



STUDIES ON KINETICS AND MECHANISM OF THE OXIDATION OF COBALT(III) BOUND AND UNBOUND α -HYDROXY ACIDS BY 4-(DIMETHYLAMINO) PYRIDINIUM CHLOROCHROMATE

**KANNAN POWNSAMY^{*}, SAROJINI GOPALAKRISHNAN^a and
BEZUAYEHU BEFEKADU**

Department of Chemistry, College of Natural and Computational Sciences, Dilla University,
P. O. Box 419, DILLA, ETHIOPIA

^aDepartment of Chemical (Thermal) Engineering, College of Engineering and Technology,
Dilla University, P. O. Box 419, DILLA, ETHIOPIA

ABSTRACT

A variety of Chromium(VI) complexes have been prepared and tested to be effective oxidants, 4-(dimethylamino)pyridinium chlorochromate is one of them. The kinetics of 4-(dimethylamino)pyridinium chlorochromate (DMAPCC) oxidation reaction with cobalt (III) bound and unbound α -hydroxy acids have been studied in $0.10 \text{ mol dm}^{-3} \text{ HClO}_4$ at $30 \pm 0.2^\circ\text{C}$. From the kinetic and stoichiometric results with product analyses a suitable mechanism has been proposed.

Key words: DMAPCC, Cobalt (III) bound α -hydroxy acids, Oxidation, Kinetics.

INTRODUCTION

In recent years, a variety of chromium(VI) complexes have been prepared and tested to be effective oxidants. Potassium dichromate is a standard oxidizing agent in chemical analysis and chromium trioxide is a common reagent for the oxidation of organic compounds. Later on mechanistic interest in chromium(VI) oxidants began with the inception of chemical kinetics as a tool for these studies. As a result of the pioneering work in this field by Westheimer and his collaborations¹ and many of the investigations which followed, the details of mechanisms of these reactions are in many cases fairly well understood. Review of such chromium(VI) and oxidations are well documented in literature²⁻⁴.

* Author for correspondence; E-mail: apkannan03@yahoo.co.in

DMAPCC is one of the chromium(VI) complex. It is a mild selective reagent for the oxidation of organic compounds⁵⁻⁷. Hydroxy acids can be oxidized, either like alcohols⁸ yielding corresponding oxoacids, or may undergo oxidative decarboxylation to yield a ketone⁹. In continuation of earlier work on the oxidation of cobalt(III) bound and unbound α -hydroxy acids by Mn(VII)¹⁰, vanadium(V)¹¹ and another chromium(VI)¹². In this present study, first DMAPCC has been used as an time oxidant for the oxidation of cobalt(III) bound and unbound α -hydroxy acids. From the kinetic and stoichiometric results with product analyses a suitable mechanism has been proposed.

EXPERIMENTAL

The materials, kinetic method and product analysis for this study are as follows.

Materials

The α -hydroxy acids were of reagent grade [BDH] and were used after checking their physical constants. The cobalt(III) complexes of mandelic acid, lactic acid and glycolic acids were prepared by the method of Fan and Gould¹³. DMAPCC was prepared by the reported literature method⁵. All other chemicals used were of analytical grade.

Kinetics

The reactions were carried out at $30 \pm 0.2^\circ\text{C}$. Under pseudo-first order conditions by maintaining a large excess of the cobalt(III) complex over DMAPCC in 100% aqueous medium. The reactions were followed upto 90% completion and the unreacted DMAPCC estimated by iodometric procedure periodically.

Product analysis

The product analysis was carried out under kinetic conditions. The amount of one of the expected product cobalt(II) was estimated after nine-half-lives. 2.5 cm^3 of the reaction mixture was diluted to 25 cm^3 with concentrated HCl, allowing the evolution of chlorine to cease and then measuring the absorbance for the cobalt(II) chloro complex at 692 nm ($\epsilon = 560 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$)¹⁴. The amount of cobalt(II) formed was negligibly small.

The other products such as phenylglyoxylic acid and phenylglyoxylato cobalt(III) complex were analyzed as follows. In a typical experiment, the reaction mixture was allowed to stand in dark for 24 hours to ensure completion of the reaction. Most of the solvent was removed by distillation under reduced pressure. The residue was then treated with an excess of a freshly prepared saturated solution of 2,4-dinitrophenylhydrazine in HCl (1 mol dm^{-3})

and kept overnight in a refrigerator. The precipitated 2,4-dinitrophenylhydrazone was filtered off, dried, weighed, recrystallized from ethanol and reweighed. The product was identical to an authentic sample of the DNP of phenylglyoxylic acid. By similar analysis, and with the reaction mixture obtained from the DMAPCC-cobalt(III) mandelato complex, reaction yielded the phenylglyoxylato cobalt (III) complex. The IR spectrum of the product of mandelato complex with DMAPCC was recorded and it is identical to an authentic compound of Co^{III} -phenylglyoxylato complex.

The stoichiometric studies of oxidation of pentaammine cobalt(III) complexes of α -hydroxy acids and unbound ligands by DMAPCC were carried out with the oxidant in excess. The unreacted concentration of Cr(VI) was determined by iodometrically. The $[\text{H}^+]$ and ionic strength was maintained as in the corresponding rate measurements. The temperature was maintained at $30 \pm 0.2^\circ\text{C}$. The results are summarized in Table 1.

Table 1: Stoichiometric data for DMAPCC oxidation of Co^{III} bound and unbound α -hydroxy acids

$10^4[\text{compound}]$ (mol dm^{-3})	$10^3[\text{DMAPCC}]_{\text{initial}}$ (mol dm^{-3})	$10^4[\text{DMAPCC}]_{\text{final}}$ (mol dm^{-3})	$\Delta 10^4[\text{DMAPCC}]$ (mol dm^{-3})	[Compound]: Δ [DMAPCC]
Co^{III}-Mandelato				
1.00	1.00	0.880	1.20	1.00:1.20
1.50	1.00	0.814	1.86	1.00:1.24
2.00	1.00	0.764	2.36	1.00:1.18
2.50	1.00	0.695	3.05	1.00:1.12
Co^{III}-Lactato				
1.00	1.00	0.882	1.18	1.00:1.18
1.50	1.00	0.812	1.87	1.00:1.25
2.00	1.00	0.752	2.48	1.00:1.24
2.50	1.00	0.700	3.00	1.00:1.20
Co^{III}-Glycolato				
1.00	1.00	0.878	1.22	1.00:1.22
1.50	1.00	0.820	1.80	1.00:1.20
2.00	1.00	0.764	2.36	1.00:1.18
2.50	1.00	0.697	3.02	1.00:1.21

Cont...

10^4 [compound] (mol dm ⁻³)	10^3 [DMAPCC] _{initial} (mol dm ⁻³)	10^4 [DMAPCC] _{final} (mol dm ⁻³)	$\Delta 10^4$ [DMAPCC] (mol dm ⁻³)	[Compound]: Δ [DMAPCC]
Mandelic acid				
1.00	1.00	0.909	0.910	1.00:0.91
1.50	1.00	0.857	1.42	1.00:0.95
2.00	1.00	0.816	1.84	1.00:0.92
2.50	1.00	0.721	2.79	1.00:0.93
Lactic acid				
1.00	1.00	0.890	1.10	1.00:1.10
1.50	1.00	0.838	1.62	1.00:1.08
2.00	1.00	0.776	2.24	1.00:1.12
2.50	1.00	0.722	2.77	1.00:1.11
Glycolic acid				
1.00	1.00	0.883	1.17	1.00:1.17
1.50	1.00	0.830	1.69	1.00:1.13
2.00	1.00	0.770	2.30	1.00:1.15
2.50	1.00	0.705	2.95	1.00:1.18

RESULTS AND DISCUSSION

The kinetics of 4-(dimethylamino)pyridinium chlorochromate (DMAPCC) reaction with cobalt(III) bound and unbound α -hydroxy acids have been studied in 0.10 mol dm⁻³ HClO₄ at 30 \pm 0.2°C.

Dependence of rate on DMAPCC concentration

In a typical experiment between DMAPCC and pentaamminecobalt(III) complexes of mandelic, lactic and glycolic acids, the specific rates calculated using integrated first order rate equation from the change in the concentration of DMAPCC are the same, indicating that the order with respect to DMAPCC is one. When increasing the concentration of DMAPCC from 1.00 x 10⁻³ mol dm⁻³ to 4.00 x 10⁻³ mol dm⁻³, the specific rates are nearly the same, the rate of the reaction depends upon the first power of [DMAPCC] (Table 2).

Under identical conditions, DMAPCC oxidation of unbound mandelic, lactic and glycolic acids have been studied to look into the consequence of ligation with cobalt(III) center. In any specific run, from the rate of disappearance of DMAPCC, the specific rates calculated using integrated first order rate equation are constant (Table 3). Also the plot of

logarithm of DMAPCC concentration versus time are linear and from the slopes of these plots specific rates calculated are agree with those calculated from integrated rate equation. This indicate first order dependence on DMAPCC oxidation of unbound α -hydroxy acids when the concentration of DMAPCC is varied from $1.00 \times 10^{-3} \text{ mol dm}^{-3}$ at a fixed $[\alpha\text{-hydroxy acid}]$ and $[\text{HClO}_4]$, the specific rate remain constant (Table 3) in keeping with the first order dependence on DMAPCC concentration.

Table 2: Kinetic data for the oxidation of $[\text{Co}(\text{NH}_3)_5\text{L}]^{2+}$ complexes by DMAPCC

$10^3[\text{DMAPCC}]$ (mol dm^{-3})	$10^2[(\text{NH}_3)_5\text{Co}^{\text{III}}\text{-L}]$ (mol dm^{-3})	$10^5 k_1$ (s^{-1})	$10^3 k_2$ ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)
L=Mandelato			
1.00	1.00	1.06	--
2.00	1.00	1.11	--
3.00	1.00	1.13	--
4.00	1.00	1.09	--
1.00	1.50	1.61	1.08
1.00	2.00	2.14	1.07
1.00	2.50	2.65	1.06
1.00	3.00	3.23	1.08
1.00	3.50	3.72	1.06
1.00	4.00	4.27	1.07
L=Lactato			
1.00	1.00	2.02	--
2.00	1.00	2.08	--
3.00	1.00	2.12	--
4.00	1.00	2.09	--
1.00	1.50	2.89	1.93
1.00	2.00	3.98	1.99
1.00	2.50	4.96	1.98
1.00	3.00	6.01	2.00
1.00	3.50	7.05	2.01
1.00	4.00	7.96	1.99

Cont...

$10^3[\text{DMAPCC}]$ (mol dm ⁻³)	$10^2[(\text{NH}_3)_5\text{Co}^{\text{III}}\text{-L}]$ (mol dm ⁻³)	$10^5 k_1$ (s ⁻¹)	$10^3 k_2$ (dm ³ mol ⁻¹ s ⁻¹)
L=Glycolato			
1.00	1.00	0.708	--
2.00	1.00	0.728	--
3.00	1.00	0.812	--
4.00	1.00	0.798	--
1.00	1.50	1.07	0.714
1.00	2.00	1.41	0.706
1.00	2.50	1.79	0.716
1.00	3.00	2.08	0.693
1.00	3.50	2.46	0.702
1.00	4.00	2.85	0.712

Table 3: Kinetic data for the oxidation of α -hydroxy acids by DMAPCC

$10^3[\text{DMAPCC}]$ (mol dm ⁻³)	$10^2 [\alpha\text{-Hydroxy acid}]$ (mol dm ⁻³)	$10^4 k_1$ (s ⁻¹)	$10^2 k_2$ (dm ³ mol ⁻¹ s ⁻¹)
Mandelic acid			
1.00	1.00	1.16	--
2.00	1.00	1.42	--
3.00	1.00	1.23	--
4.00	1.00	1.18	--
1.00	1.50	1.76	1.17
1.00	2.00	2.18	1.09
1.00	2.50	2.86	1.14
1.00	3.00	3.33	1.11
1.00	3.50	4.05	1.15
1.00	4.00	4.84	1.21

Cont...

$10^3[\text{DMAPCC}]$ (mol dm^{-3})	$10^2 [\alpha\text{-Hydroxy acid}]$ (mol dm^{-3})	$10^4 k_1$ (s^{-1})	$10^2 k_2$ ($\text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$)
Lactic acid			
1.00	1.00	0.512	--
2.00	1.00	0.502	--
3.00	1.00	0.477	--
4.00	1.00	0.515	--
1.00	1.50	0.771	0.514
1.00	2.00	1.04	0.502
1.00	2.50	1.27	0.511
1.00	3.00	1.57	0.526
1.00	3.50	1.80	0.514
1.00	4.00	2.06	0.517
Glycolic acid			
1.00	1.00	0.623	--
2.00	1.00	0.627	--
3.00	1.00	0.654	--
4.00	1.00	0.634	--
1.00	1.50	0.936	0.624
1.00	2.00	1.23	0.617
1.00	2.50	1.54	0.618
1.00	3.00	1.87	0.623
1.00	3.50	2.18	0.624
1.00	4.00	2.54	0.635

Dependence of rate on the concentration of cobalt(III) bound and unbound α -hydroxy acids

At a particular DMAPCC concentration with increasing mandelato/lactate/glycolatocobalt(III) concentration, there is proportional increase in the rate of oxidation (Table 2). When a plot of graph of logarithm of specific rate versus logarithm of cobalt(III) concentration dependence the slope is equal to 0.97.

Under identical conditions, the effect of changing unbound α -hydroxy acids concentration has been studied with all these substrates. There is a monoatomic increase in the rate of DMAPCC oxidation with unbound α -hydroxy acids with increasing concentration of substrates (Table 3). The rate law for the DMAPCC oxidation of unbound α -hydroxy acid is similar to the observed with cobalt(III) bound ligands.

Effect of increasing HClO_4 concentration

The DMAPCC oxidation of cobalt(III) complexes of α -hydroxy acids is an acid catalyzed reaction and the effect of HClO_4 concentration on the rate of DMAPCC oxidation has been studied in the concentration range from 0.02 mol dm^{-3} to 0.10 mol dm^{-3} at a constant ionic strength (Table 4). With increasing HClO_4 concentration, the rate of DMAPCC oxidation increase proportionally and the plot of logarithm of specific rates versus logarithm of HClO_4 concentration the slope is equal to 0.61.

Oxidation of α -hydroxy acids by DMAPCC is an acid catalyzed reaction and the effect of HClO_4 concentration on the rate of DMAPCC oxidation has been studied in the concentration 0.02 mol dm^{-3} to 0.10 mol dm^{-3} at constant ionic strength (Table 4).

Table 4: Effect of increasing concentration of HClO_4 on the oxidation of cobalt(III) bound and unbound α -hydroxy acids by DMAPCC

$[\text{HClO}_4]$ (mol dm^{-3})	$[\text{NaClO}_4]$ (mol dm^{-3})	$10^5 k_1$ (s^{-1})
L=Mandelato		
0.02	0.08	0.412
0.04	0.06	0.594
0.06	0.04	0.702
0.08	0.02	0.896
0.10	0.00	1.06
L=Lactato		
0.02	0.08	0.724
0.04	0.06	1.20
0.06	0.04	1.37
0.08	0.02	1.81
0.10	0.00	2.02

Cont...

[HClO ₄] (mol dm ⁻³)	[NaClO ₄] (mol dm ⁻³)	10 ⁵ k ₁ (s ⁻¹)
L=Glycolato		
0.02	0.08	0.275
0.04	0.06	0.381
0.06	0.04	0.501
0.08	0.02	0.612
0.10	0.00	0.708
Mandelic acid		
0.02	0.08	4.78
0.04	0.06	6.02
0.06	0.04	7.58
0.08	0.02	9.45
0.10	0.00	11.6
Lactic acid		
0.02	0.08	1.44
0.04	0.06	2.63
0.06	0.04	3.34
0.08	0.02	4.49
0.10	0.00	5.12
Glycolic acid		
0.02	0.08	1.99
0.04	0.06	3.31
0.06	0.04	4.16
0.08	0.02	5.48
0.10	0.00	6.23

Effect of temperature on the reaction rate

The rate of DMAPCC oxidation of cobalt(III) bound and unbound α -hydroxy acids were measured at 303 K to 323 K (Table 5). From the Eyring's plot of $\log k_2/T$ Vs $1/T$, the

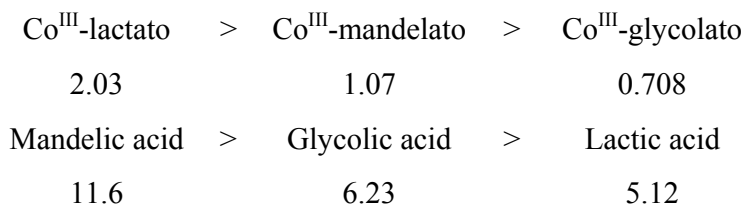
activation parameters are evaluated. The activation parameters (ΔH^\ddagger , ΔS^\ddagger and ΔG^\ddagger) shown in Table 5, clearly confirm the bimolecular nature of the reaction. The negative values of ΔS^\ddagger shown to a transition state that is more ordered than the reactant, as would be expected in a bimolecular reaction.

Table 5: Temperature dependence and activation parameters for the oxidation of Co^{III} bound and unbound α -hydroxy acids by DMAPCC

Substrate	$10^5 k_1$ (s ⁻¹)					ΔH^\ddagger (kJ mol ⁻¹)	ΔS^\ddagger (JK ⁻¹ mol ⁻¹)	ΔG^\ddagger (kJ mol ⁻¹)
	303K	308K	313K	318K	323K			
L-Mandelato	1.06	1.59	2.17	2.91	3.92	49.66	-137.81	92.81
L-Lactato	2.02	2.76	3.81	4.74	6.28	42.99	-154.64	89.88
L-Glycolato	0.708	0.958	1.37	1.89	2.64	51.20	-139.59	93.95
Mandelic acid	11.6	16.2	22.4	31.7	43.5	50.84	-114.39	86.65
Lactic acid	5.12	7.27	10.1	13.3	18.5	49.00	-127.13	88.79
Glycolic acid	6.23	9.45	13.1	18.9	24.7	53.52	-110.46	88.09

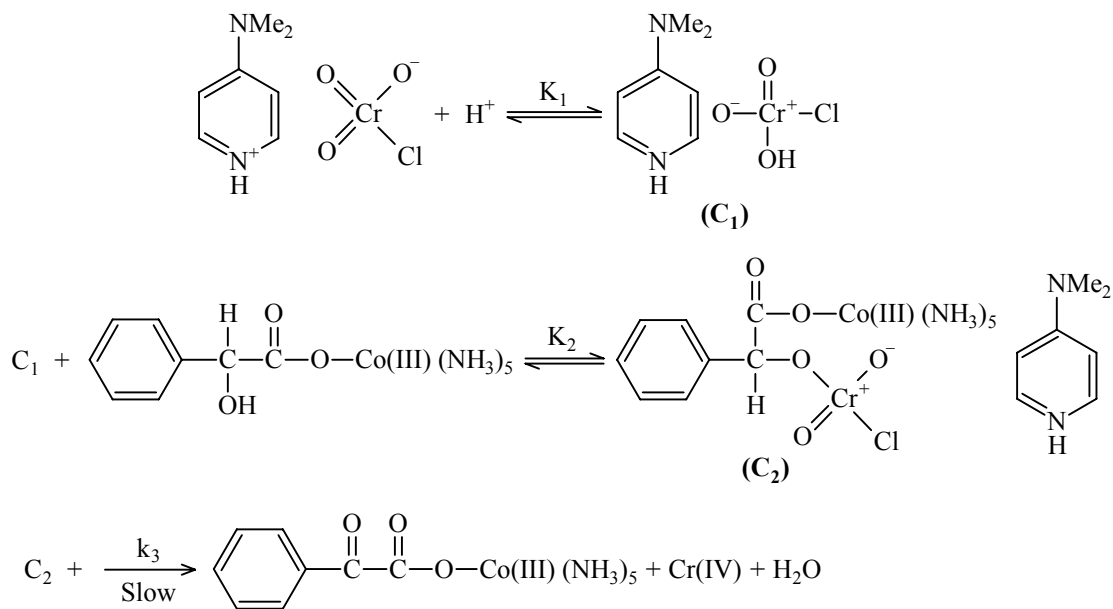
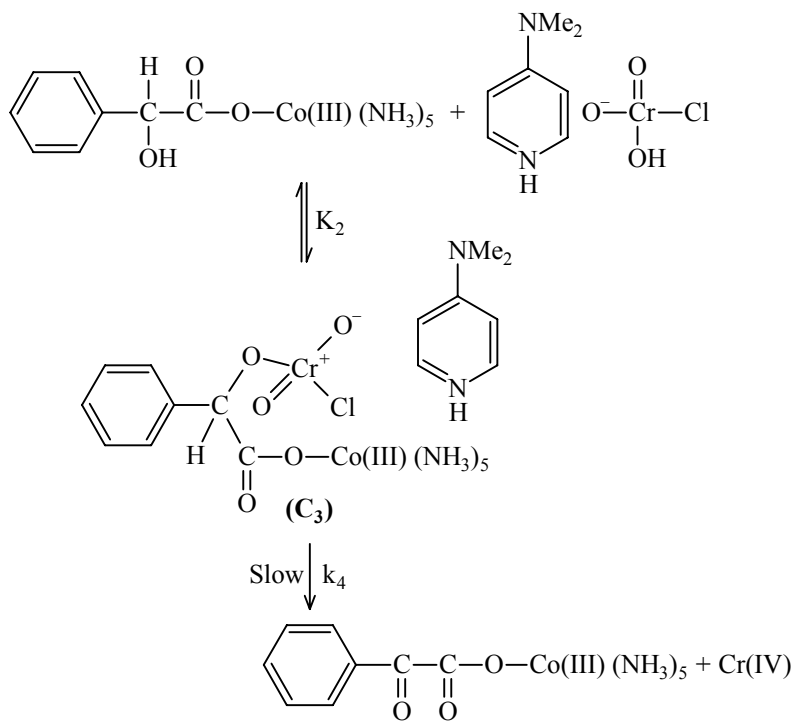
The rate of the oxidation reaction by DMAPCC is not affected by the addition of 4-(dimethylamino)pyridine.

The rate of oxidation of Co(III) bound and unbound α -hydroxy acids by DMAPCC can be summarized as –



The specific rate of the lactate complex is more when compared to other two complexes, deserves an explanation. The ligation of lactic acid to cobalt(III) center has probably increased its reactivity towards DMAPCC and this effect seems to be more specific for this ligand only.

To account for these experimental observations, the following mechanistic Schemes have been proposed.

**Scheme 1: Acid dependent****Scheme 2: Acid independent**

According to both the schemes, first it forms bimolecular complex between protonated species of DMAPCC and mandelatopentaammine cobalt(III) complex, then it gives phenylglyoxylatopentaammine cobalt(III) complex and Cr(IV).

REFERENCES

1. F. H. Westheimer, *Chem. Revs.*, **45**, 419 (1949).
2. R. Stewart, *Oxidation Mechanism, Application to Organic Chemistry*, Benjamin, New York (1964).
3. W. A. Waters, *Mechanism of Oxidation of Organic Compound*, Methuen, London (1964).
4. K. B. Wiberg, *Oxidation in Organic Chemistry, Part A*, Academic Press, New York (1973).
5. F. S. Guziee and F. A. Luzzio, *J. Org. Chem.*, **47**, 1787 (1982).
6. K. Krishnasamy, D. Devanathan and J. Dharmaraja, *Trans. Met. Chem.*, **32(7)**, 922 (2007).
7. G. Rajarajan, N. Jayachandramani, S. Manivarman, J. Jayabharathi and V. Thanikachalam, *Trans. Met. Chem.*, **33(3)**, 393 (2008).
8. K. K. Banarji, *J. Chem. Res(s)*, 193 (1978).
9. P. Levesley and W. A. Waters, *J. Chem. Soc.*, 217 (1995).
10. P. Kannan and K. R. Sankaran, *Trans. Meat. Chem.*, **29**, 757 (2004).
11. K. R. Sankaran and V. S. Srinivasan, *Indian J. Chem.*, **26A**, 1023 (1987).
12. C. Anbuselvan and K. R. Sankaran, *Oxid. Comm.*, **21**, 257 (1998).
13. F. R. Fan and E. S. Gould, *Inorg. Chem.*, **13**, 2639 (1974).
14. E. S. Gould and H. Taube, *J. Am. Chem. Soc.*, **86**, 1318 (1964).

Accepted : 18.03.2015