National Journal of Advanced Research
ISSN: 2455-216X
Impact Factor: RJIF 5.12
www.allnationaljournal.com
Volume 4; Issue 1; January 2018; Page No. 90-93

Redox reactions of cobalt (iii) complexes of α-hydroxy Acids by Quinolinium di chromate (QDC) in presence micelles

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Abstract

The kinetics of one electron transfer mode seems to be unavailable for QDC with Cobalt (III) bound and unbound complexes of α-hydroxy acids in surfactant medium, QDC oxidizes Cobalt (III) bound and unbound α- hydroxyl 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 Ammonium Lauryl sulfate. (ALS). Similar trends has been observed in lactato, glycolato and Mandelato Co (III) complexes.

Keywords: quinolinium di chromate (QDC), ALS, dimethyl diocta decyl ammonium chloride (DDAC)

1. Introduction

Evolution60 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 Quinolinium Di Chromate 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 results in nearly 100% reduction at Cobalt (1II) centre with synchronous C- C bond fission and decarboxylation. Such an electron transfer route seems to be unavailable for Quinolinium Di Chromate in its reaction with cobalt (Ill) bound and unbound α-hydroxy acids in surfactant medium. Quinolinium Di Chromate oxidizes cobalt (III) 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 QDC oxidation of cobalt (III) Mandelato, Lactato and Glycolato complexes depends on the first power of QDC concentration. Similarly the reaction between QDC and unbound α-hydroxy acid exhibits first order kinetics with respect to concentration of QDC. Of the three complexes lactate Cobalt (III) complexes react faster than mandelato and glycolato complexes, and similar trend is followed in the unbound ligands Ammonium Lauryl sulfate. (ALS). 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. QDC 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.

2. Materials and Methods

The surfactants used in the present work are Ammonium Lauryl sulfate. (ALS) and Dimethyl Diocta Decyl Ammonium Chloride (DDAC). The surfactants are purified by adopting earlier procedure. The surfactants Ammonium Lauryl sulfate. (ALS) and DDAC were purchased from (Sigma-Aldrich India 98%), mandelic, lactic and glycolic acids from (Karnataka Fine chemical. India95%) Pentaamminecobalt (III) complexes of α-hydroxy acids were prepared using 'Fan and Gould2, 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 QDC oxidation of Co (III) Complexes of α-hydroxy acids and unbound ligands11, 12. The rate measurement were made at 34 ± 0.2°C in 100% aqueous medium and temperature was controlled by electrically operated thermostat. The total volume of reaction mixture in the spectrophotometric cell was kept as 2.5 ml in each kinetic run. An Evolution60 Thermo spectrophotometer fitted with recording and thermosetting arrangement was used to follow the rate of their action. Rate of this QDC oxidant 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 ln A versus time. Reproducible result obtained giving good first order plot. The stiochiometric studies for the QDC oxidation of pentaamminecobalt (III) complexes of α-hydroxy acid and unbound ligand in the presence of micelles were carried out at 36± 2°C. It was observed that the cobalt (II) formation was negligibly small.

3. Result and Discussion

Kinetic study of the oxidation of pentaamminecobalt (III) complexes of α-hydroxy acid by QDC in surfactant medium dependence of rate on QDC concentration in bound ligand. The rate of oxidation of lactate cobalt (III) complexes depends on QDC concentration, the specific rate calculated remains constant (Table 1) and Graph of logarithm of QDC 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 QDC concentration.

When the concentration of QDC is varied from 1.00 to 5.00 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 by equation. (1)

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

At a particular QDC 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). 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 order rate dependence of rate on [Co(III)]. Hence the rate law for the Cr (VI) oxidation of cobalt (III) bound of α-hydroxy acids is given by equation.(2).

$$-d\,[Cr\,(VI)]/dt = k2\,[Cr\,(VI)]\,[Co\,(III)] \qquad \ldots (2)$$

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

Hydroxyacid: The rate of oxidation of lactato Cobalt (III) complexes depends on QDC concentration. In any specific run the change in concentration of QDC, the specific rate calculated remains constant (Table-3) and graphs of logarithm of QDC 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 QDC concentration. When concentration of QDC is varied from 1.00 to 4.00 x 10-3mol 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.

$$-d\,[Cr\,(VI)/dt = K1\,[Cr\,(VI)] \qquad \ldots (3)$$

Dependence of rate on the concentration of α-hydroxy acid in Ammonium Lauryl sulfate. (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 dm- 3by keeping other variables constant. The near consistency in the k2 values (Tables 4 and 5) and the slope of nearly unity is obtained from a linear graph of 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] (Figs. 3 and 4). Hence the rate law for the Cr (VI) oxidation α-hydroxy acid of is given below equation 4.

$$-d\,[Cr\,(VI)]\,/\,dt = k2\,[Cr\,(VI)]\,[\alpha\text{- hydroxy acid}] \ldots (4)$$

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

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 QDC 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 satirically hindered in the case of Mandela to and glycolato complexes.

4. Mechanism

Oxidation of Pentaamminecobalt (III) complexes of both bound and unbound ligands in surfactant medium. Thus, the kinetics of two electron transfer route seems to be unavailable for QDC with Cobalt(III) bound and unbound complexes of α-hydroxy acid in surfactant medium, QDC 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 surfactant concentration an increase in the rate is observed. The added DDAC enhances the rate of oxidation of a reaction much more than Ammonium Lauryl sulfate. (ALS). Similar trends has been observed in lactato and glycolato Co (III) complexes.

Table 1

$[(NH3)^5Co^{III}\text{-}L]^{2+}$ = 2.00 X 10^{-2} mol dm^{-3}
[QDC] = 2.00 X 10^{-2}mol dm^{-3}
[$HClO_4$] = 1.00 mol dm^{-3}
[Surfactants] = 1.00 X 10^{-4} mol dm^{-3}
Temperature = 36± 0.2ºC

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

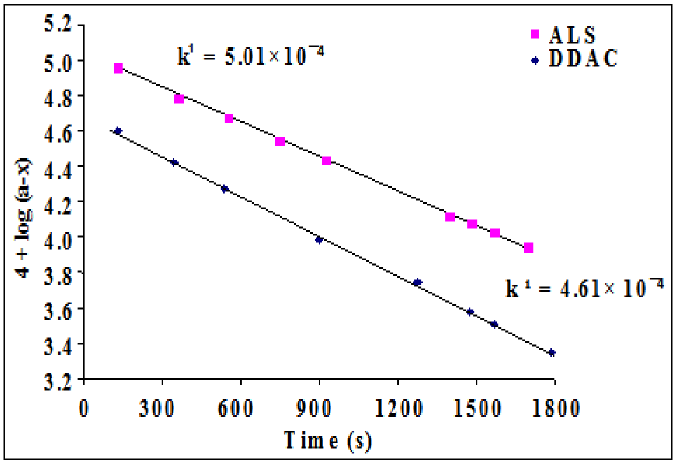

Fig 1: First order dependence plots

Table 2

[QDC] = 2.00× 10^{-3} mol dm^{-3}
$[HClO_4]$ = 1.00 mol dm^{-3}
[ALS] = 1.00× 10^{-4} mol dm^{-3}
Temperature = 36±0.2ºC

$[(NH_3)_5Co^{III}$ –L] 10^2 mol dm^{-3}		10^4 k_1 (S^{-1})	10^2 k_2 dm^3 mol^{-1} s^{-1}
L= 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

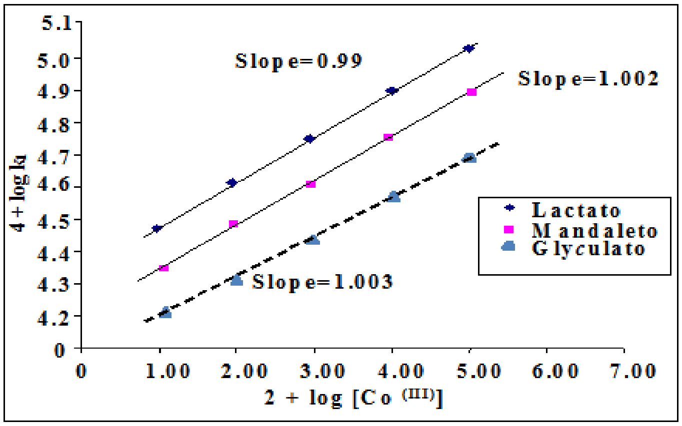

Fig 2: Dependence of rate on $[Co^{III}]$ in Ammonium Lauryl sulfate.

Table 3

[QDC] = 2.00× 10^{-3} mol dm^{-3}
$[HClO_4]$ = 1.00 mol dm^{-3}
[DDAC] = 1.00× 10^{-4} mol dm^{-3}
Temperature = 36±0.2ºC

$[(NH_3)_5Co^{III}$ –L] 10^2 mol dm^{-3}		10^4 k_1 (S^{-1})	k_2 10^2 dm^3 mol^{-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

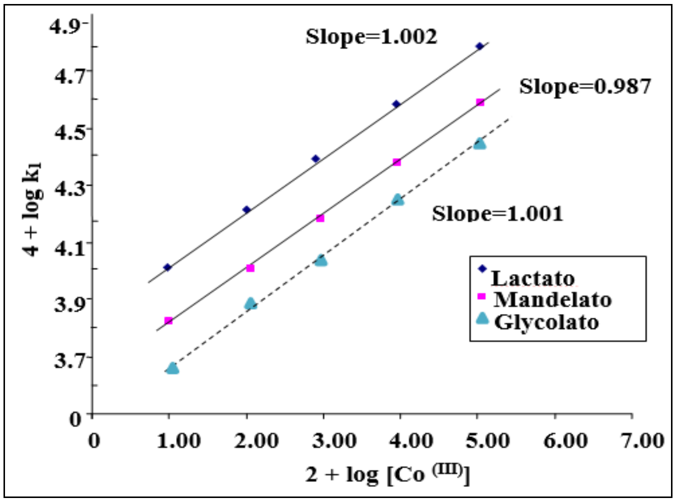

Fig 3: Dependence of rate on $[Co^{III}]$ in DDAC

Table 4

[QDC] = 2.00× 10^{-3} mol dm^{-3}
$[HClO_4]$ = 1.00 mol dm^{-3}
[ALS] = 1.00× 10^{-4} mol dm^{-3}
Temperature = 36±0.2º.

[α – Hydroxy acid]10^2 mol dm^{-3}		10^4 k_1 (S^{-1})	10^2 k_2 dm^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

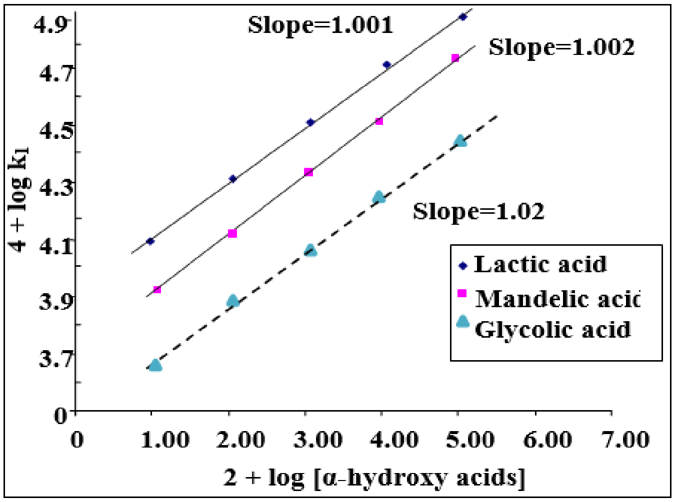

Fig 4: Dependence of rate on [α – hydroxy acid] in ALS

Table 5

[QDC] = 2.00×10^{-3} mol dm^{-3}
[$HClO_4$] = 1.00 mol dm^{-3}
[DDAC] = 1.00×10^{-4} mol dm^{-3}
Temperature = 36±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

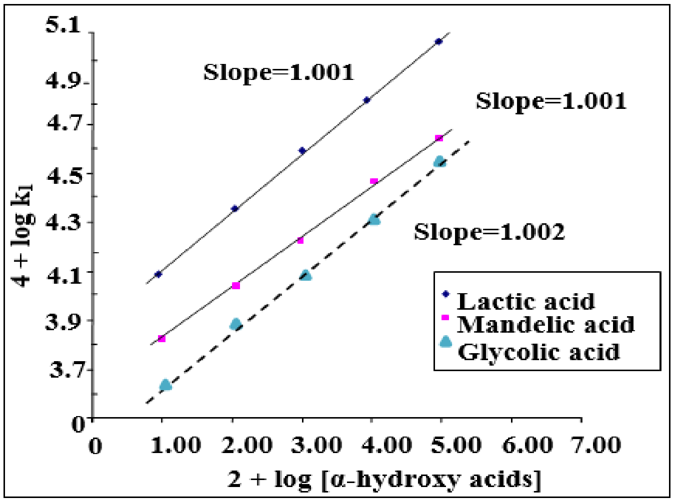

Fig 5: Dependence of rate on [α –Hydroxy acid] in DDAC

5. Conclusion

The oxidation reactions of Cobalt (III) complexes of α -hydroxy acids viz, lactic acid, glycolic acid and mandelic acid 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 Ammonium Lauryl sulfate. (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 Ammonium Lauryl sulfate. (ALS).

6. Acknowledgments

Authors are thanks to the Management of Vaniyambadi Muslim Educational Society and PG& Research Department of Chemistry, Islamiah College Vaniyambadi for providing the necessary facilities for the successful completion of this research work. At last I thanks to my friend R. Kalaivani M.A., for his kind help in processing the complete this work in computer.

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