KINETIC STUDIES ON PENTAAMMINE COBALT(III) COMPLEXES OF α-HYDROXY ACIDS BY MANGANESE(IV) HETEROPOLYANION IN MICELLAR MEDIUM

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ABSTRACT

The oxidation of pentaamminecobalt(III) complexes of α-hydroxy acids by manganese(IV) heteropolyanion (HPA) in micellar medium yields nearly 100% of carbonyl compounds and 100% Co(II) as ultimate products. In this reaction, the rate of oxidation shows first order kinetics each in [Co(III)] and [HPA]. The unbound α-hydroxy acids yield about 100% of carbonyl compounds in presence of micelles. The rate of oxidation of Co(III) complexes of both; bound and unbound α-hydroxy acids are enhanced more in the presence of cationic micelle of cetyltrimethylammonium bromide (CTAB), when compared to the anionic micelle of sodium dodecyl sulphate (SDS). The 1 mole of cobalt(III) complexes of α-hydroxy acids reacts with nearly 0.5 mole of Mn(IV) heteropolyanion, similarly 1 mole of α-hydroxy acids reacts with nearly 1 mole of Mn(IV) heteropolyanion. The kinetic and stoichiometric results have been accounted by a suitable mechanism.

Key words: Mn(IV) heteropolyanion (HPA), α-Hydroxy acids, Micelles, Stoichiometry, Cetyltrimethylammonium bromide (CTAB), Sodium dodecyl sulphate (SDS).

INTRODUCTION

Manganese is a metal with important industrial metal alloy used, particularly in stainless steels. The kinetics studies[1-3] employed Mn(IV) heteropolyanion as an efficient reagent for oxidation of primary and secondary alcohols to carbonyl compounds. In recent years, a variety of Mn(IV) heteropolyanion[4-6] complexes have been prepared and tested to be effective oxidants. Mn(IV) heteropolyanion is one of them. Introduction of Mn(IV) heteropolanion is economic and effective reagents for oxidation under mild and anhydrous conditions constitute a standing challenge. A novel manganese(IV)-containing symmetrical heteropolyvanadate was prepared by the transformation of $K_7[MnV_{13}O_{38}] \cdot 18H_2O$ (K_7MnV_{13}) to $K_4Li_2[MnV_{14}O_{40}] \cdot 21H_2O$ at pH 4. The heteropolyanion $[MnV_{14}O_{40}]^{6-}$ (MnV_{14}) is composed of a MnO_6 octahedron surrounded by 14 edge-sharing VO_6 octahedra. It liberates iodine almost instantaneously from KI. Little work has been done on Mn(IV) heteropolyanion as oxidant in micellar medium.

A large class of organic compounds was oxidized by Mn(IV) heteropolyanion. Induced electron transfer in pentaamminecobalt(III) complexes of α-hydroxy acids with various oxidants have been studied[7].

Induced electron transfer reactions in pentaamminecobalt(III) complexes of α-hydroxy acids result in nearly 100% reduction at cobalt(III) centre with synchronous C-C bond fission and decarboxylation[8-10]. Such an electron transfer route seems to be unavailable for Mn(IV) heteropolyanion in its reaction with cobalt(III) bound and unbound α-hydroxy acids to respective keto acid cobalt(III) complexes in sodium dodecyl sulphate (SDS)[11] and cetyltrimethylammonium bromide (CTAB)[12]; possibly the transition state is more electron deficient. Such a transition state can be envisaged only, when the C-H bond fission occurs in the slow step with hydride ion transfer. The rate of HPA oxidation of cobalt(III) complexes of α-hydroxy acids depends on the first power of HPA concentration. Similarly, the reaction between Mn(IV) heteropolyanion and unbound α-hydroxy acids exhibits first order kinetics with respect to concentration of HPA[13]. The 1 mole of Co(III) complexes of α-hydroxy acids consumes 0.5 mole of Mn(IV) heteropolyanion, whereas 1 mole of unbound α-hydroxy acids consumes 1.0 mole of Mn(IV) heteropolyanion.

EXPERIMENTAL

The kinetics studies were carried out by allowing reactions in glass stopper Corning glass vessels[14]. All ingredients of the reaction mixture were taken in separate flasks and the latter were suspended in a temperature controlled water bath. The solution of temperature pre-equilibrated Mn(IV) heteropolyanion of desired concentration was withdrawn and then immediately discharged into the reaction mixture. From this mixture, 5 mL of solution was titrated against sodium thiosulphate using starch as an indicator. Then this titration was continued at regular time intervals for about 75% of the reaction. The rate of the reaction (-dc/dt) in each kinetic run was determined by the slope of the tangent drawn at fixed concentration of Mn(IV) heteropolyanion. The order of the reaction with respect to each reactant was determined by the relation between initial rate, i.e., (-dc/dt) and initial [reactant].

Table 1: Stoichiometric data for HPA oxidation of Co(III) bound and unbound α-hydroxy acids in the presence of SDS and CTAB

10^3[Compound] mol dm^{-3}	10^2[HPA]$_{initial}$ mol dm^{-3}	10^2[HPA]$_{final}$ mol dm^{-3}	$\Delta 10^3$[HPA] mol dm^{-3}	[Compound]: Δ[HPA]
Mandelic acid				
1.0	1.0	0.89	1.10	1.00 : 1.10
2.0	2.0	1.80	2.00	1.00 : 1.00
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	1.81	1.90	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	1.78	2.20	1.00 : 1.10
4.0	2.0	1.57	4.30	1.00 : 1.07

[H$_2$SO$_4$] = 0.25 mol dm^{-3} [SDS] = 1.00 x 10^{-3} mol dm^{-3} [CTAB] = 1.00 x 10^{-3} mol dm^{-3}
Temperature = 29 ± 0.2°C

The concentration of α-hydroxy acids was varied in the range $[0.5\text{-}2.5] \times 10^2$ mol dm^{-3} at fixed concentrations of other reaction ingredients. A plot of initial rate versus [α-hydroxy acids] yielded a straight line passing through the origin confirming first order dependence. The concentration of SDS and CTAB was varied in the range of $[1 \times 10^{-3}, 10 \times 10^{-3}, 1 \times 10^{-4}, 5 \times 10^{-3}, 5 \times 10^{-4}]$ mol dm^{-3} at concentrations of other reaction ingredients. A plot of initial rate versus [Micelles] yielded a straight line passing through the origin confirming first order dependence. The second order plots were also made for comparable concentrations of α-hydroxy acids and micelles. The reaction is first order with respect to the α-hydroxy acids. The excess of the oxidant was used in kinetic runs. It gives pseudo first order rate constant. The pseudo first order rate constants calculated using the following integrated rate equations,

$$k = 2.303/t \log [a/a\text{-}x]$$

Where a initial concentration of oxidant and [a-x] concentration of oxidant at time t, are expressed in sec^{-1}. The values reported are averages of least two runs. The stoichiometry was calculated from the ratio between reacted [oxidant] and [substrate]. The stiochiometric studies for the Mn(IV) heteropolyanion oxidation of pentaamminecobalt(III) complexes of α-hydroxy acids and unbound ligand in the presence of micelles. It was observed that the cobalt(II) formation was negligibly small. The stoichiometric results indicate that for one mole of cobalt(III) complex, about 0.5 mole of HPA is consumed, whereas with the unbound ligands for 1 mole of α-hydroxy acids about 1.0 mole of HPA is consumed[15].

RESULTS AND DISCUSSION

Dependence of rate on cobalt(III) complexes of α-hydroxy acids in micellar medium

The rate of HPA[16] oxidation of pentaamminecobalt(III) complexes of α-hydroxy acids had been followed under pseudo first order condition by keeping excess of the complex concentration than the reagent. The rate constants were calculated by the integrated rate equation. The graph of logarithm of concentration versus time was linear and the rate constants calculated from the slope of the graph agreed with the experimental value, which shows first order dependence on $[(NH_3)_5Co(III)\text{-}L]^{2+}$. This was further substantiated from the study of changing the concentration of pentaamminecobalt(III) complexes of α-hydroxy acids from $[0.5 \text{ to } 2.5] \times 10^2$ mol dm^{-3} at a fixed concentration in micellar medium. The rate of disappearance of complexes in this concentration range studied is given as in Fig. 1 (Table 2).

$$-d[(NH_3)_5Co(III)\text{-}L]^{2+}/dt = k_1[(NH_3)_5Co(III)\text{-}L]^{2+} \qquad \ldots(1)$$
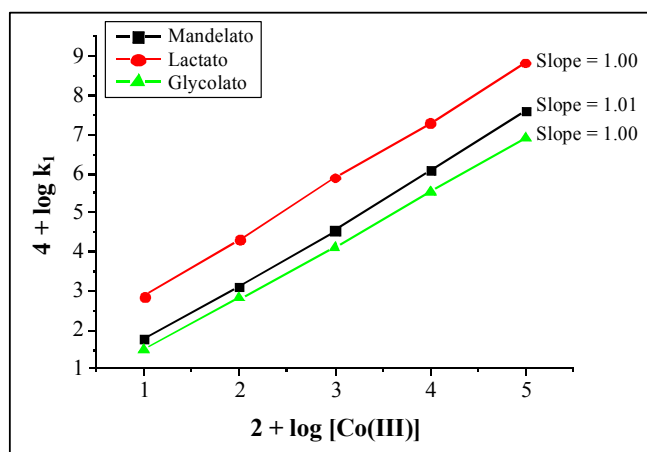
Fig. 1: Dependence of rate on [Co(III)]

Table 2

10^2[(NH$_3$)$_5$Co(III) - L] mol dm^{-3}	10^4 k$_1$ (s^{-1})	10^2k$_2$dm^3 mol^{-1}s^{-1}	SDS		CTAB	
			10^4 k$_1$ (s^{-1})	10^2k$_2$dm^3 mol^{-1}s^{-1}	10^4 k$_1$ (s^{-1})	10^2k$_2$dm^3 mol^{-1}s^{-1}
Mandelato						
0.5	1.765	3.124	1.981	3.602	2.398	4.440
1.0	3.112	3.179	3.602	3.612	4.402	4.407
1.5	4.557	3.163	5.398	3.654	6.614	4.416
2.0	6.089	3.120	7.013	3.691	8.922	4.427
2.5	7.606	3.118	8.720	3.648	11.31	4.480
Lactato						
0.5	2.862	4.361	2.486	4.362	3.906	6.232
1.0	4.314	4.327	4.362	4.317	6.216	6.278
1.5	5.900	4.345	6.244	4.302	8.520	6.238
2.0	7.302	4.312	8.352	4.386	10.804	6.298
2.5	8.852	4.336	9.901	4.317	13.001	6.222
Glycolato						
0.5	1.495	2.885	1.683	3.375	1.231	3.221
1.0	2.816	2.814	3.375	3.371	3.221	3.212
1.5	4.126	2.841	3.960	3.376	5.124	3.223
2.0	5.529	2.865	4.650	3.386	7.033	3.202
2.5	6.927	2.849	6.235	3.342	9.159	3.220

[SDS] = 0.08 mol dm^{-3} [H$_2$SO$_4$] = 0.25 mol dm^{-3} [Micelles] = 1.00 x 10^{-3} mol dm^{-3}, Temp. = 29 ± 0.2°C

Dependence of rate on cobalt(III) complexes oF H$_2$SO$_4$ in the presence of micelles

The rate of HPA oxidation of pentaamminecobalt(III) complexes of H$_2$SO$_4$ had been followed under pseudo first order condition by keeping excess of the complex concentration than the reagent. The rate constants were calculated by the integrated rate equation. The graph of logarithm of concentration versus time was linear and the rate constants calculated from the slope of the graph agreed with the experimental value, which shows first order dependence on [H$_2$SO$_4$]. This was further substantiated from the study of changing the concentration of pentaamminecobalt(III) complexes of H$_2$SO$_4$ from [0.1 to 0.5] x 10^2 mol dm^{-3} at a fixed concentration in micellar medium. The rate of disappearance of complexes in this concentration range studied is given in Fig. 2 (Table 3).

$$\text{Rate} = k_{obs}[\text{HPA}] \, [\text{Co(III)}] \, [\text{H}_2\text{SO}_4] \qquad \qquad …(2)$$

Table 3

10^2[H$_2$SO$_4$] mol dm^{-3}	SDS		CTAB	
	10^4 k$_1$ (s^{-1})	10^2k$_2$dm^3 mol^{-1}s^{-1}	10^4 k$_1$ (s^{-1})	10^2k$_2$ dm^3 mol^{-1}s^{-1}
Co(III) - Mandelato				
0.10	0.655	1.711	0.882	1.770
0.30	2.875	1.756	2.721	1.709
0.50	5.175	1.716	4.801	1.705

$10^2[H_2SO_4]$ mol dm^{-3}	SDS		CTAB	
	$10^4 k_1$ (s^{-1})	$10^2 k_2$ dm^3 mol^{-1}s^{-1}	$10^4 k_1$ (s^{-1})	$10^2 k_2$ dm^3 mol^{-1}s^{-1}
Co(III) - Lactato				
0.10	1.154	2.308	1.287	2.307
0.30	3.488	2.316	3.312	2.395
0.50	5.762	2.396	5.436	2.346
Co(III) - Glycolato				
0.10	0.312	1.224	0.480	1.288
0.30	2.281	1.206	2.215	1.258
0.50	4.562	1.207	4.221	1.265

$[(NH_3)_5Co(III)-L]^{2+}$=0.5 mol dm^{-3} [SDS] = 0.08 mol dm^{-3} [Micelles] =1.00 x 10^{-3} mol dm^{-3} Temp. =29 ± 0.2°C

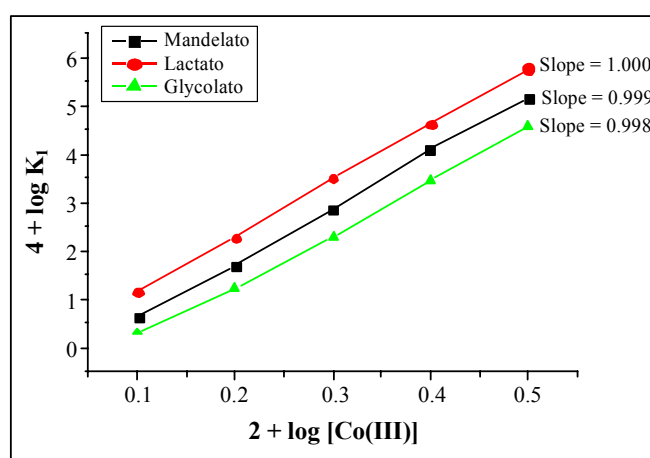**Fig. 2: Dependence of rate on Co(III) complexes of [H$_2$SO$_4$] in SDS**

Mechanism of HPA oxidation of pentaamminecobalt(III) complexes of both; bound and unbound α-hydroxy acids in micellar medium

HPA oxidizes OH centre of the α-hydroxy acids at a rate comparable to that of the free ligand. There is 100% reduction at the proton centre, forms a HPA ester, which can decompose in a slow step, and proceeds through C-C bond fission leading to the formation of carbonyl compounds with the evolution of carbon dioxide and H$_2$ gas. Considering these facts and findings, the following reaction schemes has been proposed for the HPA oxidation of pentaamminecobalt(III) complexes of both; bound and unbound α-hydroxy acids.
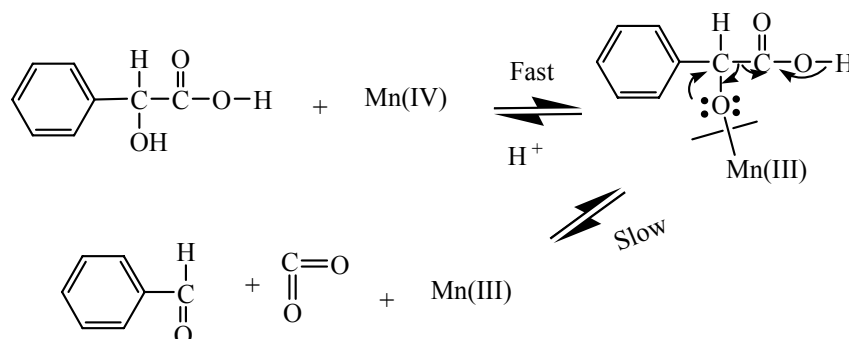
Scheme 1
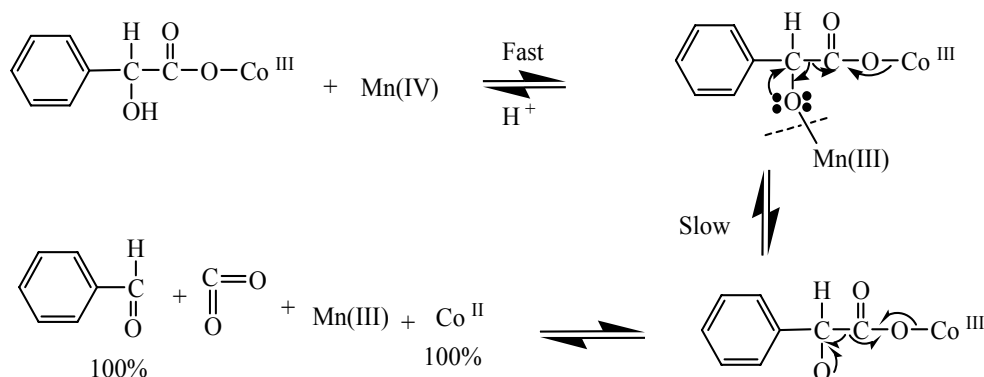
Scheme 2

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 SDS and CTAB. The reaction exhibits second order kinetics. In these reactions, the rate of oxidation shows first order kinetics each in [cobalt(III)] and [HPA]. Product and stoichiometric analysis were carried out for the oxidation of complexes and free ligands in different (anionic and cationic) micellar medium with increasing micellar concentration, where an increase in the rate is observed. Mn(IV) heteropolyanion oxidizes cobalt (III) bound and unbound α-hydroxy acids through free radical. 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 SDS. 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 HPA, whereas 1 mole of unbound α-hydroxy acids consumes 1.0 mole of HPA. The reaction goes by free radical mechanism and it has been proved by acrylonitrile polymerization. The appropriate methodology has been inducted.

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