1}
30	3.23	52.0	–70.3	73.1
35	4.50	52.0	–70.3	73.2
40	5.93	53.0	–70.3	73.2
45	9.32	52.1	–70.4	73.3
50	12.20	52.2	–70.4	73.4
	Average	52.0	–70.3	73.2

Mn(III) pyrophosphate exists as $\text{Mn}(\text{H}_2\text{P}_2\text{O}_7)_3^{3-}$ in acidic medium[6]. In the present case due to association (Table-2) the species can be represented as

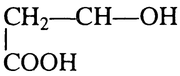
$$\text{Mn}(\text{H}_2\text{P}_2\text{O}_7)_3^{3-} + \text{H}^+ \overset{K}{\rightleftarrows} \text{Mn}(\text{H}_3\text{P}_2\text{O}_7)(\text{H}_2\text{P}_2\text{O}_7)_2^{2-} \qquad (1)$$

The following reaction steps can now be proposed:

$$\text{C}_4\text{H}_6\text{O}_5 + \text{Mn}(\text{H}_3\text{P}_2\text{O}_7)(\text{H}_2\text{P}_2\text{O}_7)^{2-} \overset{K_2}{\rightleftarrows} \underset{\text{complex}}{[\text{Mn}(\text{H}_3\text{P}_2\text{O}_7)(\text{H}_2\text{P}_2\text{O}_7)(\text{C}_4\text{H}_6\text{O}_5)]} + \text{H}_2\text{P}_2\text{O}_7^{2-} \qquad (2)$$

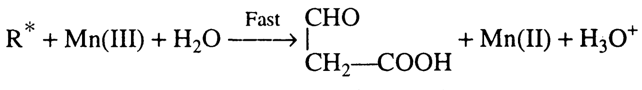
This cyclic complex then disproportionates in a slow step producing free radical by a C—C bond fission.

$$\text{Complex} \xrightarrow[\text{slow}]{K_s} \underset{\text{Free Radical}}{R^*} + \text{Mn}(\text{H}_2\text{P}_2\text{O}_7) + \text{H}_4\text{P}_2\text{O}_7 + \text{CO}_2 \qquad (3)$$

where R* =


$$\begin{array}{l}\text{CH}_2\text{—CH—OH} \\ | \\ \text{COOH}\end{array}$$

The free radical thus formed further breaks to produce in a fast step:



$$R^* + \text{Mn(III)} + \text{H}_2\text{O} \xrightarrow{\text{Fast}} \begin{array}{l}\text{CHO} \\ | \\ \text{CH}_2\text{—COOH}\end{array} + \text{Mn(II)} + \text{H}_3\text{O}^+ \qquad (4)$$

Formyl acetic acid

Thus on the basis of steps (1)–(4) the final rate law can be derived as

$$\frac{-d[\text{Mn(III)}]}{dt} = \frac{K_S K K_2\, [\text{malic acid}][\text{Mn(III)}]\, [\text{H}^+]}{[\text{H}_2\text{P}_2\text{O}_7^{2-}] + K_2\, [\text{malic acid}]}$$

As there is no kinetic evidence of complex formation (Table-1), K_2 should be very small; hence

$$\frac{-d[\text{Mn(III)}]}{dt} = \frac{K_S K K_2\, [\text{Malic Acid}][\text{Mn(III)}]\, [\text{H}^+]}{[\text{H}_2\text{P}_2\text{O}_7^{2-}]} = K_1[\text{Mn(III)}]$$

where $K_1[Mn(III)]$ is observed pseudofirst order rate constant.

Due to coordination the activation energy for C—C bond fission is lowered[7] and this is in agreement with the observed value of ΔE. The negative value of ΔS* also explains the C—C bond fission in the reaction. Waters *et al.*[9] suggested the similar C—C bond fission in 2-hydroxy acids oxidation by Mn(III) pyrophosphate.

The above proposed steps and the rate law incorporate the kinetic results satisfactorily.

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