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Kinetic study on induced electron transfer reaction in Pentaamminecobalt (III) complexes of A-Hydroxy acids by Quinolinium Dichromate (QDC) in Micellar Medium

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Abstract

Quinolinium DiChromate (QDC) oxidation of pentaamminecobalt (III) complexes of α-hydroxy acids in micellar medium yielding nearly 100% of carbonyl compounds are ultimate products. The decrease in UV-visible absorbance at l=502 nm for Co (III) complex corresponds to nearly 100% of the initial absorbance. The stoichiometry of unbound ligand and cobalt (III) complex is accounting for about 100% reduction at the cobalt (III) centre. The kinetic and stoichiometric results have been accounted by a suitable mechanism.

Keywords: Quinolinium DiChromate (QDC), Pentaammine cobalt (III) complexes, Induced electron transfer reaction, ALS, Dimethyl Diocta decyl Ammonium Chloride (DDAC)

Introduction

Quinolinium DiChromate (QDC) is an efficient reagent for oxidation of primary and secondary alcohols to carbonyl compounds. A large class of organic compounds were oxidized by QDC has been reported1-5. Since induced electron transfer in pentaamminecobalt (III) complexes of α-hydroxy acids with various oxidants have been studied6-11. The extent of QDC oxidation of pentaamminecobalt (III) complexes of α-hydroxy acids in micellar medium as an oxidis able hydroxyl group is separated from carboxyl bound to Co(III) centre by a saturated fragment namely C-C bond12. The cation radical is formed due to the oxidation of hydroxyl group by QDC is nearly in a synchronous fashion of electron transfer resulting in a C-C, O-H bonds scission and reduction at cobalt(III) center.

2. Experimental section

2.1 Preparation of Quinolinium DiChromate. (QDC).

A known quantity of Quinoline was slowly added to a cooled solution of Chromium trioxide in water with stirring. After 30 min, the solution was diluted with acetone and cooled to -20 ºC for 2 to3 hours. The Orange solid which separated out, was filtered, washed with acetone, dried in vacuum and the recrystalised from water. Melting point.159.

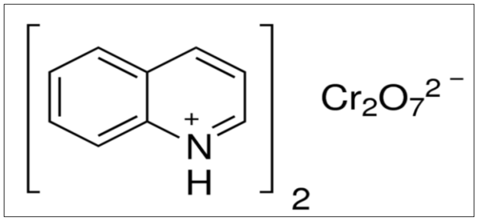

Fig 1

2.2 Kinetic measurements

The tris (*α*-hydroxo) complex; $(NH_3)_3$ Co $(OH)_3$ Co $(NH_3)_3$ $(ClO_4)_3$ (triol) has been prepared by the procedure of Siebert and Co workers 14,15. And unbound ligands in the presence of micelles were carried out at 34 ± 0.2 0C in an electrically operated thermostat bath. The concentrations of unreacted QDC was determined iodometrically. The disappearance of Co (III) was followed spectrophotometrically by following the decrease in absorbance at 470 nm. (For the monomeric Co (III) complex). Ionic strength was maintained by the addition of suitable quantities of $NaClO_4$. The specific rates estimated from the optical density measurements agree with the values from the volumetric procedure within ±7% curiously, the change in absorbance observed at 470 nm Co (III) complexes of α-hydroxy acids corresponds to nearly 100% of the initial concentration of Co(III), while the change in optical density at 374 nm for QDC corresponds to nearly 100% of [Co(III)] initial. Co(II) was estimated after completion of reaction, by diluting the reaction mixture 10-fold with concentrated HCl, Allowing the evolution of chlorine gas to cease and then measuring the absorbance of yellow Quinolinium complex of Co(II) at 660 nm (e =560 dm3 mol-1cm-1)16,17. The amount of Co (II) estimated in all these cases corresponds to nearly 100% of [Co (II)]initial. After 48 h, the product was extracted with diethyl ether and analyzed iodometrically for the amount of benzaldehyde formed was determined by measuring absorbance at 229 nm [e=11,400 dm3 mol-1 cm-1]18,19. The yield of benzaldehyde in all these cases was nearly 100% [Co (III)] initial Table 1 & 2.

Table 1: Stoichiometric data for QDC oxidation of Co(III) bound and unbound α –hydroxy acids in presence of Ammonium Lauryl Sulfate (ALS) at 34 ± 0.2 ºC.

$[HClO_4]$ = 1.00 mol dm^{-3}.
[ALS] = 1.00×10^{-4} mol dm^{-3}.
Temperature = 34 ± 0.2ºC

103[Compound] mol dm-3	102 [QDC] initial mol dm-3	102 [QDC] Final mol dm-3	Δ103 [QDC] mol dm-3	[Compound] : Δ [QDC]
Lactic acid				
4.0	2.0	1.62	3.80	1.00 : 0.95
5.0	2.0	1.54	4.60	1.00 : 0.92
6.0	3.0	2.41	5.82	1.00 : 0.97
Mandelic acid				
4.0	2.0	1.62	3.76	1.00 : 0.94
5.0	2.0	1.52	4.80	1.00 : 0.96
6.0	3.0	2.45	5.46	1.00 : 0.91
Glycolic acid				
4.0	2.0	1.61	3.88	1.00 : 0.97
5.0	2.0	1.53	4.65	1.00 : 0.93
6.0	3.0	2.46	5.40	1.00 : 0.90
CoIII Lactato				
4.0	2.0	1.61	3.84	1.00 : 0.96
5.0	2.0	1.51	4.65	1.00 : 0.98
6.0	3.0	2.44	5.40	1.00 : 0.93
CoIII Mandelato				
4.0	2.0	1.64	3.60	1.00 : 0.90
5.0	2.0	1.56	4.35	1.00 : 0.87
6.0	3.0	2.50	4.92	1.00 : 0.82
CoIII Glycolato				
4.0	2.0	1.67	3.24	1.00 : 0.81
5.0	2.0	1.60	4.00	1.00 : 0.80
6.0	3.0	1.54	4.92	1.00 : 0.82

Table 2: Stoichiometric data for QDC oxidation of Co (III) bound and unbound α-hydroxy acids in presence of Dimethyl Diocta decyl Ammonium Chloride (DDAC) at 34 ± 0.2 ºC.

$[HClO_4]$ = 1.00 mol dm^{-3}.
[DDAC] = 1.00×10^{-4} mol dm^{-3}.
Temperature = 34 ± 0.2ºC.

103[Compound] mol dm-3	102 [QDC] initial mol dm-3	102 [QDC] Final mol dm-3	Δ103 [QDC] mol dm-3	[Compound] : Δ [QDC]
Lactic acid				
4.0	2.0	1.61	3.84	1.00 : 0.96
5.0	2.0	1.53	4.65	1.00 : 0.93
6.0	3.0	2.43	5.70	1.00 : 0.95
Mandelic acid				
4.0	2.0	1.60	3.92	1.00 : 0.98
5.0	2.0	1.53	4.70	1.00 : 0.94
6.0	3.0	2.45	5.46	1.00 : 0.91
Glycolic acid				
4.0	2.0	1.61	3.88	1.00 : 0.97
5.0	2.0	1.52	4.75	1.00 : 0.95
6.0	3.0	2.44	5.52	1.00 : 0.92
CoIII Lactato				
4.0	2.0	1.63	3.68	1.00 : 0.99
5.0	2.0	1.52	4.80	1.00 : 0.96
6.0	3.0	2.44	5.58	1.00 : 0.93
CoIII Mandelato				
4.0	2.0	1.62	3.80	1.00 : 0.95
5.0	2.0	1.54	4.66	1.00 : 0.92
6.0	3.0	2.46	5.44	1.00 : 0.90
CoIII Glycolato				
4.0	2.0	1.64	3.52	1.00 : 0.88
5.0	2.0	1.59	4.10	1.00 : 0.82
6.0	3.0	2.52	4.80	1.00 : 0.80

After neutralization of the reaction mixture with sodium bicarbonate, the pH of the aqueous layer was adjusted to about 6.0 and the aqueous layer was separated by filtration in the case of both free ligands and corresponding complexes. On evaporation of water under reduced pressure, the product separated and the percentage yield was calculated. Though the yield of cobalt(II) was 100%, the estimation of cobalt(II), Cr(V) and carbonyl compounds were quantitative, In both the cases the IR spectra of the product agreed with IR spectra of authentic samples.

3. Result and Discussion

Table 3 summarizes the kinetic data for the QDC oxidation of free α -hydroxy acids with 1N $HClO_4$ in presence of anionic and cationic micelles at 34±0.2 0C. The reaction exhibits total second order dependence on [Cobalt (III)] as well as [α-hydroxy acids]. Based on the oxidation of QDC with α-hydroxy acids the following rate law has been deduced.

Rate=k[α-hydroxy acid] [QDC]

Table 4 lists the formation constants for QDC co-complexes of α-hydroxy acid along with the specific rates. Such complex formation seems to be absent when the carboxyl and it is tied up by Co(III) and the reaction between QDC and Co(III) complexes of α-hydroxy acids exhibit uncomplicated second order kinetics.

From a comparison, the specific rates for QDC oxidation of the respective Co (III) complexes and the dimeric cobalt (III) glyoxalato complex, one can infer that the oxidation rates of α-hydroxy acids are not significantly affected by complex formation. This may be due to the point of attack lies away from the Co (III) centre so that its electrostatic influence is less felt. There is, however a considerable change in the specific rate of QDC oxidation of the Co (III) keto acid complex as the two Co (III) centers can exert greater electrostatic influence over the reacting centre. This suggests that QDC attacks the O-H centre in the slow step of the reaction, leading to ligand oxidation takes place. The rate of the reaction is increased by the addition of both Ammonium Lauryl Sulfate (ALS) and Dimethyl Diocta decyl Ammonium Chloride (DDAC). A plot of specific rate constant versus micellar concentration is sigmoidal in shape the catalytic effect is more Dimethyl Diocta decyl Ammonium Chloride (DDAC) than Ammonium Lauryl Sulfate (ALS).

The specific rate of the lactato complex is more when compared to both the rate of unbound ligand and mandelato complex is due to the ligation of lactic acid to cobalt(III) centre has probably increased its reactivity towards QDC and this effect seems to be more specific for this ligands only. In NMR spectrum of lactato complex the alpha methine proton has undergone considerable downfield shift compared to the alpha C-H proton of the unbound ligand [d C-H=1.62 ppm in lactic acid and d=C-H 2.19 ppm in lactato complex whereas d= C-H 4.62 ppm in mandelic acid d=C-H=3.73 ppm in the respective complex]. Suggesting an increase in acidic nature of methine proton of lactic acid is due to ligation to metal centre. If the reaction proceeds through a performed chromate ester, then the rate of alpha C-H will been hanced, resulting in an increased rate of oxidation of lactato complex such a precursor complex may be satirically hindered in the case of mandelato and glycolato complexes.

The stoichiometric results indicate that for 1 mole of cobalt (III) complex, about 0.65 mole of QDC is consumed, whereas with the unbound ligands for 1 mole of a-hydroxy acids about0.92 mole of QDC is consumed (Table 3 & 4). The stoichiometric results coupled with kinetic data and product analysis can be accounted for by the following the reaction Scheme 1.

Table 3: First order rate constants for QDC oxidation of α -hydroxy acids at 34 ± 0.2ºC

[QDC] = 2.00×10^{-3} mol dm^{-3}.
[$HClO_4$] = 1.00 mol dm^{-3}.
[ALS] = 1.00×10^{-4} mol dm^{-3}.
[DDAC] = 1.00×10^{-4} mol dm^{-3}.
Temperature = 34 ± 0.2ºC.

10^2[α-hydroxy acids] mol dm-3	10^4 k_1 S^{-1} ALS	102 k_2 dm-3 mol S^{-1} ALS	10^4 k_1 S^{-1} DDAC	102 k_2 dm-3 mol S^{-1} DDAC
Lactic acid				
1.00	3.33	4.5223	3.24	4.5105
2.00	4.42	4.5221	3.99	4.1500
3.00	5.54	4.5220	5.15	4.1499
4.00	8.12	4.5202	5.97	4.1500
5.00	15.05	4.5183	8.06	4.1500
Mandelic acid				
1.00	2.20	4.3924	2.17	4.3364
2.00	3.01	4.3923	2.69	4.3360
3.00	3.69	4.3920	3.24	4.3360
4.00	5.14	4.3921	4.61	4.3358
5.00	6.98	4.3920	5.54	4.3368
Glycolic acid				
1.00	1.66	4.315	1.58	4.1986
2.00	2.07	4.314	1.90	4.1980
3.00	2.59	4.313	2.81	4.1980
4.00	3.24	4.314	3.34	4.1979
5.00	4.15	4.312	3.91	4.1980

Table 4: First order rate constants for QDC oxidation of Co (III) complexes of α-hydroxy acids at 34 ± 0.2 ºC.

[QDC] = 2.00×10^{-3} mol dm^{-3}.
[$HClO_4$] = 1.00 mol dm^{-3}.
[ALS] = $1.00\times10^{-}4$ mol dm^{-3}.
[DDAC] = $1.00\times10^{-}4$ mol dm^{-3}.
Temperature = 34 ± 0.2ºC.

$10^3[(NH_3)_5Co(III)L]$ mol dm^{-3}	10^4 k_1 S^{-1} ALS	102 k_2 dm-3 mol S^{-1} ALS	10^4 k_1 S^{-1} DDAC	102 k_2 dm-3 mol S^{-1} DDAC
L = Lactato				
1.00	1.02	4.0086	0.96	3.9822
2.00	1.68	4.0085	1.43	3.9820
3.00	2.69	4.0084	2.33	3.9820
4.00	3.66	4.0082	2.66	3.9821
5.00	5.62	4.0084	4.20	3.9820
L = Mandelato				
1.00	0.67	3.8260	0.72	3.8573
2.00	0.85	3.8258	0.91	3.8570
3.00	1.33	3.8259	1.36	3.8572
4.00	2.10	3.8258	1.93	3.8571
5.00	3.17	3.8258	2.76	3.8571
L = Glycolato				
1.00	0.42	3.6234	0.49	3.6901
2.00	0.64	3.6233	0.69	3.6903
3.00	0.88	3.6230	0.93	3.6903
4.00	1.92	3.6230	1.46	3.6902
5.00	2.43	3.6230	2.41	3.6903

The reaction scheme proposes that QDC oxidizes OH center of the cobalt (III) bound α-hydroxy n acids at a rate of comparable to that of the unbound ligand and there is 100%reduction at the cobalt (III) centre, forms a chromate ester with cobalt (III) glyoxalato complex which can decompose in a slow step, proceeds through C-C bond fission leading to the formation of cobalt (II), carbonyl compounds and carbon dioxide. As 1 mole of cobalt (III) glyoxalato complex consumes 0.65 mole of QDC yielding nearly 100% of Co(II)and 100% carbonyl compounds. Similarly 1 mole of unbound α-hydroxy acid consumes nearly 0.92 mole of QDC, yielding 100% of carbonyl products and CO_2.

Scheme – I

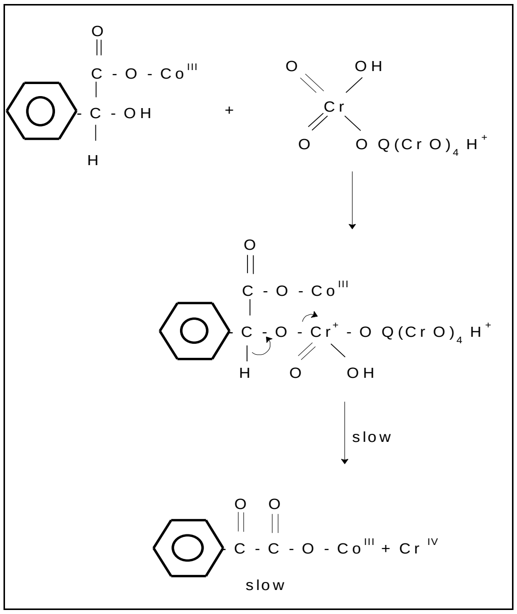

Fig 2

Scheme - II

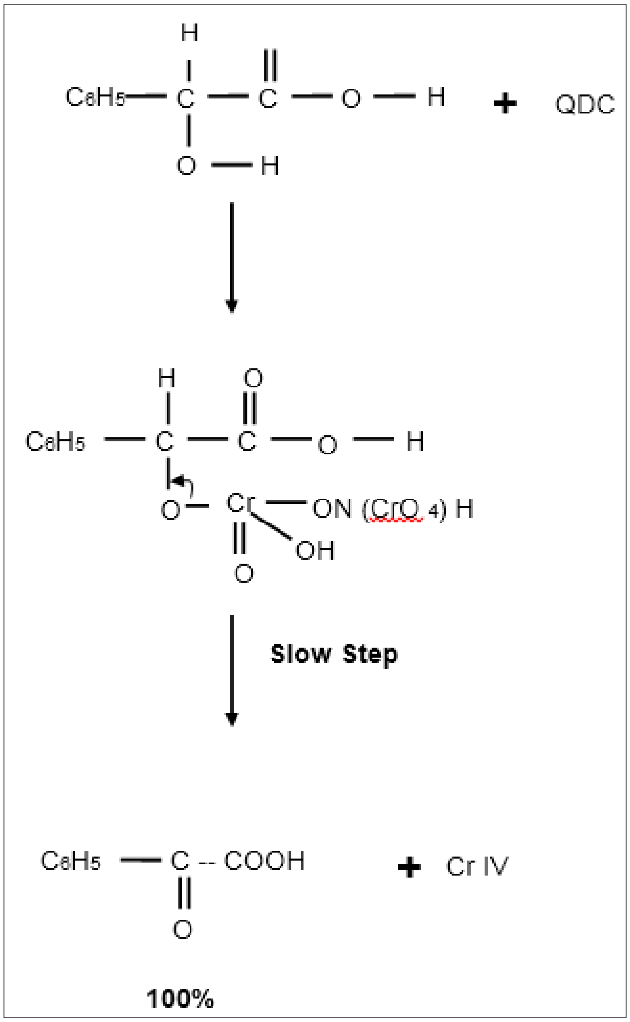

Fig 3

Quinolinium DiChromate forms a chromate ester with CO (III) mandelato complex which can decompose in a slow step leading to the formation of the keto acid complex and Cr (IV). The absence of formation of co (II) rules out the synchromous C-C bond fission and electron transfer to Co (III). The oxidation of cobalt (III) complexes of α-hydroxy acids by Quinolinium DiChromate proceeds mainly through C-H bond fission. The mechanism of QDC oxidation of Cobalt (III) lactato, glycolato, mandlic, lactic and glycolic acids will be similar to the one proposed for the Cobalt (III) mandelato complex.

4. Conclusion

It has been found that the rate of oxidation of Co (III) complexes of unbound and bound

moieties are enhanced more in the presence of Dimethyl Diocta decyl Ammonium Chloride (DDAC) when compared to the Ammonium Lauryl Sulfate (ALS). The micelles act as a positive catalyst in the present study.

5. Acknowledgment

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6. Reference

7. Nongkynrih I, Mahanti KM. Bull. Chem. Soc. Jpn, 1994; 67:2320.
8. Aruna K, Manikyamba P, Indian J. Chem. Sect. A. Inorg., Bio-Inorg., Phys., Theor Anal. Chem. 1995; 34:822.
9. Chaubey GS, Das S, Mahanti MK. Kinetics and Catalysis, 2002; 43:789.
10. Chaubey GS, Das S, Mahanti MK. Bull. Chem. Soc. Jpn, 2002; 75:2215.
11. Ramkumar B. Asian J. Chem, 2002; 14(1):463-466.
12. Chaubey GS, Das S, Mahanti MK. Can. J Chem. Rev. Can. Chim. 2003; 81:204.
13. Sekar KG. Oxidation Communication. 2003; 26:198.
14. Pandurangan P, Kavitha S, Alphonse I. Indian J Chem. 2005; 44A:715.
15. Kabilan S, Kirubashankar P, Krishnasamy P. Oxidn. Comun, 2006; 29(1):335-342.
16. Anil kumar J, Sondu S. Indian. J Chem. 2007; 46A:1702-1705.
17. Mohamed Farook NA. J Solution Chem., 2007, 36-345.
18. Krishnasamy K, Devanathan D, Dharmaraja J. Trans Met Chem, 2007; 922.
19. Mohan K, Jagadeesh MB. Indian. J Chem. 2008; 47A:226.
20. Bharad, Jagdish, *et al.*, Bull. Catl. Soc. India. 2008; 7:168-176.
21. Zwolak M, Lagerquist J, Ventra MD. J Phys. Rev. Lette, 2009; 103:102-128.
22. Nikos G, Ioanna EM. J Phys. Chem of Liquids. 2009; 47:505.
23. Jabbari M, Gharib F. J Acta. Chem. Slov., 2010; 57:325.
24. Shyamal KD, Anindha JB. J Phys. Chem, 2010; 114B:6830.
25. Priya V, Balasubramaniyan M, Mathiyalagan NJ. Chem. Pharm. Res, 2011; 3(1):522-528.
26. Rukmangathan M, Santhoshkumar V, Ramkumar B. J.Chem.pharm.Res, 2012; 4(3):1740-1744.
27. Vellaisamy M, Sharmila M. J Chem. Pharm. Res, 2013; 5(4):29-32.
28. Surya kalaa D, Asifa K, Rama krishnaa MK, Chakravarthy B, Subba PV.Chem Sci Trans, 2013; 2(4):1434-1442.
29. Samiey B, Cheng CH, Wu JJ of Chem. 2014, 14.
30. Niranjan PS, Upadhyay SK. Indian J. of Chem, 2014; 53:1402-1406.