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Redox Reactions of Pentaammine Cobalt (III) Complexes of α-Hydroxy Acids by Nicotinium Dichromate in Micealar Medium.

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ABSTRACT

The kinetics of one electron transfer mode seems to be unavailable for NDC with Cobalt (III) bound and unbound complexes of α- hydroxy acids in surfactant medium, NDC 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 in temperature. The increase in the rate is observed with increase in the concentration of the surfactant. The added DDAC enhances the rate of oxidation of a reaction much more than ALS. Similar trends have been observed in lactato, glycolato and Mandelato Co (III) complexes.

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Introduction:

Thermo spectrophotometer has been employed to study the oxidation of α-hydroxy acids such as mandelic acid, lactic acid, glycollic acid and their Cobalt (III) Complexes using Nicotinium dichromate as an oxidant in the presence of surfactant. One equivalent oxidant like Ce(IV) induced electron transfer in pentaamminecobalt (III) Complexes of α- hydroxy acid in results in nearly 100% reduction at Cobalt(lII) centre with synchronous C- C bond fission and decarboxylation. and an electron transfer route seems to be unavailable for Nicotinium dichromate in its reaction with cobalt(lll) bound and unbound α- hydroxy acid in surfactant medium. Nicotinium dichromate oxidizes cobalt(lll) bound and unbound α- hydroxy acids to respective keto acid cobalt(III)complexes in Ammonium Lauryl sulfate (ALS) and Dimethyl Diocta Decyl Ammonium Chloride(DDAC) 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 a 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 NDC oxidation of cobalt (III) Mandelato, Lactato and Glycolato complexes depends on the first power of NDC concentration. Similarly the reaction between NDC and unbound α- hydroxy acids exhibits first order kinetics with respect to concentration of NDC. Of the three complexes lactato Cobalt (III)complexes react faster than mandelato and glycolato complexes, and similar trend is followed in the unbound ligands also. NDC 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. NDC is an effective oxidant which is non-hygroscopic, non-photosensitive, stable yellow orange 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 anionic Ammonium Lauryl Sulfate (ALS) and cationic Dimethyl Diocta Decyl Ammonium Chloride (DDAC). The surfactants are purified by adopting earlier procedure. The surfactants ALS and DDAC were purchased from (Sigma-Aldrich India 98%), mandelic, lactic and glycolic acids from (Fine chemical. India

95%) Pentaamminecobalt (III) complexes of α-hydroxyl acids were prepared using 'Fan and Gould method. Double distilled water was used as a solvent and HClO4 (Merck India 95%) was standardized using standard Sodium carbonate (BDH, AR) solution with methyl orange as an indicator. For the NDC oxidation of Co (III) Complexes of α- hydroxy acid and unbound ligands.

The rate measurement were made at 320 ± 0.2°C in 100% aqueous medium and temperature was controlled by electrically operated thermostat. The total volume of reaction mixture in the spectrophotometrics cell was kept as 2.5 ml in each kinetic run. An Evolution of Thermo spectrophotometer fitted with recording and thermosetting arrangement was used to follow the rate of the reaction. Rate of this NDC oxidation with unbound ligand and Cobalt (III) bound complexes were calculated from 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 In A versus time. Reproducible result obtained giving good first order plot. The stoichiometric studies for the NDC oxidation of pentaamminecobalt (III) complexes of α -hydroxy acids and unbound ligand in the presence of micelles were carried out at 320 ± 2°C. It was observed that the cobalt (II) formation was negligibly small.

Preparation of Nicotinium dichromate (NDC):

Nicotinium (7.38g , 60m1) was added to Chromium trioxide Cr03 (12g, 120 mol), dissolved in water (12m1 at 0°C ice water bath) with vigorous stirring. After 15 min Acetone (100ml at 0.5° C) was added to the resulting red orange suspension and the mixture was stirred at 0° C —5° C for 15 min. The Product was filtered off and washed with Acetone (4x50m1) and Dichloromethane (25 ml). Apporxmatily 12g Nicotinium dichromate was obtained and usually yellow solid. m.p.216 °C.

Results and Discussion:

Kinetic study of the oxidation of pentaamminecobalt(III) complexes of α- hydroxy acids by NDC in surfactant medium dependence of rate on NDC concentration in bound ligand. The rate of oxidation of lactato cobalt(III) complexes depends on NDC concentration, the specific rate calculated remains constant (Table.1) and Graph of logarithm of NDC concentration versus time (Fig. 1) are linear.

From the slope of these graphs, the specific rate calculated agrees with those obtained from integrated rate equation suggesting first order dependence on NDC concent ration.

When the concentration of NDC is varied from 1.00 to 5.00 x 10-3 mol dm-3 at a fixed [Cobalt (III) and [HClO4]. Specific rates remain constant. Then the rate of disappearance of Cr (VI) is given by equation. (1)

$$-d [Cr (VI)] / dt = k [Cr (VI)] \quad \text{..... (1)}$$

At a particular NDC 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 of oxidation (Table.2). Hence the rate law for the Cr (VI) oxidation of cobalt (III) bound α- of hydroxy acids is given by equation.(2).

$$-d [Cr(VI)] /dt =k2 [Cr(VI)] [Cr(III)] \quad \text{..... (2)}$$

Dependence of rate on NDC concentration in surfactant for Cobalt (III) complexes of α- hydroxy acid:

The rate of oxidation of lactato Cobalt (III) complexes depends on NDC concentration. In any specific rate the change in concentration of NDC, the specific rate calculated remains constant (Table-3).The specific rate calculated agrees with those obtained from integrated rate equation, suggesting first order dependence on NDC concentration [11].

When concentration of NDC is varied from 1.00 to 4.00 x 10-3mol dm-3 at a fixed [Co (III)] and [HCIO4] specific rates remains constant. Then the rate of disappearance of Cr (VI) is given by equation …3.

$$-d [Cr(VI)] /dt = k1 [Cr(VI)] \quad \text{... (3)}$$

Dependence of rate on the concentration of α-hydroxy acids in ALS and DDAC

The oxidation studies were carried out by varying initial [α- hydroxy acid] in the range 1.00 to 4.00 x 10-3 mol drn- 3by keeping other variables constant. The near consistency in the k2 values (Tables 4 and 5) logarithm of specific rate (k1 in s-1) verses logarithm of α- hydroxy acid concentration in each case suggesting first order dependence of rate on [α-hydroxy acid] . Hence the rate law for the Cr (VI) oxidation α-hydroxy acid of is given below equation 4.

$$-d [Cr (VI)] I dt =k2(Cr VI)] [\alpha \text{ -hydroxy acid}] \quad \text{..... (4)}$$

Comparison of rates on oxidation of Pentaammine cobalt(III) complexes of both bound and unbound α-hydroxy acid by NDC:

Specific rate of the lactato complex is more compared to both the rates of oxidation of unbound ligand and Mandela to complex deserves an explanation. The ligation of lactic acid to Co (III) centre has probably increased its reactivity towards NDC 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 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 Mandelato and glycolato complexes.

Table: 1.

$[(NH_3)5CoIII\text{-}L]$ $= 2X10^{-2}$ mol dm^{-3}

[NDC] $= 2X10^{-2}$ mol dm^{-3}

HClO4 $= 1$ mol dm^3

Surfactants $= 1$ mol dm^3

Temperature $= 32^{O}C$

Time (S)	10^{-3} (a-x) mol dm^{-3}	
	ALS	**DDAC**
180	9.50	4.10
360	6.66	2.72
540	5.14	2.07
720	3.69	1.50
900	2.72	0.96
1080	1.99	1.17
1260	1.28	0.51
1440	1.07	0.37
1620	1.01	0.32
1800	0.91	0.23

Table 2

[NDC] $=2.00x\ 10^{-3}$ mol dm^{-3}

$[HC1O_4]$ $= 1.00$ mol dm^{-3}

[ALS] $= 1.00x\ 10^{-4}$ mol dm^{-3}

Temperature $= 32\pm0.2°C$

$[(N1^{-}13)5Colll\text{-}L]\ 10^2$ mol dm^{-3}	$10^4k^1(S^{-1})$	$10^2\ k^2\ dm^3\ mol^{-1}s^{-1}$
L= lactato		
1.00	2.96	2.96
2.00	3.90	2.95
3.00	5.70	2.96
4.00	7.70	2.95
5.00	10.45	2.95
L= Mandelato		
1.00	2.17	2.170
2.00	2.85	2.169
3.00	3.84	2.164
4.00	5.42	2.168
5.00	7.26	2.169
L= Glycolato		
1.00	1.65	0.364
2.00	1.98	0.368
3.00	2.55	0.372
4.00	3.41	0.352
5.00	4.32	0.366

Table 3

[NDC] $= 2.00x\ 10^{-3}$ mol dm^{-3}

$[HClO_4]$ $= 1.00$ mol dm^{-3}

[D DAC] $=1.00x\ 10^{-4}$ mol dm^{-3}

Temperature $= 32 \pm 0.2°C$

$(NH_3)_5Co^{lll}\text{-}L\ 10^2$ mol dm^{-3}	$10^4k^1(s^{-1})$	$10^2\ k^2\ dm^3\ mo1^1\ s^{-1}$
L= Lactato		
1.00	1.00	1.00
2.00	1.62	1.02
3.00	2.43	1.02
4.00	3.80	1.00
5.00	6.10	1.01
L= Mandelato		
1.00	0.64	0.64
2.00	0.96	0.64
3.00	1.55	0.64
4.00	2.25	0.64
5.00	3.44	0.64
L= Glycolato		
1.00	0.41	0.239
2.00	0.67	0.238
3.00	0.96	0.237
4.00	1.59	0.239
5.00	2.39	0.238

Table: 4.

[NDC] $= 2.00x\ 10^{-3}$ mol dm^{-3}

$[HClO_4]$ $= 1.00$ mol dm^{-3}

[ALS] $=1.00x\ 10^{-4}$ mol dm^3

Temperature $= 32\pm0.2°$.

[a - Hydroxy acid]10^2 mol dm^{-3}	$10^4k^1(S^{-1})$	$10^2\ K^2dm^3\ mol^{-1}\ s^{-1}$
L= Lactic acid		
1.00	1.23	1.23
2.00	2.01	1.23
3.00	3.19	1.25
4.00	5.12	1.24
5.00	8.01	1.28
L= Mandelic acid		
1.00	0.83	0.83
2.00	1.28	0.83
3.00	2.00	0.83
4.00	3,02	0.83
5.00	5.14	0.83
L=Glycolic acid		
1.00	0.45	0.253
2.00	0.74	0.253
3.00	1.01	0.255
4.00	1.72	0.255
5.00	2.53	0.253

Table -5

[NDC]	$=2.00 \times 10^{-3}$ mol dm^{-3}
[HC1O4]	$=1.00$ mol dm^{-3}
[DDAC]	$=1.00 \times 10^{-4}$ mol dm^{-3}
Temperature	$=32 \pm 0.2°$.

[α-hydroxy acids]10^2 mol dm^{-3}	$10^4 k_1$ (S^{-1})	$10^2 k_2 dm^{-3} mol^{-1} s^{-1}$
Lactic acid		
1.00	1.29	1.290
2.00	2.24	1.290
3.00	3.88	1.292
4.00	6.32	1.290
5.00	11.80	1.293
Mandelic acid		
1.00	0.65	0.65
2.00	1.04	0.65
3.00	1.60	0.65
4.00	2.54	0.65
5.00	3.99	0.65
Glycolic acid		
1.00	0.41	0.411
2.00	0.67	0.411
3.00	1.16	0.414
4.00	1.85	0.410
5.00	3.24	0.415

Conclusion:

The oxidation reactions of Cobalt (III) complexes of α -hydroxy acids viz, lactic add, glycolic acid and mandelic add have been carried out using a novel chromium (VI) oxidant. There is a remark able increase in the rate of the reaction has been observed in the presence of novel surfactants ALS and DDAC. These surfactants act as a positive catalyst in situ of the reaction and among which DDAC enhances the rate much more than the ALS

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