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Research Article

OXIDATION OF COBALT (III) COMPLEXES OF A-HYDROXY ACIDS BY PIPERAZINIUM DICHROMATE IN SURFACTANTS

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ABSTRACT

The kinetics of one electron transfer mode seems to be not available for PiDCwith Cobalt (III) bound and unbound complexes of α-hydroxyacids in surfactantmedium.PiDC oxidizes Cobalt (III) bound and unbound α- hydroxyacids. It rules out thesynchronous C-C bond fission and electron transfer to Cobalt (III) centre. Oxidation ofabove complexes increases with increase in temperature. The increase in the rate isobserved with increase in the concentration of the surfactant. The added Dodecyl benzyl dimethyl ammonium chlorideenhances the rate of oxidation of a reaction much more than PLS. Similartrends has been observed in lactato, glycolato and mandelatoCo (III) complexes.

Keywords: Piperazinium Dichromate **(**PiDC), Potassium Lauryl Sulphate (PLS).

INTRODUCTION

The oxidation of α hydroxyacids[1] such asmandelic acid, lactic acid, glycolic acid and their Cobalt (III) Complexes using Pyridinium dichromate[2] as anoxidant in the presence of surfactant has attempted to study. One equivalent oxidant like Ce(IV) induced electron transfer in pentaamminecobalt(III) Complexes of α-hydroxyacids results in nearly 100% reduction[3] at Cobalt(III) centre with synchronous C- C bond fission and decarboxylation. Such an electron transfer route seems to be unavailable for Pyridinium dichromate in its reaction with cobalt(III) bound and unbound α-hydroxyacids in surfactant medium. Pyridinium dichromate oxidizes cobalt(III) bound and unbound α-hydroxyacids to respective keto acid cobalt(III)complexes in potassium lauryllsulphate[4] (PLS) and Dodecyl benzyl dimethyl ammonium chloride (DBDAC)possibly the transition state is more electron deficient[5]. Such a transition state can be envisaged only when the C-H bond fission occurs in the slow step with a hydride ion transfer. The absence of formation of cobalt (II) rules out the synchronous-C bond fission[6] and electron transfer to cobalt (III). The thermodynamic parameters are in consistent with bimolecular reaction. The rate of PDC oxidation[7, 8] of cobalt (III) Mandela to, Lactato and Glycolato complexes depends on the first power of PDC concentration. Similarly the reaction between PDC and unbound α-hydroxyacid[9, 10] exhibits first order kinetics with respect to concentration of PDC. Of the three complexes lactate Cobalt (III)complexes react faster than mandelato[11, 12] and glycolato complexes, and similar trend is followed inthe unbound ligands also.

Oxidation is an important process in organic chemistry and introduction of new economic andeffective reagents for oxidation[13-17] under mild and anhydrous conditions constitutes a standingchallenge. PiDC is an effective oxidant which is non-hygroscopic, non-photosensitive, stable yelloworange solid which is freely soluble in water, acetic acid, N,N- dimethyl formamide etc.

MATERIALS AND METHODS

The surfactants used in the present work are potassium lauryl sulphate (PLS)[7]and Dodecyl benzyl dimethyl ammonium chloride (DBDAC). The surfactants are purified by adopting earlier procedure[8, 9].The surfactants PLS and DBDAC werepurchased from (Sigma-Aldrich India 98%), mandelic,lactic and glycolic acids from (SD Fine chemicals. India95%) Pentaamminecobalt (III) complexes ofα-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 standardSodiumcarbonate (BDH, AR) solution with methylorange as an indicator. For the PDC oxidation ofCo (III) Complexes of α-hydroxyacids and unbound ligands[11,12]. The rate measurements were made at33 ± 0.2°C in 100% aqueousmedium and temperature was controlled by electrically operatedthermostat[11]. The totalvolume of reaction mixture in the spectrophotometric cell was kept as 2.5 ml ineach kinetic run. An Evolution60Thermo spectrophotometer fitted with recording and thermosettingarrangement was used to follow the rate of thereaction.Rate of this PiDC oxidant with unbound ligand and Cobalt (III) bound complexes were calculatedfrom observed decrease in absorbance at 400nm. The excess of the reductant was used in kinetic runs.It gives pseudo first order rate constant. It was determined from the linear plot of the lnA versus time.Reproducible result obtained giving good first order plot. The stoichiometric studies for the PiDCoxidation of pentaamminecobalt (III) complexes of α-hydroxyacid and unbound ligand in the presenceof micelles were carried out at 33± 2°C. It was observed that the cobalt (II) formation was negligiblysmall.

RESULT AND DISCUSSION

Kinetic study of the oxidation of pentaamminecobalt(III) complexes of α-hydroxyacid by PiDCinsurfactant medium dependence of rate on PiDC concentration in bound ligand. The rate of oxidationof lactatocobalt(III) complexes depends on PiDC concentration, the specific rate calculated remainsconstant **(Table 1)** and Graph of logarithm of PiDC concentration versus time **(Fig. 1)** are linear.From the slope of these graphs, the specific rate calculated agrees with those obtained from integratedrate equation suggesting first order dependence on PiDC concentration.

When the concentration of PiDC is varied from 1.00 to 8.00 x 10^{-3}mol dm^{-3} at a fixed [Cobalt (III)]and [$HClO_4$].Specific rates remain constant. Then the of rate of disappearance of Cr (VI) is given byequation-1

-d [Cr (VI)] / dt = k [Cr (VI)] .... (1)

At a particular PiDC concentration with increases in mandelato/lactato/glycolato cobalt (III)concentration in the range 1 .00 to 4.00 x 10^{-3}mol dm^{-3} there is a proportional increases in the rate ofoxidation **(Table 2).**The slope of nearly unity is obtained from a linear graph of logarithm a **(Fig. 2)**of specific rate (k in s^{-1}) versus logarithm of Co(III) concentration in each case suggesting first orderrate dependence of rate on [Co(III)]. Hence the rate law for the Cr (VI) oxidation of cobalt (III) boundof α-hydroxy acids is given by equation-2.

-d [Cr (VI)] /dt = k2 [Cr (VI)][Co (III)] .... (2)

Dependence of rate on PiDC concentration in surfactant for Cobalt (III) complexes of α-hydroxyacid

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

From the slope of these graphs, the specificrate calculated agrees with those obtained from integrated rate equation, suggesting first orderdependence on PiDC concentration.From the slope of these graph, the specific rate calculated agree with those obtained from integrateequation suggesting first order dependence on PiDC concentration. When concentration of PiDC isvaried from 1.00 to 4.00 x 10^{-3}mol dm^{-3} at a fixed [Co (III)] and [$HClO_4$] specific rates remainsconstant. Then the rate of disappearance of Cr (VI) is given by equation 3.

-d [Cr (VI) /dt = K1 [Cr (VI)] .... (3)

Dependence of rate on the concentration of α-hydroxyacid in PLS and DBDAC:

The oxidationstudies 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 variables constant. The near consistency in the k_2 values **(Tables 4 and 5**) and theslope of nearlyunity is obtained from a linear graph of logarithm of specific rate (k_1 in s^{-1}) verseslogarithm of α-hydroxy acid concentration in each case suggesting first order dependence of rate on[α-hydroxy acid] **(Figs. 4 and 5).** Hence the rate law for the Cr (VI) oxidation α-hydroxy acid of isgiven below equation-4.

-d [Cr (VI)] / dt =k2 [Cr (VI)] [α- hydroxy acid] .... (4)

Comparison of rates on oxidation of Pentaamminecobalt(III) complexes of both bound and unbound α-hydroxyacid by PiDC

Specific rate of the lactato complex is more compared to both therates of oxidation of unbound ligand and mandela to complex deserves an explanation. The ligation oflactic acid to Co (III) centre has probably increased its reactivity towards PiDC and this effect seems tobe more specific for this ligand only. If the reaction proceeds through a preformed Chromate ester,then the rate of C-H fission will have been enhanced, resulting in an increased rate of oxidation of lactato complex such a precursor complex may be sterically hindered in the case of Mandela to andglycolato complexes.

Mechanism

Oxidation of Pentaamminecobalt(III) complexes of both bound and unbound ligands insurfactantmedium.Thus, the kinetics of two electron transfer route seems to be unavailable for PiDCwith Cobalt(III) boundand unbound complexes of α-hydroxy acid in surfactant medium, PiDCoxidizes Cobalt (III) bound and unbound α-hydroxy acids. It rules out the synchronous C-C bondfission and electron transfer to Cobalt (III) centre. Oxidation of above complexes increases withincrease of temperature. With increase in surfactant concentration an increase in therate is observed.The added DBDAC enhances the rate of oxidation of a reaction much more than PLS. Similar trends hasbeen observed in lactato and glycolatoCo(III) complexes.

CONCLUSION

The oxidation reactions of Coblat (III) complexes of α-hydroxy acids viz, lactic acid, glycolicacid and mandelic acid have been carried out using a novel chromium (VI) oxidant. There is aremarkable increase in the rate of the reaction has been observed in the presence of novel surfactantsPLS and DBDAC. These surfactants act as a positive catalyst *in-situ* of the reaction and among whichDBDAC enhances the rate much more than the PLS.

Table 1: $[(NH_3)_5Co^{III}\text{-}L]^2$ = 2. 00 X 10^{-2}mol dm^{-3}; [PiDC]= 2. 00 X 10^{-3}mol dm^{-3} $[HClO_4]$= 1. 00 X 10^{-2}mol dm^{-3}; [Surfactant]=6. 00 X 10^{-4}mol dm^{-3}; Temperature = 33±0.2 °C

Time (Sec)	PLS	DBDAC
300	1.79	1.6
600	1.6	1.4
900	1.4	1.2
1200	1.2	1
1500	1	0.8
1800	0.8	0.58
2100	0.6	0.38
2400	0.4	0.2
2700	0.2	0.03

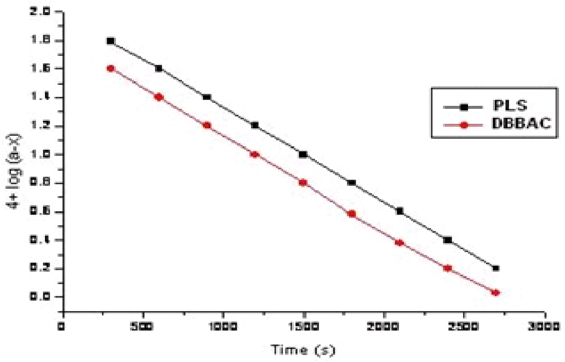

Fig. 1: First order dependence plots

Table 2: [PiDC]= 2. 00 X 10^{-3}mol dm^{-3}; [$HClO_4$]= 1. 00 X 10^{-2}mol dm^{-3}; [PLS]= 6. 00 X 10^{-4}mol dm^{-3}; Temperature = 33±0.2 ^{o}C

$[(NH_3)_5Co^{III}\text{-}L]^2 10^{-2}$mol dm^{-3}	10^4 K_1S^{-1}	10^2K_2dm^{3}mol$^{-1}S^{-1}$
L = Lactato		
1	2.97	2.97
2	5.94	2.98
4	11.88	2.97
6	17.82	2.97
8	23.76	2.97
L = Mandelato		
1	2.42	2.42
2	4.84	2.42
4	9.68	2.41
6	14.52	2.42
8	19.36	2.42
L = Glycolato		
1	1.86	1.86
2	3.72	1.85
4	7.44	1.86
6	11.16	1.86
8	14.88	1.86

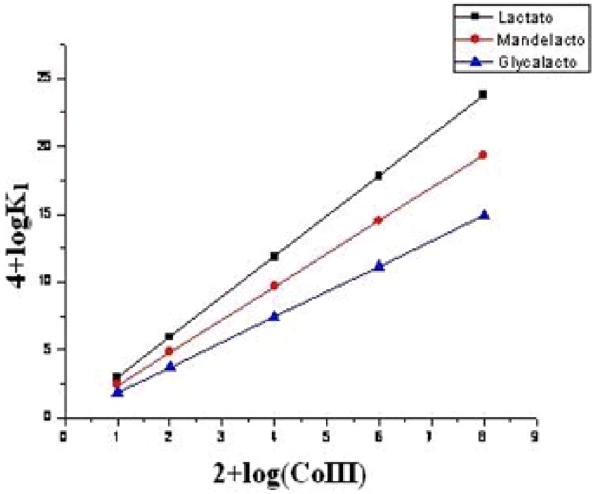

Fig. 2: Depends of rate on CoIII in PLS

Table 3: [PiDC]= 2. 00 X 10^{-3}mol dm^{-3}; [HClO$_4$]= 1. 00 X 10^{-2}mol dm^{-3}; [DBDAC]= 6. 00 X 10^{-4}mol dm^{-3}; Temperature = 33±0.2 ^{o}C

$[(NH_3)_5Co^{III}\text{-}L]^{2}10^{-2}$mol dm^{-3}	10^4 K_1S^{-1}	$10^2K_2dm^3mol^{-1}S^{-1}$
L = Lactato		
1	3.915	3.915
2	7.83	3.914
4	15.66	3.915
6	23.49	3.915
8	31.32	3.915
L = Mandelato		
1	3.49	3.49
2	6.98	3.48
4	13.96	3.49
6	20.94	3.49
8	27.92	3.49
L = Glycolato		
1	2.92	2.92
2	5.84	2.92
4	11.68	2.92
6	17.52	2.92
8	23.36	2.92

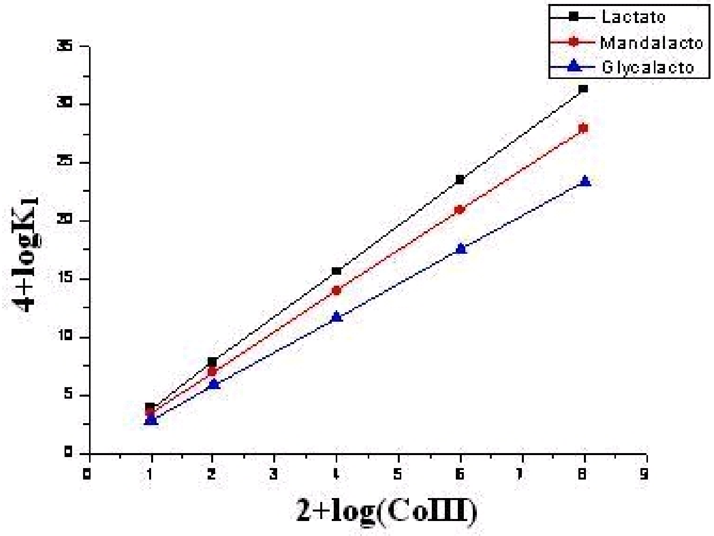

Fig. 3: Depends of rate on Co(III) in DBDAC

Table 4: [PiDC]= 2. 00 X 10^{-3}mol dm^{-3}; [$HClO_4$]= 1. 00 X 10^{-2}mol dm^{-3}; [PLS]= 6. 00 X 10^{-4}mol dm^{-3}; Temperature = 33±0.2 °C

[α-hydroxy acids] 10^2mol dm^{-3}	10^4 K_1S^{-1}	$10^2K_2dm^3mol^{-1}S^{-1}$
L = Lactato		
1	2.68	2.68
2	5.36	2.69
4	10.72	2.69
6	16.08	2.68
8	21.44	2.68
L = Mandelato		
1	2.09	2.09
2	4.18	2.09
4	8.36	2.09
6	12.54	2.09
8	16.72	2.09
L = Glycolato		
1	1.77	1.77
2	3.54	1.77
4	7.08	1.77
6	10.62	1.77
8	14.16	1.77

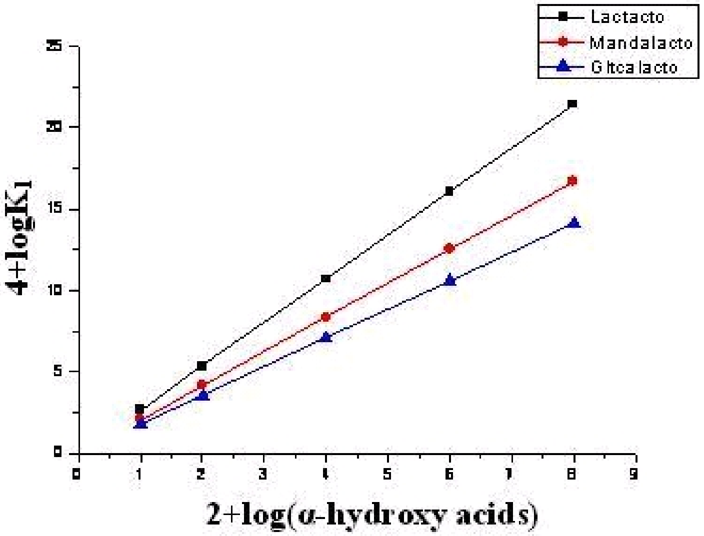

Fig. 4: Dependance of rate on α-hydroxy acids in PLS

Table 5: [PiDC]= 2. 00 X 10^{-3}mol dm^{-3}; [$HClO_4$]= 1. 00 X 10^{-2}mol dm^{-3}; [DBDAC]= 6. 00 X 10^{-4}mol dm^{-3}; Temperature = 33±0.2 °C

[α-hydroxy acids] 10^2mol dm^{-3}	10^4 K_1S^{-1}	$10^2K_2dm^3mol^{-1}S^{-1}$
L = Lactato		
1	3.58	3.58
2	7.16	3.58
4	14.32	3.58
6	21.48	3.58
8	28.64	3.58
L = Mandelato		
1	3.39	3.39
2	6.78	3.39
4	13.56	3.39
6	20.34	3.38
8	27.12	3.39
L = Glycolato		
1	2.74	2.74
2	5.48	2.75
4	10.96	2.74
6	16.44	2.74
8	21.92	2.74

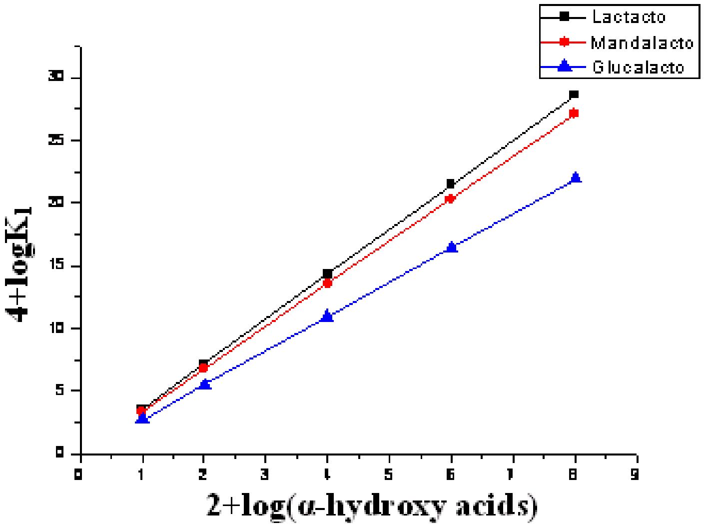

Fig. 5: Dependance of rate on α-hydroxy acids in DBDAC

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