Induced Electron Transfer Reactions in Cobalt(III) Complexes of α-Hydroxy Acids by Potassium Bromate ($KBrO_3$) in the presence of Micelles

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Abstract: The kinetics of one electron transfer way seems to be not available for Potassium bromate with Cobale (III) bound and unbound complexes of α – hydroxy acids in micellar medium. Potassium bromate oxidises Cobalt (III) bound and umbound α – hydroxy acids. It rules out synchromous c-c bond fission and electron transfer to Cobalt (III) centre. Oxidation of above complexes increases with increase of temperature with increase in micelles concentration. A remarkable increase in the reaction rate is also observed. The addition of micelle dimethyl diocta decyl ammonium chloride (DDAC) increases the rate of oxidation slightly more than another micelle used i.e., Ammonomum Lauryl Sulphate (ALS). Similar trends observed in Lactato, Glycolato and Mandelato Cobalt (III) complexes.

Keywords: Potassium bromate ($KBrO_3$), Dimethyl Diocta decyl Ammonium Chloride (DDAC), Ammonium Lauryl Sulphate (ALS), Pentaammine cobalt (III) complex.

I.Introduction:

Conventional spectro photometry has been employed to study the oxidation of α-hydroxy acids such as Lactic acid, Glycolic acid, mandelic acid and their cobalt (III) complexes using Potassium bromate ($KBrO_3$) as an oxidant in the presence of micelles. One equivalent oxidant like Ce(IV) induced electron transfer in pertammine cobalt (III) complexes of α-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 Potassium bromate ($KBrO_3$) in its reaction with Cobalt (III) bound and unbound α-hydroxy acids in micellar medium, Potassium bromate ($KBrO_3$) oxidise Cobalt (III) bound and unbound α- hydroxyacids to respective keto acid / keto acid cobalt (III) complexes in Amaonium lauryl sulphate (A.L.S) and dimenthyl dioctaadecyl 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 $KBrO_3$ oxidation of Cobalt (III) lactato, glycolato, mandelato complexes depends on the first power of $KBrO_3$ concentration. Similarly the reaction between $KBrO_3$ and unbound α-hydroxy acid exhibits first order kinetics with respect to concentration of $KBrO_3$ 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 anhydrons condition constitutes a standing challenge $KBrO_3$ (Anbuselvan and Sankaran, 1998; Das et al., 1984; Fan and Gould in 1974) is oxidant which is non hydroscopic, non photosensity, stable yellow orange solid which is freely soluble in water, Acetic acid, N-N dimethyl formamide etc., the little work has been don on PCC as oxidant in micellar media (Frechet et al 1928, Frechet et al., 1978)

II. Materials and Methods:

The Micelles used in the present work are Ammonium Lanryl sulphate (ALS) and dimelthyl decyl ammonium chloride (DDAC). The Micelles 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 (Merck chemicals, India 95%) Penta ammine cobalt (III) complexes of α-hydroxcy acids were prepared using 'Fan and Gould'. Dash etal 1984; (Bain and Hercheinson, 1955) double distilled deionised and CO_2 free water was used as a solvent and H_2So_4 (E merck of India 95%) was standardished using standard sodium carbonate (B.D.H) (AR) solution with dimenthyl orange as indicator. For the $KBrO_3$ oxidation of cobalt (III) complexes of α- hydroxyacids and unbound ligands (Mohan Hy 1982 and Yasunaga et al; 1982). The rate measurement was made at 30^0 C ±0.2^0 C in 100% aqueous medium. Temperature was controlled by electrically operated thermo stat (Mohanty and Nanda, 1982) the total volume of reaction mixture is spertrophotometric cell was kept in 2.5 ml in each kinetic run. A systemic spectrophotometers, filled with recording and thermo stating arrangement was used to follow the rate of reaction. Rate of this $KBrO_3$ oxidant with unbound ligand and Cobalt (III) bound complexes were calculated from observed decrease in aborbance 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 stoichiometric studies for the $KBrO_3$ oxidation of penta ammine Cobalt (III) complexes of α-hydroxy acid and un bound ligand in the presence of micelless were carried out at 30^0 ±0.2^0 C. It was observed that the Cobalt (II) formation was negligible.

III. Result and discussion:

Kinetic study of the oxidation of pentammine Cobalt (III) complexes of α- hydroxy acids by $KBrO_3$ in micellar medium. Dependence of rate on $KBrO_3$ concentration in micellar bound ligand; the rate of oxidation of mandelate Cobalt (III) complexes depends on $KBrO_3$ concentration. The specific rate calculated remains constant (Table – 1) and graph of logrithem of $KBrO_3$ concentration, versus time (Figure - 1) are linear from the slope of these graphs, the specific rate calculated agree with those obtained from integrated rate equitation suggesting first order dependence on $KBrO_3$ concentration.

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

$[(CH_3)^5 Co^m\text{-}L]^{2+}$	$=2.00x10^{-2}$mol dm^{-3}
$KBrO_3$	$=2.00x10^{-3}$mol dm^{-3}
H_2SO_4	=1.00x mol dm^{-3}
ALS	$=2.00x10^{-3}$mol dm^{-3}
Temperature	$=30^o\pm0.2^oC$
L	=Mandelato

10^3(a-x)moldm^{-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

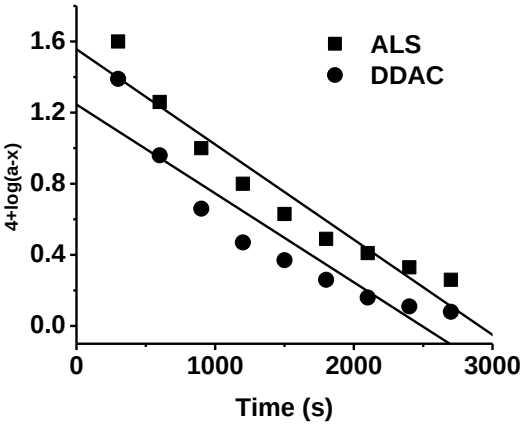

Figure – 1. I[st] order dependence plots

When the concentrations of $KBrO_3$ varied from 1.00 to 3.00 x 10^{-3}moldm^{-3} at a fixed [Cobalt(III) and H_2SO_4]. Specific rates remain constant. Then the rate of disappearance of Cr(IV) is given by equation (1).

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

At a particular concentration of $KBrO_3$ with increase in mandelato glycolato cobalt (III) concentration in the range of 1.00 to 3.00 x 10^{-3}moldm^{-3} threr is propretional increase in the rate of oxidation (Table-2). The slope of nearly unity is obtained from linear graph of logerthum (Figure-2) of specific rate (K is S^{-1}) versus log of Co(III) concentration in each case suggestions first order rate dependance of rate on [Co(III)].

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

$KBrO_3$	=2.00x10^{-3}mol dm^{-3}	
H_2SO_4	=1.00 mol dm^{-3}	
ALS	=2.00x10^{-3}mol dm^{-3}	
Temperature	=30°±0.2^{o}C	
$10^2[NH_3)_5 Co^{III}$-L]	$10^4K_1(S^{-1})$	10^2K_2dm$^{-3}S^{-1}$ mol dm^{-3}
L = Mandelato		
1.00	2.00	0.970
2.00	3.80	1.950
3.00	7.80	1.915
L = Lactato		
1.00	1.90	0.970
2.00	4.20	1.950
3.00	8.20	1.910
L = Glycolato		
1.00	1.80	0.964
2.00	3.70	1.940

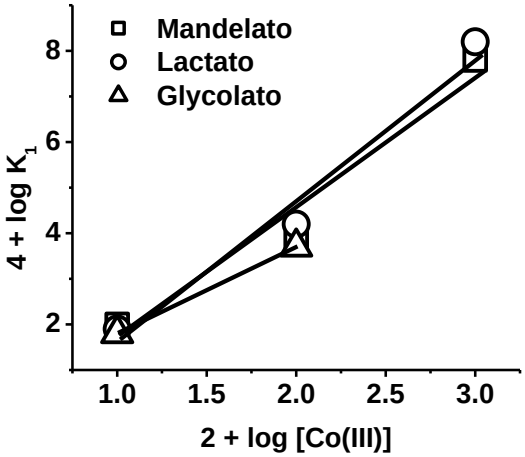

Figure – 2. Dependence of rate on Co(III) complex in the presence ALS.

Hence the rate law for Chromium(VI) oxidation of Cobale(III) bound α – hydroxy acids are given by equation (2).

$$-d[Cr(VI)]/dt=K_2[Cr(VI)][Co(III)].....(2)$$

Dependence rate on $KBrO_3$ concentration in micellar medium for α – hydroxy acid. The rate of oxidation of Mandelato Co(III) complexes depends on $KBrO_3$ concentration. In any specific run the change in concentration of $KBrO_3$, the specific rate calculated remain constant (Table-3) and graph of logoerthum of $KBrO_3$ concentration versus time are linear (Figure-3).

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

$KBrO_3$	$=2.00x10^{-3}$mol dm^{-3}	
H_2SO_4	=1.00 mol dm^{-3}	
DDAC	$=2.00x10^{-3}$mol dm^{-3}	
Temperature	$=30^o\pm0.2^oC$	
$10^2[(NH_3)_5 Co^{III}-L]$	$10^4K_1(S^{-1})$	$10^2K_2dm^{-3}$ $mol^{-1}S^{-1}$
L = Mandelato		
1.00	2.00	0.970
2.00	3.90	1.950
3.00	7.20	1.910
L = Lactato		
1.00	1.80	0.974
2.00	4.20	1.940
3.00	8.00	1.900
L-Glycolato		
1.00	1.90	0.964
2.00	3.70	1.942

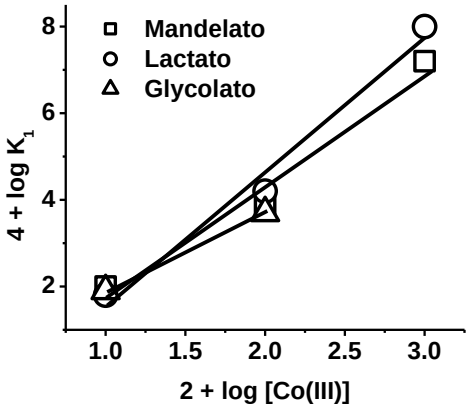

Figure-3. Dependence of rate on [Cobalt(III)] in DDAC.

When concentration of $KBrO_3$ is varied from 1.00 to 3.00 x 10^{-3} mol dm^{-3}at a fixed [Co(III)] and [H_2SO_4] specific rates remain constant. Then the rate disappearance of Cr(VI) is given by equation (3).

$$-d[Cr(VI)] / dt = K_1[Cr(VI)].....(3)$$

Dependence of rate on the concentration of α – hydroxyacid in ALS and DDAC: The oxidation studies were carried out by varying initial [α – hydroxy acid] in the range of 1.00 to 3.00 x 10^{-3} 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 unity is obtained from a linear graph of logarithm of specific rate (k_1 in S^{-1}) verses lagarithm of α – hydroxy acid concentration in each case suggesting first order dependance of rate on [α – hydroxy acid] (Figures 4 and 5). Hence the rate law for the Cr(VI) oxidation α – hydroxy acid of is given below equation (4).

$$-d[Cr(VI)] / dt = k_2 [Cr(VI)].....(4)$$

Table – 4. The rate constant values of [α-hydroxy acid] in ALS.

$KBrO_3$	=2.00x10^{-3}mol dm^{-3}	
H_2SO_4	=1.00 mol dm^{-3}	
ALS	=2.00x10^{-3}mol dm^{-3}	
Temperature	=30°±0.2°C	
10^{-3}[α-hydroxy acid] mol dm^{-3}	$10^4K_1(S^{-1})$	$10^2K_2dm^{-3}$ $mol^{-1}S^{-1}$
Mandelic acid		
1.00	0.34	0.966
2.00	0.64	1.936
3.00	1.40	1.860
Lactic acid		
1.00	0.35	0.965
2.00	0.66	1.934
3.00	1.44	1.856
Glycolic acid		
1.00	0.50	0.950
2.00	0.75	1.925
3.00	1.56	1.844

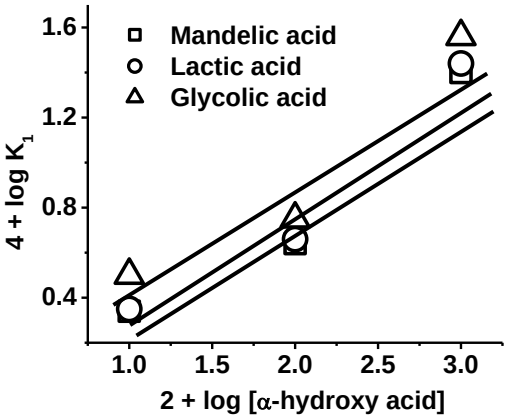

Figure-4. Dependance of rate on [α – hydroxy acid] in ALS.

Table – 5. The rate constant values of [α-hydroxy acid] in DDAC.

$KBrO_3$	$=2.00x10^{-3}$mol dm^{-3}	
H_2SO_4	$=1.00$ mol dm^{-3}	
DDAC	$=2.00x10^{-3}$mol dm^{-3}	
Temperature	$=30^o\pm0.2^oC$	
10^2[hydrixy acid]	$10^4K_1(S^{-1})$	$10^2K_2dm^{-3}mol(s)^{-1}$
Mandelic acid		
1.00	0.35	0.965
2.00	0.66	1.934
3.00	1.44	1.856
Lactic acid		
1.00	0.50	0.950
2.00	0.74	1.926
3.00	1.56	1.844
Glycolic acid		
1.00	0.40	0.960
2.00	0.70	1.930
3.00	1.60	1.840

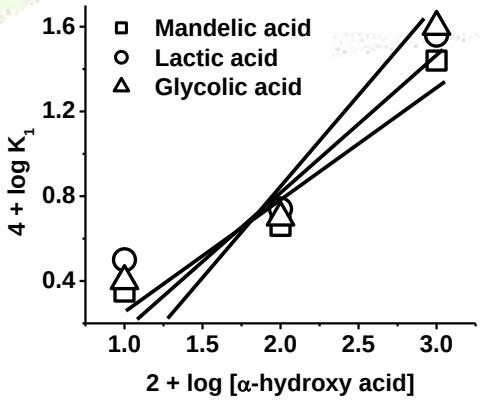

Figure-5. Dependance of rate on [α – hydroxy acid] in DDAC.

Comparison of rates on oxidation of Pentaamminecobalt (III) complexes of both bound and unbound α-hydroxy acid by $KBrO_3$.

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 porbably increased its reactivity towards $KBrO_3$ and this effect seems to be more specific for this ligand only. If the reaction proceeds through a performed Chromate ester, then the rate α-C-H fission will been 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.

IV. Conclusions:

The oxidation reactions of Cobalt(III) complexes of α-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 micelles ALS and DDAC. These micelles act as a positive catalyst in a situation of the reaction and among which DDAC enhances the rate much more than the ALS.

References:

1. Anji Reddy K, Seetha Ramaiah V and Mainsur Ahmed IJARST, 2017 (6) 707-711.
2. Udhayavani S, Subramani K, E-Journal of Chemistry, 2012; 9(2): 912-917.
3. Subramian K, Udhayavani S, Journal of Chem. Bio and Phy sciences, 2012; 2(2): 551-559.
4. Abdul Vaheith Z, Mansur Ahmed, Int. J. of Frontiers in Science and Technology, 2015; 3(3): 49-58.
5. Kannan Pownsamy, Sarojini Gopalakrishnana and Bezuayehu Befekadu: Int. J. Chem. Sci, 2015; 13 (2): 759-770.
6. Palanivel A, Rajkumar P, Palanisamy T and Dayanandhan R International Journal of Frontiers in Science and Technology, 2016 4(3), 22-31.
7. Mohanty N.K. and Nanda R.K, Transtion Met. Chem., 1982; 7: 202.