



Research Article

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Kinetic study on Induced Electron Transfer Reaction in Pentaamminecobalt(III) complexes of α -hydroxy acids by Permonosulphuric acid in micellar medium

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ABSTRACT

Permonosulphuric acid Oxidation of Pentaamminecobalt(III) complexes of α -hydroxy acids at $60 \pm 0.2^\circ\text{C}$ in micellar medium has been attempted. In this reaction the rate of oxidation shows first order kinetics each in [Cobalt(III)] and [PMS]. Permonosulphuric acid induced electron transfer in $[(\text{NH}_3)_5\text{Co(III)-L}]^{2+}$ complexes of α -hydroxy acids readily yields 100% of Cobalt(II) with nearly 100% of C-C bond cleavage products suggesting that it behaves mainly as one equivalent oxidant in micellar medium, with unbound ligand also it behaves only as C-C cleavage agent rather than C-H cleavage agent, with increasing micellar concentration an increase in the rate is observed.

Keywords: Pentaamminecobalt(III) complexes, Induced electron transfer reaction, Oxidation reaction Mechanism, Permonosulphuric acid (PMS), Sodium laurylsulphate (NaLS), Cetyltrimethyl ammoniumbromide (CTAB).

INTRODUCTION

The Kinetics studies[1-5] employing Permonosulphuric acid (PMS) is an efficient reagent for oxidation of primary and secondary alcohols to carbonyl compounds. Oxidation is an important process in organic chemistry and introduction of PMS is economic and effective reagents for oxidation under mild and aqueous conditions constitutes a standing challenge. PMS is an oxidant which is non-hygroscopic, non-photosensitive, stable yellow orange solid which is freely soluble in water, acetic acid, N,N-dimethyl formamide[6-8] etc. The little work has been done on PMS as oxidant in micellar medium[9-10].

Evolution 60 thermo spectrophotometer has been employed to study the oxidation of α -Hydroxy acids such as mandelic acid, lactic acid, glycolic acid and their Cobalt(III) complexes using Permonosulphuric acid as an oxidant in the presence of surfactant. One equivalent oxidant like Ce(IV) induced electron transfer 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. Such an electron transfer route seems to be unavailable for Permonosulphuric acid in its reaction with Cobalt(III) bound and unbound α -hydroxy acids to respective keto acid Cobalt(III) complexes in Sodium laurylsulphate (NaLS) and Cetyltrimethyl ammoniumbromide(CTAB) 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 absence of formation of Cobalt(II) rules out the synchronous C-C bond fission and electron transfer to cobalt(III). The thermodynamic parameters are in consistent with bimolecular reaction. The rate of PMS oxidation of Cobalt(III) Mandelato, Lactato and Glycolato complexes depends on the first power of PMS concentration. Similarly the reaction between PMS and unbound α -hydroxy acids exhibits first order kinetics with respect to concentration of PMS. Of the three complexes lactato Cobalt(III) complexes react faster than mandelato and glycolato complexes, where as in the unbound ligand similar trends follows[11-12].

EXPERIMENTAL SECTION

The alpha-hydroxyacids(A.R) employed as ligands were purchased from Sigma- Aldrich and used as such. The surfactants used in the present work are Sodium laurylsulphate(NaLS)[13] and Cetyltrimethyl ammoniumbromide(CTAB)[14].

The surfactants were purified by adopting earlier procedure[15-16]. The chemicals were purchased from BDH(UK), and SD Fine chemicals (INDIA), E.Merck (INDIA). Pentaamminecobalt(III) complexes of α -hydroxy acids were prepared by reported methods[17].

Double distilled water was used as a solvent. H_2SO_4 was standardized by using standard sodium bicarbonate solution with methyl orange as an indicator. For the oxidation of Co(III) complexes of α -hydroxy acids and unbound ligands the PMS was used[18]. The rate measurements were carried out on $60 \pm 0.2^\circ C$ in 100% aqueous medium. Temperature was controlled by electrically operated thermostat[19].

The total volume of reaction mixture in the spectrophotometric cell was kept as 2.5ml in each kinetic run. An Evolution 60 Thermo spectrophotometer fitted with recording and thermostating arrangement was used to follow the rate of the reaction[20]. Rate of Permonosulphuric acid oxidant with unbound ligand and Cobalt(III) bound complexes were calculated from the volumetric titration for free ligands or Co(III) complexes at 502nm. The excess of the reductant was used in kinetic runs. It gives pseudo first order rate constant Table 1.

Dependence of rate on Permono sulphuric acid concentration in micellar medium

Table 1. First order rate constants for PMS oxidation of Co(III) complexes of α -Hydroxy acids & in the presence of NaLS & CTAB at $60 \pm 0.2^\circ C$.

$[H_2SO_4] = 0.25 \text{ mol dm}^{-3}$, $[NaLS] = [CTAB] = 1.00 \times 10^{-3} \text{ mol dm}^{-3}$, Temperature= $60 \pm 0.2^\circ C$.

$10^{-4} X$ [Micelles]	$10^2 \times k_1 \text{ lit. mol}^{-1} \text{ sec}^{-1}$	
	NaLS	CTAB
2	4.85	7.53
4	9.84	14.25
6	14.83	20.97
8	19.82	27.69
10	24.81	34.41
12	29.80	41.13
14	34.79	47.85
16	39.78	54.57

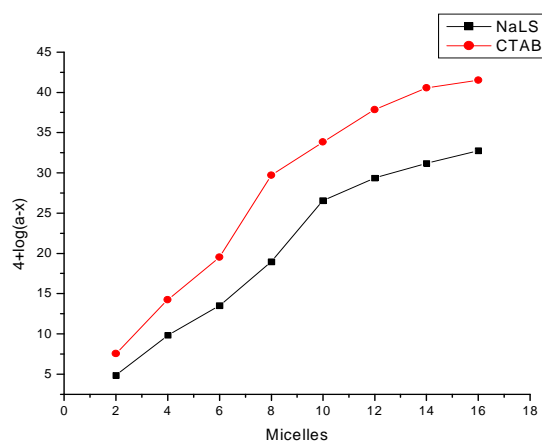


Fig.1 : First order dependence plots

The stoichiometric studies for the PMS oxidation of Pentaamminecobalt(III) complexes of α -hydroxy acids and unbound ligand in the presence of micells were carried out at $60 \pm 0.2^\circ C$. It was observed that the Cobalt(II) formation was 100%.

RESULTS AND DISCUSSION

Table 2 Summarizes the Kinetic data for the Permonosulphuric acid oxidation of free α -hydroxy acids with 2N H_2SO_4 in presence of anionic and cationic micells at $60 \pm 0.2^\circ C$. Though the reaction exhibits total second – order

dependence on [Cobalt(II)] as well as [α -hydroxy acids]. Based on the oxidation of PMS with α -hydroxy acids the following rate law has been deduced.

$$\text{Rate} = k_2 [\alpha\text{-hydroxy acids}] [\text{PMS}]$$

Table 3 lists the formation constants for PMS Co-complexes of α -hydroxy acids along with the specific rates. Such complex formation seems to be absent when the carboxyl and it is tied up by Co(III) and the reaction between PMS and Co(III) complexes of α -hydroxy acids exhibit uncomplicated second order kinetics.

The stoichiometric results indicate that for one mole of Cobalt(III) complex about 0.5 mole of PMS is consumed, whereas with the unbound ligands for 1 mole of α -hydroxy acids about 1.0 mole of PMS is consumed Table 4&5.

Table 2: First order rate constants for PMS oxidation of α -hydroxy acids & in the presence of NaLS and CTAB at $60 \pm 0.2^\circ\text{C}$

$10^2[\alpha\text{-hydroxy acids}] \text{ mol dm}^{-3}$	$10^4 k_1 \text{ s}^{-1}$	$10^2 k_2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$10^4 k_1 \text{ s}^{-1}$ NaLS	$10^2 k_2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ NaLS	$10^4 k_1 \text{ s}^{-1}$ CTAB	$10^2 k_2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ CTAB
Mandelic acid						
0.5	1.2358	2.4716	1.2441	2.4882	1.8280	3.6560
1.0	2.4646	2.4646	2.4855	2.4855	3.6561	3.6561
1.5	3.7074	2.4716	3.6053	2.4035	5.4840	3.6561
2.0	4.9238	2.4619	4.9238	2.4619	7.3120	3.6560
2.5	6.1428	2.4571	6.0798	2.4319	9.1400	3.6560
Lactic acid						
0.5	2.1441	4.2882	2.1066	4.2132	2.2861	4.5722
1.0	4.2492	4.2492	4.2353	4.2353	4.5267	4.5267
1.5	6.3295	4.2196	6.4144	4.2762	6.8383	4.5588
2.0	8.4901	4.2450	8.4359	4.2179	9.0759	4.5379
2.5	10.5516	4.2206	10.5710	4.2284	11.0310	4.4124
Glycolic acid						
0.5	1.1056	2.2112	1.1335	2.2706	1.18 00	2.3600
1.0	2.2038	2.2038	2.2631	2.2631	2.3558	2.3558
1.5	3.3054	2.2036	3.3400	2.2266	3.4540	2.3026
2.0	4.4078	2.2039	4.4609	2.2304	4.6482	2.3241
2.5	5.5434	2.2173	5.5617	2.2246	5.7596	2.3038

$$[\text{PMS}] = 0.08 \text{ mol dm}^{-3}, [\text{H}_2\text{SO}_4] = 0.25 \text{ mol dm}^{-3}, [\text{NaLS}] = 1.00 \times 10^{-3} \text{ mol dm}^{-3},$$

$$[\text{CTAB}] = 1.00 \times 10^{-3} \text{ mol dm}^{-3}, \text{Temperature} = 60 \pm 0.2^\circ\text{C}$$

Table 3: First order rate constants for PMS oxidation of Co(III) complexes of α -hydroxy acids & in the presence of NaLS and CTAB at $60 \pm 0.2^\circ\text{C}$

$$[\text{PMS}] = 0.08 \text{ mol dm}^{-3}, [\text{NaLS}] = 1.00 \times 10^{-3} \text{ mol dm}^{-3}, [\text{CTAB}] = 1.00 \times 10^{-3} \text{ mol dm}^{-3},$$

$$[\text{H}_2\text{SO}_4] = 0.25 \text{ mol dm}^{-3}, \text{Temperature} = 60 \pm 0.2^\circ\text{C}$$

$10^2[(\text{NH}_3)_5\text{Co(III)-L}]$	$10^4 k_1 \text{ s}^{-1}$	$10^2 k_2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$10^4 k_1 \text{ s}^{-1}$ NaLS	$10^2 k_2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ NaLS	$10^4 k_1 \text{ s}^{-1}$ CTAB	$10^2 k_2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ CTAB
Co(III) – Mandelato						
0.5	1.5051	3.0102	1.2811	2.5622	2.2210	4.4420
1.0	3.0110	3.0110	2.5622	2.5622	4.4420	4.4420
1.5	4.5125	3.0083	3.8842	2.5613	6.6570	4.4380
2.0	6.0245	3.0122	5.1237	2.5618	8.9421	4.4710
2.5	7.5255	3.0102	6.4057	2.5622	11.2172	4.4868
Co(III) – Lactato						
0.5	2.5121	5.0242	2.8810	5.7620	3.2182	6.4364
1.0	5.0242	5.0242	5.7620	5.7620	6.4364	6.4364
1.5	7.5272	5.0181	8.6425	5.7616	9.6514	6.4342
2.0	10.1252	5.0626	11.4527	5.7263	12.8524	6.4262
2.5	12.6882	5.0752	14.3047	5.7218	16.0574	6.4229
Co(III) – Glycolato						
0.5	1.2560	2.5120	1.3875	2.7750	1.6105	3.2210
1.0	2.5120	2.5120	2.7750	2.7750	3.2210	3.2210
1.5	3.7709	2.5139	4.1600	2.7733	4.8211	3.2140
2.0	5.0240	2.5120	5.4650	2.7325	6.4331	3.2165
2.5	6.2809	2.5123	6.8437	2.7374	8.0500	3.2200

From a comparison, the specific rates for PMS oxidation of the respective Co(III) complexes and the dimeric cobalt(III) glyoxalato complex, one can infer that the oxidation rates of α -hydroxy acids are not significantly affected by complex formation. This may be due to the point of attack lies away from the Co(III) centre so that its electrostatic influence is less felt. There is, however a considerable change in the specific rate of PMS oxidation of the Co(III) keto acid complex as the two Co(III) centres can exert greater electrostatic influence over the reacting

centre. This suggests that PMS attacks the O-H centre in the slow step of the reaction, leading to ligand oxidation takes place.

The rate of the reaction is increased by the addition of both NaLS and CTAB. A plot of specific rate constant versus micellar concentration is sigmoidal in shape the catalytic effect is more in CTAB than NaLS.

Table 4: Stoichiometric data for PMS Oxidation of Co(III) bound and unbound α -Hydroxy acids in the presence of NaLS at $60 \pm 0.2^\circ\text{C}$
 $[\text{H}_2\text{SO}_4] = 0.25 \text{ mol dm}^{-3}$, $[\text{NaLS}] = 1.00 \times 10^{-3} \text{ mol dm}^{-3}$, Temperature = $60 \pm 0.2^\circ\text{C}$

10^3 [Compound] mol dm ⁻³	10^2 [PMS] _{initial} mol dm ⁻³	10^2 [PMS] _{final} mol dm ⁻³	$\Delta 10^3$ [PMS] mol dm ⁻³	[Compound]: Δ [PMS]
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
Co(III) – Mandelato				
1.0	1.0	0.94	0.60	2.00 : 1.20
2.0	2.0	1.89	1.10	2.00 : 1.10
4.0	2.0	1.85	1.95	2.00 : 0.97
Co(III) – Lactato				
1.0	1.0	0.95	0.50	2.00 : 1.00
2.0	2.0	1.90	1.00	2.00 : 1.00
4.0	2.0	1.86	1.94	2.00 : 0.97
Co(III) – Glycolato				
1.0	1.0	0.94	0.60	2.00 : 1.20
2.0	2.0	1.88	1.20	2.00 : 1.20
4.0	2.0	1.84	1.96	2.00 : 0.98

Table 5: Stoichiometric data for PMS Oxidation of Co(III) bound & unbound α -Hydroxyacids in the presence of CTAB at $60 \pm 0.2^\circ\text{C}$.
 $[\text{H}_2\text{SO}_4] = 0.25 \text{ mol dm}^{-3}$, $[\text{CTAB}] = 1.00 \times 10^{-3} \text{ mol dm}^{-3}$

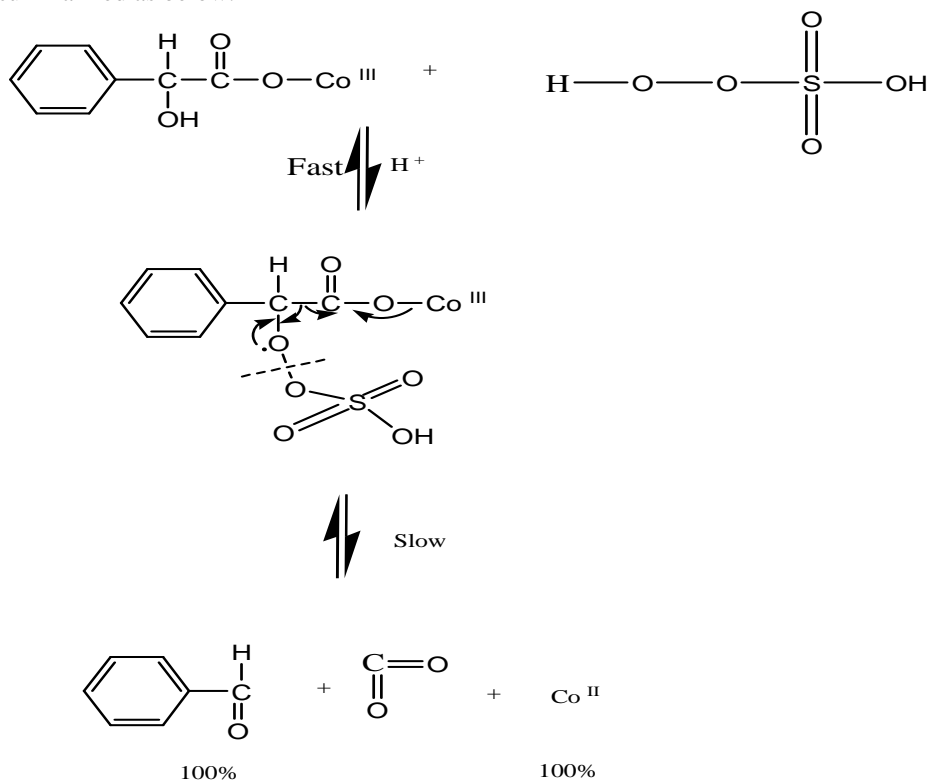
10^3 [Compound] mol dm ⁻³	10^2 [PMS] _{initial} mol dm ⁻³	10^2 [PMS] _{final} mol dm ⁻³	$\Delta 10^3$ [PMS] mol dm ⁻³	[Compound]: Δ [PMS]
Mandelic acid				
1.0	1.0	0.90	1.00	1.00 : 1.00
2.0	2.0	1.81	1.90	1.00 : 0.95
4.0	2.0	1.61	3.90	1.00 : 0.97
Lactic acid				
1.0	1.0	0.91	0.99	1.00 : 0.99
2.0	2.0	1.82	1.80	1.00 : 0.98
4.0	2.0	1.61	3.90	1.00 : 0.97
Glycolic acid				
1.0	1.0	0.89	1.10	1.00 : 1.10
2.0	2.0	1.79	2.10	1.00 : 1.05
4.0	2.0	1.58	4.20	1.00 : 1.05
Co(III) – Mandelato				
1.0	1.0	0.95	0.50	2.00 : 1.00
2.0	2.0	1.90	1.00	2.00 : 1.00
4.0	2.0	1.99	2.01	2.00 : 1.00
Co(III) – Lactato				
1.0	1.0	0.96	0.49	2.00 : 0.98
2.0	2.0	1.91	0.99	2.00 : 0.99
4.0	2.0	2.00	2.00	2.00 : 1.00
Co(III) – Glycolato				
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	1.98	2.02	2.00 : 1.01

The specific rate of the lactato complex is more when compared to both the rate of unbound ligand and mandelato complex is due to the ligation of lactic acid to cobalt(III) centre has probably increased its reactivity towards PMS and this effect seems to be more specific for ligands only. In NMR spectrum of lactato complex the alpha methine proton has undergone considerable downfield shift compared to the alpha C-H proton of the unbound ligand [δ C-H = 1.73 ppm in lactic acid and δ C-H = 2.30 ppm in lactato complex whereas δ C-H = 4.75 ppm in mandelic acid δ C-H = 3.85 ppm in the respective complex]. Suggesting an increase in acidic nature of methine proton of lactic acid

is due to ligation to metal centre. If the reaction proceeds through a performed Permonosulphuric ester, then the rate of alpha C-H will be enhanced, resulting in an increased rate of oxidation of lactato complex such a precursor complex may be sterically hindered in the case of mandelato and glycolato complexes.

MECHANISM:

Oxidation of Pentaamminecobalt(III) complexes of both bound and unbound ligands in micellar medium. The features of Permonosulphuric acid induced electron transfer in pentaamminecobalt(III) Complexes of α -Hydroxy acid are summarized as below.



CONCLUSION

The kinetics of one electron transfer route seems to be unavailable for PMS with Cobalt(III) bound and unbound complexes of α -Hydroxy acids in micellar medium, PMS oxidizes Cobalt(III) bound and unbound α -Hydroxy acids. It rules out the synchronous C-C bond fission and electron transfer to Cobalt(III) centre. Oxidation of above complexes increases with increase of temperature. 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 NaLS. Similar trends have been observed in lactato and glycolato Co(III) complexes. The 1 mole of Co(III) complex of α -Hydroxy acids consumes 0.5 mole of PMS, whereas 1 mole of unbound α -Hydroxy acids consumes 1.0 mole of PMS. The reaction goes by free radical mechanism was proved by acrylonitrile polymerization.

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