

A Study on Oxidation of Pentaammine Cobalt (III) Complexes of Lactic Acid by Using Mn (IV) Oxidant

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Abstract

The electron transfer reaction exhibits first order each in cobalt (III) and manganese (IV). A binuclear complex formation is established. One mole of lactato cobalt (III) complex consumes one mole of Mn^(IV) heteropolyanion yielding acetaldehyde, Co^(II) and CO₂. A suitable mechanism in consistent with the rate law has been proposed.

Key words: Pentaammine cobalt (III) complex, Mn^(IV), HPA, Lactic acid, electron transfer reaction.

INTRODUCTION

In all the cases of induced electron transfer reactions discussed so far but one¹⁻⁷ reaction centers on cobalt (III) complexes were separated by conjugated systems, and oxidation took place without alteration of the carbon and electron of ligand. The studies on Ce^(IV) induced electron transfer reaction in pentaammine cobalt (III) complexes of Lactic acid were interesting as the oxidisable hydroxyl group is separated from carboxyl bound to centre by a saturated fragment (viz) carbon-carbon bond scission and reduction at cobalt (III) centre⁸⁻¹². The most striking fact of this study was that with all three complexes involved, Co was formed in quantity equivalent to the (carboxylato) cobalt (III) reacting, whether the reaction was carried out with Ce^(IV) or with Co^I in excess. Indeed. This equivalency persists even when the [Ce^(IV)] : Co^{III} ratio chosen exceeded 20:1. While partition of a proposed radical intermediate between two competing paths was an important fact of past studies^{4,6}, the authors of this investigation report no indication of such a duality of reaction paths.

As Cr^(IV), generated instituted by the reaction of Cr^(VI) and V^(IV), resembles Ce^(IV)

in its reactivity, induced electron transfer reaction with pentaammine cobalt(III) complexes of α - hydroxy acids have been attempted with this oxidant. The reaction sequence proposed suggests that the Cr^(IV) oxidation necessarily occurs first at the hydroxyl center generating a radical which should collapse in such a way, that C-C fission and act of one electron transfer to Co^(III) occur synchronously or very nearly so, in the formation of Co^(III) occurs synchronously or very nearly so, in the formation of Co^(II). The striking feature of this study was that the presence of Cr^(IV) in a reaction system could be evidenced by the formation of Co^{II} as the former induces electron transfer in cobalt (III) complexes of Lactic acid. From the kinetic and stoichiometric studies made on V^(V) induced electron transfer in pentaammine cobalt (III) complexes of Lactic acid, the fraction of reaction proceeding by C-C and C-H bond fissions has been estimated. The study provided evidence for the dualistic behavior of V^(V) both as one and two - equivalent oxidant in its reaction.

EXPERIMENTAL

The stoichiometric Studies for the HPA oxidation of pentaammine Cobalt (III) complexes of Lactic acid and unbound ligands in the presence of sulphuric acid were carried out with oxidant in excess. The $[H^+]$ and ionic strength were maintained as in the corresponding rate measurements. The temperature was maintained at 28°C.

After nine half lives when the reaction was nearing completion, the concentration of unreacted HPA was determined both iodometrically and spectrometrically from the change in absorbance measured at 350nm. "[HPA] was calculated after applying due blank corrections for decomposition of HPA and aquation of Cobalt (III) Complexes of Lactic acid in the presence of sulphuric acid, similar calculations about [HPA] was made for the unbound ligands also. The stoichiometry was calculated from the ratio between reacted [oxidant] and [substrate] from the decrease in the absorbance measured for the Cobalt [III] complex, the amount of Cobalt (III) reduced was calculated. This value was then compared to the amount of Cobalt (II), and carbonyl compound. Stoichiometric data for HPA Oxidation of $Co^{(III)}$ bound and unbound.

RESULTS AND DISCUSSION

Dependence of rate

on $[(NH_3)_5 Co^{(III)} - L]^{2+}$ Complex of

Lactic acid. The kinetics of heteropolyanion

oxidation of $[(NH_3)_5 Co^{(III)} - L]^{2+}$

complexes of Lactic acids has been studied

in the acid medium. The rate of HPA

oxidation of $[(NH_3)_5 Co^{(III)} - L]^{2+}$

Complexes of Lactic depends nearly on the

first power of the concentration of cobalt

(III) complexes. The specific rates

calculated remain constant (Table 1) and the graph of time versus $(1+\log OD)$ are linear {Figure 1}. This is further substantiated from the study of changing the concentration

of $[(NH_3)_5 Co^{(III)} - L]^{2+}$ complexes of

Lactic acid, from 6.0×10^{-3} to 12.0×10^{-3} mol dm⁻³ and 8.0×10^{-4} to 60.0×10^{-4}

mol dm⁻³ depends nearly on the first order of the concentration of cobalt (III)

complexes (Table 2). The graph of $\log k$, versus $\log [Co]^{III}$ are linear with slope nearly equal to 1 [Figure 2] Hence the rate of disappearance of $Mn^{(IV)}$ is given as

$$-d[Mn^{(IV)}] / dt = k_1 [Mn^{(IV)}] [Co^{(III)}]^{-2}$$

Dependence of rate on HPA

The rate of HPA oxidation of lactic acid also depends on HPA concentration. The specific rates calculated remains constant and the for the various concentration of HPA from 1 to 8×10^{-4} mol/dm³ at a fixed concentration of lactic acid shows first order dependence. Hence the disappearance of $Mn^{(IV)}$ in the concentration range studied is given as

$$-d[Mn^{(IV)}] / dt = k_1 [Mn^{(IV)}] [\text{lactic acid}]$$

Dependence of rate on sulphuric acid concentration

The rate of HPA oxidation of lactic acid are an acid catalyzed reaction and the effect of $[H_2SO_4]$ concentration on the rate of $Mn^{(IV)}$ oxidation has been studied in the concentration range from 0.4 to 1.0 mol/dm³ and 0.1 to 0.8 mol/dm³ with increasing concentration $[H_2SO_4]$ the rate of $Mn^{(IV)}$ oxidation increases proportionally and a graph of logarithm of specific rate verses logarithm $[H_2SO_4]$ concentration is linear with slope nearly equal to unity.

$$-d[\text{Mn}^{(\text{IV})}]/dt = k_2 [\text{Mn}^{(\text{IV})}][\alpha\text{-hydroxy acids}][\text{H}^+]$$

Table 1

$[(\text{NH}_3)_5 \text{Co}^{\text{III}} - \text{L}]^{2+}$	=	$16 \times 10^{-3} \text{ mol/dm}^3$
[HPA]	=	$5 \times 10^{-4} \text{ mol/dm}^3$
$[\text{H}_2\text{SO}_4]$	=	0.1M
Temperature	=	32°C
λ	=	350 nm
L	=	Lactic acid

Time	OD (s)	$10^5 k \text{ s}^{-1}$
3600	0.903	2.512
6600	0.825	2.627
9600	0.754	2.737
12600	0.670	2.845
15600	0.612	2.858
18600	0.577	2.764
21600	0.526	2.757

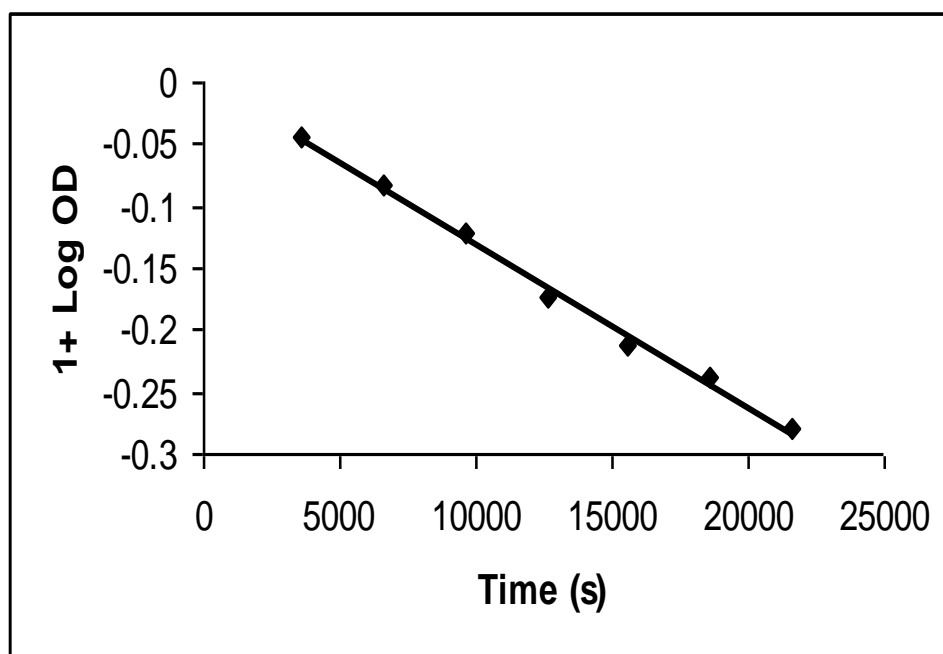
Figure – 1
FIRST ORDER PLOT

Table 2

[HPA]	=	$5 \times 10^{-4} \text{ mol/dm}^{-3}$
$[\text{H}_2\text{SO}_4]$	=	0.2M
Temperature	=	32°C

λ	=	350 nm
$10^3[(\text{NH}_3)_5 \text{Co}^{\text{III}} - \text{L}]^{2+} \text{ M}$	$10^5 k_1 \text{ s}^{-1}$	$10^3 k_2 \text{ s}^{-1}$
Lactic Acid		
8.0	1.340	1.754
16.0	2.747	1.763
32.0	5.438	1.745
60.0	10.302	1.756

Figure – 2
FIRST ORDER PLOT

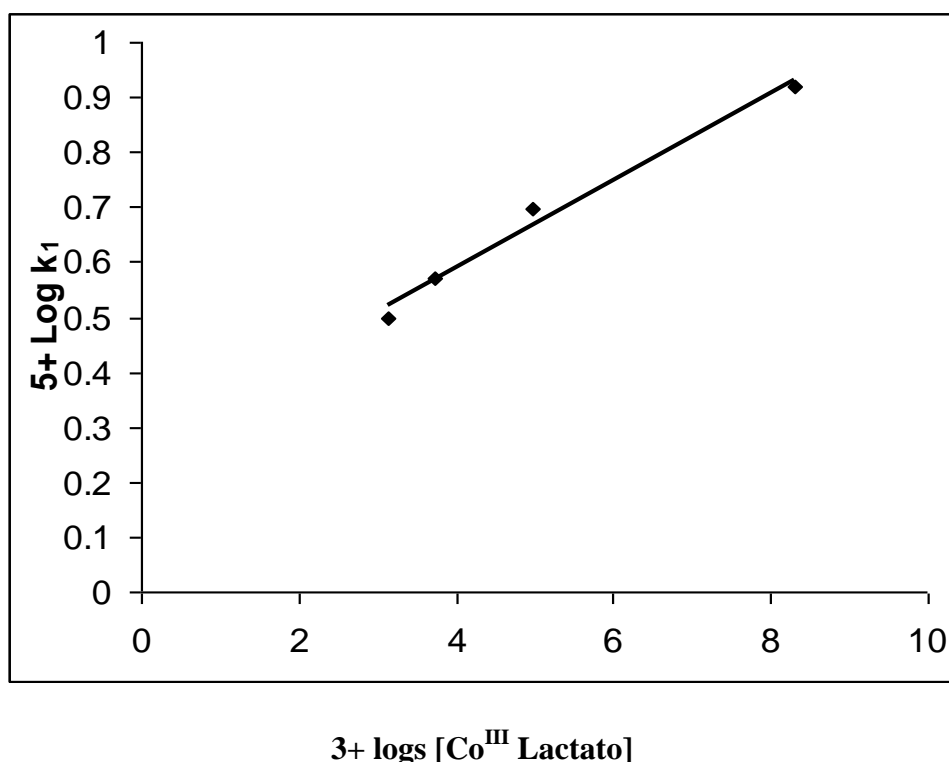


Table 3

$[(\text{NH}_3)_5 \text{Co}^{\text{III}} - \text{L}]^{2+}$	=	$5 \times 10^{-3} \text{ mol/dm}_3$
[HPA]	=	$3 \times 10^{-4} \text{ mol/dm}_3$
[H ₂ SO ₄]	=	0.4M
Temperature	=	32°C
λ	=	350nm
L	=	Lactic acid

$$10^3 [(\text{NH}_3)_5 \text{Co}^{\text{III}} - \text{L}]^{2+} \text{ M} \quad 10^4 [\text{H}_2\text{SO}_4] \text{ M} \quad 10^5 k_1 \text{ s}^{-1} \quad 10^5 k_2 \text{ s}^{-1}$$

Lactato		
0.2	1.979	9.912
0.4	3.845	9.842
0.6	5.943	9.905
0.8	7.920	9.893

Figure – 3

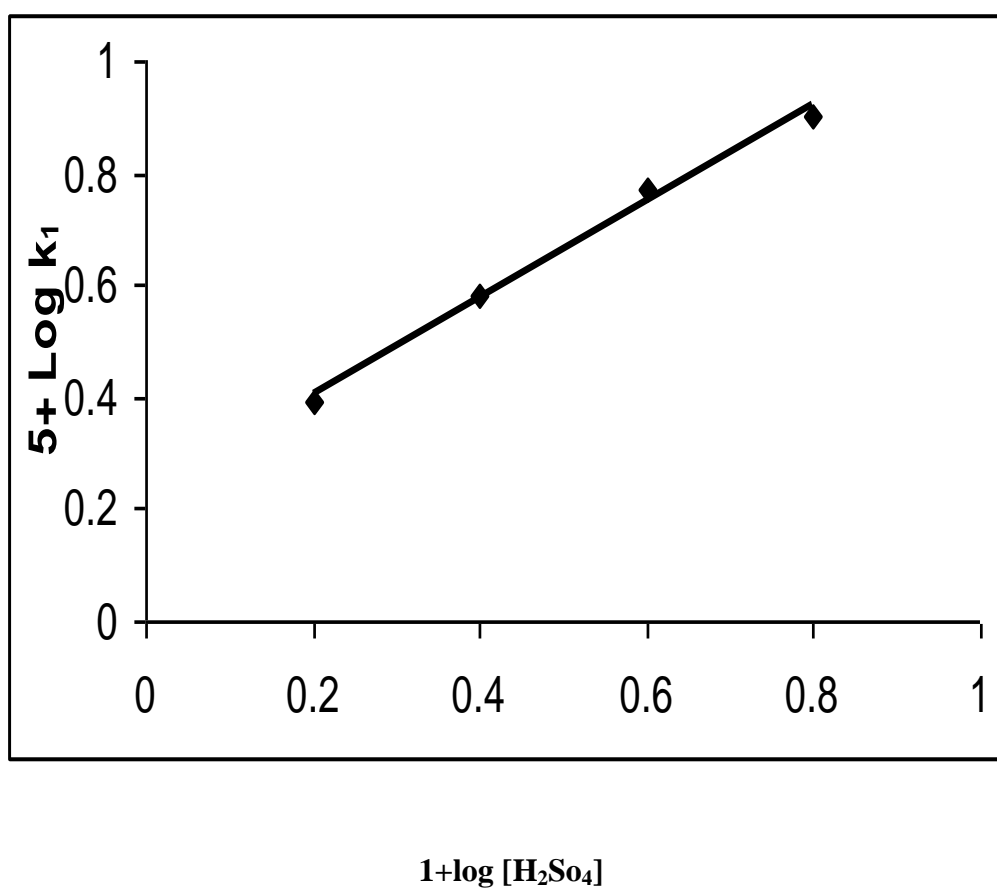
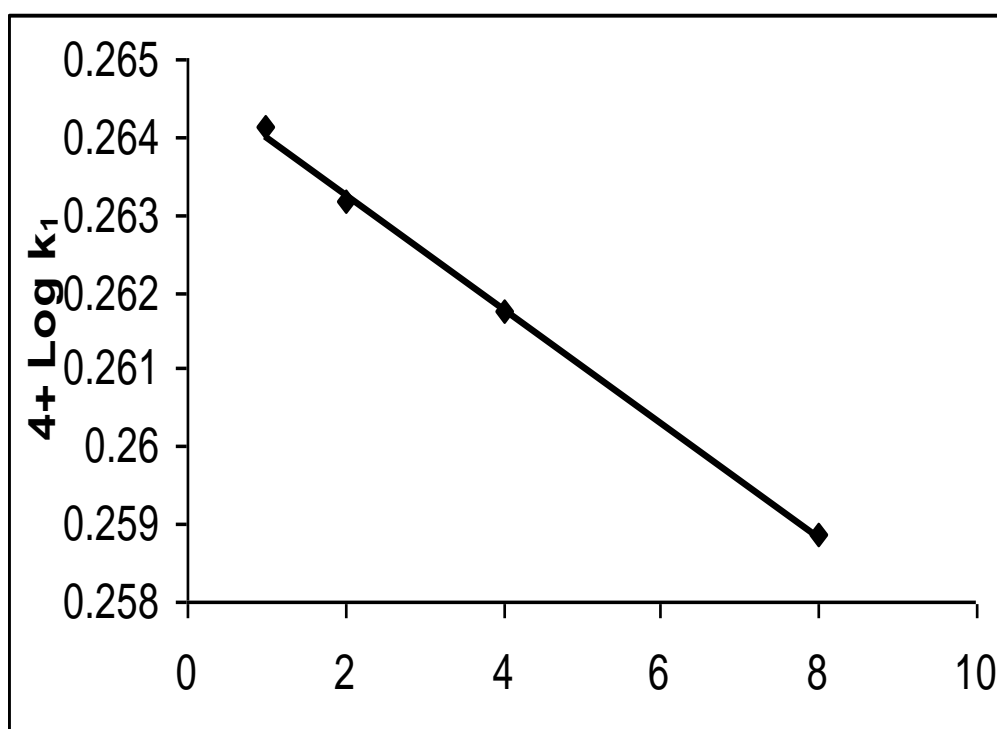


Table 4

Lactic acid	=	$1 \times 10^{-3} \text{ mol/dm}^3$
$[H_2SO_4]$	=	0.8M
Temperature	=	32°C
λ	=	350nm

10^2 (α -hydroxy acid)	10^4 [HPA] M	$10^1 k_2 s^{-1}$
L=Lactic acid		
1.0		1.827
2.0		1.862
4.0		1.814
8.0		1.815

Figure – 4
DEPENDENCE OF RATE ON [LACTIC ACID]



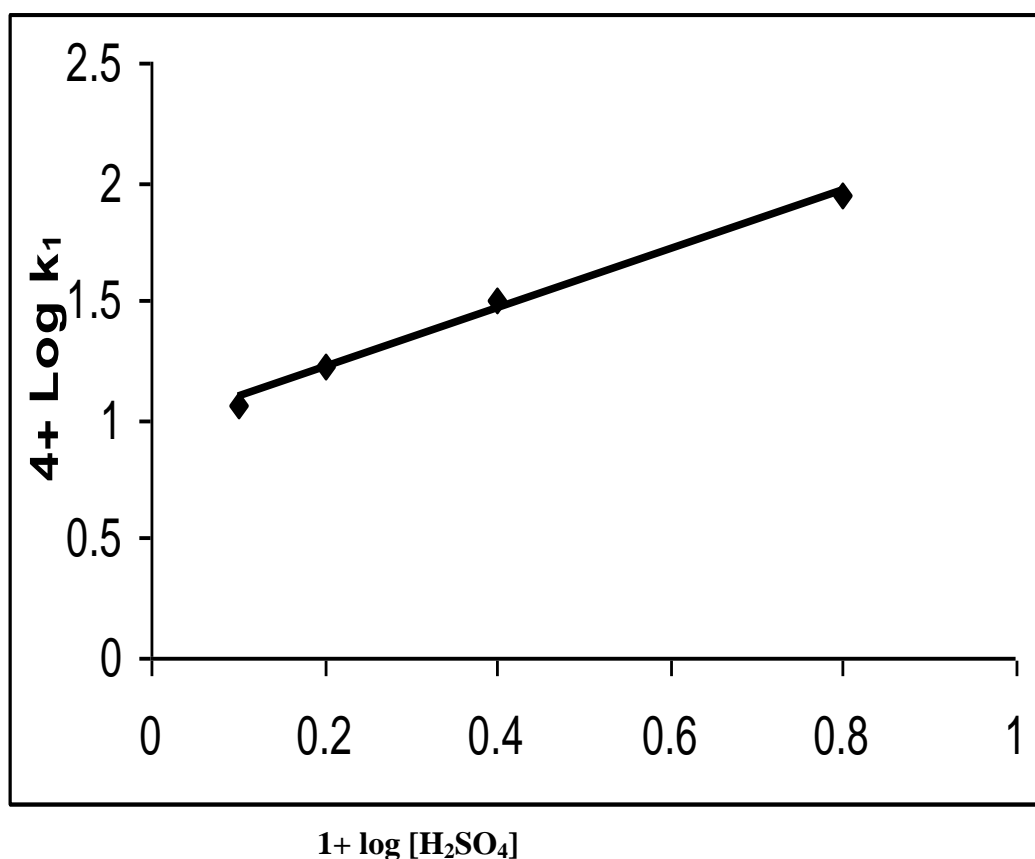
$2 + \log [\text{Lactic Acid}]$

Table 5

Lactic acid	=	$7 \times 10^{-3} \text{ mol/dm}^3$
[HPA]	=	$5 \times 10^{-3} \text{ mol/dm}^3$
[H ₂ SO ₄]	=	0.8M
Temperature	=	32°C
λ	=	350nm

$10^3 [\text{H}_2\text{SO}_4] \text{ M}$	$10^5 k_1 \text{ s}^{-1}$	$10^4 k_2 \text{ s}^{-1}$
0.1	9.371	9.441
0.2	18.826	9.415
0.4	37.756	9.433
0.8	75.236	9.405

Figure – 5
DEPENDENCE OF RATE ON $[\text{H}_2\text{SO}_4]$



MECHANISM

A brief account of the features of $\text{Mn}^{(\text{IV})}$ induced electron pentaammine cobalt (III) complexes lactic acid is furnished in this chapter before a mechanistic scheme is proposed of this reaction.

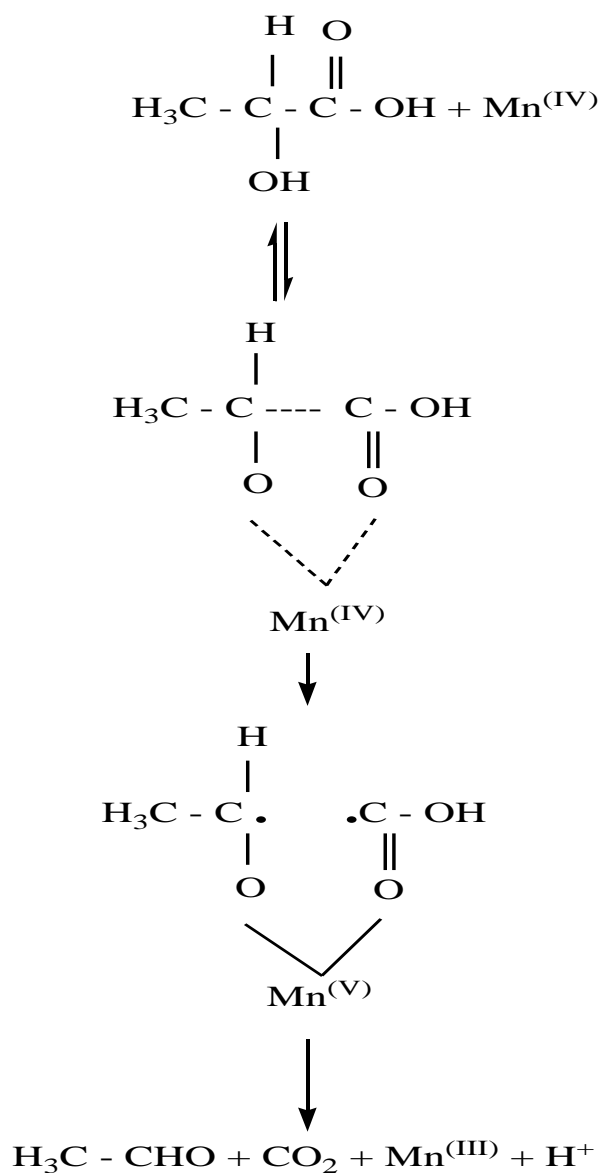
1. The rate of $\text{Mn}^{(\text{IV})}$ induced electron transfer in pentaammine cobalt (III) complexes of lactic acid depends on the

first power of concentration of cobalt (III) and the first power of concentration of $\text{Mn}^{(\text{IV})}$.

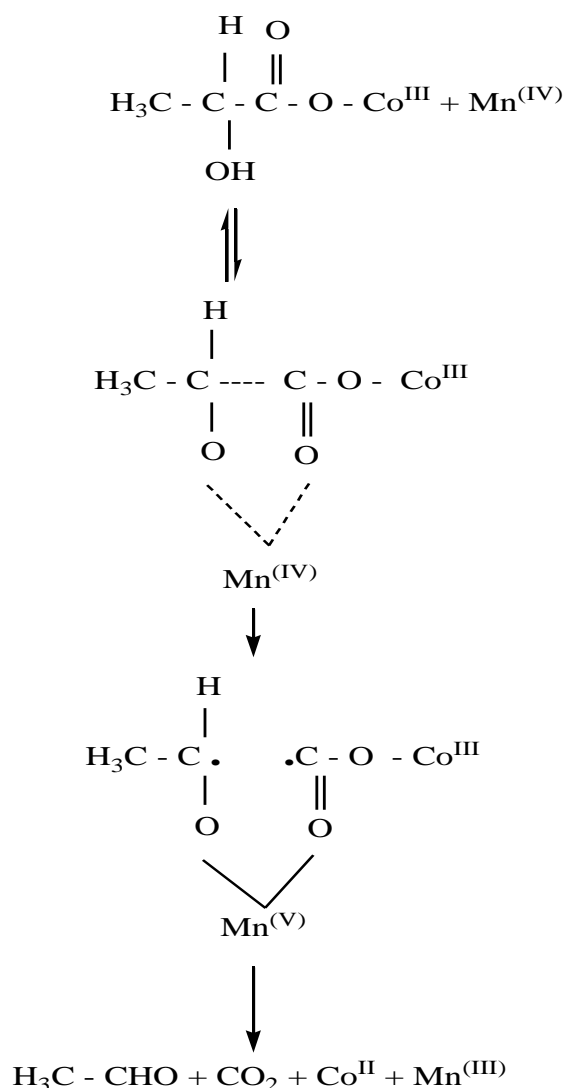
2. One mole of $\text{Co}^{(\text{III})}$ complex consumes nearly 1 mol of $\text{Mn}^{(\text{IV})}$ yielding nearly 100% acetaldehyde one mole of unbound lactic acid needs nearly 2 mole of $\text{Mn}^{(\text{IV})}$ yielding about 100% acetaldehyde

3. There is 100 % decrease in absorbance of 502 nm corresponding on the reduction of $\text{Co}^{(\text{III})}$ centre. suggesting the ligation of carboxylic acid increases the rate of induced electron transfer.
4. The rate of $\text{Mn}^{(\text{IV})}$ oxidation on bound and bound a lactic acid are different

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Scheme - 2



Scheme - 1

As the ligation of carboxylic acid (lactic acid) by $\text{Co}^{\text{(III)}}$ centre, the order with the respect to $\text{Co}^{\text{(III)}}$ complexes is unity, probably there is a possibilities of binuclear complex formation between $\text{Mn}^{\text{(IV)}}$ and $\text{Co}^{\text{(III)}}$ complex. In the presence of any such precursor complex formation, initial act of one electron transfer to $\text{Mn}^{\text{(IV)}}$ may occur by inner sphere path in the slow step.

According to the scheme I $\text{Mn}^{\text{(IV)}}$ oxidizes – OH centre and induces formation of a radical, in synchronous step undergoing C – C bond fission yielding $\text{Co}^{\text{(III)}}$. As the amount of acetaldehyde or $\text{Co}^{\text{(III)}}$ formed is

100 % of $[\text{Co}^{\text{(III)}}]$ initial (wide experimental section table: 4 and 5). As on mole of Lactato cobalt (III) complex consumes 1 mole of $\text{Mn}^{\text{(IV)}}$ yielding CH_3CHO and $\text{Co}^{\text{(II)}}$, Carbondioxide.

CONCLUSION

Induced electron transfer reaction has been attempted presently with HPA and pentaammine cobalt (III) complex of lactic acid. The reaction exhibits second order kinetics and in the case of Lactato complex the amount of cobalt (III) reduced corresponds to nearly 100%. The induced

electron transfer in cobalt (III) lactato complex, the intermediate radical formed dissociates in a nearly synchronous manner with carbon-carbon bond cleavage only to the extent of 100% and suggesting 100% C-C cleavage.

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