

Kinetic Study on Induced Electron Transfer Reaction in Pentaamminecobalt(III) complexes of α -Hydroxy Acids by Mn(III)acetate in Micellar Medium

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Abstract

The oxidation of Pentaamminecobalt(III) complexes of α -hydroxy acids by Mn(III)acetate in micellar medium yielding nearly 100% of carbonyl compounds and 100% Co(II) are ultimate products. In this reaction the rate of oxidation shows first order kinetics each in [cobalt(III)] and [Mn(III)acetate]. The unbound α -hydroxy acids yield about 100% of carbonyl compound in presence of micelles. The rate of oxidation of Co(III) complexes of both unbound and bound α -hydroxy acids are enhanced more in the presence of cationic micelle Cetyltrimethylammoniumbromide(CTAB) when compared to the anionic micelle of Sodium Dodecyl sulphate (SDS). Mn(III) acetate 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 1.00 mole of cobalt(III) complexes of α -hydroxy acids reacts with nearly 0.5 mole of Mn(III)acetate, Similarly 1.00 mole of α -hydroxy acids reacts with nearly 1.00 mole of Mn(III)acetate. The reaction goes by free radical mechanism was proved by

acrylonitrile polymerization. The appropriate methodology has been inducted.

Keywords: Mn(III)acetate, α -hydroxy acids, Sodium Dodecyl Sulphate (SDS), Stoichiometry, Cetyltrimethylammoniumbromide(CTAB).

1. Introduction

Chemical reactions are the deciding factors of the life cycle as it is known that human life is mainly depending upon chemicals in different forms. A Chemical reaction may have several aspects, one of which being oxidation. Oxidation processes are commonly been in everyday life[1]. Electron transfer is the process by which an electron moves from one atom or molecule to another atom or molecule. Electron transfer is a mechanistic description of the thermodynamic concept of redox, where in the oxidation states of both reaction partners change. Redox reactions between metal ion centers involving transfer of electron from reductant to oxidant have been studied in details in past and also reviewed by

several groups of workers[2]. The Electron transfer in Pentaamminecobalt(III) complexes of α -Amino acids with Mn(III)acetate has been already reported[3-5].

Mn(III)acetate oxidation of Pentaamminecobalt(III) complexes of α -hydroxy acids with anionic and cationic micelles as important to study the rate of decomposition of the complexes. Since micellar catalysis is an area of tremendous interest due to its occurrence in reaction important to biochemical, biotechnology, and industrial processes. The micelles used in the present work are SDS and CTAB. The rate of the reaction is increased by the addition of micelles. A plot of specific rate constant versus micellar concentration is sigmoidal in shape the catalytic effect is more in CTAB than SDS. Induced electron transfer reactions in pentaamminecobalt(III) complexes of α -hydroxy acids result in nearly 100% reduction at cobalt(III) centre with synchronous carbon-carbon bond fission and decarboxylation.

2. Materials and Methods

Preparation of Pentaamminecobalt(III) Complexes of the α -hydroxy acids

The monomeric cobalt(III) complexes of mandelic acid, lactic acid and glycolic acids were prepared as their perchlorates following the procedure of Fan and Gould[6].

10mmol of the α -hydroxy acids was dissolved in 20ml of methanol taken in a 50ml of R.B.flask and a pellet (0.50 to 1.00g) of NaOH was added. About 0.40g of finely powdered Carbanatopentaamminecobalt(III) nitrate was added and the mixture was refluxed at 70°C for 2 hours. It was then cooled under ice for 30 minutes; about 3ml of 70% perchloric acid was added drop wise while shaking the mixture was cooled again under ice for 1 hour. The cobalt(III) complex precipitated as perchlorate and was filtered through a sintered glass crucible, washed well with ethanol followed by diethyl ether, dried and preserved in a desiccator.

Manganese(III) acetate[7]

30.3 g anhydrous Mn(OAc)₂ in 440 g glacial acetic acid was refluxed for 2h. 6.82 g KMNO₄ 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.

Kinetic Method[8,9]

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 flask were standardized by usual procedure. The α -hydroxy acids (A.R) employed as ligands were purchased from Sigma-Aldrich and used as such. The chemicals were purchased from BDH(UK), and SD Fine chemicals (INDIA), E.MERCK (INDIA).

Rate Measurements[10-12]

The rate measurement were carried out on $29 \pm 0.2^\circ \text{C}$ in 100% aqueous medium for α -hydroxy acids. The Temperature was controlled by electrically operated thermostat. The rate measurement was carried out at room temperature $29 \pm 0.2^\circ \text{C}$ in 100% aqueous medium for α -hydroxy acids. The concentration of α -hydroxy acids was varied in the range $[0.5- 2.5] \times 10^2 \text{ mol dm}^{-3}$ at fixed concentrations of other reaction ingredients. A plot of initial rate versus [α -hydroxy acids] and [Micelles] yielded a straight line passing through the origin confirming first order dependence. The concentration of SDS & CTAB was varied in the range of $[1 \times 10^{-3}, 10 \times 10^{-3}, 1 \times 10^{-4}, 5 \times 10^{-3}, 5 \times 10^{-4}] \text{ mol dm}^{-3}$

Stoichiometric Studies[13,14]

The Stiochiometric Studies for the Mn(III)acetate 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. After nine half lives when the reaction was nearing completion, the concentration of unreacted Mn(III)acetate was determined iodometrically. $\Delta[\text{Mn(III)acetate}]$ was calculated after applying the due blank corrections for decomposition of Mn(III)acetate and aqation of Co(III) complex of α -hydroxy acids in the presence of micelles. Similar calculation about $\Delta [\text{Mn(III)acetate}]$ was made for the unbound ligand also. 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(III)acetate is consumed, whereas with the unbound

ligands for 1 mole of α -hydroxy acids about 1.0 mole of Mn(III)acetate is consumed (Table 1).

Table 1: Stoichiometric data for Mn(III)acetate oxidation of Co(III) bound and unbound α -hydroxy acids in the presence of Micelles.

10^3 [Compound] mol dm ⁻³	10^2 [Mn(III)] _{initial} mol dm ⁻³	10^2 [Mn(III)] _{final} mol dm ⁻³	$\Delta 10^3$ [Mn(III)] mol dm ⁻³	[Compound] : Δ [Mn(III)]
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
Mandelato				
1.0	1.0	0.95	0.50	2.00 : 1.00
2.0	2.0	1.89	1.10	2.00 : 1.10
4.0	2.0	1.99	2.01	2.00 : 1.00
Lactato				
1.0	1.0	0.96	0.49	2.00 : 0.98
2.0	2.0	1.90	1.00	2.00 : 1.00
4.0	2.0	2.00	2.00	2.00 : 1.00
Glycolato				
1.0	1.0	0.95	0.50	2.00 : 1.00
2.0	2.0	1.88	1.20	2.00 : 1.20
4.0	2.0	1.98	2.02	2.00 : 1.01

[H₂SO₄] = 0.25 mol dm⁻³, [Micelles] = 1.00 x 10⁻³ mol dm⁻³, Temperature = 29 ± 0.2°C.

3. Results and Discussion

DEPENDENCE OF RATE ON α -HYDROXY ACIDS IN MICELLAR MEDIUM

The rate of Mn(III)acetate oxidation of α -hydroxy acids depends on Mn(III)acetate concentration and

graph of logarithm of concentration versus time are linear from the slopes of the graphs, the specific rates are calculated agree with those obtained from integrated rate equation, suggesting first order dependence of [Mn(III)acetate]. This is further substantiated from the studies of changing the concentration of Mn(III)acetate from [0.5 to 2.5] X 10² mol dm⁻³ at a fixed concentration in micellar medium. The rate constants obtained for the different concentration of α -hydroxy acids were nearly a constant. Hence the rate of disappearance

of α -hydroxy acids in this concentration range studied is given as (Table - 2), (Figure - 1).

$$-d[\alpha\text{-hydroxy acids}] / dt = k_1[\alpha\text{-hydroxy acids}] \dots\dots\dots(1)$$

All the kinetic runs were repeated and the rate constants were reproducible within $\pm 2\%$ range

Table 2: First order rate constants for Mn(III)acetate oxidation of α -hydroxy acids in micellar medium at $29 \pm 0.2^\circ\text{C}$.

$10^2[\alpha\text{-hydroxy acids}]$ mol dm ⁻³	$10^4 k_1$ (s ⁻¹) SDS	$10^4 k_{cal}$ SDS	$10^4 k_1$ (s ⁻¹) CTAB	$10^4 k_{cal}$ CTA B
Mandelic acid				
0.5	1.23	2.11	1.444	2.585
1.5	3.029	2.156	3.701	2.503
2.5	4.815	2.106	5.952	2.531
Lactic acid				
0.5	1.825	2.776	2.106	3.235
1.5	3.601	2.706	4.414	3.276
2.5	5.436	2.706	6.571	3.228
Glycolic acid				
0.5	0.999	1.862	1.133	2.263
1.5	2.778	1.802	3.34	2.226
2.5	4.509	1.839	5.561	2.224

[Mn(III)acetate] = 0.08 mol dm⁻³, [H₂SO₄] = 0.25 mol dm⁻³, [Micelles] = 1.00 x 10⁻³ mol dm⁻³.

The rate of the reaction for Mn(III)acetate oxidation of bound and unbound α -hydroxy acids in micellar mediums are arranged in the following increasing order.

Glycolic acid < Mandelic acid < Lactic acid

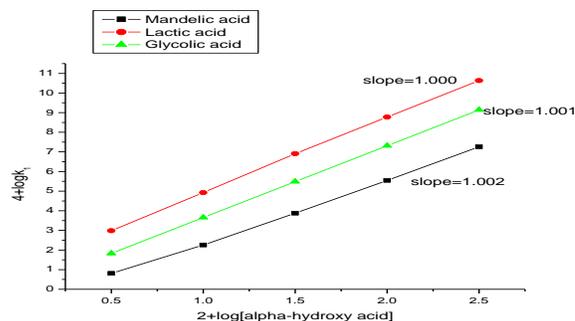


Fig. 1 Dependence of rate on $[\alpha\text{-hydroxy acids}]$ in CTAB

DEPENDENCE OF RATE ON COBALT(III) COMPLEXES OF α -HYDROXY ACIDS IN MICELLAR MEDIUM

The rate of Mn(III)acetate 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 $[(\text{NH}_3)_5\text{Co(III)-L}]^{2+}$. This was further substantiated from the study of changing the concentration of pentaamminecobalt(III) complexes of α -hydroxy acids from $[0.5 \text{ to } 2.5] \times 10^2 \text{ mol dm}^{-3}$ at a fixed concentration in micellar medium. The rate constants obtained for the different concentration of $[(\text{NH}_3)_5\text{Co(III)-L}]^{2+}$ complexes of α -hydroxy acids were nearly a constant. Hence the rate of disappearance of complexes in this concentration range studied is given as (Table - 3),(Figure -2).

$$-d[(\text{NH}_3)_5\text{Co(III)-L}]^{2+} / dt = k_1[(\text{NH}_3)_5\text{Co(III)-L}]^{2+} \dots\dots\dots(3)$$

All the kinetic runs were repeated and the rate constants were reproducible within $\pm 2\%$ range.

Table 3: First order rate constants for Mn(III)acetate of Co(III) complexes of α -hydroxy acids in micellar medium at $29 \pm 0.2^\circ\text{C}$.

$10^2[\alpha\text{-hydroxy acids}] \text{ mol dm}^{-3}$	$10^4 k_1 (\text{s}^{-1})$ SDS	$10^4 k_{\text{cal.}}$ SDS	$10^4 k_1 (\text{s}^{-1})$ CTAB	$10^4 k_{\text{cal.}}$ CTAB
Mandelato				
0.5				
1.5	1.681	2.962	2.228	4.442
2.5	4.288	2.963	6.654	4.436
Lactato	6.909	2.961	11.21	4.486
0.5				
1.5	2.486	3.762	3.956	6.232
2.5	5.144	3.762	8.558	6.238
Glycolato	7.801	3.728	13.051	6.222
0.5				
1.5	1.183	2.375	1.131	3.021
2.5	3.560	2.376	4.924	3.023
	5.935	2.342	8.959	3.020

$[\text{Mn(III)acetate}] = 0.08 \text{ mol dm}^{-3}$, $[\text{H}_2\text{SO}_4] = 0.25 \text{ mol dm}^{-3}$,
 $[\text{Micelles}] = 1.00 \times 10^{-3} \text{ mol dm}^{-3}$.

The rate of the reaction for Mn(III)acetate oxidation of bound and unbound α -hydroxy acids in micellar mediums are arranged in the following increasing order.

Glycolato < Mandelato < Lactato

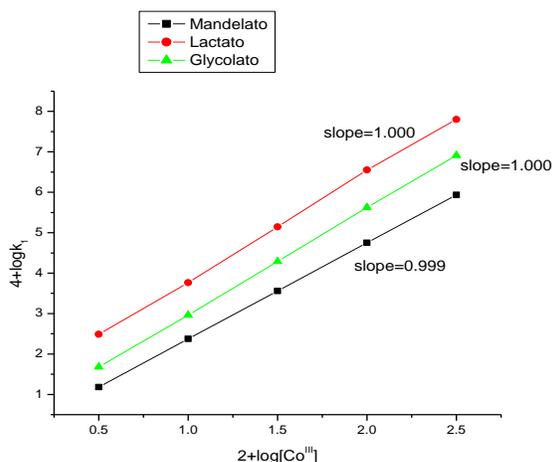


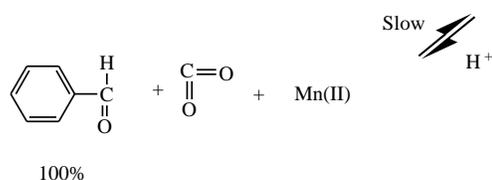
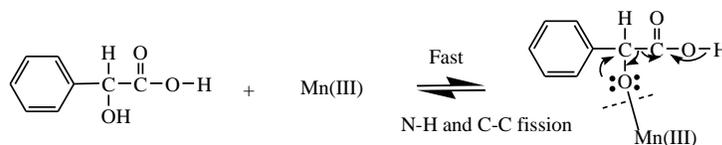
Fig.2 Dependence of rate on $[\text{Co(III)}]$ in NaLS

Mechanism

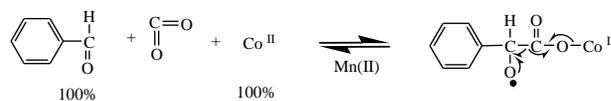
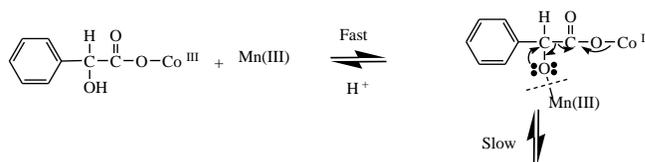
Mechanism of Mn(III) acetate oxidation of pentaamminecobalt(III) complexes of both bound and unbound α -hydroxy acids in micellar medium.

Mn(III) acetate oxidizes OH centre of the α -hydroxy acids at a rate of comparable to that of the free ligand. There is 100% reduction at the Proton centre, forms a Mn(III) acetate ester which can decompose in a slow step, proceeds through C-C bond fission leading to the formation of carbonyl compounds with the evolution of carbon dioxide and H₂ gas.

Considering these facts and findings with these results, the following reaction schemes has been proposed for the Mn(III) acetate oxidation of pentaamminecobalt(III) complexes of both bound and unbound α -hydroxy acids.



Scheme-I



Scheme-II

4. Conclusions

The kinetic analysis of one electron transfer route seems to be available for Mn(III)acetate with cobalt(III) bound and unbound complexes of α -hydroxy acids in micellar medium, Mn(III)acetate oxidizes cobalt(III) bound and unbound α -hydroxy acids through free radical. It explains the synchronous C-C bond fission and electron transfer to cobalt(III) centre. The oxidation of above complexes increases with increase in micellar concentration an increase in the rate is observed. The added CTAB enhances the rate of oxidation of a reaction much more than SDS. Similar trends has been observed in Mandelato, Lactato and Glycolato cobalt(III) complexes. 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(III)acetate, whereas 1 mole of unbound α -hydroxy acids consumes 1.0 mole of Mn(III)acetate. The reaction goes by free radical mechanism was proved by acrylonitrile polymerization. The appropriate methodology has been inducted.

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