International Journal of Chemistry and Pharmaceutical Sciences

Journal Home Page: www.pharmaresearchlibrary.com/ijcps

Research Article   **Open Access**

Kinetics and Oxidation Mechanism of Pentaamminecobalt (III) Complexes of -Hydroxy Acids by Isoquinolinium Dichromate in Micellar Mmedia

A. Palanivel*[a], P. Rajkumar[b] and K. Subramani[c]

[a]Department of Chemistry, Government Arts College (Men) (Affiliated to Periyar University, Salem)
Krishnagiri-635001, Tamilnadu, India.
[b]Department of Chemistry, Priyadarshini Engineering College (Affiliated to Anna University, Chennai),
Vaniyambadi-635751, Vellore District, Tamilnadu, India.
[c]PG & Research Department of Chemistry, Islamiah College (Affiliated to Thiruvalluvar University, Vellore),
Vaniyambadi-635752, Vellore District, Tamilnadu, India.

A B S T R A C T

Isoquinolinium Dichromate (IQDC) is a new versatile reagent for selective oxidation of primary and secondary alcohols under mild conditions. It also oxidizes vicinal and nonvicinal diols to the corresponding -hydroxy carbonyl compounds. The oxidation of pentaamminecobalt (III) complexes of -hydroxy acids by Isoquinolinium Dichromate (IQDC) in micellar medium yielding nearly 100% of carbonyl compounds and 100% Co(II) are ultimate products. In this reaction the rate of oxidation shows first order kinetics each in [Co(III)] and [IQDC]. The unbound   -hydroxy acids yield about 100% of carbonyl compounds in presence of micelles. The rate of oxidation of Co (III) complexes of both bound and unbound -hydroxy acids are enhanced more in the presence of non-ionic micelle of Polysorbate 80, when compared to the anionic micelle of Sodium lauryl Ether Sulphate (NaLES) and cationic micelle of Benzethonium Chloride (BTCl). The 1 mole of cobalt (III) complexes of -hydroxy acids reacts with nearly 0.5 mole of IQDC, similarly 1 mole of -hydroxy acids reacts with nearly 1 mole of IQDC.   A mechanism consistent with kinetic data is proposed.

Keywords: Isoquinolinium Dichromate (IQDC), -hydroxy acids, Micelles, Stoichiometry.

A R T I C L E   I N F O

CONTENTS

*Corresponding Author
A. Palanivel
Department of Chemistry, Govt. Arts College
Affiliated to Periyar University, Salem,
Krishnagiri-635001, Tamilnadu, India
Manuscript ID: IJCPS3241

PAPER-QR CODE

Citation: A. Palanivel, *et al.* Kinetics and Oxidation Mechanism of Pentaamminecobalt (III) Complexes of -Hydroxy Acids by Isoquinolinium Dichromate in Micellar Mmedia. *Int. J. Chem, Pharm, Sci.*, 2016, 4(10): 534-539.

1. Introduction

There is continued interest in the development of new chromium (VI)[1-4] reagents for the effective oxidation of organic substrates. Most of the oxidizing agents prove impractical when attempts are made to scale up the reaction process. In the past twenty five years, significant improvements were achieved by the use of new oxidizing agents such as pyridinium chlorochromate [2,3], pyridinium fluorochromate[4], quinolinium dichromate[5] and quinolinium chlorochromate. However, we have successfully used pyridinium chlorochromate for the selective oxidation of collagen [6,7]. We have now investigated the kinetic potential of Isoquinolinium Dichromate, and we have found that this reagent has certain advantages over similar oxidizing agents in terms of amounts of oxidants and solvent required, easier working up and high yields. Induced electron transfer reactions in pentaamminecobalt (III) complexes of -hydroxy acids result in nearly 100% reduction at cobalt (III) centre with synchronous carbon-carbon bond fission and decarboxylation [8-10]. Such an electron transfer route seems to be unavailable for Isoquinolinium Dichromate in its reaction with cobalt (III) bound and unbound -hydroxy acids to respective keto acid cobalt(III) complexes in Sodium lauryl Ether Sulphate [11], Benzethonium Chloride [12] and Polysorbate 80 [13] possibly 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 hydride ion transfer.   The absence of formation of cobalt (II) rules out the synchronous C-C bond fission and electron transfer to cobalt (III). The rate of IQDC oxidation of cobalt (III) complexes of -hydroxy acids depends on the first power of IQDC concentration. Similarly the reaction between IQDC and unbound -hydroxy acids exhibits first order kinetics with respect to concentration of IQDC [14].

2. Materials and Methods

Purification of Solvents

a) Ethanol: About 2 litres of rectified spirit was poured in to a 3 litre round bottomed flask and 500g of calcium oxide which has been freshly ignited in a muffle furnace and allowed to cool in desiccators was added. The flask filled with the mixture fitted with a double surface condenser carrying a calcium chloride guard-tube, was refluxed gently for 6 hours and allowed to stand overnight. The condenser was reassembled for downward distillation via a plash head adapter to prevent carryover of calcium oxide in the vapour stream. A receiver- flask with a side arm receiver-adapter, which was protected by means of calcium chloride guard-tube, was attached. Then ethanol was distilled gently discharging the first 20ml of distillate. The absolute ethanol (99.5%) was preserved in a bottle with a well fitting stopper [15].

b) Methanol [16]

The Analar grade methanol was distilled through an efficient fractionating column, to remove most of the water. Anhydrous methanol was obtained from the fractionally distilled solvent by treatment with magnesium metal.

c) Ether: A Winchester bottle of ether was divided into approximately two equal volumes and each portion was shaken in a separating funnel with 10-20ml of the iron(II) sulphate solution diluted with 100ml of water. After removing the aqueous solutions the two ether portions were combined in a clean dry Winchester bottle and 100-200g of anhydrous calcium chloride was added. This mixture was allowed to stand for 24 hours with occasional shaking; the ethanol and water were removed during the period. The ether was filtered through a large fluted filter paper in another clean dry Winchester bottle. Fine sodium wire (about 7g) was then introduced into ether with aid of sodium press. If on the following day, no bubbles or hydrogen rise and if sodium still possesses bright surface. The Winchester bottle was closed by its own screw-capped stopper and preserved in the dark. The absolute diethyl ether thus prepared was used [17].

d) Perchloric Acid [18]

$HClO_4$ 70% (E.Merck Analar) was standardized using standard sodium carbonate (BDH Analar) solution using methyl orange as indicator.

e) Other Inorganic chemicals and organic compounds [19]:
The other inorganic chemicals such as sodium dichromate, potassium dichromate, sodium thiosulphate, potassium iodide, barium hydroxide, hydrochloride acid and organic compounds such as oxalic acid dehydrate and starch power (all from BDH) were used as received. The kinetics studies were carried out by allowing reactions in glass stopper corning glass vessels. All ingredients of the reaction mixture were taken in separate flasks and the latter were suspended in a temperature controlled water bath. The solution of temperature pre-equilibrated Isoquinolinium Dichromate (IQDC) of desired concentration was withdrawn and then immediately discharged into the reaction mixture. From this mixture 5ml of solution was titrated against sodium thiosulphate using starch as an indicator. Then this titration was continued at regular time intervals for about 75% of the reaction. The rate of the reaction (-dc/dt) in each kinetic run was determined by the slope of the tangent drawn at fixed concentration of Isoquinolinium Dichromate which is written as [IQDC]. The order of the reaction with respect to each reactant was determined by the relation between initial rate, i.e., (-dc/dt) and initial [reactant]. The rate measurements were carried out on $27 \pm 0.2°C$ in100% aqueous medium for -hydroxy acids. The temperature was controlled by electrically operated thermostat. The concentration of -hydroxy acids was varied in the range $[0.1 – 0.4] \times 10^2$ mol dm^{-3} at fixed concentrations of other reaction ingredients. A plot of initial rate versus [-hydroxy acids] yielded a straight line passing through the origin confirming first order dependence. A plot of initial rate versus [Micelles] yielded a straight line passing through the origin confirming first order dependence. The second order plots were also made for comparable concentrations of -hydroxy acids and micelles. The reaction is first order with respect to the -hydroxy acids. The excess of the oxidant was used in kinetic runs. It gives pseudo first order rate constant. The pseudo first order rate constants calculated using the following integrated rate equations.

$$K_1 = 2.303/t \log [a/a-x]$$

Where a initial concentration of oxidant and [a-x] concentration of oxidant at time t, are expressed in sec^{-1}. The values reported are averages of least two runs.

The stoichiometry was calculated from the ratio between reacted [oxidant] and [substrate]. The stiochiometric studies for the IQDC oxidation of pentaamminecobalt (III) complexes of -hydroxy acids and unbound ligand in the presence of micelles were carried out at 27 ± 0.2°C. It was observed that the cobalt (II) formation was negligibly small. The stoichiometric results indicate that for one mole of cobalt(III) complex, about 0.5 mole of IQDC is consumed, whereas with the unbound ligands for 1 mole of -hydroxy acids about 1.0 mole of IQDC is consumed(**Table - 1**).

3. Results and Discussion

Dependence of rate on Cobalt (III) complexes of -hydroxy acids in micellar medium

The rate of Isoquinolinium Dichromate oxidation of pentaamminecobalt (III) complexes of -hydroxy acids had been followed under pseudo first order condition by keeping excess of the complex concentration than the reagent. The rate constants were calculated by the integrated rate equation. The graph of 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 $[(NH_3)_5Co(III)-L]^2$ (**Table - 2**), (**Figure - 1**). This was further substantiated from the study of changing the concentration of pentaamminecobalt (III) complexes of -hydroxy acids from [0.5 to 2.5] X 10^2 mol dm^{-3} at a fixed concentration in micellar medium. The rate constants obtained for the different concentration of $[(NH_3)_5Co(III)-L]^{2+}]$ complexes of -hydroxy acids were nearly a constant. Hence the rate of disappearance of complexes in this concentration range studied is given as (**Table - 3**), (**Figure - 2, 3, 4**).

$$-d[(NH_3)_5Co(III)-L]^{2+}]/d\,t = k_1[(NH_3)_5Co(III)-L]^{2+}] \ldots\ldots(2)$$

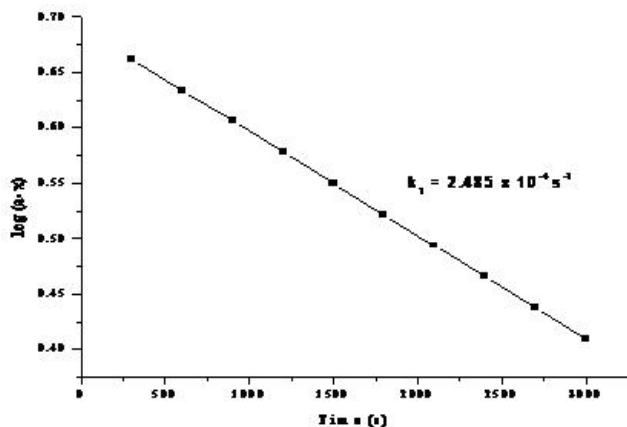All the kinetic runs were repeated and the rate constants were reproducible within ± 2% range.

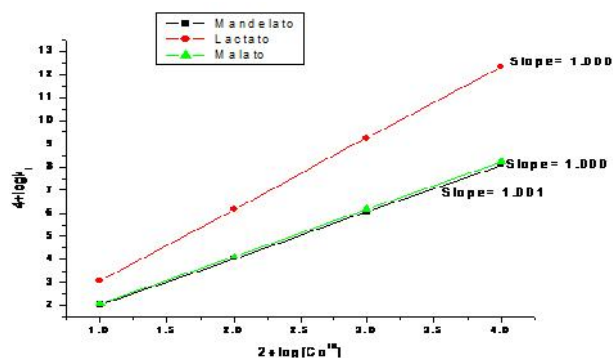**Figure 1:** First order dependence plot

Figure 2: Dependence of rate on Co(III) Complexes of [-hydroxy acids] in NaLES
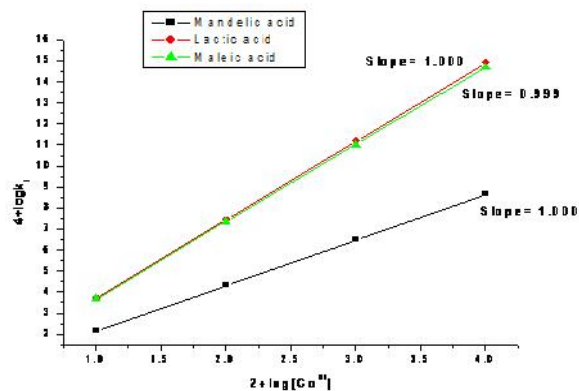

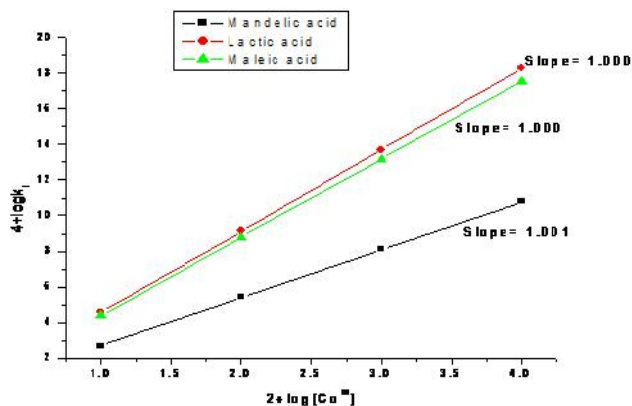**Figure 3:** Dependence of rate on Co(III) Complexes of [-hydroxy acids] in BTCl

Figure 4: Dependence of rate on Co(III) Complexes of [-hydroxy acids] in Polysorbate 80

Mechanism

Mechanism of IQDC oxidation of pentaamminecobalt (III) complexes of -hydroxy acids in micellar medium.

IQDC oxidizes OH centre of the -hydroxy acids at a rate of comparable to that of the free ligand. There is 100% reduction at the Proton centre, forms an Isoquinolinium Dichromate ester which can decompose in a slow step, proceeds 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 has been proposed for the IQDC oxidation of pentaamminecobalt(III) complexes of -hydroxy acids.

Table 1: Stoichiometric data for IQDC oxidation of Co(III) bound & unbound -hydroxy acids in the presence of Micelles.

IQDC = 0.08 mol dm^{-3} (0.04N)
[HClO$_4$] = 0.25 mol dm^{-3} (0.4N)
[Micelles] = 1.00 x 10^{-3} mol dm^{-3}
Temperature = 27 ± 0.2°C

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

Table - 2

IQDC = 0.08 mol dm^{-3} (0.04N)
[HClO$_4$] = 0.25 mol dm^{-3} (0.4N)
[Micelles] = 1.00 x 10^{-3} mol dm^{-3}
Temperature = 27 ± 0.2°C
Mandelic acid = 1.00 x 10^2 mol dm^{-3}

Time (s)	log(a-x) mol dm^{-3}	10^{4}k$_1$ (s^{-1})
300	0.662	2.481
600	0.634	2.489
900	0.606	2.496
1200	0.578	2.483
1500	0.550	2.475
1800	0.522	2.487
2100	0.494	2.489
2400	0.466	2.481
2700	0.438	2.486
3000	0.410	2.484

Table - 3

IQDC	=	0.08 mol dm^{-3} (0.04N)
[HClO$_4$]	=	0.25 mol dm^{-3} (0.4N)
[Micelles]	=	1.00×10^{-3} mol dm^{-3}
Temperature	=	$27 \pm 0.2°C$

10^2[(NH$_3$)$_5$Co(III) - L] mol dm^{-3}	$10^4 k_1$ (s^{-1})	NaLES	BTCl	POLY SORBATE 80
		$10^4 k_1$ (s^{-1})	$10^4 k_1$ (s^{-1})	$10^4 k_1$ (s^{-1})
Mandelato				
0.1	0.0915	2.0211	2.1650	2.7011
0.2	1.8301	4.0422	4.3301	5.4023
0.3	2.7495	6.0633	6.4951	8.1001
0.4	3.6600	8.0844	8.6621	10.8010
Lactato				
0.1	1.4425	3.0825	3.7250	4.5710
0.2	2.8850	6.1650	7.4502	9.1420
0.3	4.3275	9.2475	11.1750	13.7132
0.4	5.7701	12.3300	14.9001	18.2840
Malato				
0.1	1.2105	2.0551	3.6750	4.3921
0.2	2.4210	4.1102	7.3501	8.7842
0.3	3.6315	6.1650	11.0251	13.1763
0.4	4.8420	8.2201	14.7022	17.5568
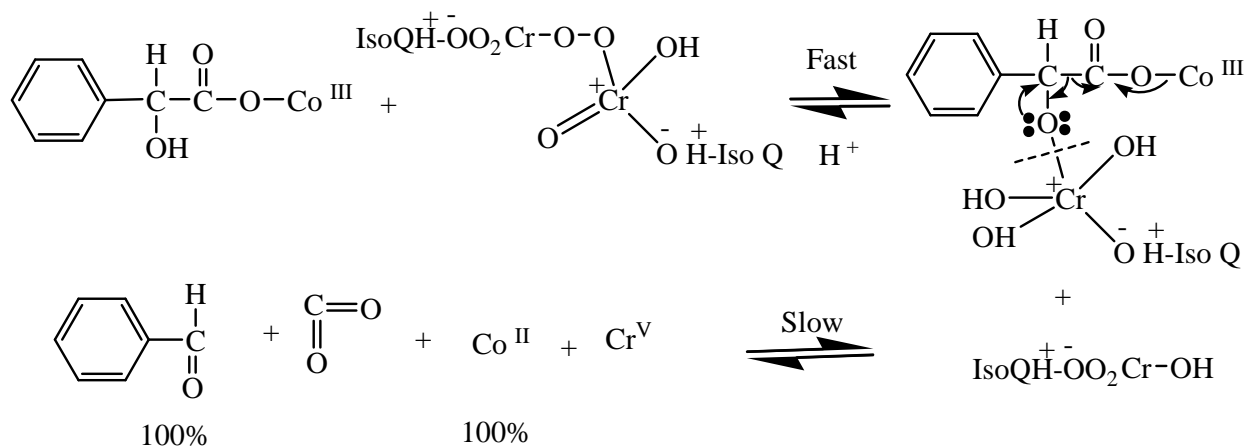
4. Conclusion

An induced electron transfer reaction has been attempted with Isoquinolinium Dichromate and pentaamminecobalt (III) complexes of -hydroxy acids in the presence of NaLES, BTCl and Polysorbate 80 medium. The reaction exhibits second order kinetics. In these reaction the rate of oxidation shows first order kinetics each in [cobalt(III)] and [IQDC]. Product and Stoichiometric analysis were carried out for the oxidation of complexes and free ligands in three different (Anionic, Cationic & Neutral) micellar medium with increasing micellar concentration an increase in the rate are observed. IQDC oxidizes cobalt(III) bound -hydroxy acids through free radical. It explains the synchronous C-C bond fission, decarboxylation and electron transfer to cobalt (III) centre. The added Micelles enhance the rate of oxidation of a reaction much more than NaLES & BTCl. Among three different micelles Polysorbate 80 is react faster than NaLES & BTCl. 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 -hydroxy acids consumes 0.5 mole of IQDC, whereas 1 mole of unbound -hydroxy acids consumes 1.0 mole of IQDC. The reaction goes by free radical mechanism was proved by acrylonitrile polymerization. The appropriate methodology has been inducted.

5. References

[1] JC Collins and WW Hess. *Org. Synthesis*, 1972, 5: 52.

[2] EJ Corey and JW Suggs. *Tetrahedron Lett*, 1975, 2647.

[3] EJ Corey and DL Boger. *Tetrahedron Lett.* 1978, 2461.

[4] FS Guziec and FA Luzzio. *Synthesis*. 1980, 691.

[5] K Anandaratchagan, B Mohammed Nawaz and K Subramani. *Acta. Chim. Pharm. Indica*. 2011, (1)1: 44-50.

[6] PK Sehgal, K Balasubramanian and KT Joseph. *Indian J. Biochem. Biophys*. 1980, 17: 98.

[7] PK Sehgal, K Balasubramanian and KT Joseph. *Leather Science*. 1984, 38.

[8] FRF Fan, and ES Gould, *Inorg. Chem*. 1974, 13: 26.

[9] H Yao, DE Richardson. *J. Am Chem Soc.* 2003, 125: 6211.

[10] Y Ogata, K Tomizawa and T Ikeda. *J. Org. Chem*. 1978, 43: 2417.

[11] P Keashwani and YK Gupta, *Indian. J. Chem*. 1982, 21A: 162.

[12] JO Edwards and JJ Muller. *Inorg Chem.* 1962: 696.

[13] AG Dash, Nanda, R.K. and Mohanti, P. *Indian. J. Chem*., 1984, 12A: 162.

[14] CA Bunton, S Diaz, LS Romsted, Valenzuela, *J. Org. Chem*., 1976, 41: 3037.

[15] LM Bhardwaj, DN Sharma and YK Gupta. *Inorg. chem.,* 1976, 15: 1695.

[16] P Maruthamuthu and P Neta *J. Phy. Chem.,* 1977, 81: 937.

[17] P Kalidoss and VS Srinivasan, *J. Chem. Soc*. *Dalton trans*., 1984: 2831.

[18] J Yasunaga, K Takeda and S Harada. *J. Colloid Interface Sci*., 1973, 42: 45

[19] P Rajkumar. *International Journal of Applied Engineering Res.* 2015, 10(10): 22974-22980.