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Oxidation of cobalt (iii) complexes of α - hydroxy acids by quinolinium chloro chromate (qcc) in the presence of polysorbate 80 – A kinetic and mechanistic study

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Abstract

The Kinetic of induced electron transfer reaction has been attempted presently with Quinolinium Chloro Chromate (QCC) and pentaammine cobalt (III) complexes of α -Hydroxy acid in the presence of micelles. The Quinolinium Chloro Chromate (QCC) oxidize cobalt (III) bound and unbound α -Hydroxy acids. In Quinolinium Chloro Chromate (QCC) induced electron transfer in the complex, the intermediate radical formed dissociates in a nearly synchronous C-C bond cleavage and the rest of it proceeding with α - C-H fission yielding to cobalt (III) complex. With increase in surfactant (Polysorbate-80) concentration an increase in the rate is observed.

Keywords: Quinolinium Chloro Chromate (QCC), Pentaammine Cobalt (III) complexes, Polysorbate-80.

1. Introduction

The oxidation of α -Hydroxy acids such as mandelic acid , Lactic acid, Glycolic acid and their pentaammine cobalt (III) complexes using Quinolinium Chloro Chromate(QCC) an oxidant in presence of Polysorbate-80. The little work has been done on Quinolinium Chloro Chromate (QCC) with pentaammine cobalt (III) complexes as oxidant in micellar media. The reaction between Quinolinium Chloro Chromate (QCC) and unbound α -Hydroxy acid exhibits second order kinetics with respect to concentration of Quinolinium Chloro Chromate (QCC). A study of induced electron transfer reaction in Co (III)-L system by an external oxidant, whether a one electron transfer reaction takes place at the bound organic ligand gets oxidized without disturbing cobalt (III) centre. Oxidation is an important process in organic chemistry and introduction of new economic and effective reagents for oxidation under mild and anhydrous conditions constitutes a standing challenge. The Quinolinium Chloro Chromate (QCC) is oxidant which is non- hygroscopic, non – photosensitive, stable dark brown solid which is freely soluble in water, Acetic acid, etc.....

2. Materials and Methods

The surfactant used in the present work is Polysorbate-80. The surfactants are purified by adopting earlier procedure. The chemicals were purchased Polysorbate-80 from (Bio Corporals, 99%, Japan) Mandelic, Lactic and glycolic acids from (Karnataka Fine Chem, 97%, India), pentaammine cobalt (III) complexes of α -Hydroxy acids were prepared using Fan and Gould. Double distilled (deionised and CO₂ free) water was used as a solvent and HClO₄ (E.Merck, India 95%) was standardized using standard sodium carbonate (BDH.AR) solution with methyl orange as an indicator. For Quinolinium Chloro Chromate (QCC) oxidation of Co (III) complexes of α -Hydroxy acids and unbound ligands. The rate measurement was made at 35 ± 0.2 °C in 10% aqueous medium and temperature was controlled by electrically operated thermostat.

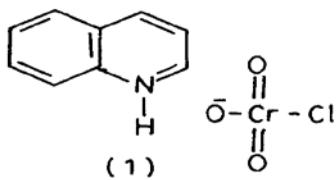
2.1. Preparation of Quinolinium Chloro Chromate (QCC).

In to a 1-1 beaker containing Hydrochloric acid (6 M, 184 ml) was added Chromium trioxide (100g, 1 mole) rapidly. The mixture was thoroughly stirred for five minutes and the resulting homogeneous solution was cooled to 15 °C. To this mixture quinoline (129.6g, 1 mole) was

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added drop wise over a period of half an hour. After the addition of quinoline was over the mixture was again cooled to 15 °C. This resulted in precipitation of Quinolinium Chloro chromate in the form of a yellow powder. The powder was filtered off and dried under vacuum for three hours, melting point 239°, 96% yield.



3. Result and Discussion

Kinetic study of the oxidation of pentaammine cobalt (III) complexes of α -Hydroxy acid by Quinolinium Chloro Chromate (QCC) in micellar medium dependence of rate on Quinolinium Chloro Chromate (QCC) concentration in micellar bound ligand. The rate of Quinolinium Chloro Chromate (QCC) oxidation of pentaammine cobalt (III) complexes of α - Hydroxy acids depends on QCC concentration, the specific rate calculated remains constant, and graph linear. From the slope of these graphs, the calculated specific rate agree rate equation suggesting first order dependence on Quinolinium Chloro Chromate (QCC) concentration. When the concentration of QCC is varied from 1.00 to 5.00×10^{-3} mol dm⁻³ at a fixed [Cobalt (III)] and [HClO₄]. A specific rate remains constant. Then the rate of disappearance of Cr (VI) is given by equation. (1).

$$-\frac{d}{dt} [\text{Cr(VI)}] = k_1 [\text{Cr(VI)}] \quad \dots \dots \dots \quad (1)$$

3.1 Dependence of rate on cobalt (III) Concentration.

The rate of QCC oxidation $[(\text{NH}_3)_5 \text{Co}-\text{L}]^{2+}$ complexes of Mandelic, Lactic and Glycolic acid, depends nearly on the first power of the concentration of Co(III) complexes, graph of log k versus log [Co (III)] are linear with slope nearly equal to one. Hence the rate law for the Cr (VI) oxidation of cobalt (III) bound of α -Hydroxy acids are given by equation. (2).

$$-\frac{d}{dt} [\text{Cr(VI)}] = k_2 [\text{Cr(VI)}] [\text{Co(III)}] \quad \dots \dots \dots \quad (2)$$

3.2 Dependence of rate on Quinolinium Chloro Chromate (QCC) concentration in micellar for α - Hydroxy acid.

At a given initial concentration of QCC in macular medium, the oxidation varies proportionately with the concentration of α - Hydroxy acids and the rate of this reaction exhibits first order dependence on α - Hydroxy acids concentration plot of log k₁ versus (α - Hydroxy acids) are linear with slope, nearly equal to one, evidencing the order is with respect to α - Hydroxy acids. Hence the rate of disappearance of Cr (VI) is given by equation. (3).

$$-\frac{d}{dt} [\text{Cr(VI)}] = k_2 [\text{Cr(VI)}] [\alpha\text{-Hydroxy acid}] \quad \dots \dots \dots \quad (3)$$

3.3 Comparison of rates on oxidation of Pentaammine Cobalt (III) complexes of both bound and unbound α - Hydroxy acid by QCC.

The specific rate of the Co (III) Lactato complex reacts faster than Co (III) Mandelato and Co (III) Glycolate complexes, because if the reaction proceeds through a performed bromated ester, then the rate of oxidation of C-H cleavage has been enhanced resulting in an increase in the rate of oxidation of Co (III) complex. Also chromate ester formation may be sterically

hindered in the case of Mandelato complex. The absence of such a steric retardation and enhanced acidity of methyl proton in the Lactato complex may account for its greater reactivity. In this work, an induced electron transfer reaction has been attempted presently with QCC and Pentaammine cobalt (III) Complexes of α - Hydroxy acid in the presence of micells.

The reaction exhibits second order kinetics and in the case of Mandelato complex, the amount, of cobalt (III) reduced to corresponds to nearly initial concentration while nearly 70 % of cobalt (III) is converted to keto acid, cobalt (III) Mandelato complex, the intermediate radical formed dissociated in a nearly synchronous manner with C—C bond cleavage only to the extent of 25 % and rest of its proceeding with α - C—H fission giving keto acid cobalt (III) complex. With increase in micelle concentration an increase in the rate of observed. The Polysorbate-80 added to enhanced the rate of oxidation. The same trends observed in Lactato and Glycolato cobalt (III) complex.

3.4 Dependence of rate on the concentration of cobalt (III) bound α - Hydroxy acids.

At a particular QCC concentration with increasing Mandelato / Lactato / Glycolato cobalt (III) concentration in the range 1.00×10^{-3} mol dm⁻³, there is a proportional increase in the rate of oxidation. The slopes of nearly unity are obtained from a linear graph of logarithm of specific rate (k_1 in S⁻¹) Versus logarithm of cobalt (III) concentration in each case suggesting first order dependence of rate law for the QCC oxidation of cobalt (III) bound α - Hydroxy acids is given by equation. (4).

$$-\frac{d}{dt} [\text{Cr(VI)}] = k_2 [\text{Cr(VI)}] [\text{Co(III)}] \quad \dots \dots \dots \quad (4)$$

$$[\text{QCC}] = 2.00 \times 10^{-3} \text{ mol dm}^{-3}$$

$$[\text{HClO}_4] = 1.00 \text{ mol dm}^{-3}$$

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

3.5 Kinetic study of the oxidation of α - Hydroxy acids by QCC

The Kinetic of QCC reaction with α -Hydroxy acids have been studied in the presence of 1.00 mol dm^{-3} HClO₄ and in the absence of micelles at a temperature of $35 \pm 0.2^\circ \text{C}$.

3.6 Dependence of rate on Quinolinium Chloro Chromate (QCC) concentration.

Under identical conditions, QCC oxidations of unbound ligand Mandelic acid has been studied to look in to the consequence of ligation with cobalt (III) centre. In any specific run, from the rate of disappearance of QC, the specific rates calculated using integrated first order rate equations are constant.

Also graphs of logarithm of QCC concentration Versus calculated, agree well with those calculated from integrated first order dependence on QCC oxidation of unbound α - Hydroxy acids. Hence the rate law is given by equation. (5).

$$-\frac{d}{dt} [\text{Cr(VI)}] = k_1 [\text{Cr(VI)}] \quad \dots \dots \dots \quad (5)$$

When the concentration of Quinolinium Chloro Chromate (QCC) is varied from 1.00 to 5.00×10^{-3} mol dm⁻³, at a fixed α - Hydroxy acids, [HClO₄] and micellar concentration, the specific rates remain constant in keeping with the first dependence on Quinolinium Chloro Chromate (QCC) concentration. Under identical conditions, the effect of changing unbound α - Hydroxy acids concentration has been

studied in the range of 1.00×10^{-3} mol dm $^{-3}$ with all the substrates in the absence of micellar medium. There is a monotonic increase in the rate of Quinolinium Chloro Chromate (QCC) oxidation with unbound α -Hydroxy acids with increasing concentration substrates.

Also a graph of logarithm of specific rate (k_1 in S $^{-1}$) Versus logarithm of α -Hydroxy acids concentration is linear with a slope nearly equal to unity with a slope nearly the rate law of Quinolinium Chloro Chromate(QCC) oxidation of unbound α -Hydroxy acids which is similar to cobalt (III) bound ligands.

$$-d[Cr(VI)] = k_2[Cr(VI)][\alpha\text{-Hydroxy acid}] \dots \dots \dots (6)$$

4. Summary

Earlier studies on induced electron transfer reaction involved mainly an one equivalent oxidant, Ce (VI) and pentaammine cobalt (III) complexes, $[(NH_3)_5 Co(III)-L]^{2+}$ with bound ligands featuring conjugated fragments. In all these reactions, ultimately, reduction at cobalt (III) centre has been achieved due to the generation of a radical at the bound organic ligand by the one equivalent oxidant. But the percentage of cobalt (III) formed differed from reaction to reaction due to the partitioning of the reaction paths.

An induced electron transfer reaction has been attempted presently with Quinolinium Chloro Chromate (QCC) and pentaammine cobalt (III) complexes of α -Hydroxy acids in the presence of Polysorbate-80 medium and also in the absence of Polysorbate-80 medium. The reaction exhibits second order kinetics and in the case of Mandelato complex, the amount of cobalt (III) reduced corresponds to nearly 20

initial concentration and the amount of cobalt (II) Ph. CHO and CO₂ formed is nearly 20%. While nearly 75 % of it is converted to keto acid, cobalt (III) complex, possibly Cr (VI) induced electron transfer in cobalt (III) Mandelato complex, the intermediate radical formed dissociate in a synchronous manner with C—C bond cleavage only to the extent of 20 %. The cobalt (III) bound α -Hydroxy acid gets oxidized at higher rate than that of unbound ligand. With increasing Polysorbate-80 concentration an increase in the rate is observed. Added Polysorbate-80 enhance the rate of oxidation of reaction much more than without Polysorbate-80.

Similar trends have been observed in Lactate and Glycolato cobalt (III) complexes.

Table 1

POLYSORBATE-80			
Time in Seconds	$10^3(a-x)$ mol dm $^{-3}$	$10^4 k_1$ (S $^{-1}$)	$4+\log(a-x)$
240	3.18	4.311	4.5024
480	2.58	4.323	4.4116
720	1.76	4.334	4.2455
960	1.58	4.341	4.1986
1200	1.23	4.356	4.0899
1440	0.90	4.366	3.9542
1680	0.81	4.373	3.9084
1920	0.65	4.382	3.8129
2160	0.59	4.389	3.7708

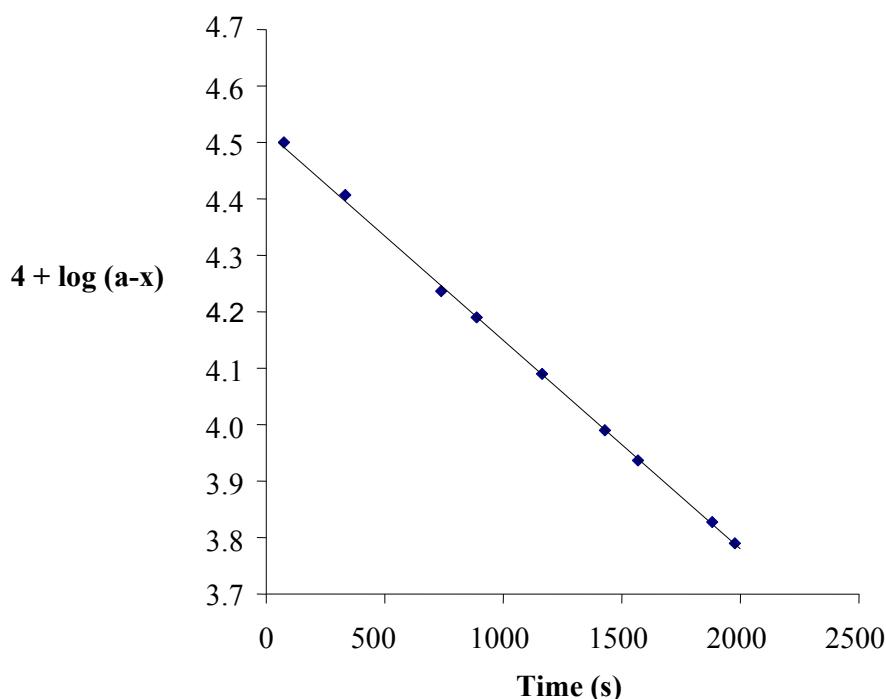


Fig 1: First order dependence plots

Table 2

POLYSORBATE-80			
$10^2 [(\text{NH}_3)\text{Co(III)} - \text{L}] \text{ mol dm}^{-3}$	$10^4 k_1 (\text{S}^{-1})$	$10^2 k_2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$4 + \log k_1$
L = Lactato			
1.00	3.33	3.33	4.5224
2.00	4.42	3.28	4.6454
3.00	5.95	3.36	4.7745
4.00	8.12	3.33	4.9095
5.00	15.05	3.35	5.1775
M = Mandato			
1.00	2.20	2.20	4.3924
2.00	3.01	2.22	4.4785
3.00	3.69	2.26	4.5670
4.00	5.14	2.21	4.7019
5.00	6.98	2.23	4.8438
G = Glycolato			
1.00	1.66	1.69	4.2201
2.00	2.07	1.71	4.3159
3.00	2.59	1.73	4.4132
4.00	3.24	1.71	4.5105
5.00	4.15	1.72	4.6180

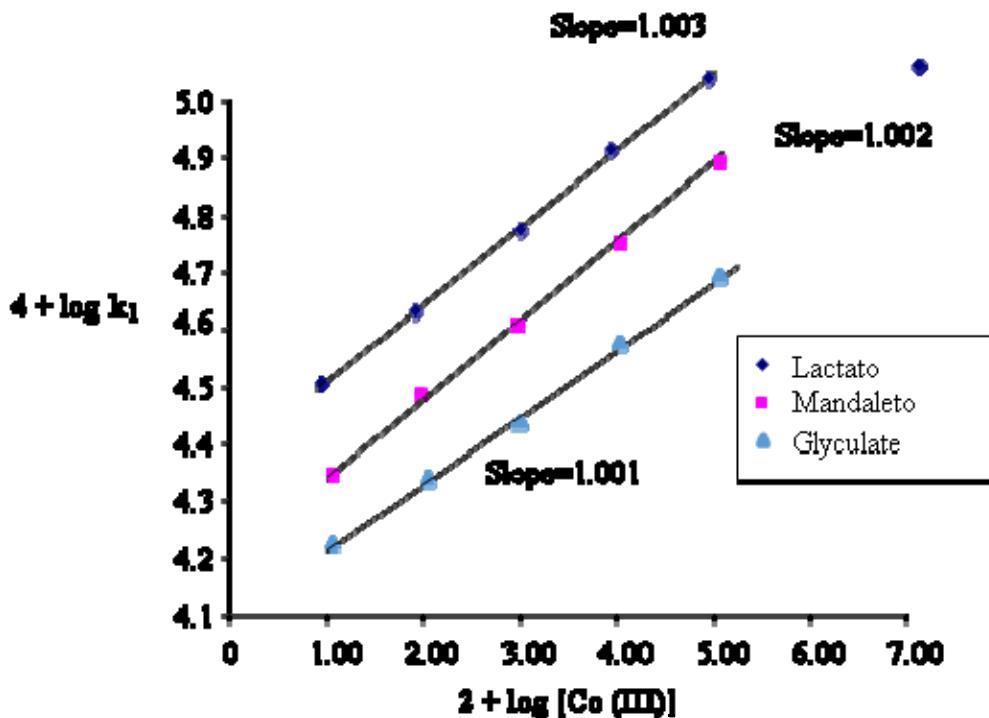
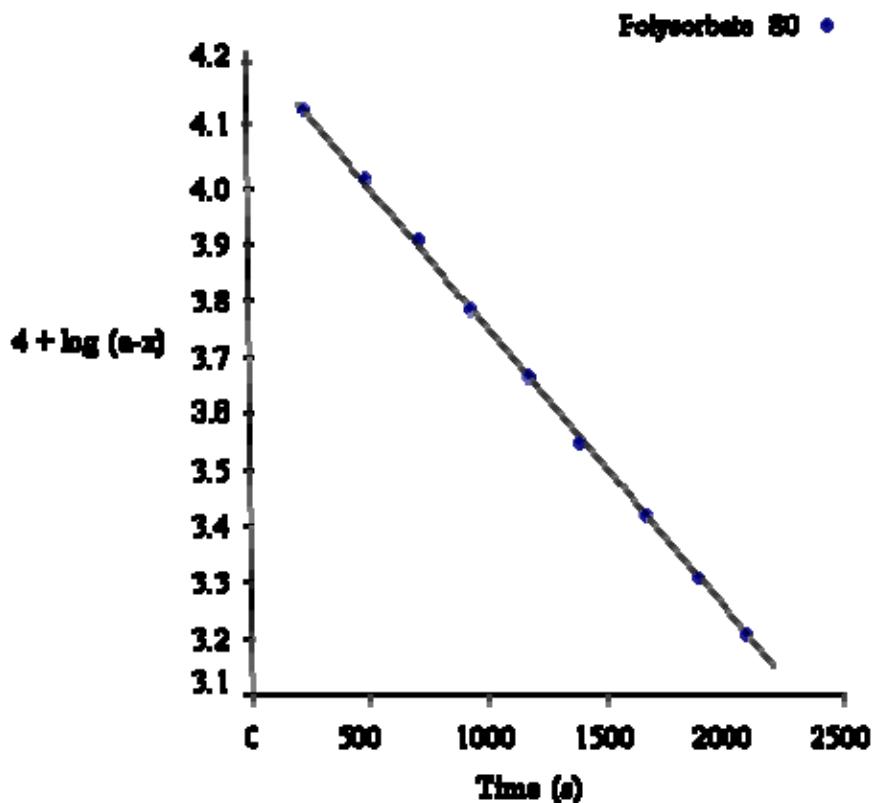


Fig 2: Dependence of rate on [Co (III)] in Polysorbate-80

Table 3

POLYSORBATE-80			
Time in Seconds	$10^3 (a-x) \text{ mol dm}^{-3}$	$10^4 k_1 (\text{S}^{-1})$	$4+\log(a-x)$
240	1.28	2.651	4.1092
480	1.01	2.653	4.0043
720	0.85	2.644	3.9294
960	0.59	2.761	3.7708
1200	0.44	2.656	3.6434
1440	0.35	2.666	3.5440
1680	0.26	2.673	3.4149
1920	0.19	2.682	3.2787
2160	0.15	2.689	3.1960

**Fig 3:** First order dependence plots**Table 4**

POLYSORBATE-80			
$10^2 [(\text{NH}_3)_5\text{Co(III)} - \text{L}] \text{ mol dm}^{-3}$	$10^4 k_1 (\text{s}^{-1})$	$10^2 k_2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$	$4 + \log k_1$
L = Lactato			
1.00	1.02	1.02	4.0086
2.00	1.68	1.02	4.2253
3.00	2.69	1.02	4.4297
4.00	3.66	1.02	4.5634
5.00	5.62	1.02	4.7497
M = Mandato			
1.00	0.67	0.67	3.8260
2.00	0.85	0.67	3.9294
3.00	1.33	0.67	4.1238
4.00	2.10	0.67	4.3221
5.00	3.17	0.67	4.5010
G = Glycolato			
1.00	0.42	0.42	3.6232
2.00	0.64	0.42	3.8161
3.00	0.88	0.42	3.9444
4.00	1.92	0.42	4.2833
5.00	2.43	0.42	4.3856

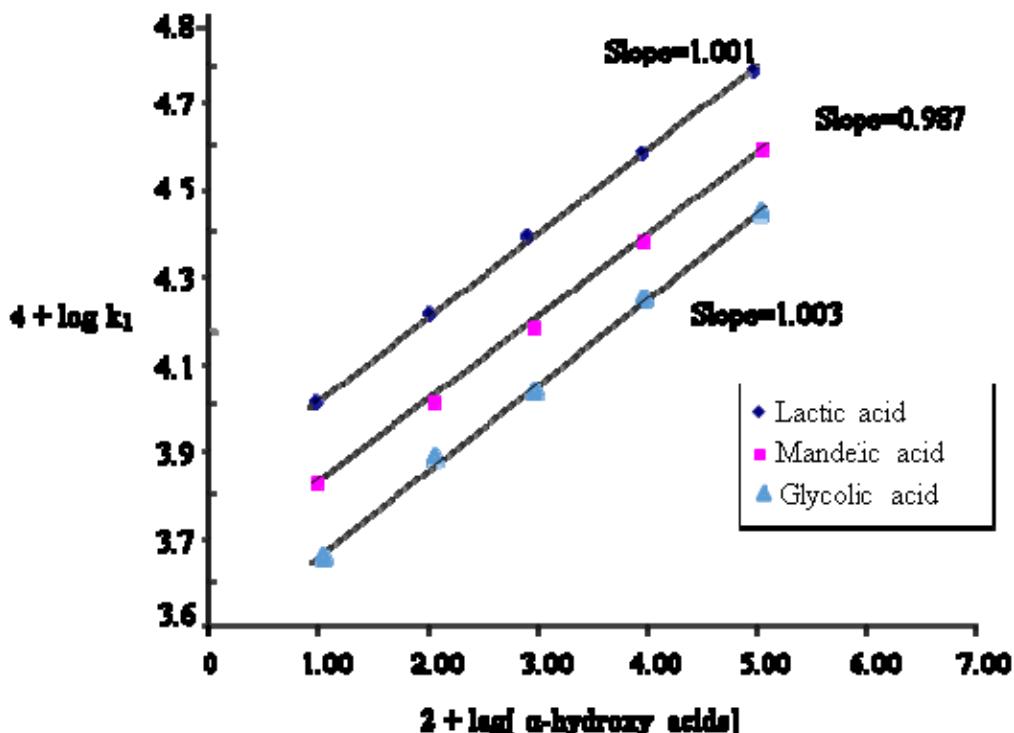


Fig 4: Dependence of rate on $[\alpha\text{-hydroxyacids}]$ in Polysorbate-80

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