

## Redox Reactions of Cobalt (III) Complexes of $\alpha$ –Hydroxy Acids by Pyridinium Bromo Chromate in the presence of Surfactants.

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### ABSTRACT

The Kinetics of one electron transfer route seems to be un available for Pyridinium bromo chromate with cobalt (III) bound and unbound complexes of  $\alpha$  –hydroxy acids in micellar medium pyridinium bromo chromate oxidises cobalt (III) bound and unbound  $\alpha$  –hydroxy acids. It rules out the synchronous C-C bond fission and electron transfer to Cobalt (III) centre. Oxidation of above complexes increases with increase of temperature with increase in micellar concentration. An increase in the rate is observed. The added dimethyl dioctadecyl ammonium chloride (DDAC) increases the rate of oxidation of a reaction much more than Ammonium lauryl sulphate (ALS). Similar trends observed in Lactato and Glycolato Cobalt (III) Complexes.

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### Introduction:

Conventional spectro photometry has been employed to study the oxidation of  $\alpha$ -hydroxy acids such as Lactic acid, Glycolic acid, mandelic acid and their cobalt (III) complexes using pyridinium bromo chromate as an oxidant in the presence of surfactant. One equivalent oxidant like Ce(IV) induced electron transfer in pentammine cobalt (III) complexes of  $\alpha$ -hydroxy acids result in nearly 100% reduction at cobalt (III) centre with synchronous carbon – carbon bond fission and decarboxilation. Such as electron transfer route seems to be un available for pyridinium bromo chromate in its reaction with cobalt (III) bound and unbound  $\alpha$ -hydroxy acids in micellar medium, pyridinium bromo chromate oxidise cobalt (III) bound and unbound  $\alpha$ - hydroxyacids to respective keto acid / keto acid cobalt (III) complexes in Ammonium lauryl sulphate (A.L.S) and dimethyl diocta decyl ammonium chloride (DDAC). Possibly the transition state is more electron deficient. Sub transition state can be envisaged only when the C-H bond fission occurs in the slow step with hydride in transfer. The absence of formation of cobalt (II) rules out the synchronous C-C- bond fission

and electron transfer to cobalt (III) the thermodynamic parameters are in consistent with bimolecular reaction. The rate of PBC oxidation of cobalt (III) lactato, glycolato, mandelato complexes depends on the first power of PBC concentration. Similarly the reaction between PBC, bound and unbound  $\alpha$ - hydroxy acid exhibits first order kinetics with respect to concentration of PBC of the three complexes, where as in the unbound ligand similar trends follows, that is lactic acid reacts faster than Glycolic and mandelic acid.

Oxidation is an important process in organic chemistry and introduction of new economic and effective reagents for oxidation under mild and anhydrous condition constitutes a standing challenge PBC (Anbuselvan and Sankaran, 1998; Das et al., 1984; Fan and Gould in 1974) is oxidant which is non-hydrosopic, non-photosensitive, stable yellow orange solid which is freely soluble in water, Acetic acid, N-N dimethyl formamide etc., the little work has been done on PCC as oxidant in micellar media (Frechet etal 1928, Frechet etal., 1978)

## Materials and Methods:

The surfactants used in the present work are Ammonium Lauryl sulphate (ALS) and dimethyl decyl ammonium chloride (DDAC). The surfactants are purified by adapting earlier procedure (Kabir-U-Din et al; 2005).

Kresheik, 1973; Long et al; 1973. The Chemicals were purchased DDAC from (B.D.H. U.K. 99%) A.L.S.Lactic, Glycolic and mandelic from (S.D. fine chemicals, India 95%) Penta ammine cobalt (III) complexes of  $\alpha$ -hydroxy acids were prepared using 'Fan and Gould'. Dash et al 1984; (Bain and Hercheinson, 1955) double distilled deionised and  $\text{CO}_2$  free) water was used as a solvent and  $\text{H}_2\text{SO}_4$  (E merck of India 95%) was standardised using standard sodium carbonate (B.D.H) (AR) solution with dimethyl orange as indicator. For the P.B.C. oxidation of cobalt (III) complexes of  $\alpha$ - hydroxyacids and unbound ligands (Mohan Hy 1982 and yasunaga et al; 1982). The rate measurement was made at  $32^\circ\text{C} \pm 0.2^\circ\text{C}$  in 100% aqueous medium. Temperature was controlled by electrically operated thermo stat (Mohanty and Nanda, 1982) the total volume of reaction mixture covered a spectro photo metric cell which was kept in 2.5 ml in each kinetic run. A systronics spectrophotometer, fitted with recording and thermo static arrangement was used to follow the rate of reaction. Rate of this PBC oxidant with unbound ligand and cobalt (III) bound complexes were calculated from observed decrease in absorbance at 350 nm. The excess of the reductant was used in the kinetic runs. It gives pseudo first order rate constant. It was determined from linear plot of the concentration versus time. Reproducible result obtained giving good first order plot.

The stiochiometric studies for the PBC oxidation of penta ammine cobalt (III) complexes of  $\alpha$ - hydroxy acids and un bound ligand in the presence of micelles were carried out at  $32^\circ \pm 0.2^\circ\text{C}$ . It was observed that the cobalt (II) formation was negligible.

## Result and Discussion:

Kinetic study of the oxidation of pentammine cobalt (III) complexes of  $\alpha$ - hydroxy acids by PBC in micellar medium. Dependence of rate on PBC concentration in micellar bound ligand ; the rate of oxidation of mandelato cobalt (III) complexes depends on PBC concentration. The specific rate calculated remains constant (table – 1) and graph of logarithm of PBC concentration, versus time (Fig.1) are linear. From the slope of these graphs, the specific rate calculated; agree with those obtained from integrated rate equation suggesting first order dependence on PBC concentration.

When the concentrations of PBC varied from 1.00 to  $3.00 \times 10^{-3} \text{mol dm}^{-3}$  at a fixed [Cobalt(III) and  $\text{H}_2\text{SO}_4$ ]. Specific rates remains constant. Then the rate of disappearance of Cr(IV) is given by equation 1.

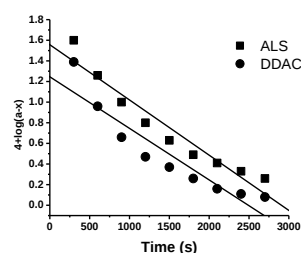
$$-d[\text{Cr(VI)}]/dt = K[\text{Cr(VI)}] \dots\dots\dots (1)$$

**Table: 1.** The specific rate calculated values of ALS and DDAC.

| Components                                              | Concentrations                            |
|---------------------------------------------------------|-------------------------------------------|
| $[(\text{CH}_3)_5\text{Co}^{\text{III}}\text{-L}]^{2+}$ | $=2.00 \times 10^{-2} \text{mol dm}^{-3}$ |
| PBC                                                     | $=2.00 \times 10^{-3} \text{mol dm}^{-3}$ |
| $\text{H}_2\text{SO}_4$                                 | $=1.00 \times \text{mol dm}^{-3}$         |
| ALS                                                     | $=2.00 \times 10^{-3} \text{mol dm}^{-3}$ |
| Temperature                                             | $=32^\circ \pm 0.2^\circ\text{C}$         |
| L                                                       | =Mandelato                                |

| $10^3(a-x) \text{mol dm}^{-3}$ |      |      |
|--------------------------------|------|------|
| Time(s)                        | ALS  | DDAC |
| 300                            | 1.60 | 1.39 |
| 600                            | 1.26 | 0.96 |
| 900                            | 1.00 | 0.66 |
| 1200                           | 0.80 | 0.47 |
| 1500                           | 0.63 | 0.37 |
| 1800                           | 0.49 | 0.26 |
| 2100                           | 0.41 | 0.16 |
| 2400                           | 0.33 | 0.11 |
| 2700                           | 0.26 | 0.08 |



**Figure: 1.** 1<sup>st</sup> order dependence plots

At a particular concentration of PBC with increase in mandelato, glycolato cobalt (III) concentration in the range of  $1.00$  to  $3.00 \times 10^{-3} \text{mol dm}^{-3}$  there is proportional increase in the rate of oxidation (Table-2). The slope of nearly units is obtained from linear graph of logarithm (Figure-2) of specific rate ( $K$  is  $\text{S}^{-1}$ ) versus log of Co(III) concentration in each case suggesting that first order rate dependence of rate on  $[\text{Co(III)}]$ .

**Table: 2.** The rate constant values of [Cobalt(III)] in ALS.

| Components              | Concentrations                            |  |
|-------------------------|-------------------------------------------|--|
| PBC                     | $=2.00 \times 10^{-3} \text{mol dm}^{-3}$ |  |
| $\text{H}_2\text{SO}_4$ | $=1.00 \text{mol dm}^{-3}$                |  |
| ALS                     | $=2.00 \times 10^{-3} \text{mol dm}^{-3}$ |  |
| Temperature             | $=32^\circ \pm 0.2^\circ\text{C}$         |  |

| $10^2[\text{NH}_3)_5\text{Co}^{\text{III}}\text{-L}]$ | $10^4 K_1(\text{S}^{-1})$ | $10^2 K_2 \text{dm}^{-3} \text{S}^{-1} \text{mol dm}^{-3}$ |
|-------------------------------------------------------|---------------------------|------------------------------------------------------------|
| L = Mandelato                                         |                           |                                                            |
| 1.00                                                  | 3.80                      | 3.80                                                       |
| 1.50                                                  | 5.81                      | 3.87                                                       |
| 2.00                                                  | 7.60                      | 3.81                                                       |
| 2.50                                                  | 9.62                      | 3.84                                                       |
| 3.00                                                  | 11.58                     | 3.87                                                       |
| L = Lactato                                           |                           |                                                            |
| 1.00                                                  | 4.40                      | 4.40                                                       |
| 1.50                                                  | 6.80                      | 4.56                                                       |
| 2.00                                                  | 8.92                      | 4.45                                                       |
| 2.50                                                  | 11.18                     | 4.42                                                       |
| 3.00                                                  | 13.44                     | 4.43                                                       |
| L-Glycolato                                           |                           |                                                            |
| 1.00                                                  | 2.52                      | 2.52                                                       |
| 2.25                                                  | 6.38                      | 2.50                                                       |
| 3.00                                                  | 7.80                      | 2.60                                                       |

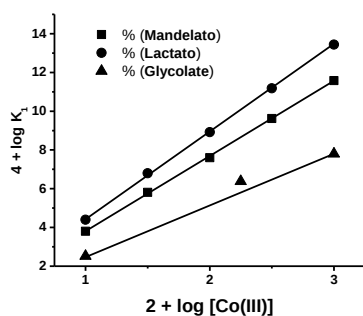


Figure 2. Dependence of rate on [Cobalt(III)] in ALS.

Hence the rate law for Chromium(VI) oxidation of Cobalt (III) bound  $\alpha$  – hydroxy acids are given by equation (2)

$$-d[\text{Cr(VI)}]/dt = K_2[\text{Cr(VI)}][\text{Co(III)}] \dots\dots 2$$

Dependence rate on PBC concentration in micellar medium for  $\alpha$  – hydroxy acid. The rate of oxidation of Mandelato Co(III) complexes depends on PBC concentration. In any specific run the change in concentration of PBC, the specific rate calculated remain constant (Table-3) and graph of logarithm of PBC concentration versus time are linear (Figure-3).

Table 3. The rate constant values of [Cobalt(III)] in DDAC

| Components                     | Concentrations                             |
|--------------------------------|--------------------------------------------|
| PBC                            | $=2.00 \times 10^{-3} \text{ mol dm}^{-3}$ |
| H <sub>2</sub> SO <sub>4</sub> | $=1.00 \text{ mol dm}^{-3}$                |
| DDAC                           | $=2.00 \times 10^{-3} \text{ mol dm}^{-3}$ |
| Temperature                    | $=32^\circ \pm 0.2^\circ \text{C}$         |

| $10^2[(\text{NH}_3)_5\text{Co}^{\text{III}}\text{-L}]$ | $10^4 K_1 (\text{S}^{-1})$ | $10^2 K_2 \text{ dm}^{-3} \text{ mol}^{-1} \text{ S}^{-1}$ |
|--------------------------------------------------------|----------------------------|------------------------------------------------------------|
| L = Mandelato                                          |                            |                                                            |
| 1.00                                                   | 6.2                        | 6.2                                                        |
| 2.00                                                   | 12.2                       | 6.05                                                       |
| 2.50                                                   | 15.8                       | 6.28                                                       |
| 3.00                                                   | 18.2                       | 6.06                                                       |
| L = Lactato                                            |                            |                                                            |
| 1.00                                                   | 7.20                       | 7.20                                                       |
| 1.50                                                   | 10.7                       | 7.13                                                       |
| 2.00                                                   | 14.5                       | 7.25                                                       |
| 3.00                                                   | 21.2                       | 7.06                                                       |
| L-Glycolato                                            |                            |                                                            |
| 1.00                                                   | 4.70                       | 4.70                                                       |
| 2.00                                                   | 7.22                       | 4.81                                                       |
| 2.50                                                   | 9.70                       | 4.85                                                       |
| 3.00                                                   | 11.90                      | 4.76                                                       |

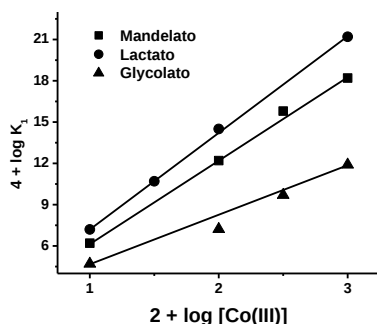


Figure-3. Dependence of rate on Cobalt(III) in DDAC.

When concentration of PBC is varied from 1.00 to  $3.00 \times 10^{-3} \text{ mol dm}^{-3}$  at a fixed  $[\text{Co(III)}]$  and  $[\text{H}_2\text{SO}_4]$  specific rates remain constant. Then the rate disappearance of Cr(VI) is given by equation 3.

$$-d[\text{Cr(VI)}] / dt = K_1[\text{Cr(VI)}] \dots\dots\dots 3$$

#### Dependence of rate on the concentration of $\alpha$ – hydroxyacid in ALS and DDAC:

The oxidation studies were carried out by varying initial  $[\alpha$  – hydroxy acid] in the range of 1.00 to  $3.00 \times 10^{-3} \text{ mol dm}^{-3}$  by keeping other variable constant. The near constancy in the  $K_2$  values (Tables 4 and 5) and the slope of nearly unit is obtained. From linear graph of logarithm of specific rate ( $k_1$  in  $\text{S}^{-1}$ ) versus logarithm of  $\alpha$  – hydroxy acid concentration in each case suggesting first order dependence of rate on  $[\alpha$  – hydroxy acid] (Figures 4 and 5). Hence the rate law for the Cr(VI) oxidation  $\alpha$  – hydroxy acid is given below equation 4.

$$-d[\text{Cr(VI)}] / dt = k_2 [\text{Cr(VI)}] \dots\dots\dots 4.$$

Table 4. The rate constant values of  $[\alpha$  – hydroxy acid] in ALS

| Components                     | Concentrations                             |
|--------------------------------|--------------------------------------------|
| PBC                            | $=2.00 \times 10^{-3} \text{ mol dm}^{-3}$ |
| H <sub>2</sub> SO <sub>4</sub> | $=1.00 \text{ mol dm}^{-3}$                |
| ALS                            | $=2.00 \times 10^{-3} \text{ mol dm}^{-3}$ |
| Temperature                    | $=32^\circ \pm 0.2^\circ \text{C}$         |

| $10^{-3}[\alpha\text{-hydroxy acid}] \text{ mol dm}^{-3}$ | $10^4 K_1 (\text{S}^{-1})$ | $10^2 K_2 \text{ dm}^{-3} \text{ mol}^{-1} \text{ S}^{-1}$ |
|-----------------------------------------------------------|----------------------------|------------------------------------------------------------|
| Mandelic Acid                                             |                            |                                                            |
| 1.00                                                      | 1.62                       | 1.62                                                       |
| 1.50                                                      | 2.43                       | 1.64                                                       |
| 2.00                                                      | 3.27                       | 1.67                                                       |
| 2.50                                                      | 4.15                       | 1.66                                                       |
| 3.00                                                      | 4.88                       | 1.63                                                       |
| Lactic Acid                                               |                            |                                                            |
| 1.00                                                      | 2.22                       | 2.23                                                       |
| 1.50                                                      | 3.41                       | 2.27                                                       |
| 2.00                                                      | 4.52                       | 2.25                                                       |
| 2.50                                                      | 5.63                       | 2.26                                                       |
| Glycolic Acid                                             |                            |                                                            |
| 1.00                                                      | 1.36                       | 1.36                                                       |
| 2.00                                                      | 2.82                       | 1.41                                                       |
| 2.50                                                      | 3.55                       | 1.42                                                       |
| 3.00                                                      | 4.18                       | 1.40                                                       |

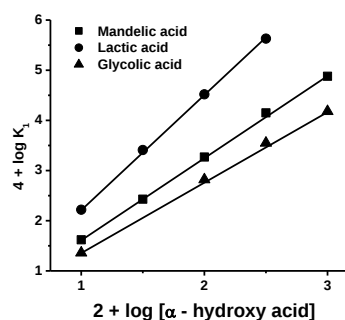


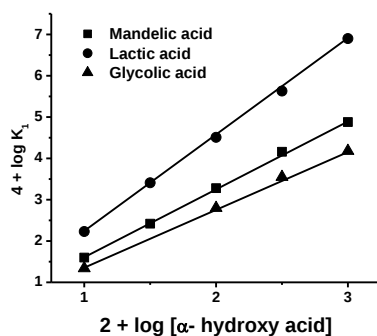
Figure-4. Dependence of rate on  $[\alpha$  – hydroxy acid] in ALS.

**Table: 5.** The rate constant values of [ $\alpha$  – hydroxy acid] in DDAC

| Components                     | Concentrations                            |  |
|--------------------------------|-------------------------------------------|--|
| PBC                            | $=2.00 \times 10^{-3} \text{mol dm}^{-3}$ |  |
| H <sub>2</sub> SO <sub>4</sub> | $=1.00 \text{mol dm}^{-3}$                |  |
| DDAC                           | $=2.00 \times 10^{-3} \text{mol dm}^{-3}$ |  |
| Temperature                    | $=32.0 \pm 0.2^\circ \text{C}$            |  |

| $10^{-3}[\alpha\text{-hydroxy acid}] \text{ mol dm}^{-3}$ | $10^4 K_1 (\text{S}^{-1})$ | $10^2 K_2 \text{ dm}^{-3} \text{ mol}^{-1} \text{ S}^{-1}$ |
|-----------------------------------------------------------|----------------------------|------------------------------------------------------------|
| Mandelic Acid                                             |                            |                                                            |
| 1.00                                                      | 1.60                       | 1.60                                                       |
| 1.50                                                      | 2.42                       | 1.62                                                       |
| 2.00                                                      | 3.28                       | 1.65                                                       |
| 2.50                                                      | 4.16                       | 1.62                                                       |
| 3.00                                                      | 4.88                       | 1.64                                                       |
| Lactic Acid                                               |                            |                                                            |
| 1.00                                                      | 2.23                       | 2.24                                                       |
| 1.50                                                      | 3.41                       | 2.27                                                       |
| 2.00                                                      | 4.51                       | 2.25                                                       |
| 2.50                                                      | 5.63                       | 2.28                                                       |
| 3.00                                                      | 6.90                       | 2.20                                                       |
| Glycolic Acid                                             |                            |                                                            |
| 1.00                                                      | 1.34                       | 1.34                                                       |
| 2.00                                                      | 2.80                       | 1.42                                                       |
| 2.50                                                      | 3.55                       | 1.40                                                       |
| 3.00                                                      | 4.18                       | 1.36                                                       |

**Figure-5.** Dependence of rate on [ $\alpha$  – hydroxy acid] in DDAC.

### Comparison of rates on oxidation of Pentaamminecobalt (III) complexes of both bound and unbound $\alpha$ -hydroxy acid by PBC:

Specific rate of the lactato complex is more compared to both the rates of oxidation of unbounded ligand and mandelato complex deserves an explanation. The ligation of lactic acid to Co(III) centre has probably increased its reactivity towards PBC and this effect seems to be more specific for this ligand only. If the reaction proceeds through a performed Chromate ester, then the rate  $\alpha$ -C-H fission will be enhanced, resulting in an increased rate of oxidation of lactato complex such a precursor complex may be sterically hindered in the case of mandelato and glycolato complexes.

### Conclusions:

The oxidation reactions of Cobalt(III) complexes of  $\alpha$ -hydroxy acids viz, mandelic acid, lactic acid and glycolic acid addition have been carried out using a novel chromimum (VI) oxidant. There is a remarkable increase in the rate of novel surfactants i.e. ALS and DDAC. These surfactants act as a positive catalyst in situation of the reaction and among which DDAC enhances the rate much more than the ALS.

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