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KINETIC STUDY OF OXIDATION OF PENTAAMMINECOBALT (III) COMPLEXES OF α-AMINO ACIDS BY Mn (III) ACETATE, Mn (IV) HETEROPOLYANION AND Mn (III) PERCHLORATE IN MICELLAR MEDIUM

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ABSTRACT

Oxidation of pentaamminecobalt (III) complexes of α-amino acids by Mn (III) acetate, Mn (IV) heteropolyanion and Mn (III) perchlorate in micellar medium yielding nearly 100% of carbonyl compounds are ultimate products. This oxidation as a diagnostic tool to find out the fraction proceeding by synchronous cleavages of N-H and C-C bonds. It has been found the rate of oxidation of Co (III) complexes of unbound and bound moieties are enhanced more in the presence of CTAB when compare to the NaLS.

Key words: Pentaamminecobalt (III) complexes, Induced electron transfer reaction, Mn (III) acetate, Manganese (IV) heteropolyanion and Mn (III) perchlorate, Micelles, NaLS, CTAB.

INTRODUCTION

Induced electron transfer, wherein the interaction of a one-electron oxidant with a metal complex leads to the formation of the one-electron reduced metal center, remains an intriguing mechanistic problem[1]. Manganese (III) acetate dehydrate was prepared by following the procedure in the literature[2].

A study of the kinetic of oxidation of cobalt (III) bound α-amino acids is important both from the mechanistic point of view and its bearing on the mechanism of amino acid metabolism. The effect of organized assemblies on the equilibrium and rates of reactions has attracted increasing attention in recent years[3]. This interest is based on the realization that many biochemical processes proceed in a micro heterogeneous system which contains an aqueous and a lipophilic moiety[4]. Among the biochemical functions, the redox processes, in which electron transport occurs, represent reactions of primary importance[5]. The investigation of electron-transfer processes in micelles system has been carried out by examining properly selected reactions[6].

Several surfactants are able to aggregate in non-aqueous solvents to yield reverse micelles[7,8] in which the polar head groups of the surfactant monomers cluster to form a micellar core and are directed towards the centre of the assemble, and the hydrophobic tails extend outwards into the bulk organic phase[9].

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Several transition metal complexes have been used for studying electron-transfer reactions[10]. Several transition metal complexes have been used for studying electron transfer of difference environments such as micelles[11,12], vesicle[13], DNAs[14-16].

EXPERIMENTAL

Carbonatopentaamminecobalt (III) nitrate

Carbonatopentaamminecobalt (III) nitrate was prepared by dissolving 58 g of powdered ammonium carbonato in 60 mL of water and 100 mL of concentration aqueous ammonia, adding a solution of 30 g of cobalt (II) nitrate. 6 hydrate in 40 mL of water and then bubbling air very slowly through the mixture (20 bubbles/min.) for 20 days. The solution was cooled to 0^o and 600 mL of methanol was added slowly with stirring. The preparation was kept at 0^o for 3 days, and the precipitated carbonato nitrate was filtered off. This was purified by dissolving in twice its weight of water, adding LiCl (1 g of LiCl / 2 g of complex), filtering and then slowly adding an equal volume of methanol. The solution was kept 0^o for 10 hr and the crystalline complex was filtered off and dried in vacuum.

Pentaaminecobalt (III) complexes of α-amino acids

10 mmol of the acid and 5 mmol of LiOH (or) NaOH were added to 20 mL of absolute methanol, and to the mixture was added 400 mg of finely ground carbonatopentaamminecobalt (III) nitrate. The mixture was refluxed for 2 hr. with frequent shaking. The preparation was cooled to under ice, and 1 mL of conc. $HClO_4$ was added, after which the preparation was kept at 0^o for an additional 30 min. the precipitate, if any was filtered off and washed with ether. The mother liquor was shaken with 150 mL of ether, generally precipitation an additional portion of the desired complex.

Manganese (III) acetate (dehydrate)

30.3 g anhydrous Mn $(OAc)_2$ in 440 g glacial acetic acid was refluxed for 2 hours. 6.82 g $KMnO_4$ was added and the solution further refluxed for 45 min. The solution was allowed to cool while 75 mL water was added drop wise. After 3 days standing, the precipitate was filtered off.

Preparation of $[Mn^{IV}Mo_9O_{32}]^{6-}$

An aqueous solution of manganese sulphate containing the oxidant sodium peroxydisulphate was added to the solution of ammonium hepta molybdate. The resulting mixture was boiled for five minutes with constant stirring, quickly filtered and cooled. The orange red crystals were recrystalised from hot water.

Preparation of Mn (III) perchlorate

10 g of manganese (III) perchlorate kept at 0ºC was added 15 mL of 12 M $HClO_4$. The 20 mL of a saturated solution of $KMnO_4$ in water was added slowly with stirring until it becomes decolorized. The solution was then filtered, and the manganese (III) perchlorate in the filtrate was estimated by an iodometric procedure.

Kinetic method

All the glass apparatus were made of pyrex glass and stoppers were well ground. The loss of solvent, tested in standard flask and in reaction bottles, was found to be negligible. Burettes, pipettes and standard flasks were standardized by usual produce.

Rate measurement

For the manganese (II) perchlorate oxidant of Co (III) complexes of α-amino acids and unbound ligands, the rate of measurements were made at 28°C in 100% aqueous medium. The standard solution prepared and required amount solutions were pipette out into a 1 cm cell. The total volume of the reaction mixture in the spectrophotometer cell was kept as 2.5 mL in each kinetic run. A UV-Visible spectrophotometer was used to follow the rate of the reaction. Rates of these unbound ligand and Co (III) bound complexes were calculated from the observed decrease in absorbance at 350 nm. For all the kinetic experiments, conversion were followed at least for four half-lives and specific rates from successive half-lives agreed with + or 7% and the average values did not differ from a plot of logarithmic change in concentration verse time calculated using integrated rate equation.

Stoichiometric studies

The stoichiometric studies for the Mn (III) acetate oxidation of pentaamminecobalt (III) complexes of α-amino acids and unbound ligands in the presence of micelles (Table 1 and 2) were carried out with the oxidant in excess. The $[H^+]$ and ionic strength were maintained as in the corresponding rate measurements. The temperature was maintained at 28 ± 0.2°C. After 100 hours when the reaction was nearing completion, the concentration of unreacted Mn (III) acetate was determined both Iodometrically and spectrophotometrically from the change in absorbance measured at 350 nm. The stoichiometric studies for the Mn (III) perchlorate oxidation of pentaamminecobalt (III) complexes of α-amino acids and unbound ligands in the presence of micelles (Tables 3 and 4) were carried out at 28 ± 0.2°C. The stoichiometric studies for the Mn (IV) heteropolyanion oxidation of pentaamminecobalt (III) complexes of α-amino acids and unbound ligands in the presence of micelles (Table 5 and 6) were carried out at 28 ± 0.2°C.

Table 1: Stoichiometric data in the Mn (III) acetate oxidation of Co (III) bound α-aminoacids.

10^2 $[Co^{III}\text{-}L]_{initial}$ mol dm^{-3}	10^2 [Mn (III) acetate]$_{initial}$ mol dm^{-3}	10^2 [Mn (III) acetate]$_{final}^{a}$ mol dm^{-3}	Δ[[Mn (III) acetate] /Co (III)$_{initial}^{b}$ mol dm^{-3}	10^3 [Co (II)] (%) mol dm^{-3}
Glycine				
1.0	10.0	8.9	1.1	1.0
1.0	5.0	4.0	1.0	1.0
Alanine				
1.0	10.0	8.8	1.2	0.98
1.0	5.0	3.9	1.1	1.0
Valine				
1.0	10.0	9.0	1.0	1.0
2.0	10.0	8.1	0.95	2.0
N-acetyl glycine				
1.0	10.0	9.1	0.9	1.0
1.0	5.0	4.0	1.0	1.0
N-benzoyl glycine				
1.0	10.0	9.2	0.8	1.0
2.0	5.0	4.1	0.9	1.0

[a] [Mn (III) acetate]$_{final}$ was estimated iodometrically after 100 hours at 28 ± 0.2°C and Δ[[Mn (III) acetate] was calculated.

[b] Suitable Blank reactions were done and correction for the hydrolysis of the Co (III) complexes was applied

Table 2: Stoichiometric data in the Mn (III) acetate oxidation of Co (III) unbound α-amino acids

10^2 [Ligand] mol dm^{-3}	10^2 [Mn (III) acetate]$_{initial}$ mol dm^{-3}	10^2 [Mn (III) acetate]$_{final}$^{a} mol dm^{-3}	Δ [[Mn (III) acetate]/[Ligand]$_{initial}$ mol dm^{-3}
Glycine			
1.0	5.0	3.2	1.8
1.0	10.0	7.8	2.2
Alanine			
1.0	10.0	7.9	2.1
1.0	20.0	18.0	2.0
Valine			
1.0	5.0	3.0	2.0
1.0	10.0	7.8	2.2
N-acetyl glycine			
1.0	10.0	9.1	0.9
1.0	5.0	4.0	1.0
N-benzoyl glycine			
1.0	10.0	9.2	0.8
2.0	5.0	4.1	0.9

[a] [Mn (III) acetate]$_{final}$ was estimated iodometrically after 100 hours at 28 ± 0.2°C and Δ [Mn (III) acetate] was calculated

Table 3: Stoichiometric data in the HPA oxidation of Co (III) bound α-aminoacids.

10^2[Co^{III}L]$_{initial}$ mol dm^{-3}	10^2[HPA]$_{initial}$ mol dm^{-3}	10^2[HPA]$_{final}$ mol dm^{-3}	Δ[[HPA]/ Co(III)$_{initial}$ mol dm^{-3}	10^3[Co(II)]Mm (%) mol dm^{-3}
Glycine				
1.0	10.0	8.9	1.1	1.0
1.0	5.0	4.0	1.0	1.1
Alanine				
1.0	10.0	8.8	1.2	0.98
1.0	5.0	3.9	1.1	1.0
Valine				
1.0	10.0	9.0	1.0	1.1
1.0	5.0	4.1	1.2	1.1
N-acetyl glycine				
1.0	10.0	9.1	1.0	1.1
1.0	5.0	4.2	1.0	1.0
N-benzoyl glycine				
1.0	10.0	9.8	1.2	1.0
2.0	5.0	4.4	0.96	1.1

Table 4: Stoichiometric data in the HPA oxidation of Co (III) unbound α-amino acids

10^2[Ligand] mol dm^{-3}	10^2[HPA]$_{initial}$ mol dm^{-3}	10^2[HPA]$_{final}$ mol dm^{-3}	Δ[[HPA]/[Ligand]$_{initial}$ mol dm^{-3}
Glycine			
1.0	5.0	3.2	1.8
1.0	10.0	8.8	1.2
Alanine			
1.0	10.0	8.9	1.1
1.0	20.0	9.0	1.0
Valine			
1.0	5.0	4.0	1.0
1.0	10.0	8.7	1.3
N-acetyl glycine			
1.0	5.0	4.5	1.2
1.0	10.0	9.1	1.1
N-benzoyl glycine			
1.0	5.0	4.9	1.0
1.0	10.0	9.5	1.2

Table 5: Stoichiometric data in the Mn (III) perchlorate oxidation of Co (III) bound α-aminoacids

10^2 [Co^{III}-L] $_{initial}$ mol dm^{-3}	10^2 [Mn (III) perchlorate]$_{initial}$ mol dm^{-3}	10^2 [Mn (III) perchlorate] $_{final}$^{a} mol dm^{-3}	Δ [[Mn (III) perchlorate]/ Co (III)$_{initial}$^{b}mol dm^{-3}	10^3 [Co(II)](%) mol dm^{-3}
Glycine				
1.0	10.0	9.0		1.0
1.0	5.0	4.2	1.1 1.0	1.0
Alanine				
1.0	10.0	8.7		9.8
1.0	5.0	4.0	1.2 1.1	1.0
Valine				
1.0	10.0	9.2		1.0
2.0	10.0	8.5	1.0 9.5	2.0
N-acetyl glycine				
1.0	10.0	9.5	1.0	1.1
1.0	5.0	4.2	1.0	1.0
N-benzoyl glycine				
1.0	10.0	9.8		1.0
2.0	5.0	4.6	1.2 1.0	1.2

[a][Mn (III) perchlorate]$_{final}$ was estimated iodometrically after 100 hours at 28 ± 0.2°C and Δ[[Mn (III) perchlorate] was calculated

[b]Suitable Blank reactions were done and correction for the hydrolysis of the Co (III) complexes was applied

Table 6: Stoichiometric data in the Mn (III) perchlorate oxidation of Co (III) unbound α-amino acids

10^2[Ligand] mol dm^{-3}	10^2[Mn (III) perchlorate]$_{initial}$ mol dm^{-3}	10^2[Mn (III) perchlorate]$_{final}{}^{a}$ mol dm^{-3}	Δ[Mn (III) perchlorate]/ [Ligand]$_{initial}$ mol dm^{-3}
Glycine			
1.0	5.0	3.9	1.5
1.0	10.0	8.6	2.1
Alanine			
1.0	10.0	8.6	2.1
1.0	20.0	19.5	2.0
Valine			
1.0	5.0	4.5	2.1
1.0	10.0	9.5	2.1
N-acetyl glycine			
1.0	5.0	4.9	1.0
1.0	10.0	9.8	1.1
N-benzoyl glycine			
1.0	5.0		1.0
1.0	10.0	4.9 9.7	1.1

[a][Mn (III) perchlorate]$_{final}$ was estimated iodometrically after 100 hours at 28 ± 0.2°C and Δ [[Mn (III) perchlorate] was calculated

RESULTS AND DISCUSSION

Kinetic oxidation of unbound and cobalt (III) bound α-amino acids

The kinetics of Mn (III) acetate, Mn (IV) heteropolyanion and Mn (III) perchlorate oxidation of Cobalt (III) bound Glycine, Alanine, Valine, N-acetyl glycine and N-benzoyl glycine have been studied in 60% AcOH – 40% H_2O at temperature = 28 ± 0.2°C. The analytical work involved gross estimation of Mn (III) acetate all rate constants are calculated using Mn (III) acetate determined.

Oxidation of pentaamminecobalt (III) complexes of α-amino acids: In a typical Mn (III) acetate, Mn (IV) heteropolyanion and Mn (III) perchlorate induced electron transfer in pentaamminecobalt (III) complexes of α-amino acids the initial concentration used as follow:

$[(NH_3)_5\,CO^{(III)}\text{-}L] = 4 \times 10^{-3}$ mol dm^{-3},

[Mn (III) acetate], = [Mn (IV) heteropolyanion] = [Mn (III) perchlorate] = 2×10^{-1} mol dm^{-3},

60% AcOH – 40% H_2O Temperature = 28 ± 0.2°C, [NaLS] = [CTAB] = 4×10^{-3} mol dm^{-3}

The reaction are carried out under pseudo-first-order conditions with Mn (III) acetate, Mn (IV) heteropolyanion and Mn (III) perchlorate in excess with performed in a spectrophotometer.

Dependence of rate on cobalt (III) concentrations in NaLS and CTAB: (Table 7, 11 and 15)

The dependence of rate cobalt (III) concentration has been studied at fixed concentration of Mn (III) acetate, Mn (IV) heteropolyanion and Mn (III) perchlorate (2×10^{-1} mol dm^{-3}), 60% AcOH – 40% H_2O at 28 ± 0.2°C in the concentration range 4×10^{-3} mol dm^{-3} – 20.0×10^{-3} mol dm^{-3} for the pentaamminecobalt (III) complexes of Glycine, Alanine, Valine, N-acetylglycine and N-benzoylglycine with increasing concentration of cobalt (III) complexes, there is a proportional increase in rate and graphs of logarithm of specific rate versus logarithm of concentration of cobalt (III) complexes are linear. In each case the slope obtained from the linear graph is nearly fractional showing that the order with respect to [Co (III)] is fractional-order. Hence the rate of disappearance of cobalt (III) complex can be given by Eq. 1.

$$-d[Co^{III}] / dt = k_1[Co^{III}] \qquad \ldots(1)$$

Dependence of rate on H_2SO_4 concentration in NaLS and CTAB: (Table 8, 12 & 16)

The rate of Mn (III) acetate, Mn (IV) heteropolyanion and Mn (III) perchlorate induced electron transfer in Glycinato, Alanato, Valinato, N-acetyl Glycinato and N-benzyl glycinatopentaamminecobalt (III) sulphate is increased by increasing H_2SO_4 concentration in the range 4 x 10^{-3} mol dm^{-3} - 20.0 x 10^{-3} mol dm^{-3}. A graph of logarithm of specific rate (in s^{-1}) versus logarithm of H_2SO_4 concentration is linear with slope equal to fractional indicating the order with respect to H_2SO_4 concentration is 1. Hence the rate law for such an acid catalysed reaction given as Eq. 2.

$$Rate = K_{Obs} [Co^{III}] [Mn (III) acetate] [H^+] \qquad \ldots(2)$$

Table 7: First order rate constant for Mn (III) acetate oxidation of [α-amino acids] and in the presence of NaLS and CTAB at 28 ± 0.2°C [Mn (III) acetate] = 2 x 10^{-1} mol dm^{-3}, [NaLS] = [CTAB] = 4 x 10^{-3} mol dm^{-3}, 60% AcOH – 40% H_2O, [H_2SO_4] = 2 x 10^{-1} mol dm^{-3}

$10^3[(NH_3)_5$-Co (III)-L] mol dm^{-3}	10^5 k_1 s^{-1}	10^3 k_2 dm^3 mol^{-1} s^{-1}	10^5 k_1s^{-1} (NaLS)	10^3 k_2dm^3 mol^{-1} s^{-1} (NaLS)	10^5 k_1s^{-1} (CTAB)	10^3 k_2dm^3 mol^{-1} s^{-1} (CTAB)
L = Glycinato						
4.0	2.2	5.3	3.2	3.1	7.7	7.5
8.0	4.5	5.6	4.8	4.6	8.2	8.1
12.0	6.9	5.8	6.0	5.9	8.5	8.4
16.0	9.2	5.9	7.6	7.5	8.6	8.5
20.0	11.6	6.0	8.0	7.8	8.9	8.7
L = Alaninato						
4.0	3.1	5.4	3.0	3.1	3.0	3.1
8.0	6.2	5.7	4.5	4.4	3.5	3.4
12.0	9.3	5.9	5.5	5.3	3.9	3.7
16.0	12.4	6.0	6.0	5.9	4.0	3.8
20.0	15.6	6.1	6.1	6.0	4.1	4.0
L = Valinato						
4.0	3.4	5.5	4.6	4.4	5.4	5.2
8.0	6.9	5.8	5.5	5.3	5.8	5.7
12.0	10.4	6.0	6.0	5.9	6.2	6.1
16.0	13.9	6.1	6.2	6.1	6.3	6.2
20.0	17.4	6.2	6.3	6.2	6.5	6.4
L = N-acetyl glycinato						
4.0	4.2	5.6	5.7	5.7	6.2	5.7
8.0	8.5	5.9	10.0	6.0	10.5	5.8
12.0	12.7	6.1	14.2	6.2	14.7	6.0
16.0	17.0	6.2	18.5	6.4	19.0	6.1
20.0	21.2	6.3	22.7	6.7	23.2	6.2

Cont…

10^3[$(NH_3)_5$-Co (III)-L] mol dm^{-3}	10^5 k_1s^{-1}	10^3 k_2 dm^3 $mol^{-1}s^{-1}$	10^5 k_1s^{-1} (NaLS)	10^3 k_2dm^3 mol^{-1} s^{-1} (NaLS)	10^5 k_1s^{-1} (CTAB)	10^3 k_2dm^3 mol^{-1} s^{-1} (CTAB)
L = N-benzoyl glycinato						
4.0	6.1	5.7	7.6	5.8	7.1	5.7
8.0	12.2	6.0	13.7	6.1	13.0	5.9
12.0	18.3	6.2	19.8	6.4	19.1	6.0
16.0	24.4	6.3	25.9	6.6	25.2	6.2
20.0	30.6	6.4	32.1	6.9	31.2	6.3

Table 8: First order rate constant for Mn (III) acetate oxidation of [H_2SO_4] and in the presence of NaLS and CTAB at 28 ± 0.2°C. L = Glycine, Alanine, Valine, N-acetyl glycine, N-benzoyl glycine = 4 x 10^{-3} mol dm^{-3}, [Mn (III) acetate] = 2 x 10^{-1} mol dm^{-3}, 60% AcOH – 40% H_2O, Temperature = 28 ± 0.2°C, [NaLS] = [CTAB] = 4 x 10^{-3} mol dm^{-3}

[H_2SO_4] 10^{-1} mol dm^{-3}	10^5 k_1s^{-1}	10^3 k_2 dm^3 $mol^{-1}s^{-1}$	10^5 k_1s^{-1} (NaLS)	10^3 k_2dm^3 mol^{-1} s^{-1} (NaLS)	10^5 k_1s^{-1} (CTAB)	10^3 k_2dm^3 mol^{-1} s^{-1} (CTAB)
Glycinato						
4.0	1.9	5.2	2.0	5.3	2.2	5.3
8.0	3.8	5.5	4.1	5.6	4.5	5.6
12.0	5.7	5.7	6.3	5.7	6.8	5.8
16.0	7.6	5.8	7.5	5.8	9.1	5.9
20.0	9.5	5.9	9.8	5.9	11.4	6.0
Alaninato						
4.0	2.3	5.3	2.5	5.3	2.7	5.4
8.0	4.6	5.6	5.1	5.7	5.4	5.7
12.0	6.9	5.8	7.9	5.8	8.1	5.9
16.0	9.2	5.9	9.8	5.9	10.8	6.0
20.0	11.5	6.0	11.6	6.0	13.5	6.1
Valinato						
4.0	2.1	5.3	2.2	5.3	2.9	5.4
8.0	4.2	5.6	4.9	5.6	5.8	5.7
12.0	6.3	5.7	7.8	5.8	8.7	5.9
16.0	8.4	5.9	10.6	6.0	11.6	6.0
20.0	10.5	6.0	13.7	6.1	14.5	6.1
N-acetyl glycinato						
4.0	2.5	5.3	2.8	5.4	3.1	5.49
8.0	5.0	5.6	7.9	5.8	6.2	5.79
12.0	7.5	5.8	9.0	5.9	9.3	5.96
16.0	10.0	6.0	12.1	6.0	12.4	6.09
20.0	12.5	6.0	15.1	6.1	15.5	6.19
N-benzoyl glycinato						
4.0	2.7	5.4	2.9	5.4	3.3	5.5
8.0	5.4	5.9	6.3	5.7	6.6	5.8
12.0	8.1	5.8	9.5	5.9	9.9	5.9
16.0	10.8	6.1	12.9	6.1	13.2	6.1
20.0	13.5	6.2	16.1	6.2	16.5	6.2

Dependence of rate on NaLS in concentration in oxidant of α-amino acids

Table 9: First order rate constant for Mn (III) acetate oxidation of [α-amino acids] and in the presence of NaLS at 28 ± 0.2°C. L = Glycine, Alanine, Valine, N-acetyl glycine, N-benzoyl glycine = 4 x 10^{-3} mol dm^{-3}, [Mn (III) acetate] = 2 x 10^{-1} mol dm^{-3}, 60% AcOH – 40% H_2O, Temperature = 28 ± 0.2°C, [H_2SO_4] = 2 x 10^{-1} mol dm^{-3}

10^3[NaLS] mol dm^{-3}	10^5 k_1 s^{-1} Glycine	10^3 k_2 dm^3 mol^{-1} s^{-1} Glycine	10^5 k_1 s^{-1} Alanine	10^3 k_2 dm^3mol^{-1} s^{-1} Alanine	10^5 k_1 s^{-1} Valine	10^3 k_2 dm^3 mol^{-1} s^{-1} Valine	10^5 k_1 s^{-1} N-acetyl glycine	10^3 k_2 dm^3 mol^{-1} s^{-1} N-acetyl glycine	10^5 k_1 s^{-1} N-benzoyl glycine	10^3 k_2 dm^3 mol^{-1} s^{-1} N-benzoyl glycine
4.0	1.8	5.25	2.2	5.34	2.6	5.41	2.75	5.43	2.9	5.46
8.0	4.1	5.61	4.9	5.69	5.5	5.74	5.85	5.76	6.2	5.79
12.0	6.4	5.80	7.6	5.88	8.4	5.92	8.95	5.95	9.5	5.97
16.0	8.7	5.93	10.3	6.01	11.3	6.05	12.05	6.08	12.8	6.10
20.0	11.0	6.04	13.0	6.11	14.2	6.15	15.15	6.18	16.1	6.20

Table 10: First order rate constant for Mn (III) acetate oxidation of [α-amino acids] and in the presence of CTAB at 28 ± 0.2°C.L = Glycine, Alanine, Valine, N-acetyl glycine, N-benzoyl glycine = 4 x 10^{-3} mol dm^{-3}, [Mn (III) acetate] = 2 x 10^{-1} mol dm^{-3}, 60% AcOH – 40% H_2O, Temperature = 28 ± 0.2°C, [H_2SO_4] = 2 x 10^{-1} mol dm^{-3}

10^3[CTAB] mol dm^{-3}	10^5 k_1 s^{-1} Glycine	10^3 k_2 dm^3 mol^{-1} s^{-1} Glycine	10^5 k_1 s^{-1} Alanine	10^3 k_2 dm^3mol^{-1} s^{-1} Alanine	10^5 k_1 s^{-1} Valine	10^3 k_2 dm^3 mol^{-1} s^{-1} Valine	10^5 k_1 s^{-1} N-acetyl glycine	10^3 k_2 dm^3 mol^{-1} s^{-1} N-acetyl glycine	10^5 k_1 s^{-1} N-benzoyl glycine	10^3 k_2 dm^3 mol^{-1} s^{-1} N-benzoyl glycine
4.0	2.0	5.30	2.4	5.38	2.8	5.44	2.95	5.46	3.1	5.49
8.0	4.3	5.63	5.1	5.70	5.7	5.75	6.05	5.78	6.4	5.80
12.0	6.6	5.81	7.9	5.89	8.6	5.93	9.15	5.96	9.7	5.98
16.0	8.9	5.94	10.5	6.02	11.5	6.05	12.25	6.08	13.0	6.11
20.0	11.2	6.04	13.2	6.12	14.4	6.15	15.35	6.18	16.3	6.21

Table 11: First order rate constant for Mn (IV) heteropolyanionsoxidation of [α-amino acids] and in the presence of NaLS and CTAB at 28 ± 0.2°C. [Mn (IV) heteropolyanions] = 2 x 10^{-1} mol dm^{-3}, [NaLS] = [CTAB] = 4 x 10^{-3} mol dm^{-3}, 60% AcOH – 40% H_2O, [H_2SO_4] = 2 x 10^{-1} mol dm^{-3}

10^3[$(NH_3)_5$-Co (III)-L] mol dm^{-3}	10^5 k_1 s^{-1}	10^3 k_2 dm^3 mol^{-1} s^{-1}	10^5 k_1 s^{-1} (NaLS)	10^3 $k_2 dm^3$ mol^{-1} s^{-1} (NaLS)	10^5 $k_1 s^{-1}$ (CTAB)	10^3 $k_2 dm^3$ mol^{-1} s^{-1} (CTAB)
Glycinato						
4.0	2.1	1.9	2.8	3.0	4.8	4.5
8.0	2.4	2.2	3.0	3.1	9.9	8.9
12.0	2.7	2.5	3.2	3.4	14.7	14.1
16.0	3.0	2.8	3.4	3.5	20.1	19.8
20.0	3.3	3.1	3.7	3.9	24.5	23.6
Alaninato						
4.0	1.9	1.8	2.0	2.1	5.2	4.9
8.0	2.1	2.0	2.3	2.4	8.9	7.9
12.0	2.3	2.2	2.5	2.6	11.8	11.5
16.0	2.5	2.4	2.7	2.8	15.3	15.0
20.0	2.7	2.6	3.0	3.2	19.9	19.1
Valinato						
4.0	3.9	3.7	4.7	4.9	7.7	7.5
8.0	4.2	4.0	4.9	5.1	9.5	9.4
12.0	4.5	4.3	5.0	5.2	13.8	13.7
16.0	4.8	4.6	5.2	5.4	18.9	18.8
20.0	5.1	4.9	5.4	5.6	21.3	21.1
N-acetyl glycinato						
4.0	4.1	4.0	5.0	5.2	9.9	9.5
8.0	4.3	4.2	5.2	5.3	13.8	13.7
12.0	4.5	4.4	5.4	5.5	16.5	16.4
16.0	4.7	4.6	5.6	5.7	20.8	20.7
20.0	4.9	4.8	5.8	6.0	24.7	24.6
N-benzoyl glycinato						
4.0	5.0	5.2	6.1	6.3	11.5	11.3
8.0	5.3	5.4	6.3	6.5	15.9	15.7
12.0	5.5	5.6	6.4	6.7	19.5	19.3
16.0	5.8	5.7	6.6	6.9	23.3	23.0
20.0	6.0	5.9	6.8	7.0	27.4	27.1

Table 12: First order rate constant for Mn (IV) heteropolyanion soxidation of [H_2SO_4] and in the presence of NaLS and CTAB at 28 ± 0.2°C. L = Glycine, Alanine, Valine, N-acetyl glycine, N-benzoyl glycine = 4 x 10^{-3} mol dm^{-3}, [Mn (IV) heteropolyanions] = 2 x 10^{-1} mol dm^{-3}, 60% AcOH – 40% H_2O, Temperature = 28 ± 0.2°C, [NaLS] = [CTAB] = 4 x 10^{-3} mol dm^{-3}

[H_2SO_4] 10^{-1} mol dm^{-3}	10^5 k_1s^{-1}	10^3 k_2 dm^3 mol^{-1}s^{-1}	10^5 k_1 s^{-1} (NaLS)	10^3 $k_2$dm^3 mol^{-1} s^{-1} (NaLS)	10^5 k_1s^{-1} (CTAB)	10^3 $k_2$dm^3 mol^{-1} s^{-1} (CTAB)
Glycinato						
4.0	3.0	4.9	2.0	5.3	2.2	5.3
8.0	4.8	4.2	4.1	5.6	4.5	5.6
12.0	6.0	4.5	6.3	5.7	6.8	5.8
16.0	7.2	4.7	7.5	5.8	9.1	5.9
20.0	9.4	4.9	9.8	5.9	11.4	6.0
Alaninato						
4.0	2.4	5.1	2.5	5.3	2.7	5.4
8.0	5.0	5.4	5.1	5.7	5.4	5.7
12.0	7.8	5.7	7.9	5.8	8.1	5.9
16.0	9.7	5.8	9.8	5.9	10.8	6.0
20.0	11.3	5.9	11.6	6.0	13.5	6.1
Valinato						
4.0	2.0	5.0	2.2	5.3	2.9	5.4
8.0	4.1	5.2	4.9	5.6	5.8	5.7
12.0	6.2	5.4	7.8	5.8	8.7	5.9
16.0	8.3	5.6	10.6	6.0	11.6	6.0
20.0	10.4	5.8	13.7	6.1	14.5	6.1
N-acetyl glycinato						
4.0	5.4	5.8	2.8	5.4	3.1	5.49
8.0	7.5	6.0	7.9	5.8	6.2	5.79
12.0	8.6	6.2	9.0	5.9	9.3	5.96
16.0	11.7	6.4	12.1	6.0	12.4	6.09
20.0	13.8	6.6	15.1	6.1	15.5	6.19
N-benzoyl glycinato						
4.0	2.5	5.9	2.9	5.4	3.3	5.5
8.0	5.7	6.1	6.3	5.7	6.6	5.8
12.0	8.9	6.3	9.5	5.9	9.9	5.9
16.0	12.1	6.5	12.9	6.1	13.2	6.1
20.0	15.3	6.7	16.1	6.2	16.5	6.2

Table 13: First order rate constant for Mn (IV) heteropolyanion soxidation of [α-amino acids] and in the presence of NaLS at 28 ± 0.2°C. L = Glycine, Alanine, Valine, N-acetyl glycine, N-benzoyl glycine = 4 x 10^{-3} mol dm^{-3}, [Mn (IV) heteropolyanions] = 2 x 10^{-1} mol dm^{-3}, 60% AcOH – 40% H_2O, Temperature = 28 ± 0.2 °C, [H_2SO_4] = 2 x 10^{-1} mol dm^{-3}

10^3[NaLS] mol dm^{-3}	10^5 k_1 s^{-1} Glycine	10^3 k_2 dm^3 mol^{-1} s^{-1} Glycine	10^5 k_1 s^{-1} Alanine	10^3 k_2 dm^3 mol^{-1} s^{-1} Alanine	10^5 k_1 s^{-1} Valine	10^3 k_2 dm^3 mol^{-1} s^{-1} Valine	10^5 k_1 s^{-1} N-acetyl glycine	10^3 k_2 dm^3 mol^{-1} s^{-1} N-acetyl glycine	10^5 k_1 s^{-1} N-benzoyl glycine	10^3 k_2 dm^3 mol^{-1} s^{-1} N-benzoyl glycine
4.0	2.9	6.35	3.3	6.44	3.7	6.51	3.85	6.53	4.0	6.56
8.0	5.2	6.71	6.0	6.79	4.3	6.56	4.2	6.58	4.32	6.59
12.0	7.5	7.07	8.7	7.14	4.9	6.61	4.55	6.63	4.64	6.62
16.0	9.8	7.43	11.4	7.49	5.5	6.66	4.9	6.68	4.96	6.65
20.0	12.1	7.79	14.1	7.84	6.1	6.71	5.25	6.73	5.28	6.68

Table 14: First order rate constant for Mn (IV) heteropolyanion soxidation of [α-amino acids] and in the presence of CTAB at 28 ± 0.2°C.L = Glycine, Alanine, Valine, N-acetyl glycine, N-benzoyl glycine = 4 x 10^{-3} mol dm^{-3}, [Mn (IV) heteropolyanions] = 2 x 10^{-1} mol dm^{-3}, 60% AcOH – 40% H_2O, Temperature = 28 ± 0.2 °C, [H_2SO_4] = 2 x 10^{-1} mol dm^{-3}

10^3[CTAB] mol dm^{-3}	10^5 k_1 s^{-1} Glycine	10^3 k_2 dm^3 mol^{-1} s^{-1} Glycine	10^5 k_1 s^{-1} Alanine	10^3 k_2 dm^3 mol^{-1} s^{-1} Alanine	10^5 k_1 s^{-1} Valine	10^3 k_2 dm^3 mol^{-1} s^{-1} Valine	10^5 $k_1 s^{-1}$ N-acetyl glycine	10^3 k_2 dm^3 mol^{-1} s^{-1} N-acetyl glycine	10^5 k_1 s^{-1} N-benzoyl glycine	10^3 k_2 dm^3 mol^{-1} s^{-1} N-benzoyl glycine
4.0	2.2	5.5	2.6	5.58	3.0	5.64	3.4	5.91	3.8	6.19
8.0	4.5	5.83	5.3	5.90	5.9	5.94	6.5	6.23	7.1	6.5
12.0	6.8	6.16	8.0	6.22	8.8	6.26	9.6	6.55	10.4	6.81
16.0	9.1	6.49	10.7	6.54	11.7	6.57	12.7	6.87	13.7	7.12
20.0	11.4	6.82	13.4	6.86	14.6	6.88	15.8	7.19	17.0	7.43

Table 15: First order rate constant for Mn (III) perchlorateoxidation of [α-amino acids] and in the presence of NaLS and CTAB at 28 ± 0.2°C. [Mn (III) perchlorate] = 2 x 10^{-1} mol dm^{-3}, [NaLS] = [CTAB] = 4 x 10^{-3} mol dm^{-3}, 60% AcOH – 40% H_2O, [H_2SO_4] = 2 x 10^{-1} mol dm^{-3}

10^3[$(NH_3)_5$-Co (III)-L] mol dm^{-3}	10^5 k_1 s^{-1}	10^3 k_2 dm^3 mol^{-1} s^{-1}	10^5 k_1 s^{-1} (NaLS)	10^3 k_2dm^3 mol^{-1} s^{-1} (NaLS)	10^5 k_1s^{-1} (CTAB)	10^3 k_2dm^3 mol^{-1} s^{-1} (CTAB)
Glycinato						
4.0	2.4	5.5	3.5	3.6	8.0	7.9
8.0	4.7	5.8	5.0	5.4	8.2	8.1
12.0	7.0	6.1	6.9	7.0	8.4	8.3
16.0	9.3	6.4	7.5	7.9	8.6	8.5
20.0	11.6	6.7	8.8	8.9	9.0	8.7
Alaninato						
4.0	3.3	5.6	3.5	3.6	4.6	4.4
8.0	6.4	5.9	4.6	4.7	4.9	4.7
12.0	9.5	6.2	5.8	5.9	5.2	5.0
16.0	12.6	6.5	6.9	6.9	5.5	5.3
20.0	15.7	6.8	7.7	8.1	5.8	5.6
Valinato						
4.0	3.6	5.7	4.8	4.9	6.2	6.0
8.0	7.1	6.0	5.4	5.6	6.5	6.3
12.0	10.6	6.3	6.6	6.7	6.7	6.5
16.0	14.1	6.6	7.7	7.8	6.9	6.8
20.0	17.6	6.9	8.9	9.1	7.1	6.9
N-acetyl glycinato						
4.0	4.4	5.8	4.0	4.6	7.3	7.1
8.0	8.7	6.1	5.2	5.3	7.5	7.3
12.0	13.0	6.4	6.4	6.7	7.8	7.5
16.0	17.3	6.7	7.8	7.9	7.9	7.7
20.0	21.6	7.0	8.6	8.9	8.2	8.0
N-benzoyl glycinato						
4.0	5.3	5.9	4.7	4.9	5.2	5.1
8.0	12.4	6.2	5.2	5.4	5.4	5.2
12.0	19.5	6.5	6.4	6.7	5.6	5.5
16.0	26.6	6.8	7.6	7.7	5.8	5.7
20.0	33.7	7.1	8.2	8.4	6.0	5.9

Table 16: First order rate constant for Mn (III) perchlorateoxidation of [H_2SO_4] and in the presence of NaLS and CTAB at 28 ± 0.2°C. L = Glycine, Alanine, Valine, N-acetyl glycine, N-benzoyl glycine = 4 x 10^{-3} mol dm^{-3}, [Mn (III) perchlorate] = 2 x 10^{-1} mol dm^{-3}, 60% AcOH – 40% H_2O, Temperature = 28 ± 0.2°C, [NaLS] = [CTAB] = 4 x 10^{-3} mol dm^{-3}

[H_2SO_4] 10^{-1} mol dm^{-3}	10^5 k_1 s^{-1}	10^3 k_2 dm^3 mol^{-1} s^{-1}	10^5 k_1 s^{-1} (NaLS)	10^3 $k_2 dm^3$ mol^{-1} s^{-1} (NaLS)	10^5 $k_1 s^{-1}$ (CTAB)	10^3 $k_2 dm^3$ mol^{-1} s^{-1} (CTAB)
Glycinato						
4.0	1.7	5.0	2.0	5.3	2.2	5.3
8.0	3.6	5.3	4.1	5.6	4.5	5.6
12.0	5.5	5.6	6.3	5.7	6.8	5.8
16.0	7.4	5.9	7.5	5.8	9.1	5.9
20.0	9.3	6.2	9.8	5.9	11.4	6.0
Alaninato						
4.0	2.1	5.4	2.5	5.3	2.7	5.4
8.0	4.0	5.7	5.1	5.7	5.4	5.7
12.0	5.9	6.0	7.9	5.8	8.1	5.9
16.0	7.8	6.3	9.8	5.9	10.8	6.0
20.0	9.7	6.6	11.6	6.0	13.5	6.1
Valinato						
4.0	2.0	5.2	2.2	5.3	2.9	5.4
8.0	3.9	5.5	4.9	5.6	5.8	5.7
12.0	5.8	5.8	7.8	5.8	8.7	5.9
16.0	7.7	6.1	10.6	6.0	11.6	6.0
20.0	9.6	6.4	13.7	6.1	14.5	6.1
N-acetyl glycinato						
4.0	2.4	5.7	2.8	5.4	3.1	5.49
8.0	4.3	6.0	7.9	5.8	6.2	5.79
12.0	6.2	6.3	9.0	5.9	9.3	5.96
16.0	8.1	6.6	12.1	6.0	12.4	6.09
20.0	10.0	6.9	15.1	6.1	15.5	6.19
N-benzoyl glycinato						
4.0	2.6	5.9	2.9	5.4	3.3	5.5
8.0	4.5	6.2	6.3	5.7	6.6	5.8
12.0	6.4	6.5	9.5	5.9	9.9	5.9
16.0	8.3	6.8	12.9	6.1	13.2	6.1
20.0	10.2	7.1	16.1	6.2	16.5	6.2

Table 17: First order rate constant for Mn (III) perchlorateoxidation of [α-amino acids] and in the presence of NaLS at 28 ± 0.2°C. L = Glycine, Alanine, Valine, N -acetyl glycine, N-benzoyl glycine = 4 x 10^{-3} mol dm^{-3}, [Mn (III) perchlorate] = 2 x 10^{-1}mol dm^{-3}, 60% AcOH – 40% H_2O, Temperature = 28 ± 0.2 °C, [H_2SO_4] = 2 x 10^{-1} mol dm^{-3}

10^3[NaLS] mol dm^{-3}	10^5 k_1 s^{-1} Glycine	10^3 k_2 dm^3 mol^{-1} s^{-1} Glycine	10^5 k_1s^{-1} Alanine	10^3 k_2 dm^3mol^{-1} s^{-1} Alanine	10^5 k_1 s^{-1} Valine	10^3 k_2 dm^3 mol^{-1} s^{-1} Valine	10^5 k_1s^{-1} N-acetyl glycine	10^3 k_2 dm^3 mol^{-1} s^{-1} N-acetyl glycine	10^5 k_1s^{-1} N-benzoyl glycine	10^3 k_2 dm^3 mol^{-1} s^{-1} N-benzoyl glycine
4.0	3.6	6.5	4.0	6.59	4.4	6.66	4.8	6.69	5.2	6.71
8.0	5.9	6.86	6.7	6.94	7.3	6.99	7.8	7.02	8.1	7.04
12.0	8.2	7.22	9.4	7.29	10.2	7.32	10.8	7.35	11.0	7.37
16.0	10.5	7.58	12.1	7.64	13.1	7.65	13.8	7.68	13.9	7.7
20.0	12.8	7.94	14.8	7.99	16.0	7.98	16.8	8.01	16.8	8.03

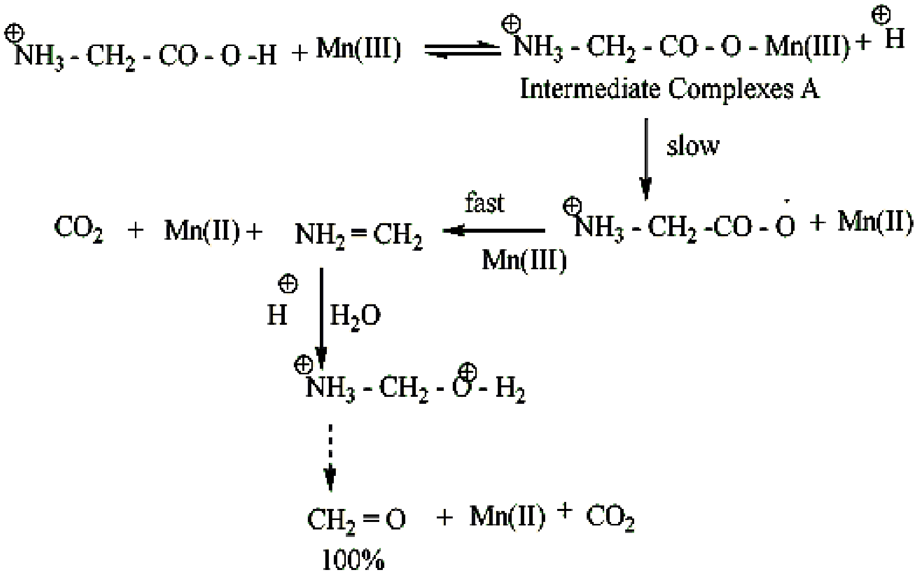
Table 18: First order rate constant for Mn (III) perchlorateoxidation of [α-amino acids] and in the presence of CTAB at 28 ± 0.2°C.L = Glycine, Alanine, Valine, N -acetyl glycine, N-benzoyl glycine = 4 x 10^{-3} mol dm^{-3}, [Mn (III) perchlorate] = 2 x 10^{-1} mol dm^{-3}, 60% AcOH – 40% H_2O, Temperature = 28 ± 0.2 °C, [H_2SO_4] = 2 x 10^{-1} mol dm^{-3}

10^3[CTAB] mol dm^{-3}	10^5 k_1 s^{-1} Glycine	10^3 k_2 dm^3 mol^{-1} s^{-1} Glycine	10^5 k_1 s^{-1} Alanine	10^3 k_2 dm^3 mol^{-1} s^{-1} Alanine	10^5 k_1 s^{-1} Valine	10^3 k_2 dm^3 mol^{-1} s^{-1} Valine	10^5 k_1s^{-1} N-acetyl glycine	10^3 k_2 dm^3 mol^{-1} s^{-1} N-acetyl glycine	10^5 k_1 s^{-1} N-benzoyl glycine	10^3 k_2 dm^3 mol^{-1} s^{-1} N-benzoyl glycine
4.0	2.5	5.7	2.9	5.78	3.3	5.86	3.7	5.94	4.1	6.02
8.0	4.8	5.83	5.6	6.1	6.2	6.18	6.6	6.26	7.0	6.34
12.0	7.1	5.96	8.3	6.42	9.1	6.5	9.5	6.58	9.9	6.66
16.0	9.4	6.09	11.0	6.74	12.0	6.82	12.4	6.9	12.8	6.98
20.0	11.7	6.22	13.7	7.06	14.9	7.14	15.3	7.22	15.7	7.3

Mechanism

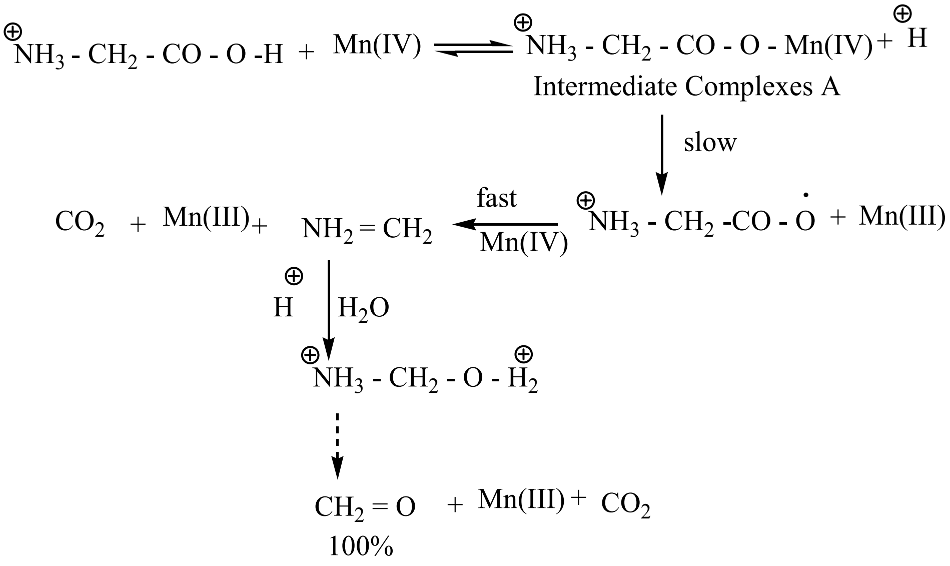
There is 100% decrease in absorbance at 502 nm corresponding on the reduction of Co(III) centre. The rate of Mn(III), Mn(IV), and oxidation of unbound α-amino acids are different suggesting the ligation of carboxylic acid increase the rate of induced electron transfer (Scheme 2A, 2B and 2C).

Mn (III) acetate oxidation of Co (III) complexes



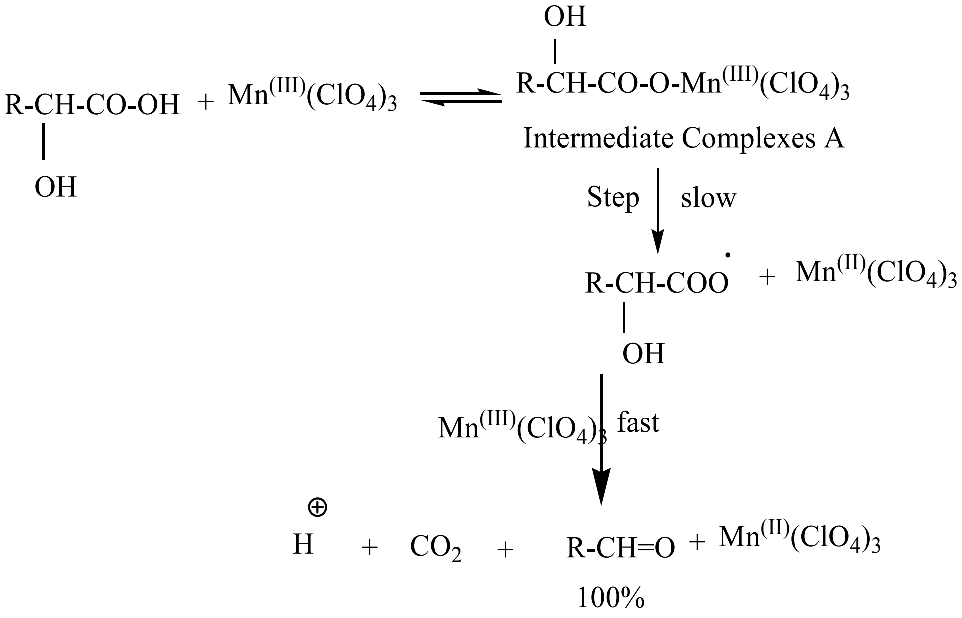
Scheme 2A

Mn (IV) heteropolyanions oxidation of Co (III) complex



Scheme 2B

Mn (III) perchlorate oxidation of Co (III) complexes



Scheme 2C

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