



OXIDATION OF COBALT (III) COMPLEXES OF α - HYDROXY ACIDS BY POTASSIUM BROMATE IN THE PRESENCE OF SURFACTANT

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ABSTRACT

An induced electron transfer reaction has been attempted presently with potassium bromate and pentaammine cobalt (III) complexes of α -hydroxy acids in the presence of micelles. The reaction exhibits second order kinetics and in the case of mandelato complexes the amount of cobalt (III) reduced corresponds to nearly 70% of mandelato complex is converted to keto acid cobalt (III) complex. In potassium bromate induced electron transfer in the complex, the intermediate radical formed dissociates in a nearly synchronous manner with C-C bond cleavage and the rest of it proceeding with α -C-H fission yielding keto acid cobalt (III) complex. With increasing the detergent concentration, an increase in the rate is observed.

Key words: Induced electron transfer, Sodium dodecyl sulphate, Acetyl trimethyl ammonium bromide, Mandelic acids, Lactic acid, Glycolic acid.

INTRODUCTION

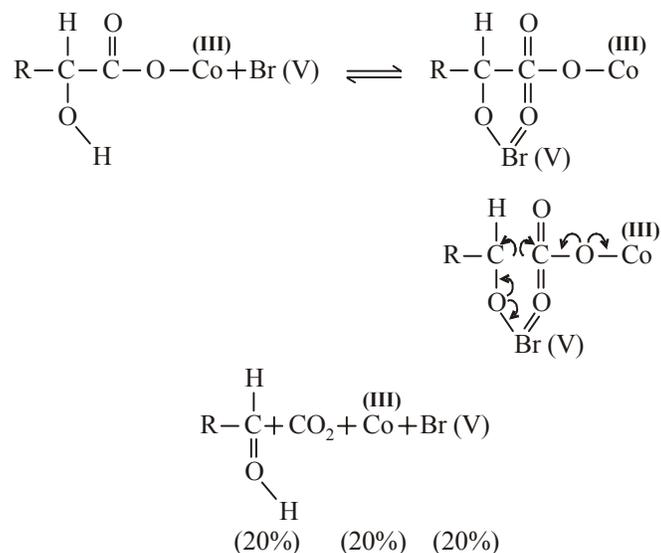
Oxidation is an important process in organic chemistry and use of new economic and effective oxidants under mild and anhydrous conditions constitutes a standing challenge. KBrO_3 is used as an oxidant¹⁻³, which is non-hygroscopic, non-photosensitive, stable yellow solid, freely soluble in water, acetic acid, N,N-dimethyl formamide etc. The little work has been done on KBrO_3 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, whether an one electron transfer takes place at the bound organic ligand gets oxidised without disturbing Co (III) center.

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EXPERIMENTAL

Mechanism of KBrO_3 oxidation of pentaammine cobalt (III) complexes of α -hydroxy acid in micellar medium.

According to **(Scheme 1)** Br (V) oxidizes $-\text{OH}$ center and induces formation of a radical, which in synchronous step undergoing C – C bond fission, yielding Co (III). As the amount of benzaldehyde or Co (III) formed is only 20% of $[\text{Co (III)}]_{\text{initial}}$. The above reaction probably contributes only 20% of total reaction.



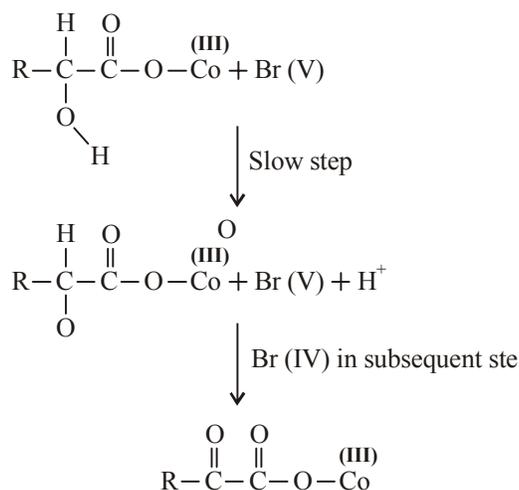
Scheme 1

According to **(Scheme 2)** envisages the formation of oxygen radical that reacts with Br (V) probably this reaction forms about 70% of total reaction on the basis of above two schemes. 0.2 Mole of Br (V) consumed by α -hydroxy acids complex can be explained. The formation of radical intermediate is evidenced by rapid initiation of acrylonitrile polymerization by this reaction mixture.

Material and method

The surfactants used in the present work are sodium dodecyl sulphate⁷ (SDS) and cetyl trimethyl ammonium bromide (CTAB). The surfactants are purified by adopting earlier procedure⁸⁻¹⁰. The chemicals were purchased CTAB from (B.D.H, UK, 99%) SDS, mandelic, lactic and glycolic acids from (SD Fine chemicals, India 95%) Pentaammine cobalt (III) complexes of α -hydroxy acid were prepared using Fan and Gould¹⁰. Double distilled

(deionised and CO₂ free) water was used as a solvent and H₂SO₄ (E.Merck India 95%) was standardised using standard sodium carbonate (BDH, AR) solution with methyl orange as indicator. For the KBrO₃ oxidation of Co (III) complexes of α -hydroxy acid and unbound ligands, the rate measurement were made at $35 \pm 0.2^\circ\text{C}$ in 100% aqueous micellar medium and temperature was controlled by electrically operated thermostat¹¹⁻¹⁶. The total volume of reaction mixture in the spectrophotometric cell was kept as 2.5 mL in each kinetic run.



Scheme 2

A systronic spectrophotometer fitted with recording and thermostating arrangement was used to follow the rate of reaction. Rate of these KBrO₃ oxidant with unbound ligand and cobalt (III) bound complexes were calculated were observed complexes decreases in absorbance at 350 nm for oxidant, and 502 nm for cobalt (III) complexes. The excess of reductant was used in kinetic runs. It gives pseudo first order rate constant were determine from the linear plot of the ln A versus time. Reproducible result obtained giving good first order plot. The stoichiometric studies for the KBrO₃ oxidation of pentaammine cobalt (III) complexes of α -hydroxy acid 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 (III) formation was negligibly small.

RESULTS AND DISCUSSION

Dependence of rate on KBrO₃ concentration in micellar bound ligand

The rate of KBrO₃ oxidation of pentaammine cobalt (III) complexes of α -hydroxy acids depends on KBrO₃ concentration. The specific rate calculated remains constant (Table 1) and Graph of logarithm of (a-x) versus time (Fig. 1) are linear. From the slope of these

graphs, the specific rates calculated were in agreement with those obtained from integrated rate equation suggesting first order dependence on KBrO_3 concentration.

When conc. of KBrO_3 is 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 Br (V) is given by equation.

$$-d[\text{Br(V)}] / dt = k[\text{Br (V)}] \quad \dots(1)$$

Table 1: Dependence of rate on cobalt (III) concentration in SDS

$$[\text{KBrO}_3] = 2.00 \times 10^{-3} \text{ mol dm}^{-3}$$

$$[\text{H}_2\text{SO}_4] = 1.00 \text{ mol dm}^{-3}$$

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

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

$10^2 [\text{NH}_3)_5\text{Co (III) -L}] \text{ mol dm}^{-3}$	$10^4 k_1 (\text{s}^{-1})$	$10^2 k_2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
L= Mandelato		
1	4.3	4.3
1.5	6.47	4.31
2	8.62	4.31
2.5	10.78	4.31
L= Lactato		
1	4.87	4.87
1.5	7.31	4.88
2	9.8	4.9
2.5	12.25	4.9
3	14.55	4.87
L = Glycolato		
1	3.52	3.52
1.5	5.26	3.51
2	7.21	3.6
2.5	8.98	3.59

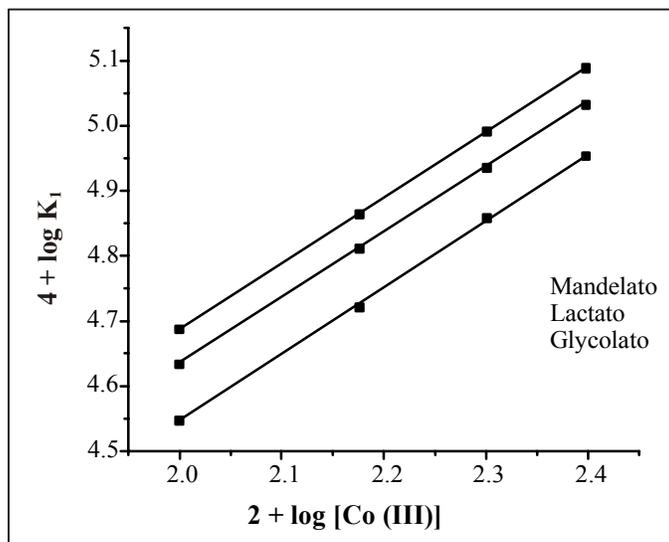


Fig. 1

Dependence of rate on cobalt (III) concentration

The rate of KBrO_3 oxidation of $[(\text{NH}_3)_5\text{Co-L}]^{2+}$ complexes of medicinal, lactic and glycolic acid, depends nearly on the first power of the concentration of cobalt (III) complexes (Tables 2 and 3), Graph of $\log k$ versus $\log [\text{Co (III)}]$ are linear with slope nearly equal to one (Figs. 2 and 3). Hence the rate of disappearance of Br (V) is given by equation 2.

$$-d[\text{Br(V)}]/dt = k_2[\text{Br (V)}][\text{Co (III)}] \quad \dots(2)$$

Table 2: Dependence of rate on Cobalt (III) concentration in CTAB

$[\text{KBrO}_3]$	=	$2.00 \times 10^{-3} \text{ mol dm}^{-3}$
$[\text{H}_2\text{SO}_4]$	=	1.00 mol dm^{-3}
$[\text{CTAB}]$	=	$2.00 \times 10^{-3} \text{ mol dm}^{-3}$
Temperature	=	$35 \pm 0.20^\circ\text{C}$

$10^2 [(\text{NH}_3)_5\text{Co(III)} - \text{L}] \text{ mol dm}^{-3}$	$10^4 k_1 (\text{s}^{-1})$	$10^2 k_2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
L = Mandelacto		
1	6.16	6.6
2	8.93	6.71

Cont...

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
2.5	10.25	6.68
3	13.27	6.61
L = Lactato		
1	7.86	7.86
1.5	11.72	7.68
2	15.82	7.92
2.5	19.73	7.89
L = Glycolato		
1	4.35	4.35
1.5	6.44	4.31
2	8.72	4.36
3	10.51	4.42

Table 3: Dependence of rate on α -hydroxy acid concentration in SDS

[KBrO ₃]	=	2.00×10^{-3} mol dm ⁻³
[H ₂ SO ₄]	=	1.00 mol dm ⁻³
[SDS]	=	2.00×10^{-3} mol dm ⁻³
Temperature	=	$35 \pm 0.20^\circ\text{C}$
10^2 [α -hydroxy acid] mol dm ⁻³	10^4 k ₁ s ⁻¹	10^2 k ₂ dm ³ mol ⁻¹ s ⁻¹
L = Mandelic acid		
1	1.3	1.3
1.5	1.98	1.32
2	2.64	1.32
2.5	3.37	1.34
L = Lactic acid		
1	1.68	1.68
1.5	2.54	1.69
2	3.34	1.67
2.5	4.29	1.71

Cont...

$10^2 [\alpha\text{-hydroxy acid}] \text{ mol dm}^{-3}$	$10^4 k_1 \text{ s}^{-1}$	$10^2 k_2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
L = Glycolic acid		
1	1.15	1.15
2	2.28	1.14
2.5	2.8	1.12
3	3.48	1.16

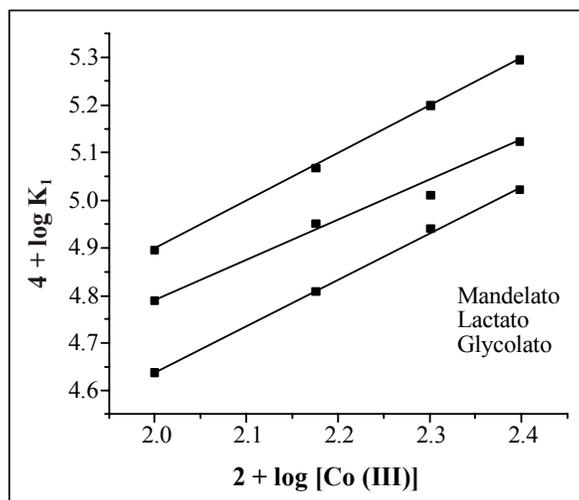


Fig. 2

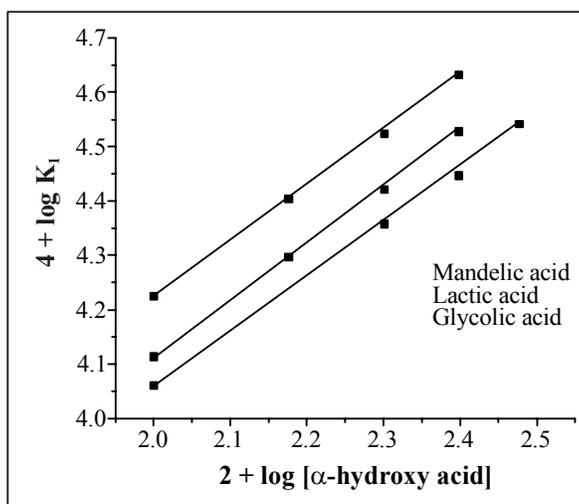


Fig. 3

Dependence of rate on the concentration of α -hydroxy acids in micellar medium

At a given initial concentration of KBrO_3 in micellar medium, the oxidation varies proportionality with the concentration of α -hydroxy acids and the rate of this reaction exhibits first order dependence on α -hydroxy acids concentration (Tables 4-5). Plot of $\log k_1$ versus $\log [\alpha\text{-hydroxy acids}]$ are linear with slope, nearly equal to one (Figs. 4-5), evidencing the order with respect to α -hydroxy acids. Hence the rate of disappearance of Br(V) is given by equation 3.

$$-d[\text{Br(V)}]/dt = k_2 [\text{Br(V)}] [\alpha\text{-hydroxy acids}] \quad \dots(3)$$

Table 4: Dependence of rate on α -hydroxy acid concentration in CTA

$[\text{KBrO}_3]$	=	$2.00 \times 10^{-3} \text{ mol dm}^{-3}$
$[\text{H}_2\text{SO}_4]$	=	1.00 mol dm^{-3}
$[\text{CTAB}]$	=	$2.00 \times 10^{-3} \text{ mol dm}^{-3}$
Temperature	=	$35 \pm 0.20^\circ\text{C}$
$10^2 [\alpha\text{-hydroxy acid}] \text{ mol dm}^{-3}$	$10^4 k_1 (\text{s}^{-1})$	$10^2 k_2 \text{ dm}^3 \text{ mol}^{-1} \text{ s}^{-1}$
L= Mandelic acid		
1	1.69	1.67
1.5	2.50	1.67
2	3.39	1.67
2.5	4.27	1.71
L= Lactic acid		
1	3.15	3.15
1.5	4.72	3.14
2	6.12	3.06
2.5	8.02	3.21
L= Glycolic acid		
1	1.64	1.4
1.5	2.15	1.43
2	2.64	1.32
3	3.19	1.34

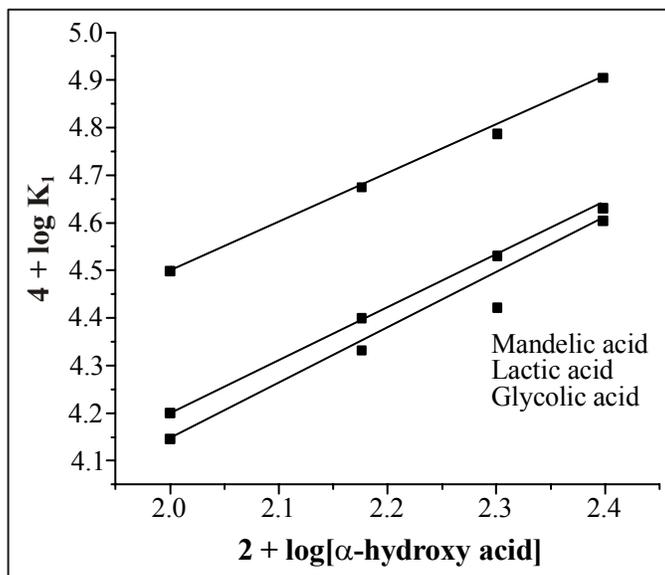


Fig. 4

Comparison of rate on oxidant of pentaammine cobalt (III) complexes of both bound and unbound α -hydroxy acids by KBrO_3

The specific rate of the Co (III) lactate complex is faster than Co (III) mandelato and Co (III) glycolato complex because if the reaction proceeds through a preformed bromate ester, then the rate of oxidation of C-H cleavage, had been enhanced resulting in an increase in the rate of oxidation of Co (III) complex. Also bromate 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 lactate complex may account for its greater reactivity.

In this work, an induced transfer reaction has been attempted presently with KBrO_3 and pentaamminecobalt (III) complexes of α -hydroxy acid in the presence of micelles. 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) complex. In potassium bromate induced electron transfer in cobalt (III) mandelato complex, the intermediate radical formed dissociated in a nearly synchronous manner with C – C bond cleavage only to the extent of 20% and the rest of it proceeding with α -C-H fission giving Keto acid cobalt (III) complex. With increase in micelle concentration an increase in the rate is observed. Added CTAB

(cationic micelle) enhance the rate of oxidation much more than SDS (cationic micelle). The same trends observed in lactato and glycolato cobalt (III) complex.

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