



ISSN (PRINT) : 2320 -1967  
ISSN (ONLINE) : 2320 -1975



## ORIGINAL ARTICLE

*CHEMXPRESS 8(2), 138-144, (2015)*

# Oxidation of cobalt (III) complexes of $\alpha$ - hydroxy acids by pyridinium bromo chromate (PBC) in the presence of ammonium lauryl sulfate – A kinetic and mechanistic study

K.Murali\*, Mansur Ahmed, Mohammed Nawaz

PG & Research Department of Chemistry, Islamiah college, Vaniyambadi, 635 752, Tamil Nadu, (INDIA)

E-mail: murali\_kana@yahoo.com

**Abstract :** The Kinetic of induced electron transfer reaction has been attempted presently with Pyridinium Bromo chromate (PBC) and pentaammine cobalt (III) complexes of  $\alpha$ -Hydroxy acid in the presence of micelles. The Pyridinium Bromo chromate (PBC) oxidizes cobalt (III) bound and unbound  $\alpha$ -Hydroxy acids. In Pyridinium Bromo chromate (PBC) 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  $\alpha$ - C-H fission yielding to cobalt (III) complex. With increase in surfactant (Ammonium lauryl sulfate) concentration an increase in the rate is observed. © Global Scientific Inc.

**Keywords :** Pyridinium bromo chromate (PBC); Pentaammine cobalt (III) complexes; Ammonium lauryl sulfate (ALS).

## INTRODUCTION

The oxidation of  $\alpha$ -Hydroxy acids such as mandelic acid, Lactic acid, Glycolic acid and their pentaammine cobalt (III) complexes using Pyridinium Bromo chromate (PBC) an oxidant in presence of Ammonium lauryl sulfate (ALS). The little work has been done on Pyridinium Bromo chromate (PBC) with pentaammine cobalt (III) complexes as oxidant in micellar media. The reaction between Pyridinium Bromo chromate (PBC) and unbound  $\alpha$ -Hydroxy acid exhibits second order kinetics with respect to concentration of Pyridinium

Bromo chromate (PBC). 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 Pyridinium Bromo chromate (PBC) is oxidant which is non- hygroscopic, non – photosensitive, stable dark brown solid which is freely soluble in water, Acetic acid, etc.

## 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  $\alpha$ -Hydroxy acids were prepared using Fan and Gould.

Double distilled (deionised and CO<sub>2</sub> free) water was used as a solvent and HClO<sub>4</sub> (E. Merck, India 95 %) was standardized using standard sodium carbonate (BDH. AR) solution with methyl orange as an indicator. For Pyridinium Bromo chromate (PBC) oxidation of Co(III) complexes of  $\alpha$  - Hydroxy acids and unbound ligands. The rate measurements were made at  $35 \pm 0.2$  ° C in 100 % aqueous medium and temperature was controlled by electrically operated thermostat.

### Preparation of pyridinium bromo chromate (PBC)

A solution of Chromium trioxide (CrO<sub>3</sub>) (20 g 0.2 mol) in water (25ml) was cooled to 0 ° C and added 47 % hydrobromic acid (38 ml, 0.21 mol) slowly with vigorous stirring. Pyridine (16.2 ml, 0.2 mol) was then added drop wise during 15 min to afford a brown solid. The reaction mixture was cooled for 4 hours and the dark brown solid obtained were filtered and dried in vacuum yield 27.5 g, molting point 108° C. [ $\lambda$  max-380nm]

## RESULT AND DISCUSSION

Kinetic study of the oxidation of pentaammine cobalt (III) complexes of  $\alpha$ -Hydroxy acid by Pyridinium Bromo chromate (PBC) in micellar medium dependence of rate on Pyridinium Bromo chromate (PBC) concentration in micellar bound ligand. The rate of Pyridinium Bromo chromate (PBC) oxidation of pentaammine cobalt (III) complexes of  $\alpha$  - Hydroxy acids depends on PBC 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 Pyridinium Bromo chromate (PBC) concentration.

When the concentration of PBC is varied from 1.00 to  $5.00 \times 10^{-3}$  mol dm<sup>-3</sup> at a fixed [Cobalt (III)] and [HClO<sub>4</sub>]. A specific rate remains constant. Then the rate of disappearance of Cr (VI) is given by equation. (1).

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

### Dependence of rate on cobalt (III) concentration

The rate of PBC 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  $\alpha$  - Hydroxy acids are given by equation. (2).

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

### Dependence of rate on pyridinium bromo chromate (PBC) concentration in micellar for $\alpha$ - Hydroxy acid

At a given initial concentration of PBC in micellar medium, the oxidation varies proportionately with the concentration of  $\alpha$  - Hydroxy acids and the rate of this reaction exhibits first order dependence on  $\alpha$  - Hydroxy acids concentration plot of log k<sub>1</sub> versus ( $\alpha$  - Hydroxy acids) are linear with slope, nearly equal to one, evidencing the order is with respect to  $\alpha$  - Hydroxy acids. Hence the rate of disappearance of Cr (VI) is given by equation. (3).

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

### Comparison of rates on oxidation of Pentaammine Cobalt (III) complexes of both bound and unbound $\alpha$ - Hydroxy acid by PBC

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

TABLE 1

| AMMONIUM LAURYL SULFATE (ALS) |                                  |                            |               |
|-------------------------------|----------------------------------|----------------------------|---------------|
| Time in Seconds               | $10^3 (a-x) \text{ mol dm}^{-3}$ | $10^4 k_1 (\text{S}^{-1})$ | $4+\log(a-x)$ |
| 240                           | 2.56                             | 4.311                      | 4.4082        |
| 480                           | 2.04                             | 4.323                      | 4.3096        |
| 720                           | 1.58                             | 4.334                      | 4.1986        |
| 960                           | 1.29                             | 4.341                      | 4.1105        |
| 1200                          | 1.09                             | 4.356                      | 4.0374        |
| 1440                          | 0.89                             | 4.366                      | 3.9493        |
| 1680                          | 0.79                             | 4.373                      | 3.8976        |
| 1920                          | 0.66                             | 4.382                      | 3.8195        |
| 2160                          | 0.52                             | 4.389                      | 3.7160        |

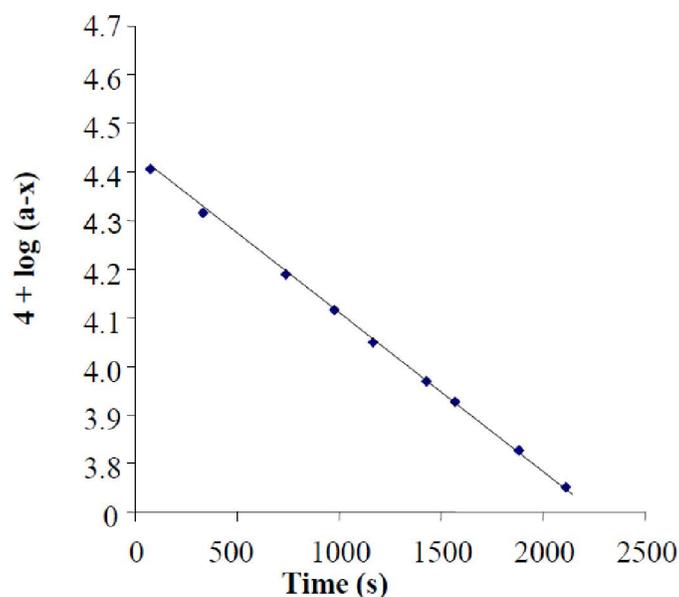


Figure 1 : First order dependence plots

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 PBC and Pentaammine cobalt (III) Complexes of  $\alpha$ -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  $\alpha$ -C—H fission giving keto acid cobalt (III) complex. With increase in micelle concen-

tration 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 $\alpha$ -Hydroxy acids

At a particular PBC concentration with increasing Mandelato / Lactato / Glycolato cobalt (III) concentration in the range  $1.00 \times 10^{-3} \text{ mol dm}^{-3}$ , 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  $\text{S}^{-1}$ ) Versus logarithm of cobalt (III) concentration in each case suggesting first order dependence of rate law for the PBC oxidation of cobalt (III) bound  $\alpha$ -Hydroxy acids is given by equation. (4).

TABLE 2

| AMMONIUM LAURYL SULFATE (ALS)                   |                     |                                                         |                |
|-------------------------------------------------|---------------------|---------------------------------------------------------|----------------|
| $10^2 [(NH_3)_5Co(III) -L] \text{ mol dm}^{-3}$ | $10^4 k_1 (S^{-1})$ | $10^2 k_2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ | $4 + \log k_1$ |
| <b>L = Lactato</b>                              |                     |                                                         |                |
| 1.00                                            | 3.24                | 3.26                                                    | 4.5105         |
| 2.00                                            | 3.99                | 3.28                                                    | 4.6009         |
| 3.00                                            | 5.15                | 3.24                                                    | 4.7118         |
| 4.00                                            | 5.97                | 3.27                                                    | 4.7759         |
| 5.00                                            | 8.06                | 3.29                                                    | 4.9063         |
| <b>M = Mandato</b>                              |                     |                                                         |                |
| 1.00                                            | 2.17                | 2.17                                                    | 4.3364         |
| 2.00                                            | 2.69                | 2.19                                                    | 4.4297         |
| 3.00                                            | 3.24                | 2.16                                                    | 4.5105         |
| 4.00                                            | 4.61                | 2.21                                                    | 4.6637         |
| 5.00                                            | 5.54                | 2.17                                                    | 4.7435         |
| <b>G = Glycolato</b>                            |                     |                                                         |                |
| 1.00                                            | 1.58                | 1.58                                                    | 4.1986         |
| 2.00                                            | 1.90                | 1.55                                                    | 4.2787         |
| 3.00                                            | 2.81                | 1.59                                                    | 4.4487         |
| 4.00                                            | 3.34                | 1.58                                                    | 4.5237         |
| 5.00                                            | 3.91                | 1.58                                                    | 4.5921         |

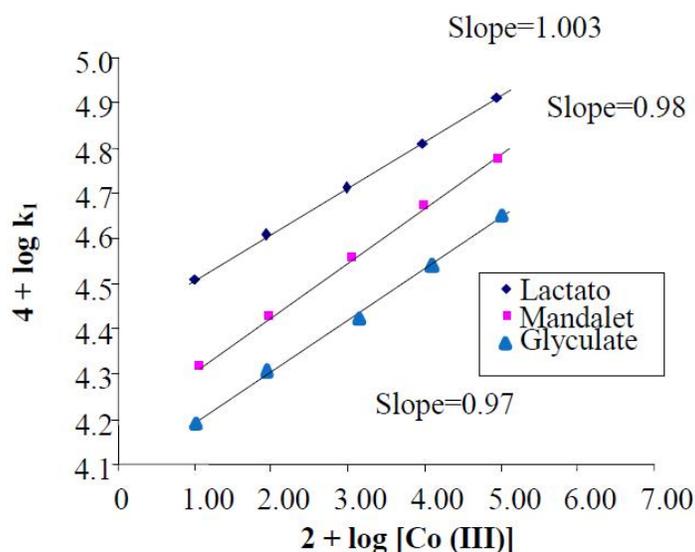


Figure 2 : Dependence of rate on [Co (III)] in ALS



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

$$[HClO_4] = 1.00 \text{ mol dm}^{-3}$$

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

### Kinetic study of the oxidation of $\alpha$ -Hydroxy acids by PBC

The Kinetic of PBC reaction with  $\alpha$ -Hydroxy

acids have been studied in the presence of  $1.00 \text{ mol dm}^{-3} \text{ HClO}_4$  and in the absence of micelles at a temperature of  $35 \pm 0.2^\circ \text{C}$ .

### Dependence of rate on Pyridinium Bromo chromate (PBC) concentration

Under identical conditions, PBC oxidations of unbound ligand Mandelic acid has been studied to look

TABLE 3

| AMMONIUM LAURAL SULFATE (ALS) |                                  |                            |               |
|-------------------------------|----------------------------------|----------------------------|---------------|
| Time in Seconds               | $10^3 (a-x) \text{ mol dm}^{-3}$ | $10^4 k_1 (\text{S}^{-1})$ | $4+\log(a-x)$ |
| 240                           | 1.55                             | 2.711                      | 4.1900        |
| 480                           | 1.30                             | 2.723                      | 4.1139        |
| 720                           | 1.01                             | 2.734                      | 4.0043        |
| 960                           | 0.87                             | 2.741                      | 3.9345        |
| 1200                          | 0.60                             | 2.756                      | 3.7781        |
| 1440                          | 0.40                             | 2.766                      | 3.6020        |
| 1680                          | 0.30                             | 2.773                      | 3.4771        |
| 1920                          | 0.21                             | 2.782                      | 3.3222        |
| 2160                          | 0.17                             | 2.789                      | 3.2304        |

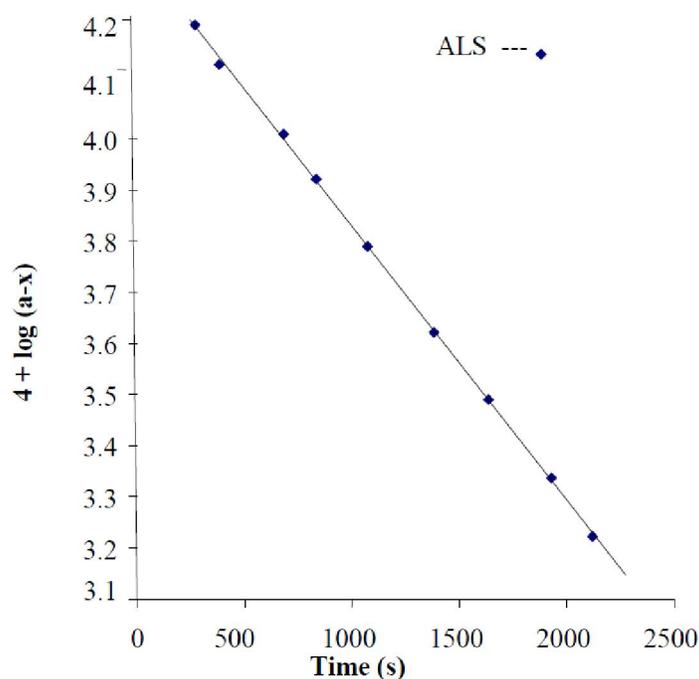


Figure 3 : First order dependence plots

in to the consequence of ligation with cobalt (III) centre. In any specific run, from the rate of disappearance of PBC, the specific rates calculated using integrated first order rate equations are constant.

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

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

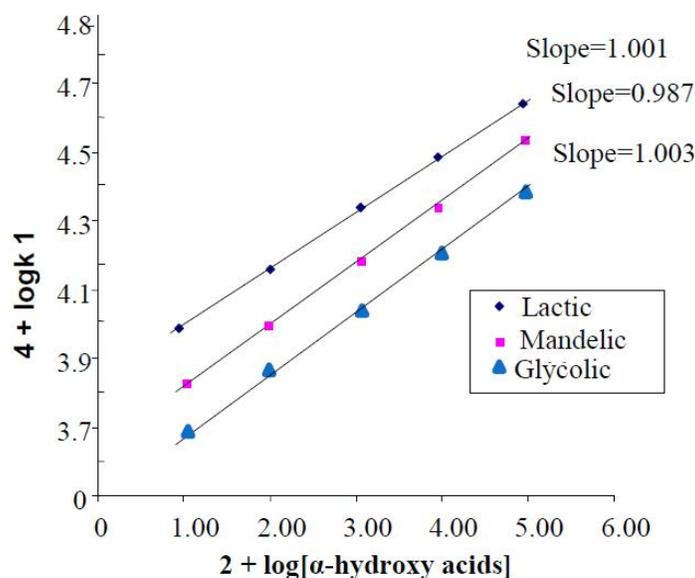
When the concentration of Pyridinium Bromo chromate (PBC) is varied from  $1.00$  to  $5.00 \times 10^{-3} \text{ mol dm}^{-3}$ , at a fixed  $\alpha$  – Hydroxy acids,  $[\text{HClO}_4]$  and micellar concentration, the specific rates remain

constant in keeping with the first dependence on Pyridinium Bromo chromate (PBC) concentration. Under identical conditions, the effect of changing unbound  $\alpha$  – Hydroxy acids concentration has been studied in the range of  $1.00 \times 10^{-3} \text{ mol dm}^{-3}$  with all the substrates in the absence of micellar medium. There is a monotonic increase in the rate of Pyridinium Bromo chromate (PBC) oxidation with unbound  $\alpha$  – Hydroxy acids with increasing concentration substrates.

Also a graph of logarithm of specific rate ( $k_1$  in  $\text{S}^{-1}$ ) Versus logarithm of  $\alpha$  – Hydroxy acids concentration is linear with a slope nearly equal to unity with a slope nearly the rate law of Pyridinium Bromo

TABLE 4

| AMMONIUM LAURAL SULFATE (ALS)                   |                     |                                                         |                |
|-------------------------------------------------|---------------------|---------------------------------------------------------|----------------|
| $10^2 [(NH_3)_5Co(III) -L] \text{ mol dm}^{-3}$ | $10^4 k_1 (S^{-1})$ | $10^2 k_2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ | $4 + \log k_1$ |
| <b>L = Lactato</b>                              |                     |                                                         |                |
| 1.00                                            | 0.96                | 0.96                                                    | 3.9822         |
| 2.00                                            | 1.43                | 0.96                                                    | 4.1553         |
| 3.00                                            | 2.33                | 0.96                                                    | 4.3673         |
| 4.00                                            | 2.66                | 0.96                                                    | 4.4248         |
| 5.00                                            | 4.20                | 0.96                                                    | 4.6232         |
| <b>M = Mandato</b>                              |                     |                                                         |                |
| 1.00                                            | 0.72                | 0.72                                                    | 3.8573         |
| 2.00                                            | 0.91                | 0.72                                                    | 3.9590         |
| 3.00                                            | 1.36                | 0.72                                                    | 4.1335         |
| 4.00                                            | 1.93                | 0.72                                                    | 4.2855         |
| 5.00                                            | 2.76                | 0.72                                                    | 4.4409         |
| <b>G = Glycolato</b>                            |                     |                                                         |                |
| 1.00                                            | 0.49                | 0.49                                                    | 3.6901         |
| 2.00                                            | 0.69                | 0.49                                                    | 3.8388         |
| 3.00                                            | 0.93                | 0.49                                                    | 3.9684         |
| 4.00                                            | 1.46                | 0.49                                                    | 4.1643         |
| 5.00                                            | 2.41                | 0.49                                                    | 4.3820         |

Figure 4 : Dependence of rate on  $[\alpha\text{-hydroxy acids}]$  in ALS

chromate (PBC) oxidation of unbound  $\alpha$ -Hydroxy acids which is similar to cobalt (III) bound ligands.

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

### SUMMARY

Earlier studies on induced electron transfer re-

action involved mainly an one equivalent oxidant, Ce (VI) and pentaammine cobalt (III) complexes,  $[(NH_3)_5Co(III)-L]^{2+}$  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.

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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 Pyridinium Bromo chromate (PBC) and pentaammine cobalt(III) complexes of  $\alpha$  - Hydroxy acids in the presence of Ammonium Lauryl Sulfate (ALS) medium and also in the absence of 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<sub>2</sub> 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 extend of 20 %. The cobalt (III) bound  $\alpha$  - Hydroxy acids 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.

## ACKNOWLEDGMENTS

With immense pleasure I express my heartfelt gratitude to Dr. MANSUR AHMED M.Sc.,M.Phil.,Ph.D., Head, P.G. & Research Department in chemistry, Vaniyambadi for his inspiring guidance, clear and explicit instruction and constant encouragement during the course of this work.

At last I thanks to my wife R. KALAIVANI M.A., for his kind help in processing the complete this work in computer.

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