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Oxidation of cobalt (III) complexes of α- hydroxy acids by quinolinium dichromate (QDC) in the presence of ammonium lauryl sulfate (ALS): A kinetic and mechanistic study

K Murali, M Shreelekha, B Divya
Department of Chemistry, Vivekanandha Arts and Science College for Women, Sankagiri, Tamil Nadu, India

Abstract
The Kinetic of induced electron transfer reaction has been attempted presently with Quinolinium DiChromate (QDC) and pentaammine cobalt (III) complexes of α-Hydroxy acid in the presence of micelles. The Quinolinium DiChromate (QDC) oxidies cobalt (III) bound and unbound α-Hydroxy acids. In Quinolinium DiChromate (QDC) 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 ALS concentration an increase in the rate is observed.

Keywords: quinolinium dichromate (QDC), pentaammine cobalt (III) complexes, ammonium lauryl sulfate (ALS)

1. Introduction

The oxidation of α-Hydroxy acids such as mandelic acid, Lactic acid, Glycolic acid and their pentaammine cobalt (III) complexes using Quinolinium DiChromate (QDC) an oxidant in presence of Ammonium Lauryl Sulfate(ALS). The little work has been done on Quinolinium DiChromate (QDC) with pentaammine cobalt (III) complexes as oxidant in micellar media. The reaction between Quinolinium DiChromate (QDC) and unbound α-Hydroxy acid exhibits second order kinetics with respect to concentration of Quinolinium DiChromate (QDC). A study of induced electron transfer reaction in Co(III)-L system by an external oxidant, whether an one electron transfer reaction take 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 DiChromate (QDC) is oxidant which is non- hygroscopic, non - photosensitive, stable dark brown solid which is freely soluble in water, Acetic acid, etc…….

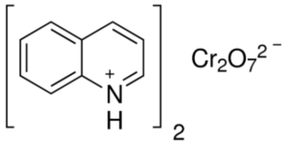
2. Material and Method

The surfactant used in the present work are Ammonium Lauryl Sulfate (ALS). The surfactants are purified by adopting earlier procedure. The chemicals were purchased Ammonium Lauryl Sulfate (ALS) 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 (de ionised and CO_2 free) water was used as a solvent and $HClO_4$ (E. Merck, India 95%) was standardized using standard sodium carbonate (BDH.AR) solution with methyl orange as an indicator. For Quinolinium DiChromate (QDC) oxidation of Co (III) complexes of α-Hydroxy acids and unbound ligands. The rate measurement were made at 36 ± 0.2 ° C in 100 % aqueous medium and temperature was controlled by electrically operated thermostat.

2.1 Preparation of Quinolinium DiChromate (QDC).

A known quantity of Quinoline was slowly added to a cooled solution of Chromium trioxide in water with stirring. After 30 min, the solution was diluted with acetone and cooled to -20 ºC for 2 to3 hours. The Orange solid which separated out, was filtered, washed with acetone, dried in vacuum and the recrystalised from water. Melting point.159.



3. Result and Discussion

Kinetic study of the oxidation of pentaammine cobalt (III) complexes of α-Hydroxy acid by Quinolinium DiChromate (QDC) in micellar medium dependence of rate on Quinolinium DiChromate (QDC) concentration in micellar bound ligand. The rate of Quinolinium DiChromat (QDC) oxidation of pentaammine cobalt (III) complexes of α-Hydroxy acids depends on QDC concentration, the specific rate calculated remains constant, and graph linear. From the slope of these graphs, the calculated specific rateagree rate equation suggesting first order dependence on Quinolinium DiChromate (QDC) concentration. When the concentration of QDC is varied from 1.00 to 5.00 $\times 10^{-3}$ mol dm^{-3} at a fixed [Cobalt (III)] and [$HClO_4$]. A specific rate remains constant. Then the rate of disappearance of Cr (VI) is given by equation. (1).

$$-d\,[Cr\,(VI)]\,/\,dt = k1\,[Cr\,(VI)] \quad \ldots\ldots\ldots\ldots\ldots\ldots\ldots\ldots..(1)$$

Dependence of rate on cobalt (III) concentration.

The rate of QDC oxidation [$(NH_3)_5$ Co-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).

$-d[Cr (VI)] / dt = k_2[Cr (VI)][Co(III)]$ …………….(2)

Dependence of rate on Quinolinium DiChromate (QDC) concentration in micellar for α - Hydroxy acid.

At a given initial concentration of QDC 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 k_1 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).

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

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

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 have 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 QDC 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 Ammonium Lauryl Sulfate (ALS) added to enhanced the rate of oxidation. The same trends observed in Lactato and Glycolato cobalt (III) complex.

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

At a particular QDC concentration with increasing Mandelato/ Lactato/ Glycolato cobalt (III) concentration in the range 1.00 $\times10^{-3}$ mol dm^{-3} there is a proportional increase in the rate of oxidation. The slopes of nearly unity is obtained from a linear graph of logarithm of specific rate (k_1 in S^{-}) versus logarithm of cobalt (III) concentration in each case suggesting first order dependence of rate law for the QDC oxidation of cobalt (III) bound α - Hydroxy acids is given by equation. (4).

$-d [Cr (VI)] = k_2 [Cr (VI)] [Co (III)]$ …………….(4)

$[QDC] = 2.00\times10^{3-}$ mol dm^{-3}
$[HClO_4] = 1.00$ mol dm^{-3}
Temperature = 36 ± 0.2º C

Kinetic study of the oxidation of α–Hydroxy acids by QDC.

The Kinetic of QDC reaction with α -Hydroxy acids have been studied in the presence of 1.00 mol dm^{-3} $HClO_4$ and in the absence of micelles at a temperature of 36 ± 0.2º C.

Dependence of rate on Quinolinium DiChromate (QDC) concentration.

Under identical conditions, QDC 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 QDC, the specific rates calculated using integrated first order rate equations are constant. Also graphs of logarithm of QDC concentration Versus calculated, agree well with those calculated from integrated first order dependence on QDC oxidation of unbound α-Hydroxy acids. Hence the rate law is given by equation. (5).

$-d [Cr (VI)] / dt = k1 [Cr (VI)]$ ………………………..(5)

When the concentration of Quinolinium DiChromate (QDC) is varied from 1.00 to 5.00 × 10^{-3} mol dm^{-3}, at a fixed α-Hydroxy acids, $[HClO_4]$ and micellar concentration, the specific rates remain constant in keeping with the first dependence on Quinolinium DiChromate (QDC) 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 DiChromate (QDC) 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 DiChromate (QDC) oxidation of unbound α-Hydroxy acids which is similar to cobalt (III) bound ligands.

$-d [Cr (VI)] = k2 [Cr (VI)] [\alpha\text{-Hydroxy acid}]$ ………….(6)

4. Summary

Earlier studies on induced electron transfer reaction involved mainly an one equivalent oxidant, Ce(VI) and pentaammine cobalt (III) complexes, $[(NH_3)_5 Co (III)\text{-}L]^{2+}$ with bound ligands featuring conjugated fragments. In all these reactions, ultimately, reduction at cobalt (III) centre have 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 DiChromate(QDC) and pentaammine cobalt(III) complexes of α-Hydroxy acids in the presence of Ammonium Lauryl Sulfate(ALS) medium and also in the absence of Ammonium

Lauryl Sulfate (ALS) medium.

The reaction exhibits second order kinetics and in the case of Mandelato complex, the amount of cobalt (III) reduced correspondence to nearly 20 initial concentration and the amount of cobalt (II) Ph. CHO and CO_2 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 Ammonium Lauryl Sulfate (ALS) concentration an increase in the rate is observed. Added Ammonium Lauryl Sulfate (ALS) enhance the rate of oxidation of reaction much more than without Ammonium Lauryl Sulfate(ALS).Similar trends has been observed in Lactate and Glycolato cobalt (III) complexes.

Table 1

Ammonium Lauryl Sulfate (ALS)			
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

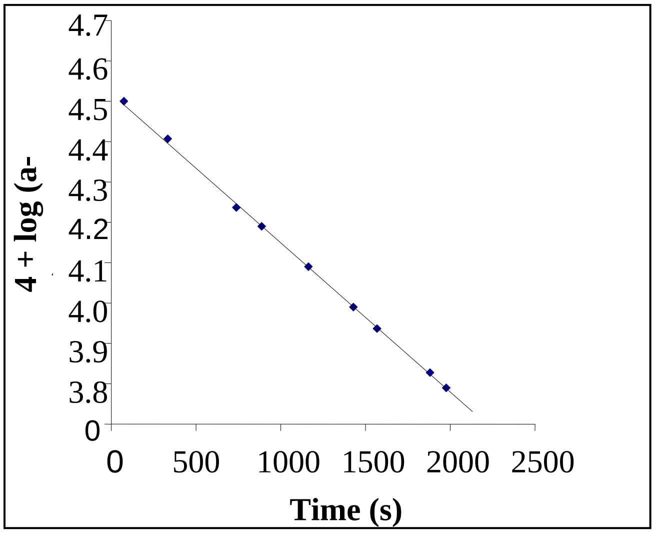


Fig 1: First order dependence plots

Table 2

Ammonium Lauryl Sulfate (ALS)			
10^2 [$(NH_3)_5$Co(III) –L] mol dm^{-3}	10^4 k_1(S^{-1})	10^2 $k_2$dm^3 mol^{-1} 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	5.54	3.36	4.7435
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

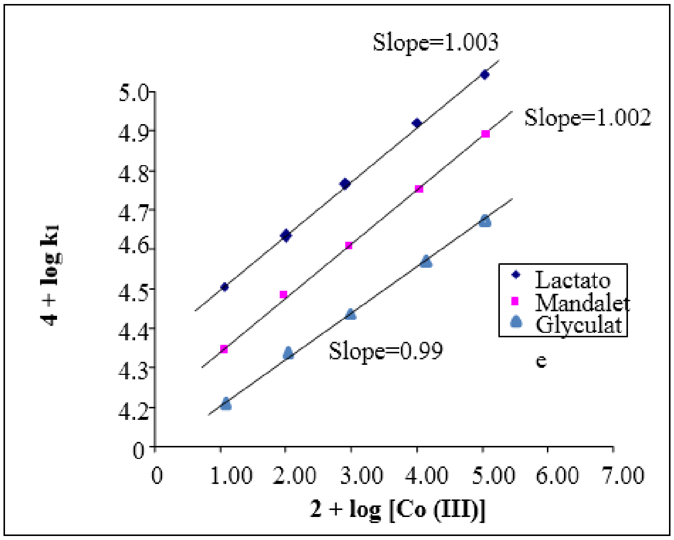


Fig 2: Dependence of rate on [Co (III)] in Ammonium Lauryl Sulfate (ALS)

Table 3

Ammonium Lauryl Sulfate(ALS)			
Time in Seconds	**10^3 (a-x) mol dm^{-3}**	**10^4 k_1(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

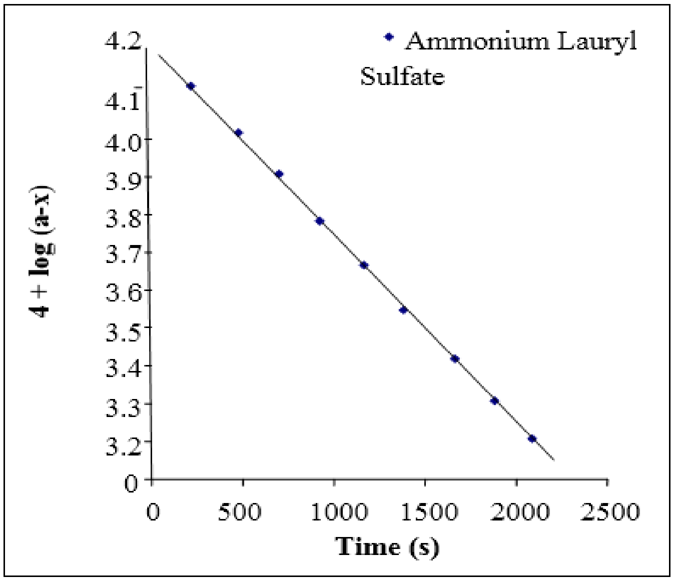


Fig 3: First order dependence plots

Table 4

Ammonium Lauryl Sulfate(ALS)			
10^2 [$(NH_3)_5$Co(III) –L] mol dm^{-3}	**10^4 k_1 (S^{-1})**	**10^2 k_2 dm^3 mol^{-1} 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

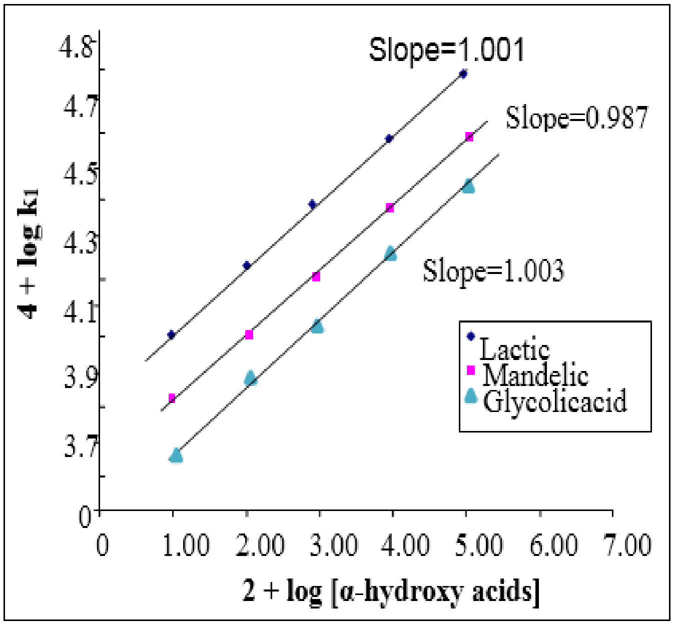


Fig 4: Dependence of rate on [α-Hydroxyacids] in Ammonium Lauryl Sulfate (ALS)

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