

Nicotinium dichromate - induced electron transfer in pentaamminecobalt (III) complexes of α -hydroxy acids in micellar medium

A. THAMINUM ANSARI¹ and K. SUBRAMANI²

¹Department of Chemistry, Ganadipathy Tulsi's Jain Engineering College, Vellore - 632 102 (India)

²PG and Research Department of Chemistry, Islamiah College, Vaniyambadi - 635 752 (India)

(Received: March 13, 2008; Accepted: April 29, 2008)

ABSTRACT

Nicotinium dichromate (NDC) oxidation of pentaamminecobalt (III) complexes of α -hydroxy acids in micellar medium yielding nearly 100% of keto acid complex is ultimate product. The decrease in UV-Visible absorbance at 502 nm for Co(III) complex corresponds to nearly 0% reduction of the initial absorbance. The stoichiometry of unbound ligand and cobalt(III) complex is accounting for no reduction at the cobalt(III) centre. The kinetic and stoichiometric results have been accounted by a suitable mechanism.

Key words: Pentaamminecobalt(III) complexes, Induced electron transfer reaction, Triol, Complex formation

INTRODUCTION

The kinetics and mechanism of diphenyl sulphide, Methyl phenyl sulphides and α -hydroxy acids in presence of perchloric acid medium by Nicotinium dichromate (NDC) have been studied^{1, 2}. Since induced electron transfer in pentaamminecobalt (III) complexes of α -hydroxy acids has been also reported³⁻⁷ and there were some inconsistencies and the work was incomplete. The extent of Nicotinium dichromate (NDC) oxidation of pentaamminecobalt(III) complexes of α -hydroxy acids as a oxidisable hydroxyl group is separated from carboxyl bound to Co(III) centre by a saturated fragment namely C-C bond⁸. The cation radical formed due to the oxidation of hydroxyl group by NDC should in nearly synchronous fashion transfer electron resulting in a C-C and O-H bonds fission and reduction at cobalt(III) centre.

RESULTS AND DISCUSSION

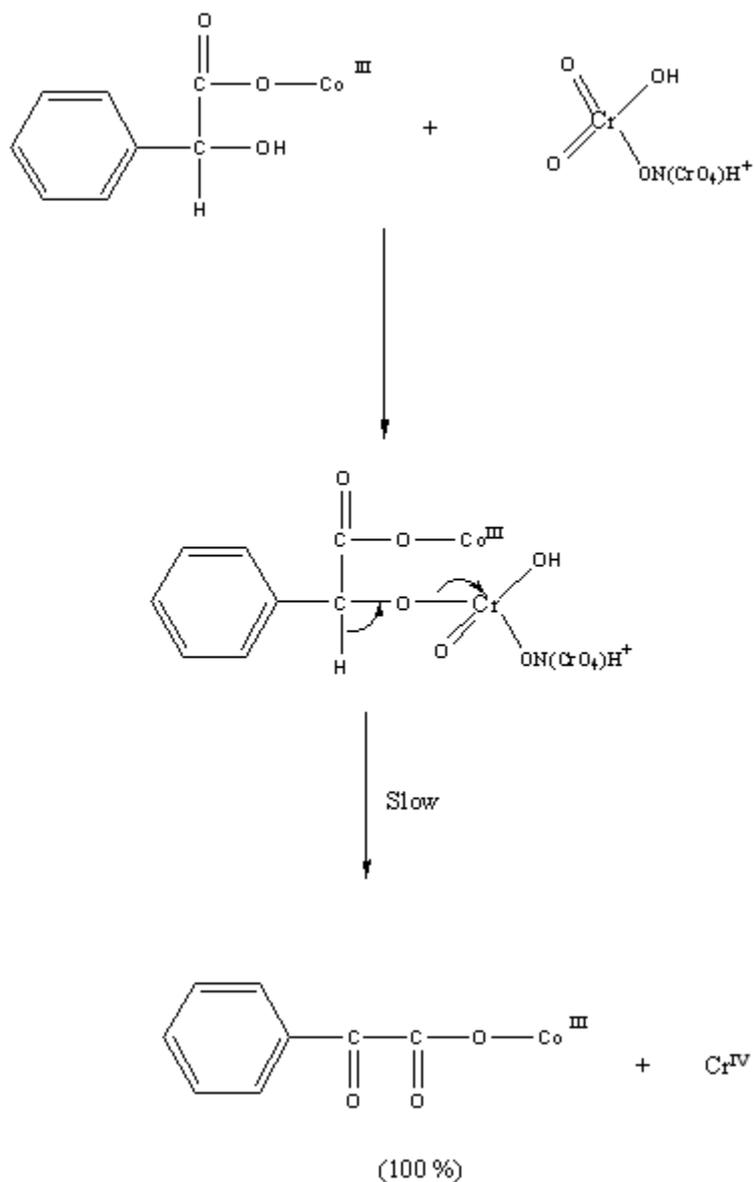
Table 1 summarizes the kinetic data for the NDC oxidation of free α -hydroxy acids with 1N H₂SO₄ in presence of anionic and cationic micelles at 35 ± 0.2°C. Though the reaction exhibits total second-order dependence on [Cobalt(II)] as well as [α -hydroxy acids]. Oxidation of NDC with α -hydroxy acids the following rate law has been deduced for this reaction.

$$\text{rate} = k [\alpha\text{-hydroxy acid}][\text{NDC}]$$

Table 2 lists the formation constants for NDC-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 NDC and Co (III) complexes of α -hydroxy acids exhibit uncomplicated second order kinetics.

From a comparison of the specific rates for NDC 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 because 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 BPC oxidation of the $\text{Co}_2^{(III)}$ keto acid complex as

the two Co (III) centres can exert greater electrostatic influence over the reacting centre. This suggests that NDC 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 NaLS and CTAB. A plot of specific rate constant versus micellar concentration is sigmoidal in shape the catalytic effect is more in CTAB than NaLS.



Scheme 1

Table 1: First order rate constants for NDC oxidation of α -hydroxy at $35 \pm 0.2^\circ\text{C}$

$10^2[\alpha\text{-hydroxy acids}]$ mol dm^{-3}	$10^4K_1(\text{S}^{-1})$ NaLS	10^2K_2dm^3 $\text{mol}^{-1}\text{s}^{-1}$ NaLS	$10^4K_1(\text{S}^{-1})$ CTAB	10^2K_2dm^3 $\text{mol}^{-1}\text{s}^{-1}$ CTAB
Mandelic acid				
1.00	2.71	2.71	3.13	3.13
1.50	4.07	2.72	4.62	3.08
2.00	5.37	2.68	6.21	3.01
2.50	6.32	2.73	7.82	3.12
3.00	8.12	2.71	9.18	3.15
Lactic acid				
1.00	3.24	3.24	3.91	3.24
1.50	4.89	3.26	5.85	3.26
2.00	6.54	3.27	7.82	3.27
2.50	7.12	3.25	9.52	3.25
3.00	9.76	3.26	11.95	3.28
Glycolic acid				
1.00	2.20	2.20	2.66	2.66
1.50	4.43	2.21	3.95	2.63
2.00	5.58	2.23	5.12	2.56
2.50	6.70	2.24	6.52	2.60
3.00	8.68	2.25	7.68	2.65

NDC = 2.00×10^{-3} mol dm⁻³ M, H₂SO₄ = 1N, NaLS = 2.00×10^{-3} mol dm⁻³ CTAB = 2.00×10^{-3} mol dm⁻³ Temperature = $35 \pm 0.2^\circ\text{C}$

Table 2: First order rate constants for NDC oxidation of α -hydroxy at $35 \pm 0.2^\circ\text{C}$

$10^2[(\text{HN}_3)_5 \text{Co}^{\text{III}}\text{-L}]$ mol dm^{-3}	$10^4K_1(\text{S}^{-1})$ NaLS	10^2K_2dm^3 $\text{mol}^{-1}\text{s}^{-1}$ NaLS	$10^4K_1(\text{S}^{-1})$ CTAB	10^2K_2dm^3 $\text{mol}^{-1}\text{s}^{-1}$ CTAB
L=Mandelato				
1.00	4.20	4.20	7.10	7.01
1.50	6.31	4.21	10.49	6.99
2.00	8.36	4.18	14.30	7.14
2.50	10.07	4.02	21.10	7.03
3.00	12.21	4.07	23.60	7.10
L-Lactato				
1.00	4.59	4.59	7.89	7.89
1.50	6.94	4.62	15.90	7.95
2.00	9.24	4.63	19.40	7.76
3.00	11.68	3.89	23.40	7.08
L=Glycolato				
1.00	3.82	3.82	6.60	6.60
1.50	7.61	3.80	9.30	6.20
2.00	9.75	3.90	12.60	6.30
3.00	11.42	3.81	15.70	6.28

NDC = 2.00×10^{-3} mol dm⁻³ M, H₂SO₄ = 1N, NaLS = 2.00×10^{-3} mol dm⁻³ CTAB = 2.00×10^{-3} mol dm⁻³

The specific rate of the lactato complex is more when compared to both the rate of oxidation of unbound ligand and mandelato complex is due to the ligation of lactic acid to cobalt(III) centre has probably increased its reactivity towards NDC and this effect seems to be more specific for this ligands only. In the NMR spectrum of lactate complex the μ -methine proton has undergone considerable downfield shift compared to the α -C-H proton of the unbound ligand [δ C-H = 1.73 ppm in lactic acid and δ C-H = 2.30 ppm in lactate complex whereas δ C-H = 4.75 ppm in mandelic acids and δ C-H = 3.85 ppm in the respective complex]. Suggesting an increase in acidic nature of methine proton of lactic acids due to ligation to metal centre. If the reaction proceeds through a performed chromate ester, then the rate of α -C-H will be enhanced, resulting in an increased rate of oxidation

of lactate complex such a precursor complex may be sterically hindered in the case of mandelato complex.

The stoichiometric results indicate that for one mole of Cobalt (III) complex and α -hydroxy acids, about 0.92 mole of NDC is consumed. In the case of cobalt(III) bound α -hydroxy acids complexes, respective keto acid cobalt(III) is formed whereas α -hydroxy acids, respective keto acid is formed as the end product. Table 3-4, the stoichiometric results coupled with kinetic data and product analysis, can be accounted for by the following reaction scheme. Scheme proposes that NDC oxidizes OH center of the cobalt (III) bound μ -hydroxy acids at a rate comparable to that of the unbound ligand and there is no reduction at the cobalt(III) centre, forms a chromate ester with

Table 3: Stoichiometric data for NDC oxidation of Co(II) bound and unbound α -hydroxy acids in presence of NaLS at 35 \pm 0.2 $^{\circ}$ C

10^3 [Compound] mol dm $^{-3}$	10^2 [NDC] $_{\text{initial}}$ mol dm $^{-3}$	10^2 [NDC] $_{\text{final}}$ mol dm $^{-3}$	$\Delta 10^3$ [NDC] mol dm $^{-3}$	[Compound Δ [NDC]
Mandelic acid				
1.0	1.00	0.912	0.880	1.00:0.88
1.5	1.00	0.865	1.350	1.00:0.90
2.0	1.50	1.410	0.900	1.00:0.92
Lactic acid				
1.0	1.00	0.913	0.870	1.00:0.87
1.5	1.00	0.873	1.270	1.00:0.54
2.0	1.50	1.910	0.850	1.00:0.85
Glycolic acid				
1.0	1.00	0.912	0.880	1.00:0.88
1.5	1.50	0.866	1.340	1.00:0.89
2.0	1.50	1.400	0.990	1.00:0.99
Co(III)-Mandelato				
1.0	1.00	0.911	0.890	1.00:0.98
2.0	1.00	0.823	1.770	1.00:0.88
3.0	1.00	2.910	0.890	1:0.89
Co(III)-Lactato				
1.0	1.00	0.970	0.893	1.00:0.89
2.0	1.00	1.950	1.680	1.00:0.84
3.0	1.00	1.910	2.670	1.00:0.89
Co(III)-Gylacalato				
1.0	1.00	0.821	0.790	1.00:0.79
2.0	1.00	0.804	1.960	1.00:0.98
3.0	1.00	0.704	2.960	1.00:0.99

[H $_2$ SO $_4$] = 1.00 mol dm $^{-3}$, [NaLS] = 2.00 \times 10 $^{-3}$, Temperature = 35 \pm 0.2 $^{\circ}$ C

cobalt(III) glyoxalato complex which can decompose in a slow step, proceeds through C-H bond fission leading to the formation of the keto acid complex and Cr(IV). As 1 mole of glyoxalato(III) complex consumes 0.92 mol of NDC yielding nearly 100% of keto acid cobalt(III) complex.

EXPERIMENTAL

Nicotinium dichromate (NDC) (Nicotinic acid (7.38g) was added to CrO_3 (12g) dissolved in 12 mL water with stirring added acetone (100 mL)-British Drug house, Analar Grade) and α -hydroxy acids employed as ligands Aldrich Products) were used as obtained.

The mono meric cobalt(III) complexes of lactic, mandelic, and glycolic acids were prepared as their perchlorates by the method of Fan and Gould.⁹ The tris (μ -hydroxo) complex $(\text{NH}_3)_3 \text{Co}(\text{OH})_3$ ($\text{Co}(\text{NH}_3)_3(\text{ClO}_4)_3$ (trio) has been prepared by the procedure of Siebert and Co workers.^{10,11}

The reaction between NDC and Co(III) complexes of α -hydroxy acids and unbound ligands in presence of micelles were carried out at $35^\circ\text{C} \pm 0.2^\circ\text{C}$ in an electrically operated thermostated bath. The concentrations of unreacted NDC was determined both iodometrically and spectrophotometrically. The disappearance of Co(III) was followed spectrophotometrically by following

Table 4: Stoichiometric data for NDC oxidation of Co(II) bound and unbound α -hydroxy acids in presence of CTAB at $35 \pm 0.2^\circ\text{C}$

$10^3[\text{Compound}]$ mol dm^{-3}	$10^2[\text{NDC}]_{\text{initial}}$ mol dm^{-3}	$10^2[\text{NDC}]_{\text{final}}$ mol dm^{-3}	$\Delta 10^3[\text{NDC}]$ mol dm^{-3}	[Compound $\Delta[\text{NDC}]$
Mandelic acid				
1.0	1.00	0.914	0.882	1.00:0.88
1.5	1.00	0.867	1.340	1.00:0.89
2.0	1.50	1.400	0.990	1.00:0.99
Lactic acid				
1.0	1.00	0.913	0.875	1.00:0.87
1.5	1.00	0.876	1.280	1.00:0.04
2.0	1.50	1.910	0.855	1.00:0.85
Glycolic acid				
1.0	1.00	0.915	0.885	1.00:0.98
1.5	1.00	0.865	1.350	1.00:0.90
2.0	1.50	1.410	0.900	1.00:0.90
Co(III)-Mandelato				
1.0	1.00	0.911	0.893	1.00:0.89
2.0	1.00	0.932	1.680	1.00:0.84
3.0	1.00	0.733	2.670	1.00:0.89
Co(III)-Lactato				
1.0	1.00	0.921	0.790	1.00:0.79
2.0	1.00	0.811	1.820	1.00:0.91
3.0	1.00	0.704	2.960	1.00:0.98
Co(III)-Gylacalato				
1.0	1.00	0.911	0.890	1.00:0.89
2.0	1.00	0.823	1.770	1.00:0.88
3.0	1.00	0.738	2.620	1.00:0.87

$[\text{H}_2\text{SO}_4] = 1.00 \text{ mol dm}^{-3}$, $[\text{CTAB}] = 2.00 \times 10^{-3}$, Temperature = $35 \pm 0.2^\circ\text{C}$

the decrease in absorbance at 502 nm. (for the monomeric Co (III) complex). Ionic strength was maintained by addition of suitable quantities of HClO_4 and NaClO_4 . The specific rates estimated from the optical density measurements agree with the values from the volumetric procedure with in $\pm 7\%$ curiously, the change in absorbance observed at 502 nm, Co (III) complexes of ∞ - hydroxy acids correspond to very nearly 0 % reduction of the initial concentration of Co (III), while the change in optical density at 502 nm for NDC corresponds to decrease of 1.00 : 0.22 of $[\text{Co (III)}]_{\text{initial}}$.

Co (II) was estimated after the completion of reaction, by diluting the reaction mixture 10- fold with concentrated HCl, allowing evolution of chlorine to cease, and then measuring the absorbance of blue chloro complex of Co(II) at 692 nm ($E=560 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)¹². The amount of Co (II) estimated in all these cases corresponds to nearly 0 % of $[\text{Co (II)}]_{\text{initial}}$.

After 48h, the product was extracted with diethyl ether and analyzed iodoimetrically, there is no carbonyl products. It was determined by measuring absorbance at 250 nm [$E = 11,400 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$].¹³ In all cases the keto acid/ keto acid cobalt(III) complex formed Table 3-4.

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 keto acid and the estimation of keto acid cobalt(III) complex were nearly quantitative. In both the cases the IR spectra of the product agreed with IR spectra of authentic samples of keto acid/keto acid cobalt (III) complex.

REFERENCES

- Chidambaram, V. *Ph.D. thesis*, Annamali University (1997).
- Anbuselvan, C., *Ph.D. thesis*, Annamalai University (1999).
- Srinivasan, V.S and Gould, E.S., *Inorg. Chem.*, **20**: 208 (1981).
- Srinivasan, V.S., *Inorg. Chem.*, **21**: 4328 (1982).
- Kalidoss, P and V.S. Srinivasan, V.S., *J. Chem. Soc., Dalton trans.*, 2831 (1984).
- Kalidoss, P and Srinivasan, V.S., *Indian Journal of Chem.*, **26A**: 924-929 (1987).
- Kalidoss, P and V.S. Srinivasan, V.S., *Indian Journal of Chem.*, **26A**: 211-214 (1987).
- Kalyan Kalisen Gupta, Amalendu Banergee and Hrishikesh Chatterjee, *Tetrahedron*, **48**, 25, 30, 5323 (1992).
- Fan, R.R.F and Gould, E.S., *Inorg. Chem.* **13**: 2639 (1974).
- Srinivasan, V.S., Singh, A.N., Wieghardt, K., Rajasekar, N., and Gould, E.S., *Inorg. Chem.*, **21**: 2531(1982).
- Siebert, H., and Anorg, Z., *Allg. Chem.* **47**: 441 (1978).
- Gould, E.S., and H. Taube, H., *Journal of Am. Chem. Soc.*, **86**: 1318 (1964).
- Dyer, J.R., applications of absorption spectroscopy of organic compounds, printice Hall, Engle wood Cliffs, 18 (1965).
- Streitwiser, Jr., A. and Heath cock, C.H., Introduction to organic chemistry, Macmillan, New York, 596 (1973).