

## Kinetic Study of the Oxidation of Pentaamminecobalt(III) Complexes of $\alpha$ -hydroxy Acids by Imidazolium Dichromate

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Kinetics of oxidation of pentaamminecobalt(III) complexes of mandelic and lactic acids by imidazolium dichromate (IDC) have been studied in the presence of  $1.00 \text{ mol dm}^{-3} \text{ HClO}_4$ . The rates of oxidation show first order kinetics each in Co(III) complex and [IDC]. Various thermodynamic parameters have been evaluated. The stoichiometry of the reaction has been determined. The formation of keto acid Co(III) complex as the product of the reaction is accounted by a suitable mechanism.

### INTRODUCTION

The kinetics and mechanism of oxidation of pentaamminecobalt(III) complexes of  $\alpha$ -hydroxy acids by various oxidants have been reported. However, there is no report on the oxidation of Co(III) complex by imidazolium dichromate. The oxidants employed in the investigation, imidazolium dichromate (IDC),  $(\text{C}_3\text{H}_5\text{N}_2^+)_2 \text{Cr}_2\text{O}_7^{2-}$ , has emerged as a very useful oxidant.

However, the kinetics of pentaamminecobalt(III) complex of  $\alpha$ -hydroxy acids by IDC has not been reported so far and hence the title investigation.

### EXPERIMENTAL

The pentaamminecobalt(III) complexes of  $\alpha$ -hydroxy acids were prepared as their perchlorates following the procedure of Fan and Gould.<sup>1</sup> Mandelic and lactic acids (Aldrich) used were of extra pure variety and their physical constants agreed with literature values. The imidazolium dichromate (IDC) was prepared by the method of Sunggak Kim *et al.*<sup>2</sup> and the purity of the sample was determined as 99% by an iodometric procedure.

Kinetic study on the imidazolium dichromate oxidation of pentaamminecobalt(III) complexes of  $\alpha$ -hydroxy acids has been made in aqueous perchloric acid medium under pseudo-first oxidation by maintaining a large excess of the Co(III) complex over oxidant. The progress of the reaction at constant temperature has been followed spectrophotometrically (UVDEC, 380, JASCO) by measuring the absorbance of the oxidant at 350 nm. The rate constants were determined by the least square method, from the given plot of log absorbances versus time.

As Ce(IV) oxidation of pentaammine cobalt(III) complex of  $\alpha$ -hydroxy acids<sup>3</sup> yields Co(II) as one of the products, 2.5 mL of the reaction mixture was made up to

25 mL pentaamine cobalt(III) complexes with conc. HCl and the absorbance of the resulting solution after nine half-lives was measured at 692 nm ( $\epsilon = 560 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$ )<sup>4</sup>  $\lambda_{\text{max}}$  of the chloro complex of cobalt(II). Almost zero absorbance noted at 692 nm suggested that the yield of cobalt(II) was negligibly small.

In the case of  $(\text{NH}_3)_5\text{Co(III)}$  mandelato complex, the product was isolated after neutralising the reaction mixture with aq.  $\text{KHCO}_3$ , and adjusting the pH to 6.0. The reaction mixture was concentrated under reduced pressure and the product isolated was a Co(II) complex, the IR spectrum of which was superimposable over that of an authentic sample of  $(\text{NH}_3)_5\text{Co(III)}$  phenylglyoxylato complex. By a similar procedure,  $(\text{NH}_3)_5\text{Co(III)}$ , pyruvato complex was isolated as one of the products of Cr(VI) oxidation of  $(\text{NH}_3)_5\text{Co(III)}$  lactato complex.

Stoichiometric studies were made with 10–20-fold excess of Cr(VI) over the Co(III) mandelato complex. After nine half-lives, it was found that 1 mole of mandelic acid/Co(III) mandelato complex required nearly 0.98 mol of imidazolium dichromate.

## RESULTS AND DISCUSSION

The reaction between imidazolium dichromate and Co(III) bound and unbound  $\alpha$ -hydroxy acids exhibits total second order kinetics: first order with respect to Co(III) complex and first order with respect to oxidant (Table-1). This is further corroborated by the linear plots of log absorbance versus time as well as the slope of unity for the plot of log [cobalt (III) complex] versus log [specific rates] ( $r = 0.98$ ).

TABLE-1  
KINETIC DATA FOR  $[\text{Co}(\text{NH}_3)_5 - \text{I}]^{2+}$  COMPLEXES WITH IMIDAZOLIUM  
DICHROMATE

[Imidazolium dichromate] =  $2.00 \times 10^{-4}$  M,  $[\text{HClO}_4] = 1.00\text{M}$ , Temp. =  $30^\circ\text{C}$

	$10^3$ [Compound] M	$k_1 \times 10^4$ $\text{s}^{-1}$	$10^2 k_2 =$ $k_1/[\text{compound}]$ $\text{dm}^3 \text{ mole}^{-1} \text{ s}^{-1}$
Co(III) mandelato	1.00	0.68	6.82
	2.00	1.32	6.60
	3.00	2.11	6.70
	4.00	2.60	6.50
	5.00	3.40	6.80
Co(III) lactato	1.00	0.79	7.90
	2.00	1.62	8.10
	3.00	2.39	7.96
	4.00	3.17	7.92
	5.00	4.01	8.02

Hence the rate law for the reaction is

$$\frac{-d[\text{Cr(VI)}]}{dt} = k_2[\text{Cr(VI)}][\text{Co(III)}] \text{ at a given } \text{H}^+$$

(where  $k_2 = k_1/[\text{Co(III)}]$  at fixed  $\text{H}^+$ )

$$\frac{-d[\text{Cr(VI)}]}{dt} = k_{\text{obs}}[\text{Cr(VI)}][\alpha\text{-hydroxy acid}][\text{H}^+]$$

where  $k_{\text{obs}} = k_1/[\alpha\text{-hydroxy acid}][\text{H}^+]$ .

The reaction between imidazolium dichromate and pentamminecobalt(III) complexes of  $\alpha$ -hydroxy acids is acid catalysed one, and with increase in  $[\text{HClO}_4]$  at a fixed ionic strength, the rate increases monotonically and the order in  $(\text{HClO}_4)$  is unity as shown by the slope of the plot of  $\log [\text{HClO}_4]$  versus  $\log k_1$ . This shows that the rate-determining step, in the presence of an acid, involves protonated Cr(VI) species.

The order of reactivity among the complexes as:



$$0.79 \qquad \qquad 0.68$$

The Co(III) lactato complex reacts faster than Co(III) mandelato complex; because if the reaction proceeds through a preformed chromate ester, then the rate of C—H cleavage should be enhanced, resulting in an increase in the rate of oxidation of Co(III) complex. Also chromate ester formation may be sterically hindered in the case of mandelato complex. The absence of such a steric retardation and enhanced acidity of methine proton in the lactato complex may account for its greater reactivity.

### Effect of Temperature

The rate of imidazolium dichromate oxidation of pentaamminecobalt(III) complexes of  $\alpha$ -hydroxy acids increases with increase in temperature in the range 30° to 50°C. From the Eyring's plot,  $\log k_2/T$  versus  $1/T$ , (Table 2) the thermodynamic parameters are calculated in the order expected for a bimolecular reaction.

TABLE-2  
EFFECT OF TEMPERATURE

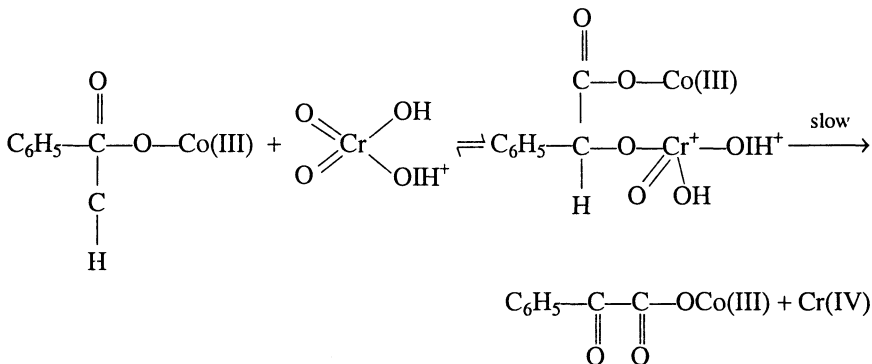
$[\text{Co(III) complex}] = 3.0 \times 10^{-3} \text{ M}$ ;  $[\text{IDC}] = 2.0 \times 10^{-4} \text{ M}$ ;  $[\text{HClO}_4] = 1.0 \text{ M}$

Substrate	$k_1 \times 10^4 \text{ s}^{-1}$			$\Delta H^\ddagger$ kJ mol <sup>-1</sup>	$\Delta S^\ddagger$ J K mol <sup>-1</sup>	$\Delta G^\ddagger$ kJ mol <sup>-1</sup>
	30°C	40°C	50°C			
Co(III)mandelato	2.11	4.57	10.4	27.13	-137.19	41.807
Co(III) lactato	2.26	5.16	11.2	27.38	-137.26	41.617

### Mechanism

Imidazolium dichromate with Co(III) mandelato/lactato complex forms a chromate ester complex. Then the chromate ester complex  $\alpha$ -C—H bond fission occurs in such a way that proton transfer take place in the slow step leading to the formation of the keto acid complex and Cr(IV). The absence of formation of Co(II) rules out the synchronous C—C bond fission and electrons transfer to

Co(III). Thus the oxidation of Co(III) complexes of  $\alpha$ -hydroxy acids by imidazolium dichromate seems to proceed mainly by C—H bond fission.



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