

Research Article

Oxidation of Cobalt (III) Complexes of Alpha Hydroxy Acids by Pyrazinium Chloro Chromate in ALS Medium – A Kinetic and Mechanistic Study

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ABSTRACT

An induced electron transfer reaction has been attempted presently with pyrazinium chloro chromate and pentamminecobalt(III) complexes of alpha hydroxyl acids in the presence of micelles. The reaction exhibits second order kinetics and in the case of mandelato complexes the amount of cobalt (III) reduced corresponds to nearly 70% of mandelato complex is converted to keto acid cobalt (III) complex. In pyrazinium chloro chromate induced electron transfer in the complex, the intermediate radical formed dissociates in a nearly synchronous manner with C-C bond cleavage and the rest of it proceeding with alpha C-H fission yielding keto acid cobalt(III) complex. With increasing the detergent concentration an increase in the rate is observed.

Keywords: Ammonium Lauryl Sulphate, Pyrazinium Chlorochromate, Cobalt (III) Complexes.

1. INTRODUCTION

Oxidation is an important process in organic Chemistry and use of new economic and effective oxidants under mild and anhydrous conditions constitutes a standing challenge. PCC is an oxidant, which is non – hygroscopic, non-photosensitive, stable solid, freely soluble in water, acetic acid, N,N-dimethyl formamide etc. The little work has been done on PCC with cobalt (III) complexes as oxidant in micellar media. A study of induced electron transfer reaction in Co(III) – L System by an external oxidant, whether an one electron transfer reaction takes place at the bound organic ligand gets oxidized without disturbing Co (III) centre.

2. MATERIAL AND METHOD

The surfactants used in the present work are ammonium lauryl sulphate (ALS). The surfactants are purified by adopting earlier procedure. The chemicals were purchased ALS from (Sigma Aldrich), mandelic, lactic and glycolic acids from (SD Fine chemicals, India). 95% pentamminecobalt(III) complexes of alpha hydroxy acid were prepared using Fan and Gould¹⁰. Double distilled water was used as a solvent and HClO₄ was standardizing using standard Sodium carbonate (BDH, AR) solution with methyl orange as

indicator. For the PCC oxidation of Co(III) Complexes of alpha hydroxyl acid and unbound ligands.

3. RESULTS AND DISCUSSION

Dependence of rate on PCC concentration in micellar bound ligand

The rate of PCC oxidation of pentamminecobalt(III) complexes of alpha hydroxyl acids depends on PCC concentration. The specific rate calculated remains constant and graph of logarithm of (a-x) versus time are linear. From the slope of these graphs, the specific rates calculated agree with those obtained from integrated rate equation suggesting first order dependence on PCC concentration. When conc. of PCC is varied from 1.00 to 3.0010⁻³ mol dm⁻³ at a fixed [Cobalt] and [HClO₄], specific rates remains constant. Then the rate of disappearance of Cr(VI) is given by equation.

$$-\frac{d[Cr(VI)]}{dt} = k[Cr(VI)] \dots\dots\dots (1)$$

Dependence of rate on Cobalt (III) concentration

The rate of PCC oxidation of [(NH₃)₅Co-L]²⁺ complex of mandelic, lactic and glycolic acid, depends nearly on the first power of the concentration of Co(III)

complexes, Graph of $\log k$ versus $\log[\text{Co(III)}]$ are linear with slope nearly equal to one. Hence the rate of disappearance of Cr(VI) is given by equation (2).

$$\frac{-d[\text{Cr(VI)}]}{dt} = k_2[\text{Cr(VI)}][\text{Co(III)}] \dots \dots (2)$$

Dependence of rate on the concentration of alpha hydroxyl acids in micellar medium

At a given initial concentration of PCC in micellar medium, the oxidation varies proportionately with the concentration of alpha hydroxy acids and the rate of this reaction exhibits first order dependence on alpha hydroxyl acids concentration plot of $\log k_1$ versus $\log[\text{alpha hydroxyl acids}]$ are linear with slope, nearly equal to one, evidencing the order is with respect to alpha hydroxyl acids. Hence the rate of disappearance of Cr (VI) is given by equation (3).

$$\frac{-d[\text{Cr(VI)}]}{dt} = k_2[\text{Cr(VI)}][\alpha\text{-hydroxy acids}] \dots \dots (3)$$

Comparison of rate on oxidation of pentaammine Cobalt(III) complexes of both bound and unbound alpha hydroxyl acids by PCC

The specific rate of the Co(III) lactato complex reacts faster than Co(III) mandelato and Co(III) glycolato complex, because if the reaction proceeds through a performed bromated ester, then the rate of oxidation of C-H cleavage has been enhanced resulting in an increase in the rate of oxidation of Co(III) complex. Also chromate ester formation may be sterically hindered in the case of mandelato complex. The absence of such a steric retardation and enhanced acidity of methyl proton in the lactato complex may account for its greater reactivity.

In this work, an induced transfer reaction has been attempted presently with PCC and pentaamminecobalt(III) complexes of alpha hydroxy acid in the presence of micelles. The reaction exhibits second order kinetics and in the case of mandelato complex, the amount of Cobalt(III) reduced corresponds to nearly initial concentration. While nearly 70% of Cobalt (III) is converted to keto acid cobalt(III) mandelato complex, the intermediate radical formed dissociated in a nearly synchronous manner with C-C

bond cleavage only to the extent of 20% and rest of its proceeding with alpha C-H fission giving keto acid Cobalt(III) complex. With increase in micelle concentration an increase in the rate is observed. ALS added to enhanced the rate of oxidation. The same trends observed in lactato and glycolato Cobalt(III) complex.

Dependence of rate on the concentration of Cobalt(III) bound alpha hydroxyl acids

At a particular PCC concentration with increasing mandelato / lactato/ glycolato Cobalt(III) concentration in the range $1.00 \times 10^{-3} \text{ mol dm}^{-3}$, there is a proportional increase in the rate of oxidation. The slopes of nearly unity is obtained from a linear graph of logarithm of specific rate (K_1 in S^{-1}). Versus logarithm of Cobalt(III) concentration in each case suggesting first order dependence of rate on $[\text{Co(III)}]$. Hence the rate law for the PCC oxidation of Cobalt(III) bound alpha hydroxyl acid is given by equation (4)

$$-d[\text{Cr(VI)}] = k_2[\text{Cr(VI)}][\text{Co(III)}] \dots (4)$$

[PCC]	= $2.00 \times 10^{-2} \text{ mol dm}^{-3}$
[HClO ₄]	= 1.00 mol dm^{-3}
Temperature	= $32 \pm 0.2 \text{ }^\circ\text{C}$

Kinetic study of the oxidation of alpha hydroxy acids by PCC

The kinetics of PCC reaction with alpha hydroxy acids have been studied in the presence of $1.00 \text{ mol dm}^{-3} \text{ HClO}_4$ and in the absence of micelles at a temperature of $32 \pm 0.2^\circ\text{C}$.

Dependence of rate on PCC concentration

Under identical conditions, PCC oxidation of unbound ligand mandelic acid has been studied to look into the consequence of ligation with Cobalt (III) centre. In any specific run, from the rate of disappearance of PCC, the specific rates calculated using integrated first order rate equations are constant.

Also graphs of logarithm of PCC concentrations versus calculated, agree well with those calculated from integrated first order equation. This indicate first order dependence on PCC oxidation of unbound alpha hydroxy acids. Hence the rate law is given by (5).

$$\frac{-d[\text{Cr(VI)}]}{dt} = k_1[\text{Cr(VI)}] \dots \dots (5)$$

When the concentration of PCC is varied from 1.00 to $3.00 \times 10^{-3} \text{ mol dm}^{-3}$, at a fixed alpha hydroxy acids, $[\text{HClO}_4]$ and micellar concentrations, the specific rates remain constant in keeping with the first dependence on PCC concentration.

Under identical conditions, the effect of changing unbound alpha hydroxy acids concentration has been studied in the range of $1.00 \times 10^{-3} \text{ mol dm}^{-3}$ with all the substrates in the absence of micellar medium. There is a monotonic increase in the rate of PCC oxidation with unbound alpha hydroxy acids with increasing concentration of substrates.

Also a graph of logarithm of specific rate (K_1 in S^{-1}) versus logarithm of alpha hydroxy acids concentration is linear with a slope nearly equal to unity with a slope nearly the rate law of PCC oxidation of unbound alpha hydroxy acids which is similar to Cobalt (III) bound ligands.

$$-d[\text{Cr(VI)}] = k_2[\text{Cr(VI)}][\alpha\text{-hydroxyacid}] \dots (6)$$

4. Summary

Earlier studies on induced electron transfer reactions involved mainly an one equivalent oxidant, Ce (IV) and pentaammine Cobalt (III) complexes, $[(\text{NH}_3)_5\text{Co III} - \text{L}]^{2+}$ with bound ligands featuring conjugated fragments. In all these reactions, ultimately, reduction at Cobalt (III) centre has been achieved due

to the generation of a radical at the bound organic ligand by the one equivalent oxidant. But the percentage of Cobalt (III) formed differed from reaction to reaction due to the partitioning of the reaction paths.

An induced electron transfer reaction has been attempted presently with PCC and pentammine Cobalt (III) complexes of alpha hydroxy acids in the presence of ALS medium and also in the absence of ALS medium. The reaction exhibits second order kinetics and in the case of mandelato complex, the amount of Cobalt (III) reduced corresponded to nearly 20 initial concentration and the amount of Cobalt (II) Ph.CHO and CO_2 formed is nearly 20%. While nearly 75% of it is converted to keto acid Cobalt(III) complex, possibly Cr(VI) induced electron transfer in Cobalt (III) mandelato complex, the intermediate radical formed dissociate in a synchronous manner with C-C bond cleavage only to the extent of 20%. The Cobalt (III) bound alpha hydroxy acid gets oxidized at higher rate than that of unbound ligand.

With increasing ALS concentration an increase in the rate is observed. Added ALS enhance the rate of oxidation of reaction much more than without ALS. Similar trends has been observed in lactate and glycolato Cobalt(III) complexes.

Table 1

ALS			
Time in Seconds	$10^3(a-x) \text{ mol dm}^{-3}$	$104 k_1 \text{ S}^{-1}$	$4+\log(a-x)$
300	2.03	4.307	4.3074
600	1.78	4.334	4.2504
900	1.56	4.362	4.1931
1200	1.37	4.354	4.1367
1500	1.2	4.366	4.0791
1800	1.05	4.381	4.0211
2100	0.92	4.384	3.9637
2400	0.81	4.367	3.9084
2700	0.71	4.370	3.8512

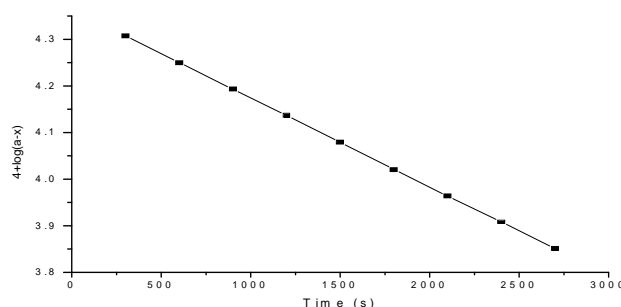
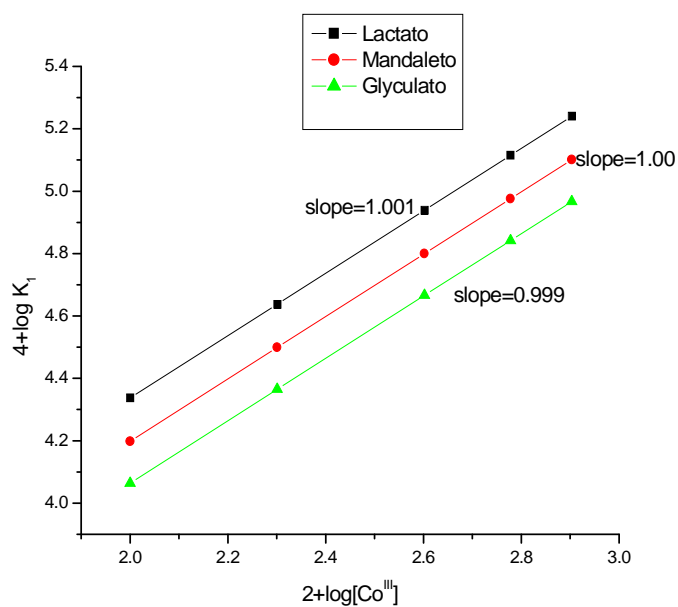


Fig. 1: First order dependence plots

Table 2

$10^2 [(NH)_5Co^{III}]$ mol dm ⁻³	ALS		
	$10^4 K_1$	$102k_2$ dm ⁻³	$4+\log K_1$
L=Lactato			
1.00	2.175	2.175	4.337
2.00	4.35	2.175	4.638
4.00	8.70	2.175	4.939
6.00	13.05	2.175	5.115
8.00	17.40	2.175	5.240
M=Mandato			
1.00	1.58	1.58	4.198
2.00	3.16	1.58	4.499
4.00	6.32	1.58	4.800
6.00	9.48	1.58	4.976
8.00	12.64	1.58	5.101
G=Glycolato			
1.00	1.16	1.16	4.064
2.00	2.32	1.16	4.365
4.00	4.64	1.16	4.666
6.00	6.96	1.16	4.842
8.00	9.28	1.16	4.967

Fig. 2: Dependence of rate on $[Co(III)]$ in ALS

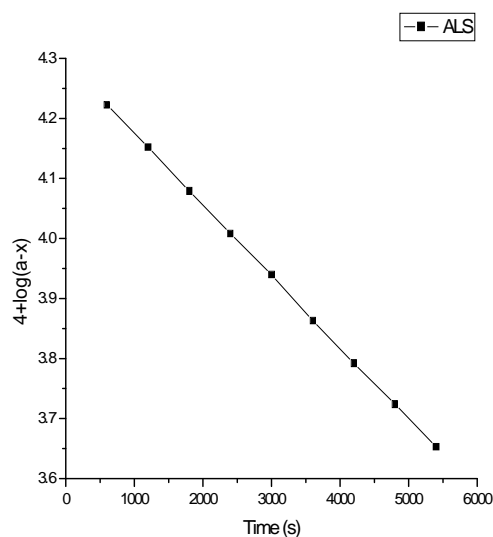


Fig. 3: First order dependence plots

Table 3

ALS			
Time in Seconds	$10^3(a-x)$ mol dm^{-3}	$10^4 k_1 \text{S}^{-1}$	$4+\log(a-x)$
600	1.67	2.753	4.2227
1200	1.42	2.728	4.1522
1800	1.2	2.753	4.0791
2400	1.02	2.743	4.0086
3000	0.87	2.724	3.9395
3600	0.73	2.758	3.8633
4200	0.62	2.753	3.7923
4800	0.53	2.735	3.7242
5400	0.45	2.734	3.6532

Table 4

$10^2 [(\text{NH})_5\text{Co}^{\text{III}}]$ mol dm^{-3}	ALS		
	$10^4 K1$	$10^2 K2 \text{ dm}^{-3}$	$4+\log K1$
L=Lactato			
1.00	1.375	1.375	4.1383
2.00	2.75	1.375	4.4393
4.00	5.5	1.375	4.7403
6.00	8.25	1.375	4.9164
8.00	11.0	1.375	5.0413
M=Mandato			
1.00	1.01	1.01	4.0043
2.00	2.02	1.01	4.3053
4.00	4.04	1.01	4.6063
6.00	6.06	1.01	4.7824
8.00	8.08	1.01	4.9074
G=Glycolato			
1.00	0.73	0.73	3.8633
2.00	1.54	0.73	4.1875
4.00	3.08	0.73	4.4885
6.00	4.38	0.73	4.6414
8.00	5.84	0.73	4.7664

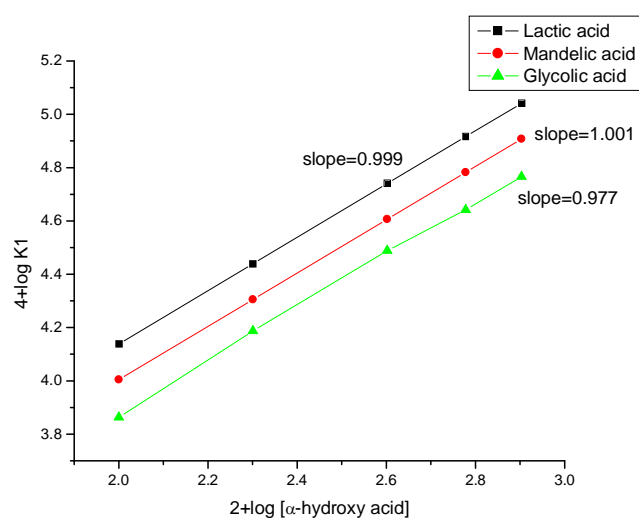


Fig. 4: Dependence of rate on [α – hydroxyl acid] in ALS

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