OXIDATION OF COBALT (III) COMPLEXES OF α-HYDROXY ACIDS BY PYRIDINIUM DICHROMATE IN THE PRESENCE OF SURFACTANTS

B. MOHAMMED NAWAZ[*], K. SUBRAMANI and K. ANANDARATCHAGAN

Department of Chemistry, Islamiah College, VANIYAMBADI – 635752 (T.N.) INDIA

ABSTRACT

The kinetics of one electron transfer route seems to be unavailable for Pyridinium dichromate (PDC) with cobalt (III) bound and unbound complexes of α-hydroxy acid in surfactant medium. PDC 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 surfactant 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 has been observed in lactato and glycolato Co (III) complexes.

Key words: Pyridinium dichromate, Sodium lauryl sulphate, Cetyl trimethyl ammonium bromide.

INTRODUCTION

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 pyridinium dichromate an oxidant in presence of surfactant. One equivalent oxidant like Ce (IV) induced electrontransfer in pentaammine cobalt (III) complexes of α-hydroxyacids result in nearly 100% reduction at cobalt (1II) centre with synchronous carbon-carbon bond fission and decarboxylation. Such an electron transfer route seems to be unavailable for pyridinium dichromate in its reaction with cobalt (Ill) bound and unbound α-hydroxyacids in micellar medium. Pyridinium dichromate oxidize cobalt (III) bound and unbound α-hydroxyacids to respective keto acid cobalt (III) complexes in sodium lauryl sulphate (NaLS) and cetyl trimethyl-ammonium bromide (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 PDC oxidation of cobalt (III) mandelato, lactato and glycolato complexes depends on the first power of PDC concentration. Similarly the reaction between PDC and unbound α-hydroxyacid exhibits first order kinetics with respect to concentration of PDC. Of these three complexes mandelato cobalt (III) complexes react faster than lactato and glycolato complexes, where as in the unbound ligand similar trends follows.

Oxidation is an important process in organic chemistry and introduction of new economic and effective reagents for oxidation under mild and anhydrous conditions constitutes a standing challenge. PDC is oxidant which is non-hygroscopic, non-photosensitive, stable yellow orange solid which is freely soluble in water, acetic acid, N, N- dimethyl formamide etc.[1-3] The little work has been done on PDC as oxidant in micellar medi[4-5].

Materials and methods

The surfactants used in the present work are sodium lauryl sulphate (NaLS) and cetyltrimethylammoniumbromide (CTAB)[6-7]. The surfactants are purified by adopting earlier procedure[8,9]. The chemicals were purchased CTAB from (B.D.H, UK. 99%) NaLS mandelic, lactic and glycolic acids from (SD Fine chemicals, India 95%) Pentaammine cobalt (III) complexes of α-hydroxyacids were prepared using Fan and Gould[2,10]. Double distilled (deionised and CO_2 free) water was used as a solvent and $HClO_4$ (E.Merck, India 95%) was standardized using standard Sodium carbonate (BDH, AR) solution with methyl orange as an indicator. For the PDC oxidation of Co (III) complexes of α-hydroxy acids and unbound ligands[11,12]. The rate measurement were made at $35 \pm 0.2°C$ in 100% aqueous medium and temperature was controlled by electrically operated thermostat[11]. The total volume of reaction mixture in the spectrophotometric cell was kept as 2.5 mL in each kinetic run. A Evolution60 Thermo spectrophotometer fitted with recording and thermostating arrangement was used to follow the rate of the reaction. Rate of these PDC oxidant with unbound ligand and cobalt (III) bound complexes were calculated from observed decrease in absorbance at 400 nm. The excess of the reductant was used in kinetic runs. It gives pseudo first order rate constant. It was determine from the linear plot of the in A versus time. Reproducible result obtained giving good first order plot.

The stiochiometric studies for the PDC oxidation of pentaammine cobalt (III) complexes of α-hydroxyl acid and unbound ligand in the presence of micelles were carried out at $35 \pm 2°C$. It was observed that the cobalt (II) formation was negligibly small.

RESULTS AND DISCUSSION

Kinetic study of the oxidation of pentaammine cobalt (III) complexes of α-hydroxyacid by PDC in micellar medium dependence of rate on PDC concentration in micellar bound ligand. The rate of oxidation of lactato cobalt (III) complexes depends on PDC concentration, the specific rate calculated remains constant (Table 1) and Graph of logarithm of PDC concentration versus time Fig. 1 are linear. From the slope of these graphs, the calculated specific rate agrees with those obtained from integrated rate equation suggesting first order dependence on PDC concentration.

When the concentration of PDC is varied from 1.00 to 8.00×10^{-3} mol dm^{-3} at a fixed [cobalt (III)] and [HCO_4]. A specific rate remains constant. Then the of rate of disappearance of Cr VI) is given by equation

$$-d\,[Cr\,(VI)]\,/\,dt = k\,[Cr\,(VI)] \qquad\qquad\qquad …(1)$$

At a particular PDC concentration with increases in mandelato/lactato/glycolato cobalt (1II) concentration in the range 1.00 to 4.00×10^{-3} mol dm^{-3} there is a proportional increases in the rate of oxidation (Table 2). The slope of nearly unity is obtained from a linear graph of logarithm. Fig. 2 of specific rate (k in s^{-1}) versus logarithm of Co (III) concentration in each case suggesting first order rate dependence of rate on [Co (III)].

Table 1

$[(NH_3)_5CoIII-L]^{2+} = 2.00 \times 10^{-2}$ mol dm^{-3}, $[PDC] = 2.00 \times 10^{-3}$ mol dm^{-3}

$[HCLO_4] = 1.00$ mol dm^{-3}, $[Micelle] = 6.00 \times 10^{-4}$ mol dm^{-3}

Temperature = $35 \pm 0.2^{\circ}$ C

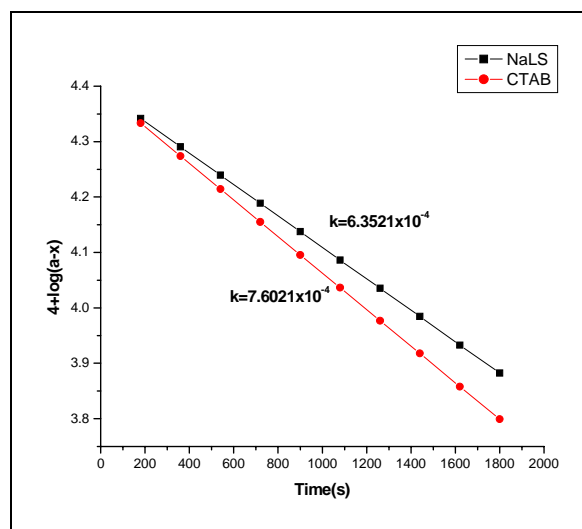| Time	$10^3(a - x)$ mol dm^{-3}	
(s)	NaLS	CTAB
180	2.19	2.15
360	1.95	1.87
540	1.73	1.63
720	1.54	1.42
900	1.37	1.24
1080	1.22	1.08
1260	1.08	0.94
1440	0.96	0.82
1620	0.85	0.72
1800	0.76	0.63

Fig. 1: First order dependence plots

Table 2

$[PDC] = 2.00 \times 10^{-3}$ mol dm^{-3}, $[HCLO_4] = 1.00$ mol dm^{-3}

$[NaLS] = 1.00 \times 10^{-4}$ mol dm^{-3}, Temperature = $35 \pm 0.2^{\circ}$C

$[(NH_3)_5Co^{III}-L]10^2$ mol dm^{-3}	$10^4.k_1$ (s^{-1})	$10^2.k_2$ (dm^3 mol^{-1}s^{-1})
L = Mandelato		
1.00	2.47	2.47
2.00	4.98	2.49

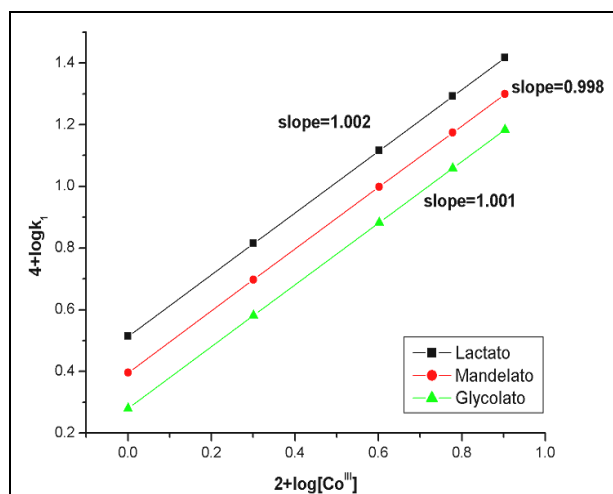| $[(NH_3)_5Co^{III}-L]10^2$ mol dm^{-3}	$10^4 \cdot k_1$ (s^{-1})	$10^2 \cdot k_2$ (dm^3 mol^{-1}s^{-1})
4.00	9.94	2.48
6.00	14.90	2.48
8.00	19.95	2.49
L = Lactato		
1.00	3.27	3.27
2.00	6.53	3.26
4.00	13.00	3.25
6.00	19.62	3.27
8.00	26.08	3.26
L = Glycolato		
1.00	1.90	1.90
2.00	3.81	1.90
4.00	7.68	1.92
6.00	11.40	1.90
8.00	15.28	1.91

Fig. 2: Dependence of rate on [Cobalt (III)] in NaLS

Hence the rate law for the Cr (VI) oxidation of cobalt (III) bound of α-hydroxy acids are given by equation 2.

$$-d\,[Cr\,(VI)]/dt = k_2\,[Cr\,(VI)]\,[Co\,(III)] \qquad \qquad \qquad …(2)$$

Dependence of rate on PDC concentration in micellar for α-hydroxyacid

The rate of oxidation of lactate cobalt (III) complexes depends on PDC concentration. In any specific run the change in concentration of PDC, the specific rate calculated remains constant (Table 3 and graphs of logarithm of PDC concentration versus time are linear Fig. 3).

From the slope of these graphs, the specific rate calculated agrees with those obtained from integrated rate equation, suggesting first order dependence on PDC concentration.
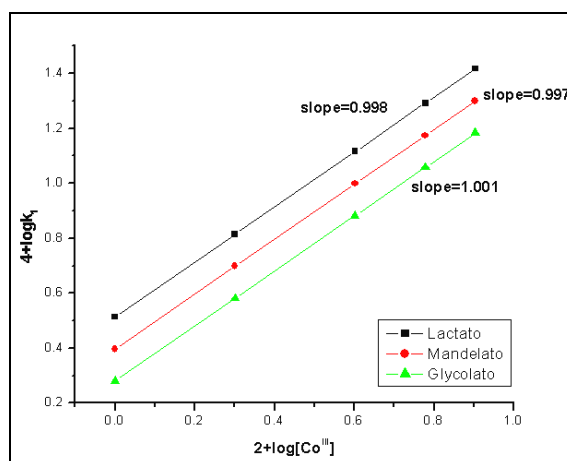
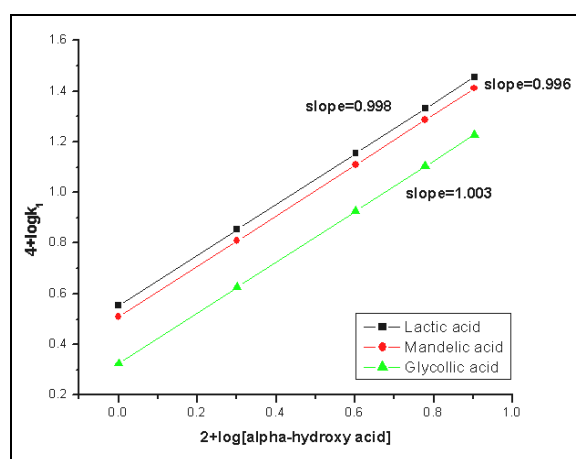**Fig. 3: Dependence of rate on [Cobalt (III)] in CTAB**

Fig. 4: Dependence of rate on [α-hydroxy acid] in NaLS

Table 3

[PDC] = 2.00 X 10^{-3} mol dm^{-3},   [$HClO_4$] = 1.00 mol dm^{-3}

[CTAB] = 1.00 X 10^{-4} mol dm^{-3} Temperature = 35 ± 0.2^{o}C

[$(NH_3)_5Co^{III}$-L]10^2 mol dm^{-3}	10^4. k_1 (s^{-1})	10^2.k_2 (dm^3 $mol^{-1}$$s^{-1}$)
L = Mandelato		
1.00	3.90	3.90
2.00	7.81	3.90
4.00	15.58	3.89
6.00	23.40	3.90
8.00	31.30	3.91
L = Lactato		
1.00	3.82	3.82
2.00	7.60	3.80
4.00	15.18	3.79
6.00	22.82	3.80
8.00	30.42	3.80

$[(NH_3)_5Co^{III}\text{-}L]10^2 \text{ mol dm}^{-3}$	$10^4 \cdot k_1 \text{ (s}^{-1})$	$10^2 \cdot k_2 \text{ (dm}^3 \text{ mol}^{-1}\text{s}^{-1})$
L= Glycolato		
1.00	2.34	2.34
2.00	4.70	2.35
4.00	9.38	2.34
6.00	14.12	2.35
8.00	18.78	2.34

When concentration of PDC is varied from 1.00 to 4.00 x 10^{-3} mol dm^{-3} at a fixed [Co (III)] and [HClO$_4$] specific rates remains constant. Then the rate of disappearance of Cr (VI) is given by equation 3.

$$-d \text{ [Cr (VI)}/dt = K_1 \text{ [Cr (VI)]} \qquad \qquad ...(3)$$

Dependence of rate on the concentration of hydroxyacid in NaLS and CTAB

The oxidation studies were carried out by varying initial [α-hydroxy acid] in the range 1.00 to 4.00 x 10^{-3} mol dm^{-3} by keeping other variable constant. The near constancy in the k_2 values (Tables 4 and 5) and the slope of nearly unity is obtained from a linear graph of logarithm of specific rate (k_1 in s^{-1}) verses logarithm of α-hydroxy acid concentration in each case suggesting first order dependence of rate on [α-hydroxy acid] (Figs. 3 and 4). Hence the rate law for the Cr (VI) oxidation α-hydroxy acid of is given below equation 4.

$$-d \text{ [Cr (VI)] } / dt = k_2 \text{ [Cr (VI)] [α- hydrox acid]} \qquad \qquad …(4)$$

Table 4

[PDC] = 2.00 X 10^{-3} mol dm^{-3},   [HClO$_4$] = 1.00 mol dm^{-3}

[NaLS] = 1.00 X 10^{-4} mol dm^{-3} Temperature = 35 ± 0.2°C

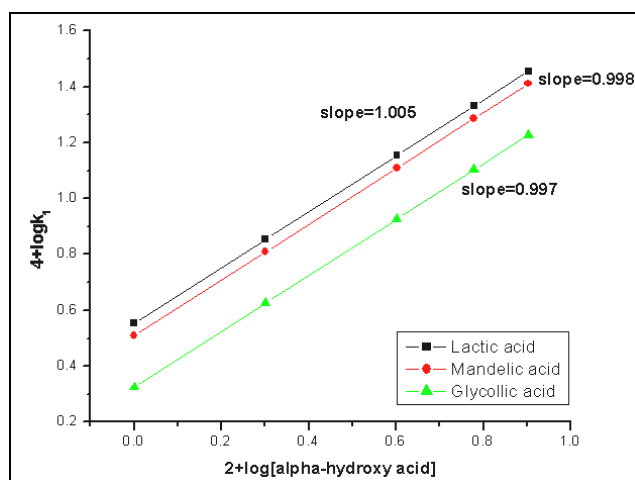| [hydroxy acid].10^2 (mol dm^{-3})	$10^4 \cdot k_1 \text{ (s}^{-1})$	$10^2 \cdot k_2 \text{ (dm}^3 \text{ mol}^{-1}\text{s}^{-1})$
Mandelic acid		
1.00	3.23	3.23
2.00	6.44	3.23
4.00	12.86	3.21
6.00	19.34	3.22
8.00	25.80	3.22
Lactic acid		
1.00	3.58	3.58
2.00	7.14	3.57
4.00	14.24	3.56
6.00	21.38	3.56
8.00	28.60	3.57
Glycolic acid		
1.00	2.13	2.13
2.00	4.25	2.12
4.00	8.52	2.13
6.00	12.70	2.11
8.00	17.02	2.12

Fig. 5: Dependence of rate on [α-hydroxy acid] in CTAB

Table 5

[PDC] = 2.00 X 10^{-3} mol dm^{-3},

[CTAB] = 1.00 X 10^{-4} mol dm^{-3}

[HClO$_4$] = 1.00 mol dm^{-3}

Temperature = 35 ± 0.2^{o}C

[hydroxy acid].10^2 (mol dm^{-3})	$10^4.k_1$ (s^{-1})	$10^2.k_2$ (dm^3 mol^{-1}s^{-1})
Mandelic acid		
1.00	3.37	3.37
2.00	6.72	3.36
4.00	13.40	3.35
6.00	20.18	3.36
8.00	26.90	3.36
Lactic acid		
1.00	3.60	3.60
2.00	7.22	3.60
4.00	14.40	3.60
6.00	21.68	3.61
8.00	28.90	3.60
Glycolic acid		
1.00	2.36	2.36
2.00	4.70	2.35
4.00	9.38	2.34
6.00	14.06	2.34
8.00	18.82	2.35

Comparison of rates on oxidation of pentaammine cobalt (III) complexes of both bound and unbound α-hydroxy acid by PDC

Specific rate of the lactato complex is more compared to both the rates of oxidation of unbound ligand and mandelato complex deserves an explanation. The ligation of lactic acid to Co (III) centre has

probably increased its reactivity towards PDC and this effect seems to be more specific for this ligand only. If the reaction proceeds through a preformed chromate ester, then the rate of C-H, fission will been 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 pentaammine cobalt (III) complexes of both bound and unbound ligands in micellar medium.

Thus, the kinetics of one electron transfer route seems to be unavailable for PDC with cobalt (III) bound and unbound complexes of α-hydroxy acid in micellar medium, PDC 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 increase 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 has been observed in lactato and glycolato Co (III) complexes.
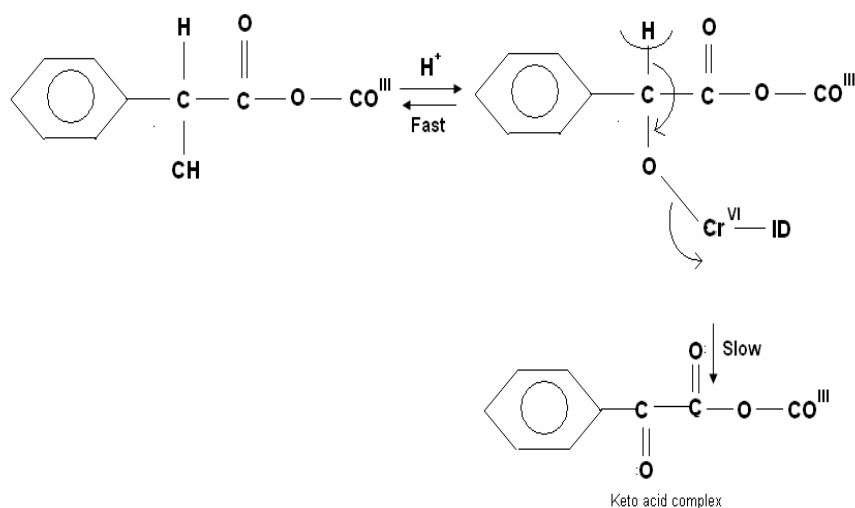
Scheme

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