Acta Chimica
&
Pharmaceutica Indica

Acta Chim. Pharm. Indica: 1(1), 2011, 44-50

INDUCED ELECTRON TRANSFER REACTIONS IN PENTAAMMINE COBALT (III) COMPLEXES OF ALPHA – HYDROXY ACIDS BY QUINOLINIUM DICHROMATE IN ACETIC ACID (70%) MEDIUM : A KINETIC STUDY

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(*Received : 11.10.2011, Revised : 22.10.2011, Accepted : 25.10.2011*)

ABSTRACT

The oxidation of pentaamminecobalt (III) perchlorate complexes of alpha-hydroxy acids by quinolinium dichromate (QDC) has been studied in 70% acetic acid. The oxidation of free alpha-hydroxy acids were also carried out under the same conditions for comparative purpose. The reaction was followed by observing the decrease in the absorbance at 440 nm for the Cr (VI) present in the reagent in a UV – Visible spectrophotometer. Product and stoichiometric analysis were carried out for the oxidation of complexes and free ligands. A mechanism involving one electron transfer for the complex and two electron transfer for the ligand was proposed.

Key words: Pentaamminecobalt (III) complexes, Alpha-hydroxy acids, Induced electron transfer reactions, Dichromates.

INTRODUCTION

Quinolinium dichromate (QDC) was found to be a mild reagent for the oxidation of organic compounds. Oxidation kinetics of primary, secondary and allylic alcohols[1], substituted benzyl alcohols[2], aliphatic aldehydes[3], aromatic aldehydes[4], heterocyclic aldehydes[5], cyclohexanones[6], β-diketones[7], aliphatic and aromatic carboxylic acids[8], styrenes[9], substituted cinnamates[10], and 2-naphthols[11], were carried out by various authors.

The mildness of QDC was demonstrated effectively in the oxidation of diols[12] where a single hydroxyl group was oxidized to give hydroxy carbonyl compound as the product. The determination of isoniazid in the pure form and in pharmaceutical formulations was carried out by Kulkarni et al.[13] Oxidation of alpha-hydroxy acids by QDC was carried out by Chimatader et al.[14] and Aruna et al.[15] in various organic solvents. A mechanism involving the C-C bond cleavage leading to the formation of aldehydes as the product was proposed. The formation of ketoacids by the C-H cleavage of the alpha-hydroxy acids was reported with many chromium (VI) oxidants[16].

In the case of complexes, the hydroxy1 group of the bound ligand is free for oxidation with C-H

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cleavage leading to the formation of keto complexes. Formation of aldehydes as a product is possible with decarboxylation and synchronous C-C cleavage accompanied by an induced electron transfer to the Co (III) in the complex and one electron transfer to the oxidant. The contest between the two mechanisms became interesting and produced definite results when mild oxidizing agents like QDC were kinetically followed.

EXPERIMENTAL

Quinolinium dichromate was prepared in the laboratory according to the procedure followed by Balasubramanian et al.[17] The alpha-hydroxy acids (A.R) employed as ligands were purchased from Sigma-Aldrich and used as such. Acetic acid was purified and conductivity water was prepared by following the standard procedure.

The monomeric cobalt (III) complexes of alpha-hydroxy acids were prepared as their perchlorates using the method of Fau and Gould[18]. Kinetic measurements of the oxidation of monomeric cobalt (III) complexes of alpha-hydroxy acids and unbound ligands were carried out under pseudo first order conditions in 70% acetic acid at 35 ± 2°C by following the concentration of QDC at 440 nm with the help of an UV-visible spectrophotometer. All the solutions for the experiments were maintained at the specified temperature in an electrically operated thermostated bath. Perchloric acid was used as the source of H^+ ions and ionic strength was maintained by $NaClO_4$. The change in absorbance observed at 440 nm for QDC corresponds to nearly 100% of the initial concentration of the reagent.

Product analysis had been carried out under kinetic conditions and the products were analyzed after the completion of 9 half life periods. The reaction mixture was diluted with water and the organic products were separated by extraction with diethyl ether. The carbonyl compounds were converted into their phenyl hydrazone derivatives and estimated. The other products namely the keto complexes of Co (III) and Co (II) were estimated according to the methods reported in the literature[19].

Stoichiometric studies for the oxidation of pentaammine cobalt (III) complexes of alpha-hydroxy acids and unbound ligands by QDC were carried out with the oxidant in excess. The $[H^+]$ and ionic strength were maintained as such in the corresponding rate measurements. After nine half lives when the reaction was nearing completion the concentration of unreacted QDC was determined spectrophotometrically. The difference in the concentration of the oxidant [QDC] was measured and then the stoichiometry was calculated from the ratio between reacted [oxidant] and [substrate]. The amount of cobalt (III) reduced was also calculated from the decrease in the absorbance measured for the Co (III) complex (Table 1).

RESULTS AND DISCUSSION

The kinetic data for the oxidation of alpha-hydroxy acids and their complexes by QDC in presence of perchloric acid is summarized in the Table 2. The reaction, catalysed by perchloric acid, shows a total second order dependence on the substrates and the oxidant. Among the alpha-hydroxy acids, there was a smaller difference in the rate of the reaction between lactic and glycolic acids, which was not observed with other chromium halochromates. An explanation for the higher reactivity of lactic acid involving C-H cleavage was given based on the higher acidity of C-H proton. In the present investigation, the absence of such an observation leads to C-C cleavage. The product analysis confirmed the formation of aldehydes due to C-C cleavage and not keto acids as a product. QDC undergoes two electron transfer and the overall reaction between QDC and alpha-hydroxy acid could be written as:

$$\begin{array}{l} \mathrm{ArCH(OH)COOH} \\ \quad + \\ \mathrm{Q^{+}H^{-}OCrO_2OCrO_2O^{-}H^{+}Q} \end{array} \rightarrow \mathrm{Ar\text{-}CHO + HOCrO\text{-}O^{-}H^{+}\,Q + HOCrO_2OH^{+}Q + H_2O + CO_2} \qquad \ldots(1)$$

The rate equation for this reaction could be deduced as –

$$\text{Rate} = K\ [\text{alpha-hydroxy acid}]\ [\text{QDC}] \qquad \ldots(2)$$

The kinetic data for the oxidation of the pentaamminecobalt (III) complexes by QDC in presence of acid catalyst is given in the Table 2. The behaviour of the complexes were similar to the unbound ligands and the reaction showed a total second order dependence on them and the reagent. The trend observed in the rate of oxidation among the complexes was very similar to that of the unbound ligands. But the rate of oxidation of complexes were found to be higher than the corresponding free ligands showing that the oxidation was facilitated by complexation. Further the absence of keto complexes in the product and formation of aldehydes as the only organic product confirm the C-C cleavage. The reduction of Co (III) to Co (II) to an extent of 98% showed an induced electron transfer from the ligand to the metal due to decarboxylation and synchronous cleavage of the C-C bond in the complexes. QDC undergoes a one electron change and the overall reaction between QDC and the complexes could be written as:

$$\begin{array}{l} [\mathrm{ArCH(OH)COO - Co^{III}}] \\ \quad + \\ \mathrm{Q^{+}H^{-}OCrO_2OCrO_2O^{-}H^{+}Q} \end{array} \rightarrow \mathrm{Ar{-}CHO + Cr^{V} + Co^{II} + CO_2} \qquad \ldots(3)$$

The rate equation for the oxidation could be deduced as:

$$\text{Rate} = K\ [\mathrm{Co^{III}} - \text{Complex}]\ [\text{QDC}] \qquad \ldots(4)$$

Table 1: Stoichimetric data for the oxidation of alpha-hydroxyl acids and their pentaammine cobalt (III) complexes by quinolinium dichromate [QDC]

[$HClO_4$] = 1.00 mol dm^{-3} Temperature = 35 ± 0.2°C

10^3[Compound] mol dm^{-3}	**10^2 [QDC] mol dm^{-3} initial**	**10^2 [QDC] mol dm^{-3} Final**	**▲10^3 [QDC] mol dm^{-3}**	**10^4 [C_o^{11}] mol dm^{-3} %**	**[Compound] ▲[QDC]**
Mandelic acid					
1	1	0.928	0.720	-	1.0 : 0.72
2	2	1.852	1.480	-	1.0 : 0.74
4	2	1.712	2.880	-	1.0 : 0.72
Lactic acid					
1	1	0.932	0.680	-	1.0 : 0.68
2	2	1.968	1.320	-	1.0 : 0.66
4	2	1.736	2.640	-	1.0 : 0.66
Glycolic acid					
1	1	0.937	0.630	-	1.0 : 0.63
2	2	1.872	1.280	-	1.0 : 0.64
4	2	1.740	2.600	-	1.0 : 0.65

Cont…

10^3[Compound] mol dm^{-3}	10^2 [QDC] mol dm^{-3} initial	10^2 [QDC] mol dm^{-3} Final	▲10^3 [QDC] mol dm^{-3}	10^4 [C_o^{11}] mol dm^{-3} %	[Compound] ▲[QDC]
Co^{III} – Mandelato					
1	1	0.964	0.36	9.8 (98%)	1.0 : 0.36
2	2	1.928	0.72	19.4 (97%)	1.0 : 0.36
4	2	1.856	1.44	19.8 (99%)	1.0 : 0.36
Co^{III} – Lactato					
1	1	0.969	0.31	9.7 (97%)	1.10 : 0.31
2	2	1.942	0.58	18.8 (94)	1.10 : 0.29
4	2	1.884	1.16	19.8(99%)	1.10 : 0.29
Co^{III} –Glycolato					
1	1	0.966	0.34	9.4 (94%)	10 : 0.34
2	2	1.930	0.70	19.4(97%)	10 : 0.35
4	2	1.864	1.36	19.6(98%)	10 : 0.34

Table 2: Kinetic data for the oxidation of pentaammine Co^{III} complexes of alpha-hydroxy acids and unbound ligands by QDC

[$HClO_4$] = 1.00 mol dm^{-3} Temperature = 35 ± 0.2°C

		Rate constant K10^4 S^{-1}					
[QDC] 10^3 mol dm^{-3}	**[Sub] 10^1 mol dm^{-3}**	**Co^{III} – Mandelato**	**Co^{III} – Lactato**	**Co^{III} – Glycalato**	**Mandelic acid**	**Lactic acid**	**Glycolic acid**
1	1	3.4867	2.8117	2.4987	3.1895	2.4669	2.2418
2	1	3.1393	2.3856	2.1137	2.8335	2.1275	1.9316
3	1	2.8335	2.1042	1.8967	2.5469	1.9873	1.7987
4	1	2.6128	1.9267	1.6739	2.1435	1.8812	1.6259
5	1	2.5087	1.8123	1.5143	2.0698	1.6924	1.5134
2	0.4	1.2558	0.9542	0.8453	1.1343	0.8503	0.7762
2	1	3.1393	2.3856	2.1134	2.8335	2.1275	1.9316
2	2	6.3018	4.7896	4.2268	5.6670	4.2519	3.9132
2	4	12.4963	9.4424	8.5636	11.3349	8.5136	7.7294
2	6	18.9135	14.3136	12.5804	17.0110	12.7554	11.5896
2	8	25.2201	19.1264	16.9072	22.6591	17.0172	15.4493

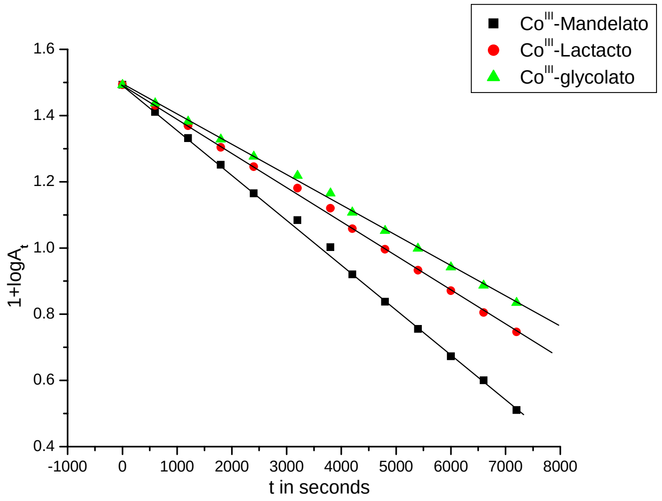


Fig. 1: Oxidation of pentaamminecobalt (III) complexes of alpha-hydroxy acids by quinolinium dichromate. First order dependence of rate on [QDC]

$[Co^{III}] = 1 \times 10^{-1}$ mol dm^{-3} $[QDC] = 2 \times 10^{-3}$ mol dm^{-3}

$[HClO_4] = 5 \times 10^{-2}$ mol dm^{-3} Temp = 35 ± 0.2°C

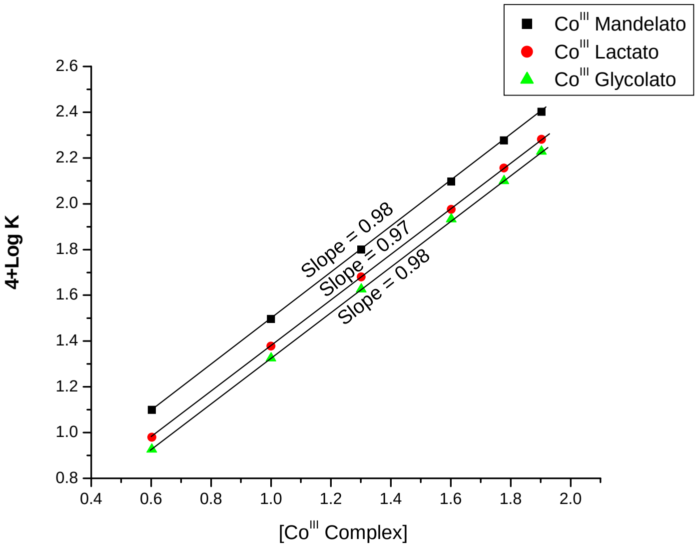


Fig. 2: Dependence of rate on pentaamminecobalt (III) complexes of alpha-hydroxy acids. order plots

$[Co^{III}] = 0.4X10^{-1}$ Mol dm^{-3} to $8X10^{-1}$ Mol dm^{-3} $[QDC] = 2X10^{-3}$ Mol dm^{-3}

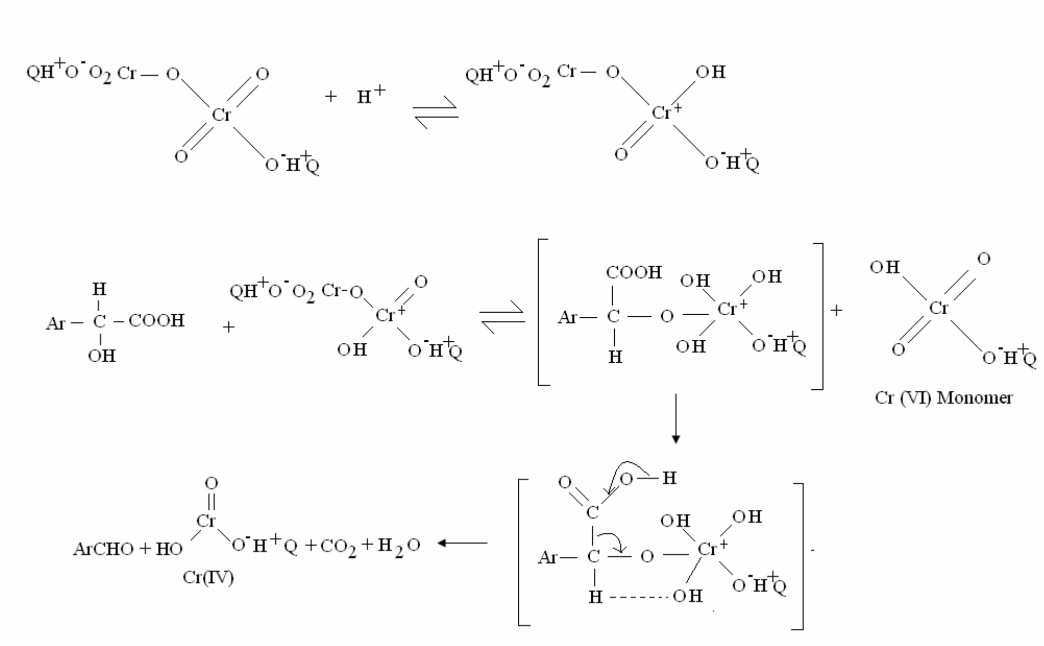
$[HClO_4] = 5X10^{-2}$ Mol dm^{-3} Temp = 35 $\pm$ 0.2°C

MECHANISM

The oxidation of alpha-hydroxy acids and their complexes by QDC in an atmosphere of nitrogen failed to induce the polymerization of acrylonitrile which discounts the possibility of any radical formation. The oxidation of alpha-hydroxy acids and their complexes was catalysed by perchloric acid, which may well be attributed to the protonation of QDC to give a stronger oxidant and electrophile.

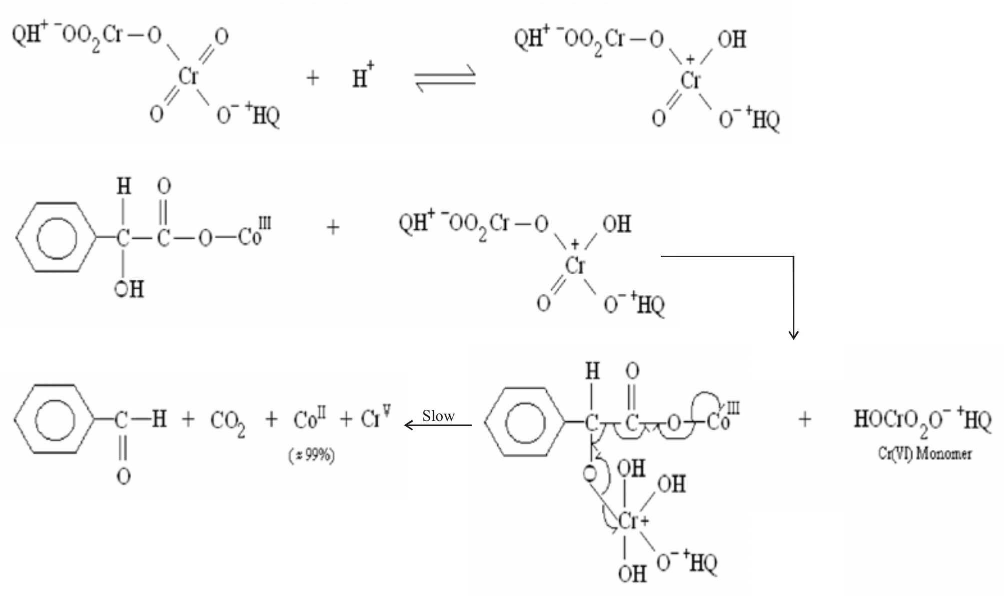
The formation of a protonated Cr (VI) species has been postulated earlier. The kinetic results and absence of keto acids as a product leads to a mechanism involving two electron transfer to Cr (VI) with C-C cleavage and decarboxylation **[Scheme 1]**.

In the oxidation of the complexes, the available evidence point out the absence of two electron transfer to Cr (VI) and C-H cleavage. Hence, a mechanism involving one electron transfer to Cr (VI) and an induced electron transfer to Co (III) by the decarboxylation and synchronous cleavage of C-C was proposed.



Scheme 1

The mechanism for the oxidation of lactato and glycolato complexes will be similar to the mechanism for the oxidation of mandelatopentaammine Co (III) perchlorate.



Scheme 2: One electron transfer with induced one electron transfer to Co^{III}
Q=Quinolinium

REFERENCES

1. I. Nongkynrin, E. Kharpuria, J. C. Dkhar and M. K. Mahanti, Oxid. Commun., **23**, 399 (2000).
2. D. Dey and M. K. Mahant, J. Org. Chem., **55**, 5848 (1990).
3. G. S. Chaubey and M. K. Mahanti, Oxid. Commun., **23**,500 (2000).
4. H. A. A. Medien, Z. Natuforsch, **58**, 1201 (2003).
5. G. S. Chaubey, S. Das and M. K. Mahanti, Oxid. Commun., **26**, 532 (2003).
6. S. Das and M. K. Mahant. Oxid. Commun., **23**, 495 (2000).
7. S. Das, G. S. Chaubey and M. K. Mahant. Oxid. Commun., **26**, 540 (2003).
8. H. Suante and M. K.Mahanti, Oxid. Commun., **27**, 335 (2004).
9. H. Suante and M. K. Mahant, Oxid. Commun., **28**, 910 (2005).
10. K. Aruna and P. Manikyamba, Indian J. Chem., **34A**, 822 (1995).
11. P. Manikyamba and K. Aruna, Ultra Scientists Phys. Sci., **15**, 85 (2003).
12. B. Kuotsu, E. Tiewsoh, A. Debroy and M. K. Mahant, J. Org. Chem., **61**, 8875 (1996).
13. R. K. Kulkarni, D. C. Bilehal and S. T. Nandibewoor, Anal. Sci., **20**, 743 (2004).
14. A. A. Chimatadar, S. B. Koujalagi and S. T. Nandibewoor, Oxid. Commun., **27**, 81 (2004).
15. K. Aruna, P. Manikyamba and E. V. Sundaram, Collect. Czech. Chem. Commun., **58**, 1624 (1993).
16. Sabita Patel and B. K. Mishra, Tetrahedron, **63**, 4367 (2007).
17. K. Balasubramanian and V. Pratibha, Indian J. Chem., **25(B)**, 326 (1986).
18. R. R. F. Fau and E. S. Gould, Inorg. Chem., **13**, 2636 (1974).
19. E. S. Gould and H. Taube, J. Am. Chem. Soc., **86**, 1318 (1964).