



**MANGANESE (IV) HETEROPOLYANION-INDUCED ELECTRON
TRANSFER IN PENTAAMMINECOBALT (III) COMPLEXES OF
 α -HYDROXY ACIDS. EVIDENCE FOR THE FRACTION OF REACTION
WITH SYNCHRONOUS C-C AND O-H BOND FISSIONS**

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ABSTRACT

Manganese (IV) heteropolyanion (HPA) oxidation of pentaamminecobalt (III) complexes of α -hydroxy acids of in micellar medium yielding nearly 100% of Co(II) and 100% carbonyl compounds are ultimate products. The decrease in UV-visible absorbance at $\lambda = 502$ nm for Co(III) complex corresponds to nearly 100% of the initial absorbance. The stoichiometric of unbound ligand and cobalt(III) complex is accounting for about 100% reduction at the cobalt (III) centre. The kinetic and stoichiometric results have been accounted by a suitable mechanism.

Key words: Pentaamminecobalt (III) complexes, Induced electron transfer reaction, Complex formation, Mn(IV)HPA, Micelles.

INTRODUCTION

Manganese (IV) heteropolyanion (HPA) is an efficient reagent for oxidation of primary and secondary alcohols to carbonyl compounds a large class of organic compounds where oxidizing by Mn(IV) HPA has been reported¹. Since induced electron transfer in pentaamminecobalt(III) complexes of α -hydroxy acids with various oxidants have been studied. The extent of Mn(IV) HPA oxidation of pentaamminecobalt(III) complexes of α -hydroxy acids in micellar medium as a oxidisable hydroxyl group is separated from carbonyl bound to Co(III) centre by a saturated fragment namely C-C bond. The cation radical formed due to the oxidation of hydroxyl group by Mn(IV) HPA should be in nearly synchronous fashion electron transfer resulting in C-C and O-H bond fission and reduction at cobalt(III) centre. The micelles used in the present work are Sodium laurylsulphate (NaLS)² and Cetyltrimethylammonium bromide(CTAB)³. The micelles were purified by adopting earlier procedure. The stoichiometric results indicate that for one mole of cobalt(III) complex, about 0.5 mole of Mn(IV) HPA is consumed, where as with the unbound ligands for one mole of α -hydroxy acids about 1.00 mole of micelles is consumed.

EXPERIMENTAL

Purification of solvents

(a) Ethanol⁴

About 2 litres of rectified spirit was poured in to a 3 litre round bottomed flask and 500 g of calcium oxide which has been freshly ignited in a muffle furnace and allowed to cool in desiccators was added. The flask filled with the mixture fitted with a double surface condenser carrying a calcium chloride guard-tube, was refluxed gently for 6 hrs and allowed to stand overnight. The condenser was reassembled for downward distillation via a splash head adapter to prevent carryover of calcium oxide in the vapour stream. Then ethanol was distilled gently discharging the first 20 mL of distillate. The absolute ethanol (99.5%) was preserved in a bottle with a well fitting stopper.

(b) Methanol^{5,6}

The Analar grade methanol was distilled through an efficient fractionating column, to remove most of the water. Anhydrous methanol was obtained from the fractionally distilled solvent by treatment with magnesium metal.

(c) Perchloric acid⁷

HClO₄ 70% (E. Merck Analar) was standardized using standard sodium carbonate (BDH Analar) solution using methyl orange as indicator.

(d) Other inorganic chemicals and organic compounds⁸

The other inorganic chemicals such as sodium dichromate, potassium dichromate, sodium thiosulphate, potassium iodide, barium hydroxide, hydrochloride acid and organic compounds such as oxalic acid dehydrate and starch power (all from BDH) were used as received.

(e) Micelles⁹

The micelles used in the present work are Sodium laurylsulphate (NaLS) and Cetyltrimethyl ammonium bromide (CTAB). The micelles are purified by the following procedure available in the literature. The commercial samples of the surfactants were repeatedly washed with anhydrous ether and recrystallised several times from alcohol with the addition of anhydrous ether. Manganese(IV) heteropolyanion (184 mL of 6M HCl was added to 100 g of MnO₂ with stirring cooled and 79.1 g of Manganese was added over 100 min. British drug house, Analar Grade and α -hydroxy acids employed as ligands Aldrich products) were used as obtained.

The monomeric cobalt(III) complexes of lactic, mandelic and glycolic acids were prepared as their perchlorates by the method of Fan and Gould. The tris (μ -hydroxo) complex (NH₃)₃Co(OH)₃ (Co(NH₃)₃(ClO₄)₃ (triol) has been prepared by the procedure of siebert and co-workers. The reaction between Mn(IV) HPA and Co(III) complexes of α -hydroxy acids and unbound ligands in presence of micelles were carried out at 29 \pm 0.2°C in an electrically operated thermostated bath. The concentrations of unreacted micelles was determined both iodometrically¹⁰. The disappearance of Co(III) was followed spectrometrically by following the decrease in absorbance at 502 nm. (for the monomeric Co(III) complex). Ionic strength was maintained by addition of suitable quantities of HClO₄ and NaClO₄. The specific rates estimated from the optical density measurements agree with the values from the volumetric procedure within \pm 7% curiously, the change in absorbance observed at 502 nm Co(III) complexes of α -hydroxy acids correspond to very nearly 100% of the initial concentration of Co(III), while the change in optical density at 350 nm for Mn(IV) HPA corresponds to 100% of Co(III)_{initial}. Co(III) was estimated after the completion of

reaction, by diluting the reaction mixture 10-fold with concentrated HCl, allowing evaluation of chlorine to cease, and then measuring the absorbance of blue chloro complex of Co(II) at 692 nm ($c = 560 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$). The amount of Co(II) estimated in all these cases corresponds to nearly 100% of $\text{Co(II)}_{\text{initial}}$.

After neutralization of the reaction mixture with sodium bicarbonate, the pH of the aqueous layer was adjusted to about 6.0 and the aqueous layer was separated by filtration in the case of both free ligands and corresponding complexes. On evaporation of water under reduced pressure, the product separated and the percentage yield was calculated¹¹. Through the yield of cobalt(II) was 100% the estimation of cobalt(II), Mn(IV) and carbonyl compounds were quantitative. In both the cases the IR spectra of the product agreed with IR spectra of authentic samples^{12,13}.

RESULTS AND DISCUSSION

Table 1 Summarizes the kinetic data for the Mn(IV) HPA oxidation of free α -hydroxy acids with 1N H_2SO_4 in presence of anionic and cationic micelles at $29 \pm 0.2^\circ\text{C}$. Though the reaction exhibits total second-order dependence on [cobalt(II)] as well as [α -hydroxy acids]. Oxidation of Mn(IV)HPA with α -hydroxy acids the following rate law has been deduced for this reaction.

$$\text{Rate} = K[\alpha\text{-hydroxy acids}] [\text{Mn(IV)HPA}]$$

Table 1: First order rate constant for Mn(IV) oxidation of α -hydroxy acids at $29 \pm 0.2^\circ\text{C}$

10^2 (α -hydroxy acids) mol dm^{-3}	$10^4 K_1$ (S^{-1}) NaLS	$10^2 k_2 \text{dm}^3$ $\text{mol}^{-1} \text{s}^{-1}$ (NaLS)	$10^4 K_1$ (S^{-1}) CTAB	$10^2 k_2 \text{dm}^3$ $\text{mol}^{-1} \text{s}^{-1}$ (CTAB)
Mandelic acid				
1.00	1.32	1.33	1.64	1.64
1.50	1.98	1.31	2.39	1.62
2.00	2.61	1.29	3.32	1.66
2.50	3.43	1.35	4.19	1.63
3.00	4.04	1.33	4.84	1.61
Lactic acid				
1.00	2.23	2.24	2.41	2.41
1.50	3.34	2.27	3.58	2.39
2.00	4.38	2.21	4.77	2.41
2.50	5.46	2.19	4.99	2.43
3.00	6.74	2.25	7.20	2.43
Glycolic acid				
1.00	1.11	1.11	1.31	1.31
1.50	2.14	1.08	2.53	1.28
2.00	2.75	1.09	3.28	1.32
2.50	3.07	1.10	3.49	1.34
3.00	3.34	1.12	3.94	1.32

Mn(IV) = $2.00 \times 10^{-3} \text{ mol dm}^{-3}$, $\text{H}_2\text{SO}_4 = 1\text{N}$, NaLS = 2.00×10^{-3} , CTAB = $2.00 \times 10^{-3} \text{ mol dm}^{-3}$,
Temperature = $29 \pm 0.2^\circ\text{C}$

Table 2 lists the formation constants for Mn(IV)HPA - Co complexes of α -hydroxy acids along with the specific rates, such complex formation seems to be absent when the carbonyl and it is tried up by Co(III) and the reaction between Mn(IV)HPA and Co(III) complexes of α -hydroxy acids exhibit uncomplicated second order kinetics.

Table 2: First order constants for Mn(IV) oxidation of Co(III) complexes of α -hydroxy acids at $29 \pm 0.2^\circ\text{C}$

$10^2((\text{NH}_3)_5\text{Co(III)-L})$ mol dm^{-3}	$10^4\text{K}_1(\text{S}^{-1})$ NaLS	$10^2\text{K}_2 \text{ dm}^3\text{mol}^{-1}\text{S}^{-1}$ NaLS	$10^4\text{K}_1(\text{S}^{-1})$ CTAB	$10^2\text{K}_2 \text{ dm}^3\text{mol}^{-1}\text{S}^{-1}$ CTAB
L = Mandelato				
1.00	2.79	2.79	3.30	3.31
1.50	4.18	2.83	5.67	3.26
2.00	5.57	2.86	6.45	3.27
2.50	7.02	2.88	8.13	3.29
3.00	8.38	2.84	9.94	3.35
L = Lactato				
1.00	3.69	3.69	4.17	4.17
1.50	5.57	3.72	6.28	4.20
2.00	7.35	3.69	8.35	4.19
2.50	9.16	3.68	10.26	4.21
3.00	11.07	3.71	12.55	4.22
L = Glycolato				
1.00	2.12	2.12	2.35	2.35
1.50	3.48	2.09	3.51	2.37
2.00	4.15	2.11	4.58	2.35
2.50	5.25	2.13	5.74	2.31
3.00	6.37	2.14	7.49	2.32

Mn(IV) HPA = $2.00 \times 10^{-3} \text{ mol dm}^{-3}$ $\text{H}_2\text{SO}_4 = 1\text{N}$, NaLS = $2.00 \times 10^{-3} \text{ mol dm}^{-3}$,

CTAB = $2.00 \times 10^{-3} \text{ mol dm}^{-3}$, Temperature = $29 \pm 0.2^\circ\text{C}$

The stoichiometric studies¹⁴⁻¹⁶ for the Mn(IV) HPA oxidation of pentaamminecobalt(III) complexes of α -hydroxy acids and unbound ligand in the presence of micelles were carried out at $29 \pm 0.2^\circ\text{C}$. It was observed that the cobalt(II) formation was negligibly small. The stoichiometry was calculated from the ratio between reacted [oxidant] and [substrate]. The stoichiometric results indicate that for one mole of cobalt(III) complex, about 0.5 mole of Mn(IV) HPA is consumed, whereas with the unbound ligands for 1 mole of α -hydroxy acids about 1.0 mole of Mn(IV) HPA is consumed (Table 3).

Table 3: Stoichiometric data for Mn(IV)HPA oxidation of Co(III) bound & unbound α -hydroxy acids in the presence of NaLS & CTAB

$10^3[\text{Compound}]$ mol dm ⁻³	$10^2[\text{Mn(IV)}]_{\text{initial}}$ mol dm ⁻³	$10^2[\text{Mn(IV)}]_{\text{final}}$ mol dm ⁻³	$\Delta 10^3[\text{Mn(IV)}]$ mol dm ⁻³	[Compound]: $\Delta[\text{Mn(IV)}]$
Mandelic acid				
1.0	1.0	0.89	1.10	1.00 : 1.10
2.0	2.0	1.81	1.90	1.00 : 1.05
4.0	2.0	1.60	4.00	1.00 : 1.00
Lactic acid				
1.0	1.0	0.90	1.00	1.00 : 1.00
2.0	2.0	1.79	2.10	1.00 : 0.95
4.0	2.0	1.60	4.00	1.00 : 1.00
Glycolic acid				
1.0	1.0	0.88	1.20	1.00 : 1.20
2.0	2.0	1.80	2.00	1.00 : 1.10
4.0	2.0	1.57	4.30	1.00 : 1.07

[H₂SO₄]= 1N, NaLS = 2.00 x 10⁻³ mol dm⁻³, CTAB = 2.00 x 10⁻³ mol dm⁻³, Temperature = 29 ± 0.2°C

Comparison of rates of oxidation of α -hydroxy acids and their pentaamminecobalt(III) complexes by Mn(IV)HPA

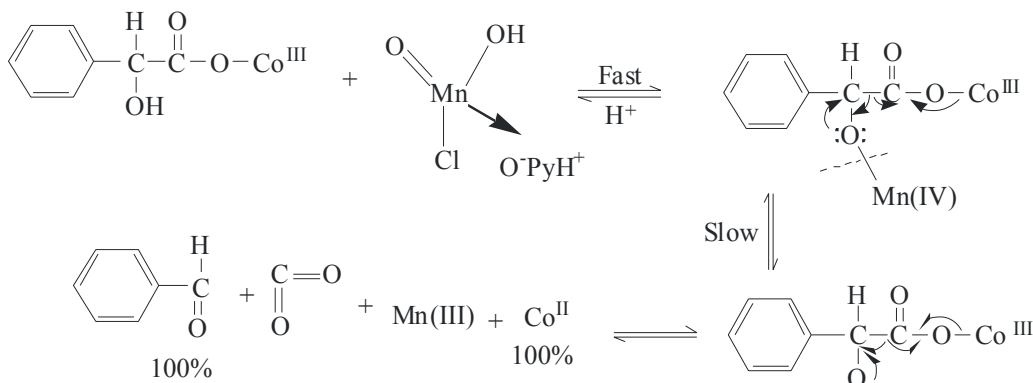
The rate of permonosulphuric acid oxidation of α -hydroxy acids in NaLS & CTAB medium can be summarized as –

	Lactic acid	>	Mandelic acid	>	Glycolic acid
NaLS :	2.23		1.32		1.11
CTAB:	2.41		1.64		1.31
	Co(III) lactato > Co(III) mandelato > Co(III) glycolato				
NaLS :	3.69		2.79		2.12
CTAB:	4.17		3.30		2.35

The Mn(IV)HPA oxidation of lactic acid reacts faster than Mn(IV) HPA oxidation of mandelic acid and glycolic acid, because if the reaction proceeds through a performed bromate ester, than the rate of C-H cleavage had been enhanced resulting in an increase in the rate of oxidation of α -hydroxy acids. Also bromate ester formation may be sterically hindered in the case of mandelic acid. The absence of such a steric retardation and enhanced acidity of methyl proton in the lactic acid may account for its greater reactivity, similarly for their complexes¹⁷.

Mechanism

Mechanism proposes that Mn(IV) HPA oxidizes OH centre cobalt (III) bound α -hydroxy acids at a rate comparable to that of the unbound ligand and there is 100% reduction at the cobalt (III) centre, forms a chromate ester with cobalt(III) glyoxalato complex, which can decompose in a slow step, proceeds through C-C bond fission leading to the formation of cobalt(II), carbonyl compounds and CO₂.



CONCLUSION

An induced electron transfer reaction has been attempted with Manganese (IV) heteropolyanion (HPA) and pentaamminecobalt (III) complexes of α -hydroxy acids in the presence of NaLS and CTAB medium. The reaction exhibits second order kinetics. In these reaction the rate of oxidation shows first order kinetics each in [cobalt(III)] and [Mn(IV)HPA].

Product and stoichiometric analysis were carried out for the oxidation of complexes and free ligands in three different (Anionic & Cationic) micellar medium with increasing micellar concentration increase in the rate is observed. Mn(IV)HPA oxidizes cobalt(III) bound and unbound α -hydroxy acids. It explains the synchronous C-C bond fission, decarboxylation and electron transfer to cobalt(III) centre. The added CTAB enhances the rate of oxidation of a reaction much more than NaLS. A mechanism involving the one electron transfer for the complex and two electron transfer for the ligand was proposed i.e., the 1 mole of Co(III) complexes of α -hydroxy acids consumes 0.5 mole of Mn(IV)HPA, whereas 1 mole of unbound α -hydroxy acids consumes 1.0 mole of Mn(IV)HPA. The appropriate methodology has been inducted.

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