

ORIGINAL ARTICLE

EVIDENCE FOR THE SYNCHRONOUS CLEAVAGE OF C-C AND C-H BONDS
IMIDAZOLIUM FLUORO CHROMATE(IFC) OXIDATION OF COBALT(III)BOUND AND
UNBOUND α -HYDROXY ACIDS

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ABSTRACT

Imidazoliumfluorochromate(IFC) of pentaammine cobalt(III) bound and unbound mandelic, lactic and glycolic acids have been studied in 50%(v/v)aqueous acetic acid medium. The reaction exhibits total second order kinetics first order in each reactant. The reaction of imidazoliumfluorochromate with $[\text{Co}(\text{NH}_3)_5]^{2+}$ complexes of α -hydroxy acids,yield Co(II) and a carbonyl compound to the extent of 12%. The other product of the reaction,phenylglyoxalato cobalt(III) complex is obtained in 88% yield by a two electron oxidation.

Keywords :Imidazoliumfluorochromate, induced electron transfer, pentaamminecobalt(III) complex.

1.INTRODUCTION

The induced electron-transfer reactions, in which a Co(III) bound organic ligand suffers a net two-electron oxidation initiated by an external oxidant such as Ce(IV), yielding a carbon radical intermediate, have been studied in detail by Taube and coworkers¹. The cation radical formed subsequently undergoes an intramolecular second one-electron transfer, resulting in the reduction at the cobalt(III) center without altering the carbon skeleton of the ligand, except in the case of Co(III)-bound oxalato². The extension of this work to Ce(IV) oxidation of Co(III) complex of the α -hydroxy acid mandelic, lactic and glycolic acids³ showed no evidence for partition of the intermediate, even when the Ce(IV):Co(III) ratio taken exceeded 20:1 and the results are consistent with a mechanisms in which electron transfer to the oxidants and C-C fission are synchronous.

The presentwork concerns the highly reactive oxidant imidazoliumfluorochromate oxidation of pentaamminecobalt(III) complexes of mandelic,lactic and glycolic acids has been employed for an induced electron-transfer reaction involving Co(III) complexes.

MATERIALS AND METHODS

IFC was prepared the reported method⁴ and is purity checked by the iodometric method⁵. Solution of IFC of required conditions were made by dissolvingweighed amounts of glacial acetic acid. The cobalt(III) complexes of mandelic, lactic and glycolic acids were prepared as their perchlorates by the method of Fanand and Gould⁶. Cobalt analysis⁷ of these complexes are in agreement with the assigned structures. Acetic acid was purified by boiling it under reflux with chromic oxide and acetic anhydride for 6h and then fractionally distilling it.

The reaction were carried out at $30 \pm 0.2^\circ\text{C}$.the specific rates for the reaction under pseudo first order conditions are viz.[Substrate] \gg [IFC].the solvent wasa 1:1(v/v)AcOH-H₂O mixture.

The reactions were followed up to 90% completion by monitoring the decrease in [IFC] at 529 nm.The pseudo first order rate constant k_{obs} were computed from the linear($r > 0.990$) least squares plot of $\log[\text{IFC}]$ versus time. Co^{II} was estimated after 9 half lives of reaction in presence of an excess of IFC by diluting 10-fold with conc. HCl, allowing evolution of chlorine to ease, and then measuring the absorbance at 692 nm($\epsilon=560$).this corresponded to nearly 12% of the initial concentration of the cobalt(III) complex.

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Absorbance with blank solutions containing IFC were also measured to apply suitable correction which came to less than 2% of the absorbance done to the chloro-complex of Co^{II}. The other product of the oxidation involving (NH₃)₅Co^{III}-mandelato or (NH₃)₅Co^{III}-lactato or (NH₃)₅Co^{III}-glycolato as the reductants, was found to be (NH₃)₅Co^{III}-phenylglyoxalato or (NH₃)₅Co^{III}-pyruvato respectively. After the reactions were complete, the reaction mixture were neutralized to pH=6.0 by the addition of a saturated solution of KHCO₃ when the excess of oxidants. IFC precipitated as their hydroxides and ClO₄⁻ precipitated as KClO₄ which were removed by filtration. The filtrate was transferred to a 50 cm³ R.B.flask and distilled at 60°C under reduced pressure to remove the solvent, the product separated and identified by using infrared spectrum, the infrared spectrum of the product in identical with that of the authentic sample (glyoxalato cobalt(III) complex). Carbon dioxide was estimated by carrying out the reaction with excess oxidant at 30°C for 24 h.

Similar experiments with the other Co^{III}- complex yielded corresponding Co^{III}-oxoacids in 85-88% yields after recrystallisation. Stoichiometry determination under excess of IFC in a 50:50%(v/v) acetic acid – water mixture showed that 1.20 mol of IFC were consumed for 1 mol of the cobalt(III) complex (Table 1).

Table 1 Stoichiometry data for IFC oxidation of cobalt(III) bound / unbound -hydroxy acids

10 ⁴ [comp] (mol dm ⁻³)	10 ³ [PBC] _{in} (mol dm ⁻³)	10 ³ [PBC] _{in} (mol dm ⁻³)	10 ⁴ [PBC] (mol dm ⁻³)	10 ⁴ [Co ^{II}] ^b (mol dm ⁻³)	[Comp] [PBC]
Co ^{III} - mandelato					
1.00	1.00	0.872	1.28	0.109(10.7)	1.00:1.2
2.00	1.00	0.750	2.50)	8
3.00	1.00	0.632	3.68	0.204(10.3)	1.00:1.2
)	5
				0.296(10.8)	1.00:1.2
)	2
Co ^{III} - Lactato					
1.00	1.00	0.871	1.29	0.107(13.7)	1.00:1.2
1.00	1.00	0.752	2.48)	9
2.00	1.00	0.630	3.70	0.206(10.3)	1.00:1.2
3.00)	4
				0.299(10.9)	1.00:1.2
)	3
Co ^{III} - glycolato					
1.00	1.00	0.872	1.28	0.110(11.0)	1.00:1.2
1.00	1.00	0.750	2.50)	8
2.00	1.00	0.632	3.68	0.210(10.4)	1.00:1.2
3.00)	5
				0.300(12.3)	1.00:1.2
)	2

^a These reaction were carried out in 50:50 (v/v) acetic acid – water medium at 30± 0.2°C

^b Amount of cobalt(II) formed was calculated with respect to [Co^{III}]_{initial}

3.RESULTS AND DISCUSSION

The kinetics of IFC oxidation of cobalt(III)-bound and unbound -hydroxy acids has been studied in the presence of 0.30 mol dm⁻³ HClO₄ at 30±0.2°C. The reaction between IFC and -hydroxy acids / cobalt(III) complex exhibits second order kinetics – first order with respect to each reactant (Table 2). This is also confirmed by the linear plots of logarithm of IFC concentration *versus* time, as well as the

unity slope for the plot of logarithm of [cobalt(III) complex] / logarithm of [-hydroxy acids] *versus* logarithm of specific rates (r=0.99). Hence the rate law for each one of the reactions is given by the equations (1) and (2)

Table 2. Kinetic data for the oxidation of pentaamminecobalt(III) complex of -hydroxy acids by IFC.

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)
L-Mandelato		
0.50	1.02	2.04
1.00	2.05	2.05
1.25	2.60	2.08
1.50	3.01	2.01
2.00	4.10	2.05
2.50	5.20	2.08
L-Lactato		
0.50	0.59	1.18
1.00	1.16	1.16
1.25	1.40	1.12
1.50	1.74	1.16
2.00	2.32	1.16
2.50	2.80	1.12
L-glycolato		
0.50	0.86	1.72
1.00	1.76	1.76
1.25	2.12	1.70
1.50	2.58	1.72
2.00	3.52	1.76
2.50	4.37	1.75

$$\frac{d[\text{I}]}{dt} = k_2[\text{IFC}][\text{Co(III)}] \dots\dots\dots(1)$$

At a given H⁺

$$\frac{d[\text{I}]}{dt} = k_{\text{obs}}[\text{IFC}] [\text{-hydroxy acids}][\text{H}^+] \dots\dots\dots(2)$$

The reaction between IFC and pentaammine cobalt(III) bound and unbound -hydroxy acids in an acid – catalyzed one, and with the increase in HClO₄ at affixed ionic strength the rate increase monotonically and the order in [HClO₄] in unity as shown by the slope of the plot of log [HClO₄] *versus* log k₁. This shown that the rate determining step in the presence of an acid, involves a protonated Cr(VI) species.

Rates of oxidation were determined in solvents containing different proportions of AcOH in water. The rate decrease with an increase in the amount of AcOH in the solvent mixture. The result show that the rate constant for the decomposition of the complex increase with an increase in the amount of acetic acid in the solvent mixture of acetic acid and water (Table 3).

Table 3. Effect of solvent composition of oxidation of cobalt(III) complex by IFC

AcOH : H ₂ O (v/v)	D	10 ⁴ k ₁ (s ⁻¹)
L-Mandelato		
40:60	49.98	1.74
50:50	42.84	2.05

60:40	35.70	2.72
70:30	27.90	3.92
L-Lactato	-	0.82
-	-	1.16
-	-	1.45
-	-	2.15
L-glycolato	-	1.42
-	-	1.76
-	-	2.12
-	-	2.86

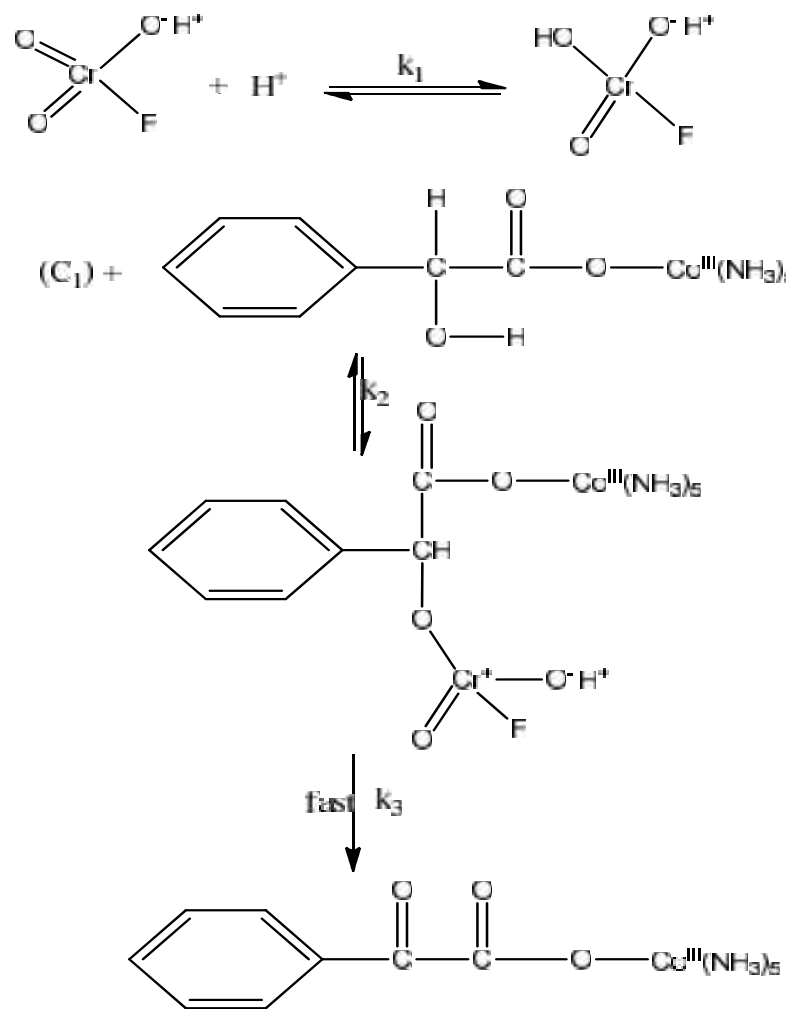
Addition of imidazole at different concentration by keeping other factors constant.

It was found that there is no appreciable change in the rate. This rules out the possibility of a pre equilibrium involving imidazole. The rates of oxidation of Co^{III} complex were obtained at different temperatures between 303K and 318K and the activation parameters were evaluated (Table 4).

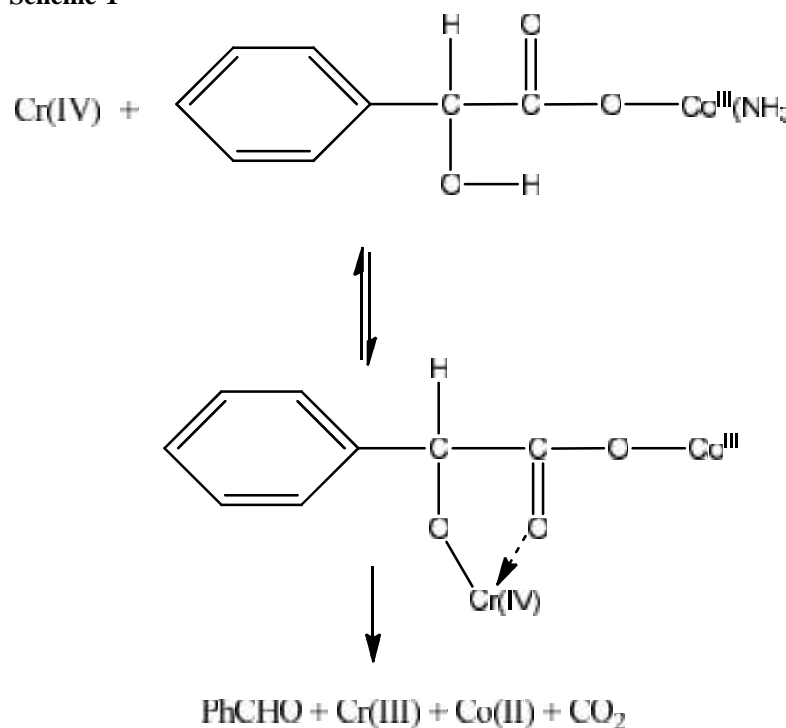
Table 4 Temperature dependence and activation parameters of the oxidation of pentaamminecobalt(III) complex of α -hydroxy acids by IFC.

[(NH ₃) ₅ Co ^{III} -L]	10 ⁴	308	313	318	H#	k-S [#]	G [#]
	(s ⁻¹)	K	K	K			
	303				kJ	JK ⁻¹	kJ
	K				mol ⁻¹	mol ⁻¹	mol ⁻¹
L-mandelato	2.05	3.18	4.47	6.22	55.4	128.8	94.4
L-lactato	1.16	1.58	2.16	2.87	44.3	121.7	81.2
L-glycolato	1.76	2.14	2.76	3.40	32.2	122.7	69.3

In the mechanisms shown in (scheme-I) envisages the formation of a binuclear between IFC and the mandelato complex. The binuclear complex undergoes nearly synchronous carbon - hydrogen fission to yield phenylglyoxalato complex (88%) whereas the same binuclear complex undergoes synchronous carbon - carbon fission to yield cobalt(II) (12) (Scheme II).



Scheme-1



Scheme-II

In all cases, ligation of the cobalt(III) center reduces the rate of IFC oxidation of ligands due to the electrostatic influence of the cobalt(III) center. This effect seems to be preferentially

marked with mandelic acid as compared with other two substrates. Thus IFC oxidation of the substrates seem to be susceptible to polar influences to some extent. Introduction of one phenyl group (mandelato) in both the rate of oxidation of lactic, glycolic acids and all the three complexes, in the mandelic acid in the presence of phenyl ring necessarily boosts the rate of oxidation when compared to other substrates. The formation of cobalt(II) and CO₂ to the extent of nearly 12% of [Co¹¹¹]_{initial} in the IFC oxidation of mandelato-pentaammine cobalt(III) complex suggests that the cleavage of C-C bonds, occurs to the extent of 12% in a synchronous fashion. As this formation is only 12% of the total reaction, the reaction is also accompanied by the formation of phenyl glyoxalato-pentaamminecobalt(III) complexes (88%) in which these are only C-H cleavages. The above observations are also in agreement with the observed decreases in absorbance at 502 nm for the mandelato-pentaamminecobalt(III) complex which is only ca. 12% of the initial absorbance. IFC oxidizes and induces the formation of a radical which in a synchronous step undergoes C-C bond cleavage, yielding cobalt(II) and CO₂ to the extent of 12% suggesting that this reaction path forms only 12% of a total reaction. IFC is known to be a good C-C cleaving reagent like Ce(IV)⁷. The formation of a radical as intermediate is also evidenced by initiation of acrylonitrile polymerization by this reaction mixture only.

4. CONCLUSION

Chromium(IV) induces electron transfer in pentaammine cobalt(III) complexes of α -hydroxy acids resulting in nearly 100% reduction in cobalt(II) center with synchronous carbon-carbon bond fission and decarboxylation. Such an induced electron transfer reaction has been attempted presently with

Imidazoliumfluorochromate(IFC) and pentaammine cobalt(III) complexes of α -hydroxy acids in perchloric acid medium. The amount of cobalt(II) formed is nearly 12% and around 88% of ketoacid-Co(III) complex is formed. Kinetic results coupled with stoichiometry data have been accounted for a suitable mechanistic scheme

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