

Pyridinium chloro chromate – Induced electron transfer in Pentaammine Cobalt (III) complexes of α -hydroxy acids in micellar medium

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Abstract: Pyridinium chloro chromate(PCC) oxidation of pentaamminecobalt (III) complexes of α - hydroxy acids in micellar medium yielding nearly 100% of Co(II), and 100% of carbonyl compounds are ultimate products. The decrease in UV-Visible absorbance at $\lambda = 502$ 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: Pentaamminecobalt(III) complexes, Induced electron transfer reaction, Triol, Complex formation.

Introduction

Pyridinium Chloro Chromate(PCC) is an efficient reagent for oxidation of primary and secondary alcohols to carbonyl compounds. A large class of organic compounds were oxidized by PCC has been reported.¹ Since induced electron transfer in pentaamminecobalt (III) complexes of α - hydroxyl acids with various oxidants have been studied.²⁻⁷ The extent of PCC oxidation of pentaamminecobalt (III) complexes of α - hydroxy acids in micellar medium 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 PCC should in nearly synchronous fashion transfer electron resulting in C- C and O-H bonds fission and reduction at cobalt(III) centre.

Results and Discussion

Table I summarizes the kinetic data for the PPC oxidation of free α - hydroxy acids with 1N H₂SO₄ in presence of anionic and cationic micelles at $35 \pm 0.2^\circ$ C. Though the reaction exhibits total second – order dependence on [Cobalt(II)] as well as [α - hydroxy acids] .

Oxidation of PCC with α - hydroxy acids the following rate law has been deduced for this reaction.

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

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

From a comparison of the specific rates for PCC 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 PCC oxidation of the Co₂^(III) keto acid complex as the two Co (III) centres can exert greater electrostatic influence over the reacting centre. This suggests that PCC 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.

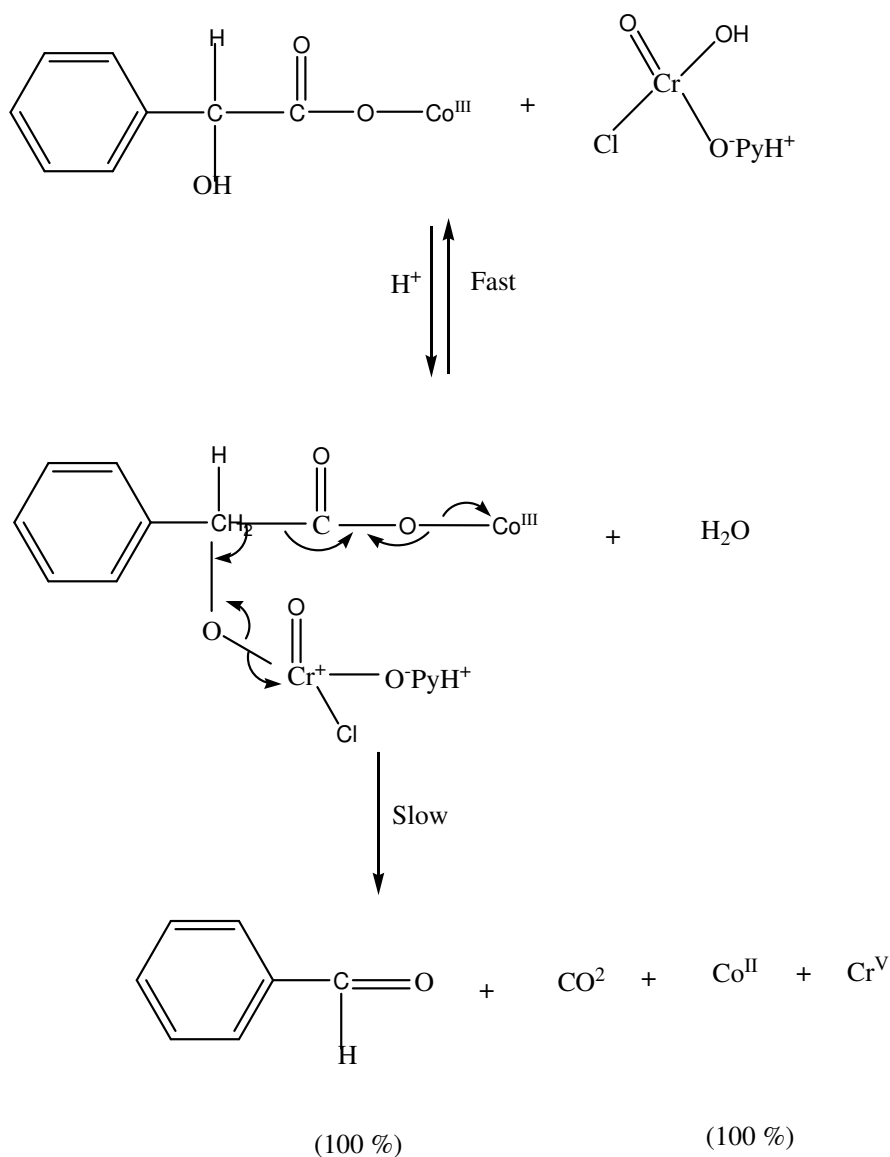
The specific rate of the lactato complex is more when compared to both the rate of oxidation of unbound ligand and mandelato complex is due to the ligation of lactic acid to cobalt(III) centre has probably increased its reactivity towards PCC and this effect seems to be more specific for this ligands only. In the NMR spectrum of lactato complex the α -methine proton has undergone considerable downfield shift compared to the α -C-H proton of the unbound ligand [∂ 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 liagtion 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 and glycolato complexes.

The stoichiometric results indicate that for one mole of Cobalt (III) complex, about 0.92 mole of PCC is consumed, whereas with the unbound ligands for one mole of α - hydroxy acids about 0.65 mole of BPC is consumed. **Table III & IV.** The stoichiometric results coupled with kinetic data and product analysis, can be accounted for by the following reaction scheme.

Scheme proposes that PCC oxidizes OH center of the cobalt (III) bound α - hydroxy acids at a rate 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 cobali(II), carbonyl compounds and carbondioxide. As 1 mole of cobalt(III) glyoxalato complex consumes 0.92 mol of PCC yielding nearly 100 % of Co(II) and 100 % carbonyl compounds. Similarly 1 mole of unbound α - hydroxy acid consumes nearly 0.65 mole of PCC, yielding 100% of carbonyl products and CO₂.

Scheme



Experimental section

Pyridinium chloro chromate, (184 mL of 6 M HCl was added to 100 g of CrO₃ with stirring, cooled and 79.1 g of pyridine was added over 100 min.- 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 (NH₃)₃ Co (OH)₃ (Co (NH₃)₃ (ClO₄)₃ (triol) has been prepared by the procedure of Siebert and Co workers.^{10,11}

The reaction between PCC and Co III complexes of α - hydroxy acids and unbound ligands in presence of micelles were carried out at 35°C \pm 0.2°C in an electrically operated thermostated bath. The concentrations of unreacted BPC was determined both iodometrically. The disappearance of Co (III) was followed spectrophotometrically by following the decrease in absorbance at 502 nm. (for the monomeric Co (III) complex). Ionic strength was maintained by addition of suitable quantities of HClO₄ and NaClO₄. 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 α - hydroxy acids correspond to very nearly 100% of the initial concentration of Co (III), while the change in optical density at 350 nm for PCC corresponds to 100% of [Co (III)]_{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 (ϵ = 560 dm³ mol⁻¹ cm⁻¹).^{12,13} The amount of Co (II) estimated in all these cases corresponds to nearly 100% of [Co (II)]_{initial}.

After 48h, the product was extracted with diethyl ether and analyzed iodoimetrically for the amount of benzaldehyde formed was determined by measuring absorbance at 250 nm [ϵ = 11,400 dm³ mol⁻¹ cm⁻¹].^{14,15} The yield of benzaldehyde in all these cases is nearly 100% [Co (III)]_{initial} **Table III& IV.**

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.

Table –I: First order rate constants for PCC oxidation of α - hydroxy acids at 35 \pm 0.2° C

10 ² [α - hydroxy acids] mol dm ⁻³	10 ⁴ k ₁ (S ⁻¹) NaLS	10 ² k ₂ dm ³ mol ⁻¹ s ⁻¹ NaLS	10 ⁴ k ₁ (S ⁻¹) CTAB	10 ² k ₂ dm ³ mol ⁻¹ s ⁻¹ CTAB
Mandelic acid	1.31	1.31	1.62	1.62
1.00	1.96	1.30	2.37	1.58
1.50	2.59	1.29	3.30	1.65
2.00	3.41	1.36	4.17	1.60
2.50	4.02	1.34	4.82	1.62
3.00				
Lactic acid				
1.00	2.21	2.21	2.39	2.39
1.50	3.32	2.22	3.56	2.37
2.00	4.36	2.18	4.75	2.38
2.50	5.44	2.17	5.97	2.39
3.00	6.72	2.24	7.18	2.39
Glycolic acid				
1.00	1.09	1.09	1.29	1.29
1.50	2.12	1.06	2.51	1.26
2.00	2.73	1.07	3.26	1.30
2.50	3.05	1.09	3.47	1.32
3.00	3.32	1.10	3.92	1.31

PCC = 2.00 x 10⁻³ mol dm⁻³ M, H₂SO₄ = 1N, NaLS = 2.00 x 10⁻³ mol dm⁻³ CTAB = 2.00 x 10⁻³ mol dm⁻³ Temperature = 35 \pm 0.2° C

Table –II: First order rate constants for PCC oxidation of Co(III) complexes of α - hydroxy acids at $35 \pm 0.2^\circ \text{C}$

$10^2[(\text{NH}_3)_5\text{Co}^{\text{III}}\text{-L}]$ mol dm^{-3}	$10^4k_1 (\text{S}^{-1})$ NaLS	$10^2k_2 \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ NaLS	$10^4k_1 (\text{S}^{-1})$ CTAB	$10^2k_2 \text{dm}^3 \text{mol}^{-1} \text{s}^{-1}$ CTAB
L = Mandelato				
1.00	2.84	2.84	3.26	3.26
1.50	4.21	2.80	5.62	3.21
2.00	5.62	2.81	6.44	3.22
2.50	7.09	2.83	8.11	3.24
3.00	8.47	2.82	9.92	3.30
L = Lactato				
1.00	3.66	3.66	4.14	4.14
1.50	5.54	3.69	6.25	4.17
2.00	7.32	3.66	8.32	4.16
2.50	9.13	3.65	10.23	4.18
3.00	11.04	3.68	12.52	4.19
L = Glycolato				
1.00	2.09	2.09	2.32	2.32
1.50	3.45	2.06	3.48	2.34
2.00	4.12	2.08	4.55	2.32
2.50	5.22	2.10	5.71	2.28
3.00	6.34	2.11	7.46	2.29

PCC = $2.00 \times 10^{-3} \text{ mol dm}^{-3} \text{ M}$, $\text{H}_2\text{SO}_4 = 1\text{N}$, NaLS = $2.00 \times 10^{-3} \text{ mol dm}^{-3}$, CTAB = $2.00 \times 10^{-3} \text{ mol dm}^{-3}$

Temperature = $35 \pm 0.2^\circ \text{C}$

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

$10^3[\text{Compound}]$ mol dm^{-3}	$10^2[\text{PCC}]_{\text{initial}}$ mol dm^{-3}	$10^2[\text{PCC}]_{\text{final}}$ mol dm^{-3}	$\Delta 10^3[\text{PCC}]$ mol dm^{-3}	[Compound] : $\Delta[\text{PCC}]$
Mandelic acid	2.00	1.74		
4.0	2.00	1.67	2.63	1.00 : 0.65
5.0	3.00	2.60	3.24	1.00 : 0.64
6.0			3.96	1.00 : 0.66
Lactic acid	2.00	1.73		
4.0	2.00	1.66	2.68	1.00 : 0.67
5.0	3.00	2.62	3.20	1.00 : 0.64
6.0			3.90	1.00 : 0.65
Glycolic acid	2.00	1.72		
4.0	2.00	1.68	2.52	1.00 : 0.63
5.0	3.00	2.60	3.25	1.00 : 0.65
6.0			3.96	1.00 : 0.66
Co(III)- Mandelato	2.00	1.86		
4.0	2.00	1.84	1.32	1.00 : 0.33
5.0	3.00	2.80	1.60	1.00 : 0.32
6.0			1.98	1.00 : 0.33
Co(III)- Lactato	2.00	1.86		
4.0	2.00	1.82	1.36	1.00 : 0.34
5.0	3.00	2.79	1.75	1.00 : 0.35
6.0			2.04	1.00 : 0.34
Co(III)- Glycalato	2.00	1.86		
4.0	2.00	1.83	1.32	1.00 : 0.33
5.0	3.00	2.78	1.70	1.00 : 0.34
6.0			2.10	1.00 : 0.35

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

Table-IV: Stoichiometric data for PCC oxidation of Co(III) 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}	$10^2[\text{PCC}]_{\text{initial}}$ mol dm^{-3}	$10^2[\text{PCC}]_{\text{final}}$ mol dm^{-3}	$\Delta 10^3[\text{PCC}]$ mol dm^{-3}	[Compound] : $\Delta[\text{PCC}]$
Mandelic acid	2.00	1.73		
4.0	2.00	1.68	2.68	1.00 : 0.67
5.0	3.00	2.61	3.25	1.00 : 0.65
6.0			3.96	1.00 : 0.66
Lactic acid	2.00	1.74		
4.0	2.00	1.67	2.63	1.00 : 0.65
5.0	3.00	2.62	3.21	1.00 : 0.64
6.0			3.92	1.00 : 0.67
Glycolic acid	2.00	1.74		
4.0	2.00	1.68	2.53	1.00 : 0.63
5.0	3.00	2.61	3.27	1.00 : 0.64
6.0			3.96	1.00 : 0.66
Co(III)- Mandelato	2.00	1.86		
4.0	2.00	1.83	1.33	1.00 : 0.34
5.0	3.00	2.79	1.62	1.00 : 0.32
6.0			2.10	1.00 : 0.35
Co(III)- Lactato	2.00	1.85		
4.0	2.00	1.83	1.36	1.00 : 0.34
5.0	3.00	2.80	1.75	1.00 : 0.35
6.0			1.98	1.00 : 0.33
Co(III)- Glycalato	2.00	1.87		
4.0	2.00	1.84	1.34	1.00 : 0.33
5.0	3.00	2.79	1.73	1.00 : 0.34
6.0			2.12	1.00 : 0.35

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

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