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KINETICS OF PENTAAMMINE COBALT(III) COMPLEXES OF α -HYDROXY ACIDS BY ISOQUINOLINIUM FLUOROCHROMATE IN MICELLAR MEDIUM

P. Rajkumar[1*], G.Saraswathy[2] , Z. Abdul Vaheith[3] and A. Fiaz Ahamed[4]
[1]Department of Chemistry, Priyadarshini Engineering College,
Vaniyambadi- 635751, (TamilNadu) India.
[2]Department of Chemistry, Government College of Engineering,
Bargur- 635104, (TamilNadu) India.
[3]Department of Chemistry, C.Abdul Hakeem College of Engineering & Technology,
Vellore- 632509 (TamilNadu) India.
[4]PG & Research Department of Chemistry, Islamiah College,
Vaniyambadi- 635752,(TamilNadu) India.
*E-mail: drprajkumar2014@gmail.com

ABSTRACT

Kinetics of oxidation of Pentaamminecobalt (III) complexes of α-hydroxy acids by Isoquinolinium Fluorochromate(IQFC) in micellar medium yielding nearly 100% of carbonyl compounds are ultimate products. This oxidation as a diagnostic tool to find out the fraction taking place by synchronous cleavages of O-H and C-C bonds. It has been set up that the rate of oxidation of Co(III) complexes of both bound and unbound α-hydroxy acids are increased more in the presence of cationic micelle of Cetyltrimethylammonium bromide (CTAB), when compared to the anionic micelle of Sodium lauryl sulfate (NaLS). The 1 mole of cobalt(III) complexes of α-hydroxy acids reacts with nearly 0.5 mole of Isoquinolinium Fluorochromate(IQFC), correspondingly 1 mole of α-hydroxy acids reacts with nearly 1 mole of Isoquinolinium Fluorochromate(IQFC). The reaction goes by free radical mechanism was proved by acrylonitrile polymerization. The suitable methodology has been proposed.

Keywords: Pentaamminecobalt(III) Complexes, Isoquinolinium Fluorochromate(IQFC), Micelles, Oxidation, NaLS, CTAB.

INTRODUCTION

The kinetics of oxidation of cobalt (III) bound α-hydroxy acids are important both from the mechanistic approach and its bearing on the mechanism of α-hydroxy acid metabolism[1,2]. Several surfactants are able to aggregate in non-aqueous solvents to yield reverse micelles in which the polar head groups of the surfactant monomers group to form a micellar center and are directed towards the center of the gather, and the hydrophobic tails expand outwards into the bulk organic segment. A number of transition metal complexes have been used for studying electron transfer of different environments such as micelles.[3,4]

A large class of organic compounds was oxidized by Isoquinolinium Fluorochromate(IQFC) has been reported[5-7]. Since induced electron transfer in pentaamminecobalt(III) complexes of α-hydroxy acids with various oxidants have been studied.[8-14] Induced electron transfer reactions in pentaamminecobalt(III) complexes of α-hydroxy acids result in nearly 100% reduction at cobalt (III) center with synchronous C-C bond fission and decarboxylation. Such an electron transfer path seems to be unavailable for Isoquinolinium Fluorochromate(IQFC) in its reaction with cobalt(III) bound and unbound α-hydroxy acids to relevant keto acid, cobalt (III) complexes in Sodium Lauryl Sulfate (NaLS)[15] and Cetyltrimethylammonium bromide(CTAB)[16,17] probably the transition state is more electron deficient. Such a transition state can be envisaged only when the C-H bond fission occurs in the slow step with

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hydride ion transfer. The rate of IQFC oxidation of cobalt(III) complexes of α-hydroxy acids depends on the first power of IQFC concentration. The 1 mole of Co(III) complexes of α-hydroxy acids consumes 0.5 mole of Isoquinolinium Fluorochromate(IQFC), while 1 mole of unbound α-hydroxy acids consume 1.0 mole of Isoquinolinium Fluorochromate(IQFC) correspondingly.

EXPERIMENTAL

Materials and Methods

Preparation of Carbonatopentaammine cobalt(III) Nitrate

Carbonatopentaamminecobalt(III) nitrate was prepared by dissolving 0.21 mol of powdered ammonium carbonato in 60 mL of water and 100 mL of concentration aqueous ammonia, adding a solution of 0.10 mol of cobalt (II) nitrate. 6 hydrate in 40 mL of water and then bubbling air very slowly through the mixture (20 bubbles/min.) for 20 days. The solution was cooled to 0^0C and 600 mL of methanol was added slowly with stirring. The preparation was set aside at 0^0C for 3 days, and the precipitated carbonato nitrate was filtered off. This was purified by dissolving in twice its weight of water, adding LiCl (1 g of LiCl / 2 g of the complex), filtering and then slowly adding an equal volume of methanol. The solution was kept 0^0C for 10 hr and the crystalline complex was filtered off and dried in vacuum[18].

Preparation of Pentaaminecobalt(III) Complexes of α-Hydroxy Acids

The monomeric cobalt(III) complexes of mandelic acid, lactic acid and malic acids[19]were prepared as their perchlorates following the method of Fan[20]and Gould.[15]

0.01 mol of the α-hydroxy acids were dissolved in 20ml of methanol taken in a 50ml of R.B.flask and a pellet (0.50 to 1.00g) of NaOH was added. About 0.001 mol of finely powdered carbanatopentaammine cobalt(III) nitrate was added and the mixture was refluxed at 70°C for 2 hours. It was then cooled under the ice for 30 minutes; about 3ml of 70% perchloric acid was added drop wise while shaking the mixture was cooled again under the ice for 1 hour. The cobalt(III) complex precipitated as perchlorate and was filtered through a sintered glass crucible, washed well with ethanol followed by diethyl ether, dried and conserved in a desiccator.

Preparation of Isoquinolinium Fluorochromate

Cr(VI) oxide (15.0g, 0.15 mol) is dissolved in water (25 ml) in a polythene beaker and 40% hydrofluoric acid (11.25 ml, 0.225 mol) is added with stirring at room temperature. To the ensuing clear orange solution, isoquinoline (17.75 ml, 0.15 mol) is added dropwise with stirring. The mixture is heated on a water bath for about 15 minutes then cooled to room temperature, and allowed to set for 40-45 minutes. The bright orange, crystalline Isoquinolinium Fluorochromate is isolated by filtration in Buchner funnel. It is recrystallized using hot water and dried in vacuums for about one hour.[21]

Kinetic Method

All the glass apparatus were made of Pyrex glass and stoppers were well ground. The loss of solvent, tested in a standard flask and in reaction bottles, was found to be insignificant. Burettes, pipettes and standard flasks were consistent by usual method.[22,23]

Rate Measurement

The Isoquinolinium Fluorochromate oxidant of Co(III) complexes of α-hydroxy acids and unbound ligand, the rate of measurements were made at 31 ± 0.2^0C in 100% aqueous medium.[24] The standard solution prepared and required amount solutions were pipette out into a 1 cm cell. The total volume of the reaction mixture in the spectrophotometer cell was kept as 2.5 mL in each kinetic run. A UV-Visible spectrophotometer was used to follow the rate of the reaction. Rates of this unbound ligand and Co(III) bound complexes were computed from the observed decrease in absorbance at 350 nm. For all the kinetic experiments, the conversion was followed at least for four half-lives and specific rates from successive half-lives fixed with + or 7% and the average values did not differ from a plot of logarithmic change in concentration versus time computed using integrated rate equation.[25]

Stoichiometric Studies

The stoichiometric studies for the Isoquinolinium Fluorochromate(IQFC) oxidation of pentaamminecobalt(III) complexes of α-hydroxy acids and unbound ligands in the presence of micelles Table-1 were carried out with the oxidant in excess. The [H^+] and ionic strength were maintained as in the corresponding rate measurements. The temperature was carried out at 31 ± 0.2^{0}C. After 100 hours when the reaction was nearing completion, the concentration of unreacted IQFC was determined both iodometrically and spectrophotometrically from the change in absorbance measured at 350 nm. Likewise, the stoichiometric studies for the IQFC oxidation of pentaamminecobalt(III) complexes of α-hydroxy acids and unbound ligands in the presence of micelles were carried out.[26,27]

Table-1: Stoichiometric Data for IQFC Oxidation of Co(III) bound and unbound α-hydroxy acids in the presence of NaLS & CTAB.

H_2SO_4= 0.5 mol dm^{-3}, [NaLS] = 1.00 X 10^3 mol dm^{-3}, [CTAB] = 1.00 X 10^3 mol dm^{-3}, Temperature 31 ± 0.2°C

10^3[Compound] mol dm^{-3}	10^2 [IQFC] Initial mol dm^{-3}	10^2 [IQFC] Final mol dm^{-3}	Δ10^3 [IQFC] mol dm^{-3}	[Compound]: Δ[IQFC]
Mandelic acid				
1.0	1.0			
2.0	2.0	0.89	1.10	1.00 : 1.10
4.0	2.0	1.80	2.00	1.00 : 1.00
Lactic acid		1.60	4.00	1.00 : 1.00
1.0	1.0			
2.0	2.0	0.90	1.00	1.00 : 1.00
4.0	2.0	1.81	1.90	1.00 : 0.95
Malic acid		1.60	4.00	1.00 : 1.00
1.0	1.0			
2.0	2.0			1.00 : 1.20
4.0	2.0	0.88	1.20	1.00 : 1.10
Mandelato		1.78	2.20	1.00 : 1.07
1.0	1.0	1.57	4.30	
2.0	2.0			2.00 : 1.00
4.0	2.0	0.95	0.50	2.00 : 1.10
Lactato		1.89	1.10	2.00 : 1.00
1.0	1.0	1.99	2.01	
2.0	2.0			2.00 : 0.98
4.0	2.0		0.49	2.00 : 1.00
Malato		0.96	1.00	2.00 : 1.00
1.0	1.0	1.90	2.00	
2.0	2.0	2.00		
4.0	2.0		0.50	2.00 : 1.00
		0.95	1.20	2.00 : 1.20
		1.88	2.02	2.00 : 1.01
		1.98		

RESULTS AND DISCUSSION

Dependence of Rate on Isoquinolinium Fluorochromate(IQFC) Oxidation Cobalt(III) Complexes of α-hydroxy Acids in Micellar Medium

The rate of Isoquinolinium Fluorochromate(IQFC) oxidation of pentaamminecobalt(III) complexes of α-hydroxy acids had been followed under pseudo-first order condition by maintaining an excess of the complex concentration than the reagent. The rate constants were calculated by the integrated rate equation. The graph of the logarithm of concentration versus time was linear and the rate constants calculated from the slope of the graph agreed with the experimental value, which shows first-order dependence on [$(NH_3)_5Co(III)\text{-}L]^{2+}$] Table-2, (Fig.-1)**.** This was further substantiated from the study of varying the concentration of pentaamminecobalt(III) complexes of α-hydroxy acids from [0.5 to 2.5] X 10^2 mol dm^{-3}at a fixed concentration in the micellar medium. The rate constants obtained for the different concentration of $[(NH3)5Co(III)\text{-}L]^{2+}]$ complexes of α-hydroxy acids were nearly a constant. Hence the rate of disappearance of complexes in this concentration range studied is given as Table-3, (Fig.-2 and 3).

$$-d[(NH3)5Co(III)\text{-}L]^{2+}] / dt = k1[(NH3)5Co(III)\text{-}L]^{2+}] \qquad (1)$$

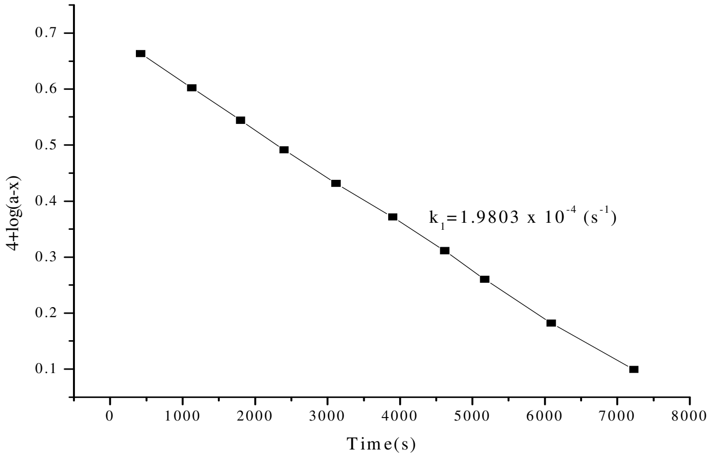


Fig.-1: First Order Dependence Plot

Table-2: First Order Rate on IQFC Oxidation of Pentaamminecobalt(III) Complexes

[IQFC] = 1.25 mol dm^{-3}, H_2SO_4= 0.5 mol dm^{-3}, Temperature = 31 ± 0.2°C, L= Mandelic Acid

Time (s)	log(a-x) mol dm^{-3}	10^4k_1 (s^{-1})
300	0.662	2.461
600	0.632	2.464
900	0.603	2.463
1200	0.574	2.471
1500	0.545	2.464
1800	0.516	2.459
2100	0.487	2.457
2400	0.458	2.461
2700	0.429	2.463
3000	0.401	2.461

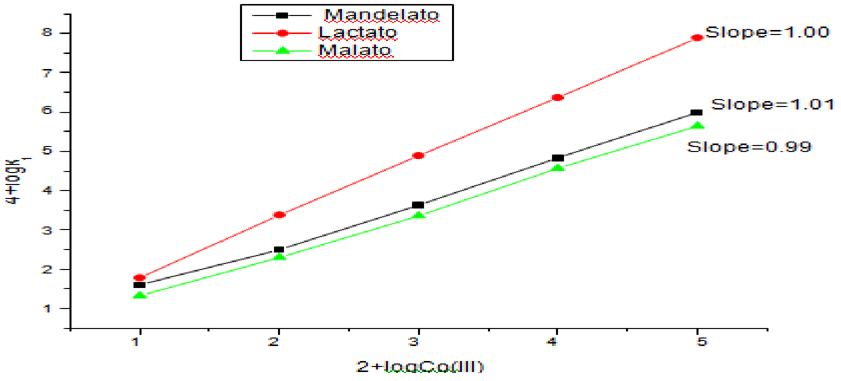


Fig.-2 Dependence of rate on [Co(III)] in NaLS

Table-3: Dependence of Rate on IQFC Oxidation Cobalt(III) Complexes of α-Hydroxy Acids in Micellar Medium $[(NH_3)_5Co(III)\text{-}L]^{2+}]$ = 1.25 mol dm^{-3}, H_2SO_4 = 0.5 mol dm^{-3}, [NaLS] = 1.00 X 10^3 mol dm^{-3}, [CTAB] = 1.00 X 10^3 mol dm^{-3}, Temperature = 31 ± 0.2°C

10^2 $[(NH_3)_5Co(III)$ - L] mol dm^{-3}	NaLS		CTAB	
	10^4 k_1 (s^{-1})	10^2 k_2dm^3 mol^{-1} s^{-1}	10^4 k_1 (s^{-1})	10^2 k_2dm^3 mol^{-1} s^{-1}
Mandelato				
0.5	1.204	1.368	1.567	1.678
1.0	2.498	2.567	3.089	3.189
1.5	3.631	3.563	4.567	4.609
2.0	4.834	4.987	6.024	6.193
2.5	5.990	5.891	7.498	7.590
Lactato				
0.5	1.783	1.670	1.906	1.897
1.0	3.378	3.276	3.859	3.894
1.5	4.890	4.906	5.794	5.367
2.0	6.368	6.287	7.637	6.736
2.5	7.891	7.704	9.521	8.209
Malato				
0.5	1.126	1.283	1.367	1.490
1.0	2.298	2.325	2.599	2.678
1.5	3.357	3.206	3.814	3.908
2.0	4.567	4.987	5.203	5.199
2.5	5.641	5.418	6.408	6.000

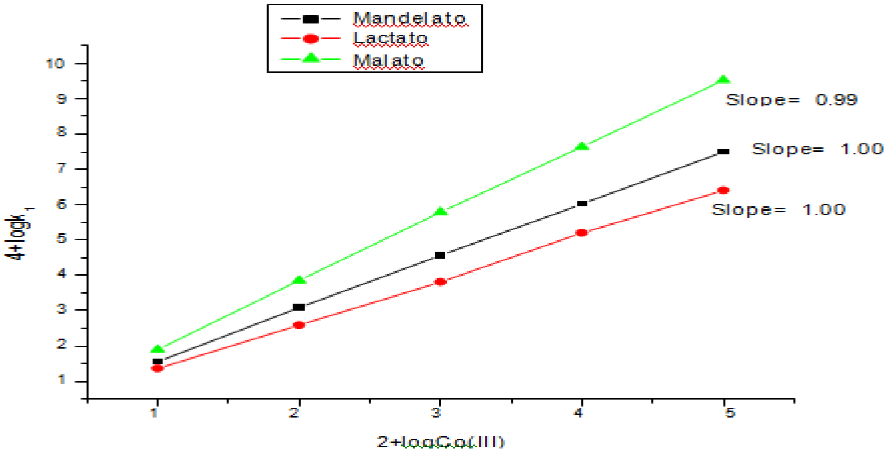


Fig.-3 Dependence of rate on [Co(III)] in CTAB

Table-4: Activation parameters and second order rate constants for the oxidation of $[(NH_3)_5Co(III)\text{-}L]^{2+}$ by IQFC $[(NH_3)_5Co(III)\text{-}L]^{2+}]$ =1.25 mol dm^{-3} ; [IQFC] =1.25 mol dm^{-3}; $[H_2SO_4]$ =0.5 mol dm^{-3}

Parameters	Lactato 10^4 $k_1(s^{-1})$	Mandelato 10^4 $k_1(s^{-1})$	Malato 10^4 $k_1(s^{-1})$
[Temperature] 298K	1.31	1.07	3.11

303K	1.71	1.57	3.62
308K	2.11	2.07	4.14
313K	2.51	2.58	4.65
[Activation parameters]			
E_aKJmol^{-1}	25.08	20.49	59.55
ΔH KJmol^{-1}	22.56	17.97	57.03
-ΔS JK^{-1}mol^{-1}	120.16	115.57	154.63
ΔG KJmol^{-1}	59.81	53.79	104.96

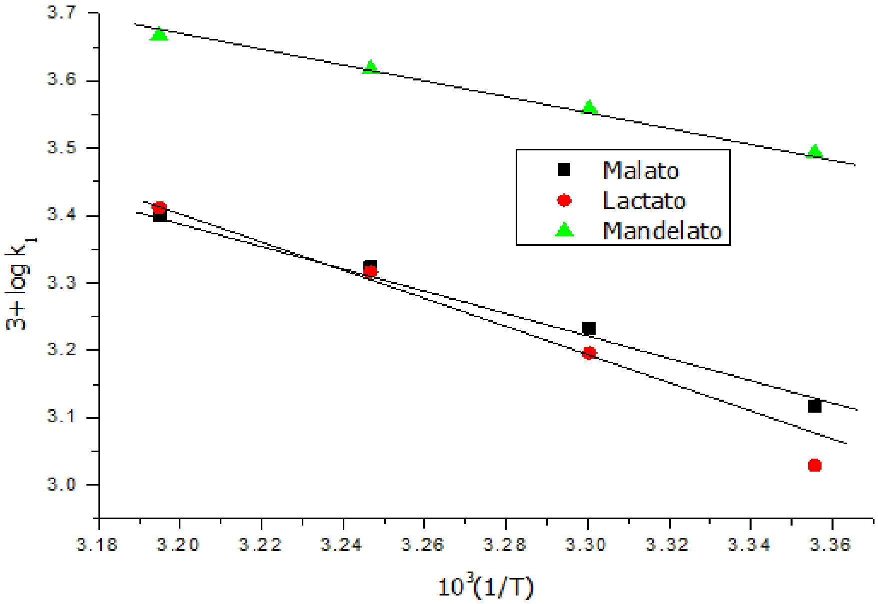


Fig.-4 Dependence of rate on [Co(III)] at various temperatures

All the kinetic runs were repetitive and the rate constants were reproducible within ± 2% range.

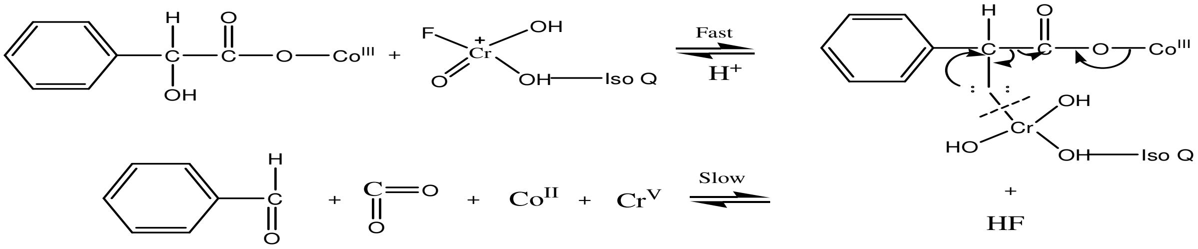
Effect of Varying the Temperature of Cobalt(III) Complexes of α-hydroxy Acids

The effect of varying the temperature on the rate of IQFC oxidation of pentaamminecobalt(III) complexes α-hydroxy acids has been investigated in the range of temperatures 25°C to 40°C ± 0.2°C which was given in Table-4 With rising the temperature, an increase in the rate is observed. A graph of logk$_1$versus temperature [1/T] is a linear (Fig.-4). At a higher temperature of α-hydroxy acids, the nearly maximum rate has been observed. The linear pattern of the curve of these catalyzed the oxidation. If the reaction species is ionic the reaction would have been accelerated and retarded in the other depending on the charge carried by it. Lower the value of Ea indicates that it is a better catalyst for the above oxidation reaction.

Mechanism of IQFC Oxidation of Pentaamminecobalt(III) Complexes of Both Bound and Unbound α-Hydroxy Acids in Micellar Medium.

Isoquinolinium Fluorochromate(IQFC) oxidizes OH center of the α-hydroxy acids at a rate of comparable to that of the free ligand. There is 100% reduction at the Proton center, forms an Isoquinolinium Fluorochromate ester which can decompose in a slow step, takings through C-C bond fission leading to the formation of carbonyl compounds with the evolution of carbon dioxide and H_2 gas.

Considering these facts and findings with these results, the following reaction schemes have been projected for the IQFC oxidation of pentaamminecobalt(III) complexes of both bound and unbound α-hydroxy acids.



Scheme-1

CONCLUSION

An induced electron transfer reaction has been attempted presently with Isoquinolinium Fluorochromate(IQFC) and pentaamminecobalt(III) complexes of α-hydroxy acids in the presence of NaLS & CTAB medium. The reaction exhibits second order kinetics. In these reactions, the rate of oxidation shows first order kinetics. The reactions have followed by observing the decrease in the absorbance at 502 nm for Co(III) complex in a UV-visible spectrophotometer.

Product and Stoichiometric analysis were carried out for the oxidation of complexes and free ligands in two different (Anionic & Cationic) micellar medium. with increasing micellar concentration an enhance in the rate is observed. IQFC oxidizes cobalt(III) bound and unbound α-hydroxy acids through free radical. It explains the synchronous C-C bond fission, decarboxylation and electron transfer to cobalt(III) center. The added CTAB enhances the rate of oxidation of a reaction much more than NaLS. A mechanism involving the one-electron transfer for the complex and two electron transfer for the ligand was proposed i.e., the 1 mole of Co(III) complexes of α-hydroxy acids consumes 0.5 mole of Isoquinolinium Fluorochromate, whereas 1 mole of unbound α-hydroxy acids consume 1.0 mole of Isoquinolinium Fluorochromate(IQFC).

In the present work, on such a reaction with pentaamminecobalt(III) complexes of α-hydroxy acids, the rate of disappearance of cobalt(III) is found to be almost the same as the rate of formation of cobalt(II) or the respective carbonyl product. The quantum yield of cobalt (III) obtained is nearly 100% for all these complexes. Nearly 100% reduction at cobalt (III) center, with the formation of 100% of cobalt (II) and respective carbonyl product is briefed by a metal-centered excitation resulting in a metal-ligand bond breaking accompanied by d → π back bonding to ligand, facilitating carbon-carbon fission, possibly in a synchronous manner. When a mixture of pentaamminecobalt(III) complexes of α-hydroxy acids with acrylonitrile is irradiated with 254nm, as polymerization does not found, the reduction of this complex, possibly, does not produce long-lived organic radical. The reaction goes by free radical mechanism was proved by acrylonitrile polymerization. The appropriate methodology has been adopted.

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