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Kinetics of Oxidation of Cobalt(III) Bound and Unbound α-Hydroxy Acids by Quinolinium Dichromate

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Quinolinium dichromate (QDC) oxidizes pentaammine cobalt(III) bound and unbound mandelic and lactic acids, in the presence of 0.50 mol dm^{-3} $HClO_4$. The reaction has unit dependence on α-hydroxy acids/cobalt(III) complex and QDC. The comparative study of QDC oxidation of cobalt(III) bound and unbound α-hydroxy acids may throw light on the mechanistic aspects of this reaction.

INTRODUCTION

The kinetics and mechanism of oxidation reactions of chromium(VI) have been fairly well studied. The mechanism of oxidation varies with the chromium(VI) species and the solvent used. The reagent employed in this investigation, quinolinium dichromate(QDC) $(C_4H_7NH^+)_2Cr_2O_7^{2-}$, has emerged as a very useful and versatile oxidant[1], which is clearly deserving of widespread application. The kinetics of quinolinium dichromate, {Cr(VI)}, oxidation of α-hydroxy acids have been studied by Aruna *et al.*[2] A mechanism involving the formation of chromate ester in the slow step has been proposed by the authors. If the carboxylic acid portion is tied up with cobalt(III) then the formation of cyclic chromate ester may not be possible. To understand the mechanistic aspects of QDC oxidation of α-hydroxy acids, kinetics of quinolinium dichromate oxidation of cobalt(III) bound and unbound α-hydroxy acids is undertaken.

EXPERIMENTAL

Quinolinium dichromate (QDC) was prepared by the reported method[1] and its purity was checked by estimating Cr(VI) iodometrically. Mandelic and lactic acid (Aldrich) was used as received. The pentaamminecobalt(III) complexes of α-hydroxy acids were prepared as their perchlorates following the procedure of Fan and Gould.[3] The reactions were performed under pseudo first order conditions by keeping a large excess of the cobalt(III) complex or unbound ligands with respect to QDC. The reactions were carried out at constant temperature and the progress of the oxidation was followed by an iodometric procedure.[4]

Stoichiometric studies and product analysis: The amount of cobalt(II) formed was estimated after nine half-lives, 2.5 mL of reaction mixture was diluted to 25 mL with conc. HCl allowing the evolution of chlorine to cease and then measuring the absorbance for the Co(II) chloro complex at 692 nm ($\varepsilon = 560$ dm^3

mol^{-1} cm^{-1}).[5] The amount of Co(II) formed was negligibly small, showing that there is no reduction at cobalt(III) centre.

The reaction mixture obtained by the reaction of Cr(VI) and mandelic acid after nine half-lives, was neutralised with K_2CO_3 solution and filtered. From the filtrate, the organic product was extracted with chloroform several times and from the chloroform extracts the organic product separated gave an IR spectrum which corresponds with IR spectrum of phenylglyoxylic acid. A similar analysis was carried out for Co(III) complex also. With Cr(VI) in 10–20-fold excess stoichiometric experiments were preformed with cobalt(III) bound and unbound mandelic acid. After the completion of reaction, from the amount of unreacted Cr(VI) estimated, it has been found that 1 mol mandelic acid/cobalt(II) mandelato complex requires nearly 1 mol of Cr(VI).

RESULTS AND DISCUSSION

The kinetic data for QDC oxidation of bound and unbound α-hydroxy acids are summarised in Tables 1 and 2. The reaction between chromium(VI) and cobalt(III) complex/α-hydroxy acids exhibits total second order kinetics- first order with respect to each reactant. These are further corroborated by the linear plots of logarithm of QDC concentration *vs.* time as will as the slope of unity for the plot of logarithm of [cobalt(III) complex]/logarithm of [α-hydroxy acid] *vs.* logarithm of specific rates (τ = 0.99). Hence the rate law for each one of the reactions is given by

$$\frac{-d[QDC]}{dt} = K_2[QDC][Co(III)] \quad \text{at given } H^+ \qquad (1)$$

$$\frac{-d[QDC]}{dt} = K_{obs}[QDC][\alpha\text{-hydroxy acid}][H^+] \qquad (2)$$

The reaction between QDC and pentaamminecobalt(III) bound and unbound α-hydroxy acids is an acid catalysed one, and with increase in $HClO_4$ at a fixed ionic strength (Tables 1 and 2) the rate increases montonically and the order in $[HClO_4]$ is unity as shown by the slope of the plot of log $[HClO_4]$ *vs.* log k_1. This shows that the rate determining step in the presence of an acid involves a protonated Cr(VI) species.

The rates of quinolinium dichromate oxidation of both Co(III) bound and unbound α-hydroxy acids are

Co(III) mandelato	>	Co(III) lactato
4.2		3.3
Mandelic acid	>	lactic acid
2.3		1.3

The specific rate of oxidation of the Co(III) mandelato complex is more when compared to both the rate of oxidation of unbound ligand and lactato complex, deserves an explanation. In the mandelate complex the presence of phenyl ring necessarily boosts the rate of oxidation. This has been attributed to the increased acidic nature of methine proton of lactic acid in its complex as revealed by the PMR spectra of respective Co(III) complex and unbound ligands.

TABLE-1
KINETIC DATA FOR [[Co(NH$_3$)$_5$–L]$^{2+}$] COMPLEXES WITH QUINOLINIUM DICHROMATE[a]

L	[Compound] 10^2 mol dm^{-3}	[Cr(VI)] 10^3 mol dm^{-3}	[HClO$_4$] mol dm^{-3}	$k_1 \times 10^4$ s^{-1}
Mandelato	1.0	1.0	0.50	4.20
	1.5	1.0	0.50	6.30
	2.0	1.0	0.50	8.50
	2.5	1.0	0.50	10.40
	3.0	1.0	0.50	12.70
	3.5	1.0	0.50	15.10
	1.0	1.5	0.50	4.40
	1.0	2.5	0.50	4.50
	1.0	3.0	0.50	4.50
	1.5	1.0	0.40[b]	4.00
	1.0	1.0	0.30[b]	2.54
	1.0	1.0	0.20[b]	1.26
	1.0	1.0	0.10[b]	0.97
Lactato	1.0	1.0	0.50	3.31
	1.5	1.0	0.50	5.22
	2.0	1.0	0.50	6.74
	2.5	1.0	0.50	8.43
	3.0	1.0	0.50	10.10
	1.0	1.5	0.50	3.10
	1.0	2.0	0.50	3.30
	1.0	2.5	0.50	3.20
	1.0	3.0	0.50	3.40
	1.0	1.0	0.40[b]	2.95
	1.0	1.0	0.30[b]	2.63
	1.0	1.0	0.20[b]	2.24

[a] Reactions were carried out at 30 ± 0.2°C

[b] The ionic strength was maintained by using HClO$_4$-NaClO$_4$ mixtures.

TABLE-2

SPECIFIC RATES FOR [Cr(VI)] OXIDATION OF α-HYDROXY ACID[a]

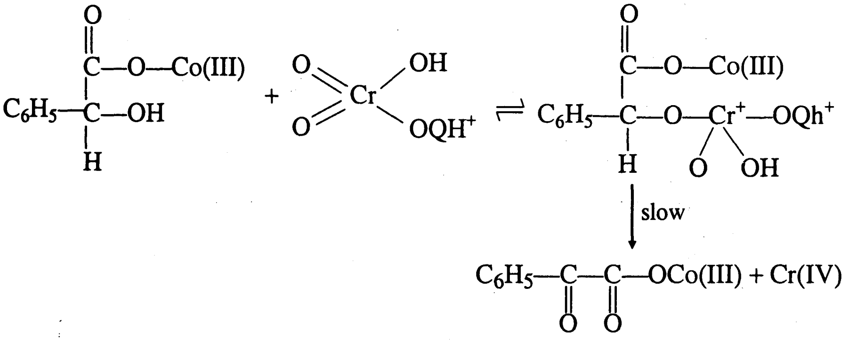
Compound	[Compound] 10^2 mol dm^{-3}	[Cr(VI)] 10^3 mol dm^{-3}	[$HClO_4$] mol dm^{-3}	$k_1 \times 10^4$ s^{-1}
Mandelic acid	1.0	1.0	0.50	2.30
	1.5	1.0	0.50	3.60
	2.0	1.0	0.50	4.80
	2.5	1.0	0.50	5.90
	3.0	1.0	0.50	6.70
	3.5	1.0	0.50	8.10
	1.0	1.5	0.50	2.50
	1.0	2.0	0.50	2.50
	1.0	2.5	0.50	2.70
	1.0	1.0	0.40[b]	1.90
	1.0	1.0	0.30[b]	1.40
	1.0	1.0	0.20[b]	0.98
Lactic acid	1.0	1.0	0.50	1.32
	1.5	1.0	0.50	2.10
	2.0	1.0	0.50	2.70
	2.5	1.0	0.50	3.20
	3.0	1.0	0.50	4.20
	1.0	1.5	0.50	1.40
	1.0	2.0	0.50	1.50
	1.0	2.5	0.50	1.70
	1.0	1.0	0.40*b*	1.06
	1.0	1.0	0.30*b*	0.79
	1.0	1.0	0.20*b*	0.51

[a] Reactions were carried out at 30 ± 0.2°C

[b] The ionic strength was maintained by using $HClO_4$—$NaClO_4$ mixtures.

Mechanism

Quinolinium dichromate with Co(III) mandelato/lactato complex forms a chromate ester (Scheme-1). The chromate ester transfer α-C—H bond fission occurs in the slow step in such a way that hydride ion transfer takes place leading to the formation of the ketoacid complex and Cr(IV). From the infuence of substituents on the rate of quinolinium dichromate oxidation of α-hydroxy acids it is found that the reaction constant p is negative which shows that the transition state is more electron deficient. Such a transition state can be envisaged only when the α-C—H bond fission occurs in the slow step with hydride ion tranfer. The absence of formation of Co(II) rules out the synchronous C—C bond fission and electron transfer to Co(III). Thus the oxidation of Co(III) complexes of α-hydroxy acids by quinolinium dichromate seems to proceeds mainly by α-C—H bond fission. The mechanism of Cr(VI) oxidation of cobalt(III) lactato, mandelic acid and lactic acid will be similar to one proposed for the cobalt(III) mandelato complex.



Scheme-1

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