



## Kinetics and mechanism of oxidation of $\alpha$ -hydroxy acids by quinoxalinium chloro chromate in aqueous acetic acid on surfactants

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### ABSTRACT

Kinetics and mechanism of oxidation of  $\alpha$ -hydroxy acids and Co (III) complexes of  $\alpha$ -Hydroxy acids by Quinoxalinium Chloro Chromate (QxCC) in 50% (v/v) Aqueous Acetic acid with surfactants have been studied. The rate of oxidation of the reaction is increased with increasing substrate concentrations, perchloric acid, Temperature, Surfactants etc., The rate of oxidation enhances by adding cationic micelles CTAB and the higher rates were observed in Lactic acid and Lactato Co (III) complexes. All the kinetic runs were carried out by spectrophotometrically at 365nm. The mechanism of reaction was suggested by Synchronous C-H Cleavage with two electron transfer and the formation of the product is  $\alpha$ -keto acids.

**Keywords:**  $\alpha$ -Hydroxyacids, Sodium Lauryl sulphate (NaLS), Oxidation, Quinoxalinium Chloro Chromate (QxCC)

### INTRODUCTION

The chemistry of Quinoxalines has attracted considerable attention in the past years [1]. Quinoxaline derivatives are exhibit biological activities like anti-viral [2], anti-cancer [3] anti-depressant [4], anti-bacterial [5] and anti-inflammatory [6]. Also used as an agricultural field like herbicides, insecticides and fungicides [7]. Therefore the search of prominent new oxidant persisted, which has now led to the synthesis of Quinoxalinium chloro chromate. A number of new Cr (VI) containing compounds, with heterocyclic bases, like Pyridinium chloro chromate [8], Quinolinium chloro chromate(QCC)[9], Quinolinium fluoro chromate(QFC)[10], Quinolinium bromo chromate(QBC)[11], Imidazolium fluoro chromate (IFC)[12], Pyridinium fluoro chromate (PFC)[13], Imidazolium dichromate(IDC)[14] and Quinolinium dichromate(QDC)[15] have been developed to improve the selectivity of oxidation of organic compounds. However, the kinetics of oxidation of  $\alpha$ -hydroxy acids by QxCC, a Cr (VI) reagent has not yet been studied. This prompted us to undertake the present investigation. The present study describes the kinetics of oxidation of  $\alpha$ -hydroxy acids by QxCC and evaluates the reaction constants. Mechanistic aspects are likewise talked about.

### MATERIALS AND METHODS

#### Materials

CrO<sub>3</sub> (99%, Merck, India), Hydrochloric acid, Lactic acid (99%, SD Fine), Mandelic acid, glycolic acid, HClO<sub>4</sub> were used as supplied and their stock solutions were prepared in double distilled Deionized and CO<sub>2</sub> free water. Acetic acid was purified by standard method and the fraction distilling at 118<sup>o</sup>C was collected.

#### Preparation of Quinoxalinium Chloro chromate

A solution of chromium trioxide (0.2 mol) in water (25 mL) was cooled to 0<sup>o</sup>C and to this aqueous hydrochloric acid (0.2 mol) was slowly added with vigorous stirring. To this resulting solution quinoxaline (0.2 mol) was added and then cooled for 2h. The resulting yellow solid was collected on a sintered glass funnel and washed with ether,

kept under suction until moderately dry, and placed under vacuum pump pressure until a dry powder, mp: 108-110 °C, Yield 80 % [16]

### Preparation of cobalt (III) Complexes

Carbonato pentaammine cobalt (III) nitrate was prepared [17]. The monomeric cobalt (III) complexes of  $\alpha$ -hydroxy acids were prepared as their perchlorates using the method of Fau and Gould [18]

### Kinetic Measurements

All kinetic measurements were carried out An Evolution 60 Thermo spectrophotometer fitted with recording and thermo stating arrangement was used to follow the rate of the reaction. The progress of the reaction was followed at 365 nm by monitoring the changes in absorbance of remaining Cr (VI). The required  $\alpha$ -hydroxy acid, HClO<sub>4</sub> and QxCC were premixed in a reaction vessel, thermo stated in an oil bath, and thermally equilibrated QxCC solution was then added prior to the absorbance measurements. Under pseudo-first-order conditions of  $\alpha$ -hydroxy acid, the plots of  $\log A$  versus time were linear up to 80% completion of the reaction with an average of linear regression coefficients are  $\geq 0.996$ . Table-1 shows the results of below the concentration of reactants with NaLS.

[QxCC]	=	1.00x10 <sup>-3</sup> mol dm <sup>-3</sup>
[HClO <sub>4</sub> ]	=	0.1 mol dm <sup>-3</sup>
Temperature	=	323K
Mandelic acid	=	1.00x10 <sup>-2</sup> mol dm <sup>-3</sup>

Table-1

Time(s)	Absorbance	log(Absorbance)	10 <sup>4</sup> k1 (s <sup>-1</sup> )
0	0.638	-0.195	0
306	0.598	-0.223	2.116
608	0.56	-0.251	2.145
906	0.526	-0.279	2.131
1204	0.493	-0.307	2.142
1506	0.462	-0.335	2.144
1810	0.434	-0.363	2.129
2105	0.408	-0.389	2.124
2407	0.383	-0.417	2.120
2708	0.359	-0.449	2.124
3015	0.336	-0.474	2.127

Figure -1 shows the graph of Time (S) versus log (Absorbance) of oxidation of  $\alpha$ -Mandelic acid with QxCC on NaLS

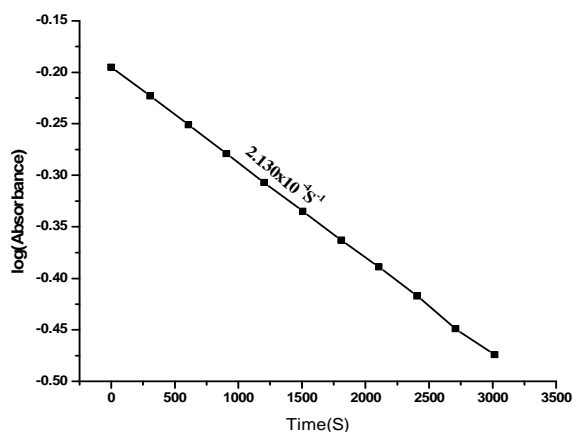


Fig.1 Dependence on first order plot

### Stoichiometric analysis

The stoichiometric studies for the oxidation of pent ammine cobalt (III) complexes of  $\alpha$ -hydroxy acids and unbound ligands by QxCC were carried out with the oxidant in excess. The H<sup>+</sup> ion concentration and ionic strength were maintained every bit in the corresponding rate measurements. After nine half lives when the reaction was nearing completion, the concentration of unreacted was determined by spectrophotometrically from the change in absorbance measured at 365 nm for free ligands and Co(III) complexes. The stoichiometry was calculated from the ratio between reacting oxidant and substrate from the reduction in the optical density measured for the cobalt (III) complex, the amount of Cr (VI) reduced was calculated. This value was then compared to the amount of Cr (IV) and

formed compound. Table-2 shows the stoichiometry data for QxCC oxidation of Co (III) bound and unbound  $\alpha$ -hydroxy acids in the presence of 0.02M of Sodium Lauryl Sulfate at 323K in 0.1M Perchloric acid medium. Stoichiometry was calculated from the ratio between reacting QxCC and free  $\alpha$ -Hydroxy acids and Co (III) of  $\alpha$ -Hydroxy acids.

Table-2

$10^2$ [Compound] mol dm <sup>-3</sup>	$10^2$ [QxCC] <sub>initial</sub> mol dm <sup>-3</sup>	$10^2$ [QxCC] <sub>Final</sub> mol dm <sup>-3</sup>	$\Delta 10^2$ [QxCC] mol dm <sup>-3</sup>	[Compound]: $\Delta$ [QxCC]
Mandelic acid				
1.0	10.0	9.32	0.68	1.00 : 0.68
2.0	10.0	8.66	1.34	1.00 : 0.67
3.0	20.0	18.05	1.95	1.00 : 0.65
Lactic acid				
1.0	10.0	9.38	0.62	1.00 : 0.62
2.0	10.0	8.70	1.30	1.00 : 0.65
3.0	20.0	18.08	1.92	1.00 : 0.64
Glycolic acid				
1.0	10.0	9.36	0.64	1.00 : 0.64
2.0	10.0	8.70	1.30	1.00 : 0.65
3.0	20.0	18.08	1.92	1.00 : 0.64
Co <sup>III</sup> Mandelato				
1.0	10.0	9.35	0.65	1.00 : 0.65
2.0	10.0	8.72	1.28	1.00 : 0.64
3.0	20.0	18.02	1.98	1.00 : 0.66
Co <sup>III</sup> Lactato				
1.0	10.0	9.34	0.66	1.00 : 0.66
2.0	10.0	8.70	1.30	1.00 : 0.65
3.0	20.0	18.08	1.92	1.00 : 0.64
Co <sup>III</sup> Glycolato				
1.0	10.0	9.36	0.64	1.00 : 0.64
2.0	10.0	8.72	1.28	1.00 : 0.64
3.0	20.0	18.02	1.98	1.00 : 0.66

### Product Analysis

Product analysis was carried out under kinetic conditions, *i.e.*, with excess of the reductant over QxCC. In a typical experiment, Lactic acid (0.10 mol), Perchloric acid (0.10mol) and QxCC (0.01 mol) were dissolved in acetic acid – water mixture (50% - 50%) and the solution was allowed to stand in the dark for about 24h to ensure completion of the reaction. The residue was treated with an excess (200 ml) of a saturated solution of 2, 4-dinitro phenyl hydrazine in 1mol HCl and kept overnight in a refrigerator. The precipitated 2, 4-dinitro phenyl hydro zone (DNP) was filtered off, dried and recrystallised from ethanol. The product was identical with melting point and mixed melting point to an authentic sample of the DNP of pyruvic acid.

## RESULT AND DISCUSSION

Kinetic study of the oxidation of  $\alpha$ -Hydroxy acids pentaammine cobalt (III) complexes of  $\alpha$ -Hydroxy acid and Pentaammine cobalt (III)  $\alpha$ -hydroxy acids by Quinoxalium Chloro Chromate (QxCC) on surfactants have been done and rates were calculated by integrated rate equation.

$$k = 2.303/t * \log (a/a-x) \text{ S}^{-1}$$

### Dependence of rate on $\alpha$ -Hydroxy acids on Surfactants

The concentration of  $\alpha$ -Hydroxy acids were varied from  $0.5 \times 10^{-2}$  to  $2.5 \times 10^{-2}$  mol dm<sup>-3</sup> at 323 K and keeping all other reactant concentrations as constant and the rates were measured. The graph of logarithms was concentration versus time linear and the rate constants calculated from the gradient of the graph agreed with the observational value. Which shows a first order dependence plot on  $\alpha$ -hydroxy acids the plot of  $\log k_1$  versus  $\log [\alpha\text{-hydroxy acids}]$  gave the slope of 0.998

$$-d [\text{QxCC}]/dt = k_1 [\text{QxCC}][\alpha\text{-Hydroxy acids}] \quad (1)$$

### Dependence of rate on Co (III) complexes of $\alpha$ -Hydroxy acids on Surfactants

The concentration of Co (III) complexes of  $\alpha$ -Hydroxy acids were varied from  $1.0 \times 10^{-2}$  to  $3.0 \times 10^{-2}$  mol dm<sup>-3</sup> at 323 K and keeping all other reactant concentrations as constant and the rates were measured. The graph of logarithms was concentration versus time linear and the rate constants calculated from the slope of the graph agreed with the

experimental value, which shows a first order dependence plot on Co (III) complexes of  $\alpha$ -hydroxy acids the plot of  $\log k_1$  versus  $\log [\text{Co (III) } \alpha\text{-hydroxy acids}]$  gave the slope of 0.998

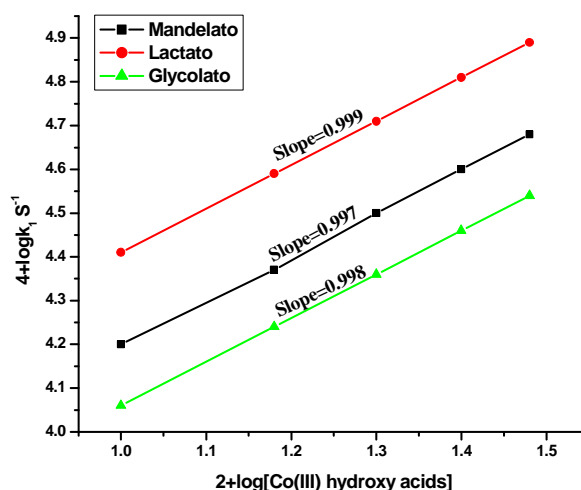
$$-d[\text{QxCC}]/dt = k_1[\text{QxCC}][\text{Co(III) } \alpha\text{-Hydroxy acids}] \quad (2)$$

Table-3 shows the results of oxidation of cobalt (III) complexes of  $\alpha$ -Hydroxy acids by QxCC on surfactants at 323K. Figure-2 shows the graph of  $\log [\text{Co (III) } \alpha\text{-hydroxy acids}]$  versus  $4+\log k_1$  for oxidation of  $\alpha$ -hydroxy acids by QxCC on NaLS.

Table-3

[QxCC]	=	$1.00 \times 10^{-3} \text{ mol dm}^{-3}$
[HClO <sub>4</sub> ]	=	$0.1 \text{ mol dm}^{-3}$
[Surfactants]	=	$1.00 \times 10^{-2} \text{ mol dm}^{-3}$

$10^2$ [(NH <sub>3</sub> ) <sub>5</sub> Co(III)-L] mol dm <sup>-3</sup>	NaLS $10^4 k_1$ (s <sup>-1</sup> )	CTAB $10^4 k_1$ (s <sup>-1</sup> )	TRITON $10^4 k_1$ (s <sup>-1</sup> )
<b>Mandelato</b>			
1.0	1.578	2.487	2.335
1.5	2.369	3.732	3.503
2.0	3.166	4.980	4.672
2.5	3.950	6.220	5.838
3.0	4.734	7.464	7.005
<b>Lactato</b>			
1.0	2.574	2.789	2.654
1.5	3.864	4.184	3.981
2.0	5.152	5.578	5.308
2.5	6.488	6.973	6.640
3.0	7.718	8.367	7.965
<b>Glycolato</b>			
1.0	1.575	2.147	1.955
1.5	2.368	3.221	2.933
2.0	3.159	4.294	3.914
2.5	3.942	5.371	4.888
3.0	4.730	6.445	5.865

Fig.2 Dependence of rate on Co (III) complexes of  $\alpha$ -hydroxy acids with NaLS

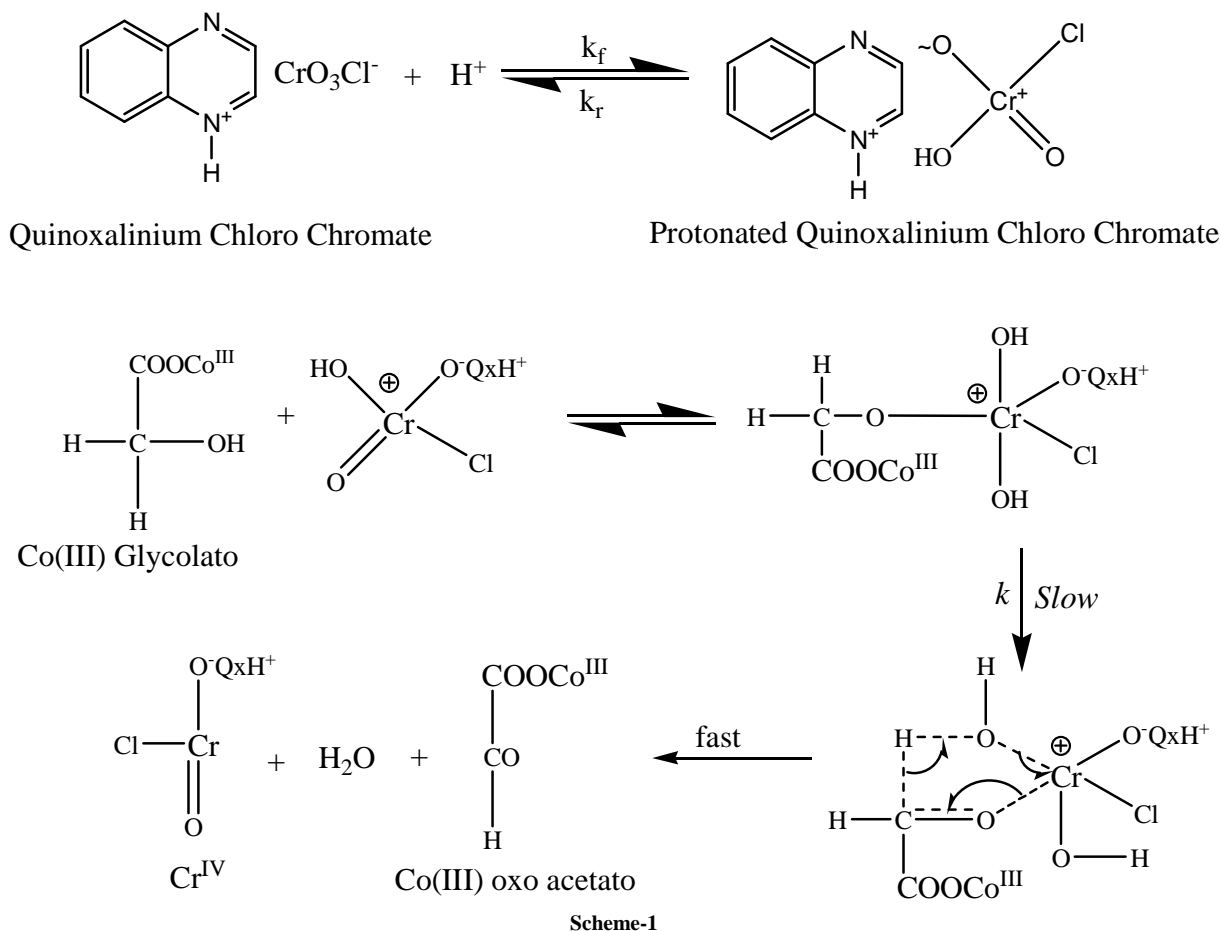
### Dependence of rate on Varying Temperature in Surfactants

The rate of oxidation of reaction was observed in varying the temperature from 323K to 343K and keeping all other reactant concentrations as constant. The rate of oxidation of reaction increased with increasing the Temperature in both free ligands and Co (III) complexes.

### Mechanistic Aspects

The oxidation of  $\alpha$ -hydroxy acids and their complexes by QxCC in an atmosphere of nitrogen failed to induce the polymerization of acrylonitrile which discounts the possibility of any radical formation. The oxidation of  $\alpha$ -hydroxy acids and their complexes was catalyzed by perchloric acid, which may well be attributed to protonation of QxCC to

give a stronger oxidant and electrophile. The formation of a protonated Cr (VI) species has been postulated earlier. The kinetic and absence of aldehydes as a product leads to a mechanism involving two electron transfer from Cr(VI) with synchronous C-H cleavage. It was confirmed by product analysis, that formation of DNP. Hence, synchronous C-H fission and hydride ion transfer are rate determining step was suggested. The mechanism is proposed for the formation of Co (III) of pyruvate as a product from lactic acid. A similar trend was proposed for Co (III) of lactate complexes. Scheme-1 shows the mechanism of cobalt (III) complexes of Glycolato.



### CONCLUSION

The kinetics and oxidation of cobalt (III) complexes of  $\alpha$ -hydroxy acids like glycolic acid, Mandelic acid and Lactic acid by novel Quinoxalinium chloro chromate in perchloric acid medium have been studied. The rate of oxidation of reaction increases in the presence of surfactants like NaLS, CTAB and TRITON-X 100 has been observed. The rate of oxidation of cobalt (III) complexes of bound hydroxy acids much more than the free hydroxy acids with surfactants has been observed. Among the surfactants, the cationic surfactant CTAB enhances the rate much more than the others. The temperature increases the rate of the reaction increases. The mechanism suggested the synchronous C-H bond fission with two electron transfer from Cr (VI) and formation of oxoacetate.

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