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Kinetics of Oxidation of Cobalt(III) Complexes of α -Hydroxy Acids by Hydrogen Peroxide in the Presence of Surfactants

MANSUR AHMED* and K. SUBRAMANI

Department of Chemistry, Islamiah College, Vaniyambadi-2, India.

chem_islamiah@fastmail.us

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Abstract: Hydrogen peroxide oxidation of pentaamminecobalt(III) complexes of α -hydroxy acids at 35 °C in micellar medium has been attempted. In this reaction the rate of oxidation shows first order kinetics each in [cobalt(III)] and [H₂O₂]. Hydrogen peroxide induced electron transfer in [(NH₃)₅CoIII-L]²⁺ complexes of α -hydroxy acids readily yields 100% of cobalt(II) with nearly 100% of C-C bond cleavage products suggesting that it behaves mainly as one equivalent oxidant in micellar medium. With unbound ligand also it behaves only as C-C cleavage agent rather than C-H cleavage agent. With increasing micellar concentration an increase in the rate is observed.

Keywords: Sodium lauryl sulphate, Cetyl trimethyl ammonium bromide, Induced electron transfer micellar medium. Mandelic acid, Glycolic acid, Hydrogen peroxide.

Introduction

Oxidation is an important process in organic chemistry and use of new economic and effective oxidants under mild and anhydrous conditions constitutes a standing challenge. H₂O₂ is an oxidant¹⁻³, which is non-hygroscopic non-photosensitive, stable yellow orange solid, freely soluble in water, acetic acid, *N,N*-dimethylformamide *etc.* Only few works have been done on H₂O₂ with cobalt(III) complexes as oxidant in micellar media⁴⁻⁶. A study of induced electron transfer reaction in Co(III) – L system by an external oxidant is an aid. To classify the mode of action of the external oxidant, whether an one electron transfer takes place at the bound organic ligand or the bound organic ligand gets oxidized without disturbing Co(III) center.

Experimental

The surfactants used in the present work are sodium lauryl sulphate⁶ (NaLS) and cetyl trimethyl ammonium bromide⁷ (CTAB). The surfactants are purified by adopting earlier procedure^{8,9,10}. Pentaamminecobalt(III) complexes of α -hydroxyacids were prepared using Fan and Gould¹¹. Double distilled (deionised and CO₂ free) water was used as a solvent and H₂SO₄ was standardized using standard Sodiumcarbonate solution with methyl orange as indicator. For the H₂O₂ oxidation of Co(III) Complexes of α -hydroxy acid and unbound ligands, the rate measurement were made at 35 ± 0.2 °C in 100% aqueous micellar medium and temperature was controlled by electrically operated thermostat¹². The total volume of reaction mixture in the spectrophotometric cell was kept as 2.5 mL in each kinetic run. A systronic spectrophotometer fitted with recording and thermostating arrangement was used to follow the rate of the reaction. Rate of these H₂O₂ oxidant with unbound ligand and cobalt(III) bound complexes were calculated from observed decrease in absorbance at 350nm for oxidant, and 502nm for cobalt(III) complexes.

Table 1. Stoichiometric data for H₂O₂ oxidation of Co(III) bound and unbound α - hydroxy acids in the presence of NALS.

[H₂SO₄] = 1.00 mol dm⁻³, [NaLS] = 2.00 x 10⁻³ mol dm⁻³, Temperature = 35 \pm 0.2 °C

| 10 ³ [Compound] mol dm ⁻³ | 10 ² [H ₂ O ₂] initial mol dm ⁻³ | 10 ² [H ₂ O ₂] Final mol dm ⁻³ | Δ 10 ³ [H ₂ O ₂] mol dm ⁻³ | [Compound] Δ [H ₂ O ₂] |
|--|--|--|---|---|
| Mandelic acid | | | | |
| 4.0 | 2.0 | 1.60 | 4.0 | 1.00 : 1.00 |
| 5.0 | 2.0 | 1.55 | 4.5 | 1.00 : 0.90 |
| 6.0 | 3.0 | 2.42 | 5.8 | 1.00 : 0.98 |
| Lactic acid | | | | |
| 4.0 | 2.0 | 1.60 | 3.9 | 1.00 : 0.97 |
| 5.0 | 2.0 | 1.51 | 4.9 | 1.00 : 0.98 |
| 6.0 | 3.0 | 2.40 | 6.0 | 1.00 : 1.00 |
| Glycolic acid | | | | |
| 4.0 | 2.0 | 1.60 | 4.0 | 1.00 : 1.00 |
| 5.0 | 2.0 | 1.50 | 5.0 | 1.00 : 1.00 |
| 6.0 | 3.0 | 2.42 | 5.8 | 1.00 : 0.96 |
| Co(III)-Mandelato | | | | |
| 4.0 | 2.0 | 1.75 | 2.5 | 1.00 : 0.60 |
| 5.0 | 2.0 | 1.71 | 2.9 | 1.00 : 0.60 |
| 6.0 | 3.0 | 2.67 | 3.3 | 1.00 : 0.65 |
| Co(III)-Lactato | | | | |
| 4.0 | 2.0 | 1.79 | 2.1 | 1.00 : 0.52 |
| 5.0 | 2.0 | 1.74 | 2.6 | 1.00 : 0.52 |
| 6.0 | 3.0 | 2.68 | 3.2 | 1.00 : 0.53 |
| Co(III)-Glycolato | | | | |
| 4.0 | 2.0 | 1.80 | 2.0 | 1.00 : 0.50 |
| 5.0 | 2.0 | 1.76 | 2.4 | 1.00 : 0.48 |
| 6.0 | 3.0 | 2.70 | 3.0 | 1.00 : 0.50 |

The excess of the reductant was used in kinetic runs. It gives pseudo first order. The rate constant was determined from the linear plot of the $\ln A$ versus time. Reproducible result obtained giving good first order plot. The stoichiometric studies for the H₂O₂ oxidation of pentaammine

cobalt(III) complexes of α -hydroxyacid and unbound ligand in the presence of micelles were carried out at $35 \pm 0.2^\circ\text{C}$. It was observed that the cobalt(II) formation was negligibly small.

Stoichiometric studies

The stoichiometric studies for the H_2O_2 oxidation of pentaamminecobalt(III) complexes of α -hydroxy acids and unbound ligands in the presence of micelles (NaLS Table 1 & CTAB Table 2) were carried out with oxidant in excess. The $[\text{H}^+]$ and ionic strength were maintained as in the corresponding rate measurements. The temperature was maintained at $35 \pm 0.2^\circ\text{C}$. After nine half lives when the reaction was nearing completion, the concentration of unreacted H_2O_2 was determined both iodometrically and spectrophotometrically from the change in absorbance measured at 350nm. $\Delta\text{H}_2\text{O}_2$ was calculated after applying blank corrections for decomposition of H_2O_2 and aquation of cobalt(III) complex of α -hydroxy acids in the presence of micelles. Similar calculation about $\Delta[\text{H}_2\text{O}_2]$ was made for the unbound ligand also. The stoichiometry was calculated from the ratio between reacted [oxidant] and [substrate]. From the decrease in the absorbance measured for the cobalt(III) complex, the amount of cobalt(III) reduced was calculated. This value was then compare with the amount of cobalt(II) formed. Also H_2O_2 oxidation of Co(III) complexes of α -hydroxy acids polymerization test done. It confirms the reaction proceeds through radical path way.

Table 2. Stoichiometric data for BPC oxidation of Co(III) bound and unbound α -hydroxy acids in the presence of CTAB.

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

| 10^3 [Compound] mol dm^{-3} | 10^2 [BPC] initial mol dm^{-3} | 10^2 [BPC] Final mol dm^{-3} | $\Delta 10^3$ [BPC] mol dm^{-3} | 10^4 [Co(II)] mol dm^{-3} | [Compound]: Δ [BPC] |
|---|---|---|---|---|-------------------------------|
| Mandelic acid | | | | | |
| 1.0 | 1.0 | 0.950 | 0.50 | - | 1.00 : 0.50 |
| 2.0 | 2.0 | 1.926 | 0.74 | - | 1.00 : 0.37 |
| 4.0 | 2.0 | 1.844 | 1.56 | - | 1.00 : 0.39 |
| Lactic acid | | | | | |
| 1.0 | 1.0 | 0.960 | 0.40 | - | 1.00 : 0.40 |
| 2.0 | 2.0 | 1.930 | 0.70 | - | 1.00 : 0.35 |
| 4.0 | 2.0 | 1.840 | 1.60 | - | 1.00 : 0.40 |
| Glycolic acid | | | | | |
| 1.0 | 1.0 | 0.960 | 0.40 | - | 1.00 : 0.40 |
| 2.0 | 2.0 | 1.934 | 0.66 | - | 1.00 : 0.33 |
| 4.0 | 2.0 | 1.866 | 1.44 | - | 1.00 : 0.36 |
| Co(III)-Mandelato | | | | | |
| 1.0 | 1.0 | 0.964 | 0.36 | 1.9(19%) | 1.00 : 0.36 |
| 2.0 | 2.0 | 1.942 | 0.58 | 3.7(18.5%) | 1.00 : 0.29 |
| 4.0 | 2.0 | 1.915 | 0.58 | 7.8(19%) | 1.00 : 0.21 |
| Co(III)-Lactato | | | | | |
| 1.0 | 1.0 | 0.974 | 0.26 | 1.8 (18%) | 1.00 : 0.26 |
| 2.0 | 2.0 | 1.940 | 0.60 | 4.2 (21%) | 1.00 : 0.30 |
| 4.0 | 2.0 | 1.900 | 1.00 | 8.0 (20%) | 1.00 : 0.25 |

Results and Discussion

Dependence of rate on H₂O₂ concentration in micellar bound ligand.

The rate of oxidation of mandelato, lactato and glycolatocobalt(III) complexes depends on H₂O₂ concentration. In any specific run, the specific rates calculated remains constant (Table 3) and graph of logarithm of H₂O₂ concentration *versus* time (Figure 1) are linear. From the slope of these graphs, the specific rate calculated agrees with those obtained from integrated rate equation suggesting first order dependence on H₂O₂ concentration. This is further substantiated from the study of the effect of changing H₂O₂ concentration on the rate of oxidation. The constancy in the specific rates of oxidation of mandelato, lactato and glycolato cobalt(III) complexes, is in keeping with the first order dependence on H₂O₂ concentration. The rate law is given by Eq.1

$$-d [H_2O_2] / dt = k_1 [H_2O_2] \quad (1)$$

Table 3. First order values for H₂O₂ oxidation of cobalt(III) bound Ligand.

$[(NH_3)_5 Co^{III} - L]^{2+} = 2.00 \times 10^{-2} \text{ mol dm}^{-3}$, $[H_2O_2] = 2.00 \times 10^{-3} \text{ mol dm}^{-3}$,
 $[H_2SO_4] = 1.00 \text{ mol dm}^{-3}$, $[NaLS] = [CTAB] = 2.00 \times 10^{-3} \text{ mol dm}^{-3}$,
 Temperature = $35 \pm 0.2^\circ C$, L = mandelato.

| Time s | $10^3 (a-x), \text{ mol dm}^{-3}$ | |
|-----------|-----------------------------------|------|
| | NaLS | CTAB |
| 300 | 1.60 | 1.39 |
| 600 | 1.26 | 0.96 |
| 900 | 1.00 | 0.66 |
| 1200 | 0.80 | 0.47 |
| 1500 | 0.63 | 0.32 |
| 1800 | 0.49 | 0.23 |
| 2100 | 0.41 | 0.16 |
| 2400 | 0.33 | 0.11 |
| 2700 | 0.26 | 0.08 |

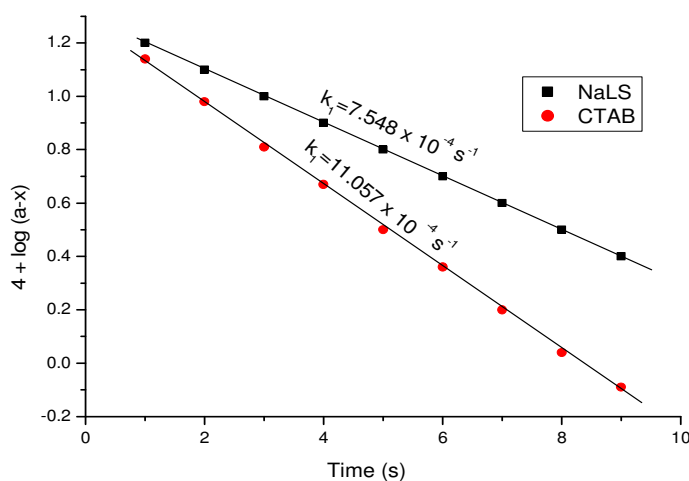


Figure 1. First order dependence plots.

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

At a particular H_2O_2 concentration with increases in manlato/lactato/glycolato cobalt(III) concentration in the range 1.00 to $3.00 \times 10^{-3} \text{ mol dm}^{-3}$ there is a proportional increases in the rate of oxidation (Table 4 & 5), as shown by the correlation coefficients of 0.9992 , 0.9998 and 0.9996 for the above respective complexes in anionic micelles. The slope of nearly unity is obtained from a linear graph of logarithm of specific rate (k in s^{-1}) versus logarithm of Co(III) concentration in each case suggesting first order rate dependence of rate on [Co(III)] (Figures 2 & 3). Hence the rate law for the H_2O_2 oxidation of cobalt(III) bound of α -hydroxy acids are given by Eq. 2

$$-d[H_2O_2] / dt = k_2 [H_2O_2] [Co(III)] \tag{2}$$

Table 4. First order values of the concentration of cobalt(III) bound α -hydroxy acids in NaLS.

$[H_2O_2] = 2.00 \times 10^{-3} \text{ mol dm}^{-3}$, $[H_2SO_4] = 1.00 \text{ mol dm}^{-3}$ $[Na LS] = 2.00 \times 10^{-3} \text{ mol dm}^{-3}$
 Temperature = $35 \pm 0.2^\circ C$.

| $10^2 [(NH_3)_5 Co^{III} - L]$, mol dm^{-3} | $10^4 k_1$, s^{-1} | $10^2 k_2$, $\text{dm}^3 \text{ mol}^{-1} s^{-1}$ |
|--|--------------------------|---|
| L= Mandelacto | | |
| 1.00 | 3.80 | 3.80 |
| 1.50 | 5.81 | 3.87 |
| 2.00 | 7.62 | 3.81 |
| 2.50 | 9.60 | 3.84 |
| 3.00 | 11.60 | 3.87 |
| L=Lactato | | |
| 1.00 | 4.40 | 4.40 |
| 1.50 | 6.82 | 4.55 |
| 2.00 | 8.90 | 4.45 |
| 3.00 | 13.40 | 4.47 |
| L= Glycolato | | |
| 1.00 | 2.51 | 2.51 |
| 2.50 | 6.35 | 2.54 |
| 3.00 | 7.84 | 2.61 |

Table 5. First order values of the concentration of cobalt (III) bound α -hydroxy acids in CTAB.
 $[H_2O_2] = 2.00 \times 10^{-3} \text{ mol dm}^{-3}$, $[H_2SO_4] = 1.00 \text{ mol dm}^{-3}$, $[CTAB] = 2.00 \times 10^{-3} \text{ mol dm}^{-3}$
 Temperature = $35 \pm 0.2^\circ C$

| $10^2 [(NH_3)_5 Co^{III} - L]$, mol dm^{-3} | $10^4 k_1$, s^{-1} | $10^2 k_2$, $\text{dm}^3 \text{ mol}^{-1} s^{-1}$ |
|--|--------------------------|---|
| L= Mandelacto | | |
| 1.00 | 6.2 | 6.20 |
| 2.00 | 12.1 | 6.05 |
| 2.50 | 15.7 | 6.28 |
| 3.00 | 18.2 | 6.06 |
| L=Lactato | | |
| 1.00 | 7.2 | 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 |
| 1.50 | 7.22 | 4.81 |
| 2.00 | 9.70 | 4.85 |
| 2.50 | 11.90 | 4.76 |

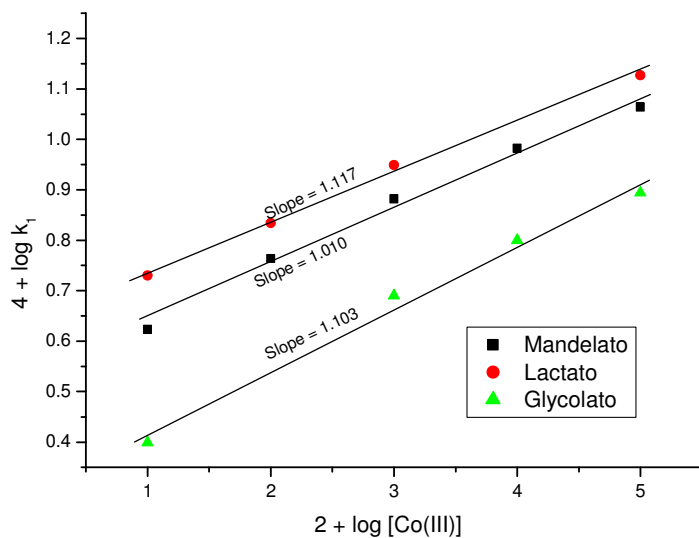


Figure 2. Dependence of rate on $[\text{Co(III)}]$ in NaLS

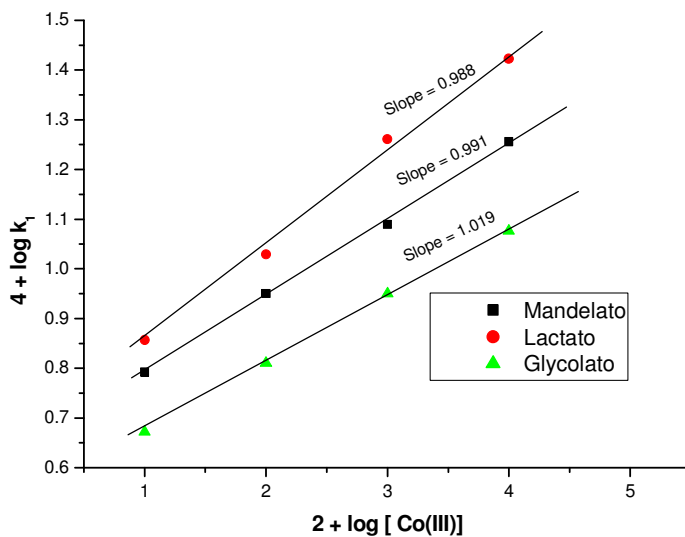


Figure 3. Dependence of rate on $[\text{Co(III)}]$ in CTAB

Dependence of rate on α -hydroxyacid concentration

Under identical conditions, the effect of changing unbound α -hydroxyacid concentration has been studied in the range 1.00 to $3.00 \times 10^{-2} \text{ mol dm}^{-3}$ with all these substrates in micellar medium.

There is a monotonic increase in the rate of H_2O_2 oxidation with unbound α -hydroxyacid with increase concentration of substrate (Table 3&4), as shown by the correlation coefficients of 0.9996. Also a graph of logarithm of specific rate (k_1 in s^{-1}) versus logarithm of α -hydroxyacid concentration is linear with a slope nearly equal to unity (Figure 6&7) with each one of the substrates and therefore, the rate law for the H_2O_2 oxidation of unbound α -hydroxyacid which is similar to cobalt(III) bound ligands, is given Eq. 3.

$$-d[\text{H}_2\text{O}_2] / dt = k_2[\text{H}_2\text{O}_2] [\alpha\text{-hydroxyacid}] \quad (3)$$

Table 6. First order values of the concentration of α -hydroxy acids in NaLS

$[\text{H}_2\text{O}_2] = 2.00 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{H}_2\text{SO}_4] = 1.00 \text{ mol dm}^{-3}$, $[\text{Na LS}] = 2.00 \times 10^{-3} \text{ mol dm}^{-3}$
 Temperature = 35 ± 0.2 °C

| 10^2 [α -hydroxy acid] mol dm^{-3} | 10^4 k_1 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 | 1.62 |
| 2.00 | 3.28 | 1.67 |
| 2.50 | 4.16 | 1.66 |
| 3.00 | 4.89 | 1.63 |
| Lactic acid | | |
| 1.00 | 2.23 | 2.23 |
| 1.50 | 3.41 | 2.27 |
| 2.00 | 4.51 | 2.25 |
| 2.50 | 5.63 | 2.26 |
| 3.00 | 6.92 | 2.20 |
| Glycolic acid | | |
| 1.00 | 1.36 | 1.36 |
| 2.00 | 2.82 | 1.41 |
| 2.50 | 3.55 | 1.42 |
| 3.00 | 4.18 | 1.39 |

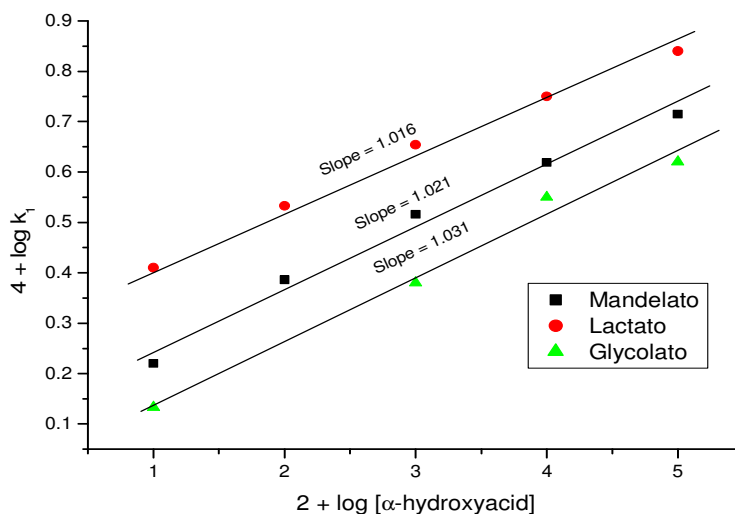


Figure 4. Dependence of rate on [α -hydroxyacid] in NaLS

Table 7. First order values of the concentration of α -hydroxy acids in CTAB
 $[\text{H}_2\text{O}_2] = 2.00 \times 10^{-3} \text{ mol dm}^{-3}$, $[\text{H}_2\text{SO}_4] = 1.00 \text{ mol dm}^{-3}$, $[\text{CTAB}] = 2.00 \times 10^{-3} \text{ mol dm}^{-3}$
 Temperature = 35 ± 0.2 °C.

| $10^2 [\alpha\text{-hydroxy acid}]$ mol dm^{-3} | $10^4 k_1$ s^{-1} | $10^2 k_2$ $\text{dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$ |
|---|-------------------------------|---|
| Mandelic acid | | |
| 1.00 | 2.06 | 2.06 |
| 1.50 | 3.13 | 2.08 |
| 2.00 | 4.18 | 2.09 |
| 2.50 | 5.26 | 2.10 |
| Lactic acid | | |
| 1.00 | 3.02 | 3.02 |
| 1.50 | 4.61 | 3.07 |
| 2.00 | 6.12 | 3.06 |
| 3.00 | 9.24 | 3.08 |
| Glycolic acid | | |
| 1.00 | 1.93 | 1.93 |
| 1.50 | 2.98 | 1.98 |
| 2.00 | 3.95 | 1.97 |
| 2.50 | 4.86 | 1.94 |

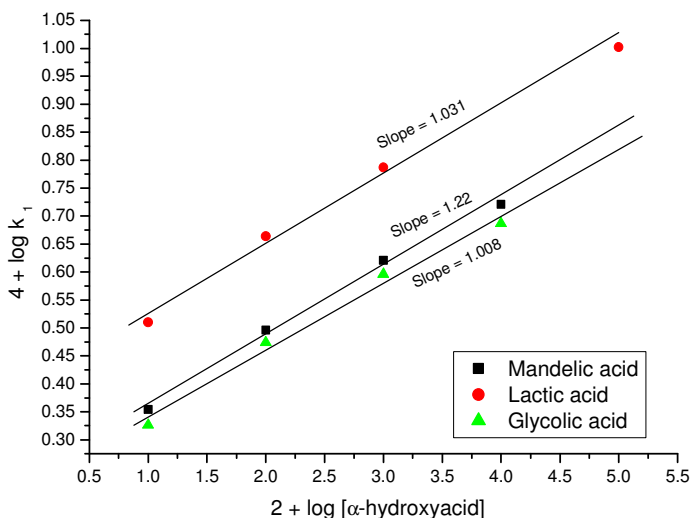


Figure 5. Dependence of rate on $[\alpha\text{-hydroxyacid}]$ in CTAB

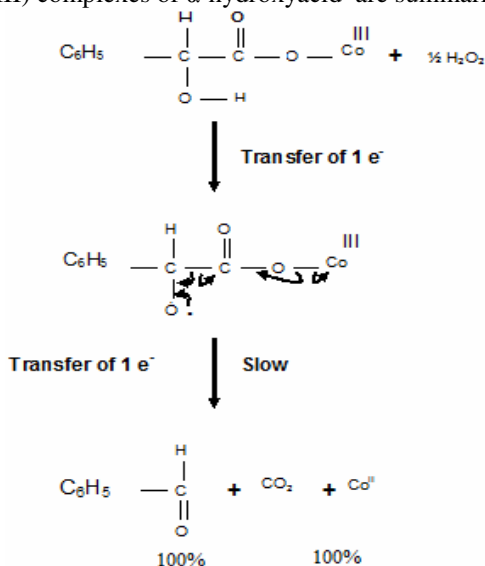
Comparison of rates on oxidation of pentaammincobalt(III) complexes of both bound and unbound α -hydroxyacid by H_2O_2 .

The cobalt(III) lactato complex is faster than cobalt(III) mandelato and cobalt(III) glycolato complex, because if the reaction proceeds through a performed radical, then the rate of C-H cleavage should be enhanced, resulting in a increase in the rate of oxidation of cobalt(III) complex. At the same concentration added CTAB enhances the rate of oxidation of reaction much more than added NaLS. Both cationic and anionic micelles act as positive catalyst,

a neutral reaction H_2O_2 species is involved in the oxidation. If the reaction species is ionic the reaction, would have been accelerated in one detergent and retarded in the other depending on the charge carried by it.

Mechanism

Oxidation of pentaamminecobalt(III) complexes of both bound and unbound ligands in micellar medium. The features of hydrogen peroxide induced electron transfer in pentaamminecobalt(III) complexes of α -hydroxyacid are summarized as below.



Conclusion

The kinetics of one electron transfer route seems to be available for H_2O_2 with cobalt(III) bound and unbound complexes of α -hydroxyacid in micellar medium, H_2O_2 oxidizes cobalt(III) bound and unbound α -hydroxyacids. It explains 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 CTAB enhances the rate of oxidation of a reaction much more than NaLS. Similar trends has been observed in lactato and glycolato co(III) complexes.

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