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Kinetics of oxidation of α -Hydroxy acids by isoquinolinium fluorochromate in presence of micelles

A Palanivel, P Rajkumar and K Subramani

Abstract

The oxidation of α -hydroxy acids by Isoquinolinium Fluorochromate (IQFC) has been studied in micellar medium. The oxidation of free α -hydroxy acids was also carried out under the same conditions for comparative purpose. The reaction was followed by observing the decrease in the absorbance at 501nm for the Cr (VI) present in the reagent in a UV-Visible spectrophotometer. The rate of oxidation of α -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). Product and stoichiometric analysis were carried out for the oxidation of complexes and free ligands. A mechanism involving two electron transfers for the ligand was proposed.

Keywords: Isoquinolinium Fluorochromate (IQFC), α -hydroxy acids, stoichiometry, sodium lauryl ether sulphate (NaLES), Benzethonium Chloride (BTCl), polysorbate 80

1. Introduction

Chemical reactions [1-4] are the deciding factors of the life cycle as it is known that human life is mainly depending upon chemicals in different forms. The study of oxidation reactions through elucidation of their mechanisms and the investigation of reaction kinetics deal with the study of change in concentration of the components of the reaction system in gas phase, as well as Liquid phase, with the passage of time.

Isoquinolinium Fluorochromate (IQFC) [5-7] is also one such oxidant developed recently. It is a more efficient and stronger oxidizing agent. This new compound is more efficient for quantitative oxidation of several organic substrates and has certain advantages over similar oxidizing agents in terms of the amount of oxidant and solvent required, short reaction times and high yields. Among the different chelating agents [8-10] that promote Cr (VI) oxidation of different types of organic substrate, oxalic acid is quite important [11-15].

Extensive studies on the mechanism of oxidation of α -hydroxy acids by different oxidants have been the subject of study by various workers [16-19]. Recently we have studied the oxidation of α -hydroxy acids by Isoquinolinium Fluorochromate (IQFC). However, no detailed kinetic study of oxidation of α -hydroxy acids by IQFC, Here we studied the kinetics of oxidation of α -hydroxy acids by IQFC in the presence of micelles.

Induced electron transfer reactions in pentaamminecobalt (III) complexes of α -hydroxy acids result in nearly 100% reduction at cobalt (III) centre with synchronous carbon-carbon bond fission [20-22]. Such an electron transfer route seems to be unavailable for Isoquinolinium Fluorochromate in its reaction with cobalt (III) bound and unbound α -hydroxy acids to respective keto acid cobalt (III) complexes in Sodium lauryl Ether Sulphate [23], Benzethonium Chloride [24] and Polysorbate 80 [25]. 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 IQFC oxidation of α -hydroxy acids depends on the first power of IQFC concentration. Similarly the reaction between IQFC and unbound α -hydroxy acids exhibits first order kinetics with respect to concentration of IQFC [26].

2. Materials and methods

2.1 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 resultant clear orange solution, isoquinoline (17.75 ml, 0.15 mol) is added drop wise with stirring.

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The mixture is heated on a water bath for about 15 minutes then cooled to room temperature, and allowed to stand 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 vacuo for about one hour.

2.2 Preparation of Carbonato pentaamminecobalt (III) Nitrate

Carbonato pentaamminecobalt (III) nitrate was prepared by dissolving 58 g of powdered ammonium carbonate in 60 mL of water and 100 mL of aqueous ammonia, adding a solution of 30 g of cobalt (II) nitrate. Hexahydrate 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 °C and 600 mL of methanol was added slowly with stirring. The preparation was kept at 0 °C 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 complex), filtering and then slowly adding an equal volume of methanol. The solution was kept 0 °C for 10 hrs. and the crystalline complex was filtered off and dried in a vacuum.

2.3 Preparation of α - hydroxy acids^[27]

Mandelic acid, Lactic acid and Malic acids were prepared as their perchlorates following the procedure of Fan and Gould. 10mmol of the α -hydroxy acids was 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 0.40g of finely powdered carbonatotetraamminecobalt (III) nitrate was added and the mixture was refluxed at 70 °C for 2 hours. It was then cooled under ice for 30 minutes; about 3ml of 70% perchloric acid was added drop wise while shaking the mixture was cooled again under 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 preserved in a desiccator.

2.4 Kinetic Measurements^[28]

All kinetic measurements were carried out An Evolution 60 Thermo spectrophotometer fitted with recording and thermostating arrangement was used to follow the rate of the reaction. The progress of the reaction was followed at 365 nm by monitoring the decreases of Cr (IV) in free α -hydroxy acids and 501nm by monitoring the changes in absorbance. The required [α -hydrox acids], [HClO₄], and [IQFC] were premixed in a reaction vessel, thermostated in an oil bath, and IQFC solution (thermally equilibrated at 323K) was then added prior to the absorbance measurements. Under pseudo-first-order conditions of α -hydroxy acid, the plots of log A versus time (A is absorbance intensity) were linear up to 80% completion of the reaction with an average of linear regression coefficients, $r \geq 0.996$.

2.5 Cobalt Analysis^[29]

Cobalt analyses of the prepared complexes were carried out by adding 2.5ml of 0.01N NaOH to 10-20mg sample of the complex. The mixture was boiled and allowed to cool. It was

then diluted to 25ml with concentrated HCl. If there was any residue it was removed by pressure filtration. The absorbance at 692nm ($\epsilon = 560\text{dm}^3 \text{mol}^{-1} \text{cm}^{-1}$), was recorded. The cobalt analyses so done were in agreement with the assigned structures.

2.6 Perchloric Acid^[30]

HClO₄ 70% (E.Merck Analar) was standardized using standard sodium carbonate (BDH Analar) solution using methyl orange as indicator.

2.7 Other Inorganic chemicals and organic compounds

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.

2.8 Micelles

The micelles used in the present work are Sodium lauryl Ether Sulphate (NaLES), Benzethonium Chloride (BTCl) and Polysorbate 80. The micelles are purified by the following procedure available in the literature. The commercial samples of the surfactants were repeatedly washed with anhydrous ether and recrystallized several times from alcohol with the addition of anhydrous ether.

After neutralization of the reaction mixture with sodium bicarbonate, the pH of the aqueous layer was adjusted to about 6.0 and the aqueous layer was separated by filtration in the case of both free ligands and corresponding complexes. On evaporation of water under reduced pressure, the product separated and the percentage yield was calculated. Through the yield of cobalt (II) was 100% the estimation of cobalt (II), Cr (VI) and carbonyl compounds were quantitative. In both the cases the IR spectra of the product agreed with IR spectra of authentic samples.

2.9 Stoichiometric Analysis^[31]

Kinetic measurements of the oxidation of α -hydroxy acids were carried out under pseudo first order conditions. The stoichiometric studies for the oxidation of α -hydroxy acids by IQFC were carried out with the oxidant in excess. After nine half-lives when the reaction was nearing completion, the concentration of unreacted was determined spectrophotometrically. The stoichiometry was calculated from the ratio between reacting [oxidant] and [substrate] from the decrease in the absorbance measured for the cobalt (III) complex, the amount of cobalt (III) reduced was calculated. This value was then compared to the amount of cobalt (II), and carbonyl compounds.

The stoichiometry was calculated from the ratio between reacted [oxidant] and [substrate]. The stoichiometric studies for the IQFC oxidation of α -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 1 mole of α -hydroxy acids about 1.0 mole of IQFC is consumed (Table - 1).

Table 1: Stoichiometric data for IQFC oxidation of α -hydroxy acids in the presence of Micelles.

$10^3[\text{Compound}] \text{ mol dm}^{-3}$	$10^2[\text{IQFC}]_{\text{initial}} \text{ mol dm}^{-3}$	$10^2[\text{IQFC}]_{\text{final}} \text{ mol dm}^{-3}$	$\Delta 10^3[\text{IQFC}] \text{ mol dm}^{-3}$	[Compound]: $\Delta[\text{IQFC}]$
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
Malic 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

IQFC= 0.08 mol dm⁻³ (0.04N), [HClO₄] = 0.25 mol dm⁻³ (0.4N), [Micelles] = 1.00 x 10⁻³ mol dm⁻³, Temperature = 27 ± 0.2 °C

3. Results and discussion

3.1 Dependence of rate on α -hydroxy acids in micellar medium

The rate of Isoquinolinium Fluorochromate oxidation of α -hydroxy acids had been followed under pseudo first order condition by keeping excess of the α -hydroxy acids 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 [α -hydroxy acids] (Table - 2), (Figure - 1). This was

further substantiated from the study of changing the concentration of α -hydroxy acids from [0.1 to 0.4] X 10² mol dm⁻³ at a fixed concentration in micellar medium. The rate constants obtained for the different concentration of α -hydroxy acids were nearly a constant. Hence the rate of disappearance of α -hydroxy acids in this concentration range studied is given as (Table - 3), (Figure - 2, 3 & 4).

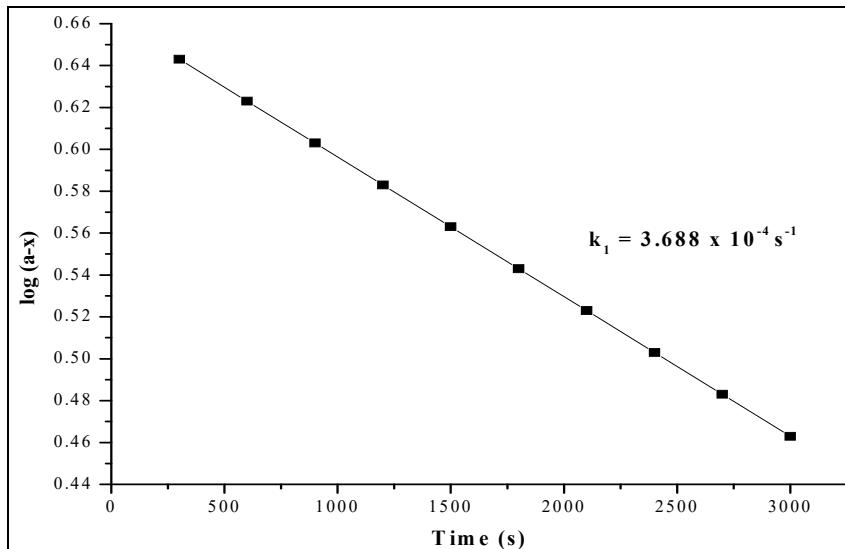
$$-\frac{d[\alpha\text{-hydroxy acids}]}{dt} = k_1[\alpha\text{-hydroxy acids}] \quad \dots\dots\dots(1)$$

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

Table 2

Time (s)	$\log(a-x) \text{ mol dm}^{-3}$	$10^4 k_1 (\text{s}^{-1})$
300	0.643	3.672
600	0.623	3.677
900	0.603	3.682
1200	0.583	3.689
1500	0.563	3.692
1800	0.543	3.689
2100	0.523	3.688
2400	0.503	3.691
2700	0.483	3.698
3000	0.463	3.690

IQFC= 0.08 mol dm⁻³, [HClO₄]= 0.25 mol dm⁻³, [Micelles] = 1.00 x 10⁻³ mol dm⁻³, Temperature= 27 ± 0.2 °C, Lactic acid= 1.00 x 10² mol dm⁻³

**Fig 1:** First order dependence plot

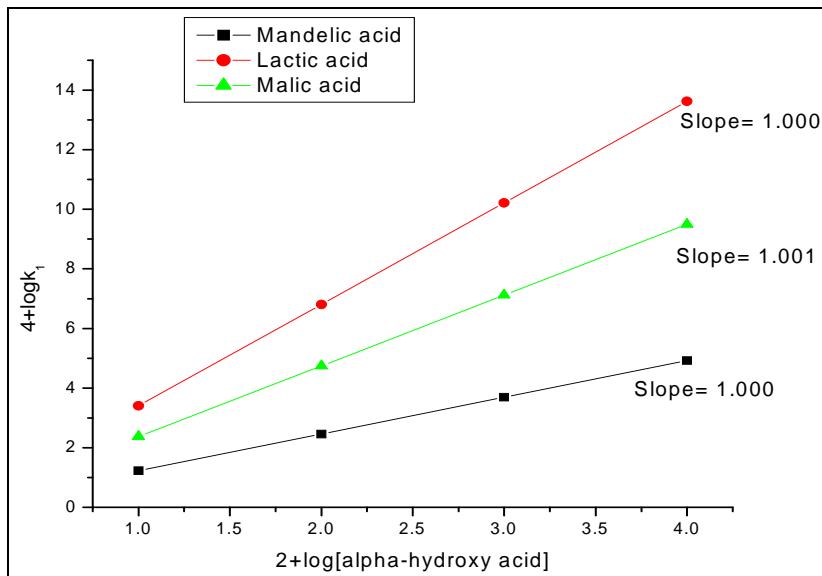
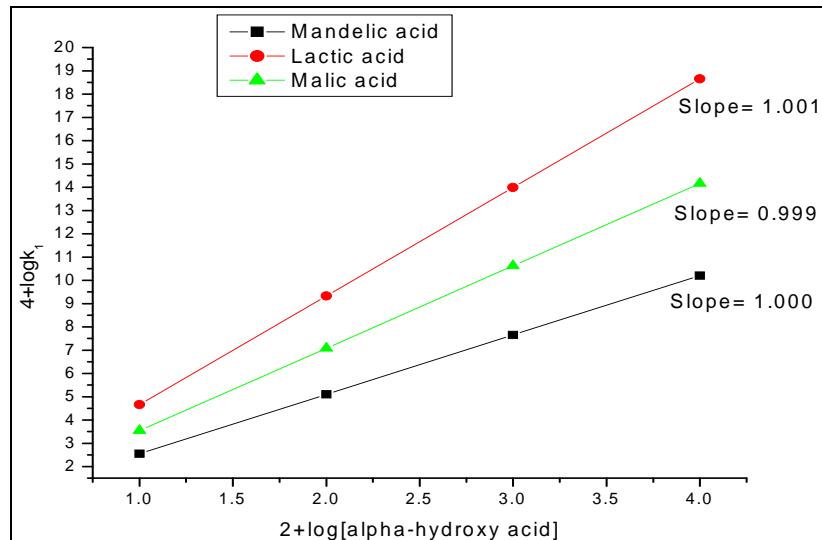
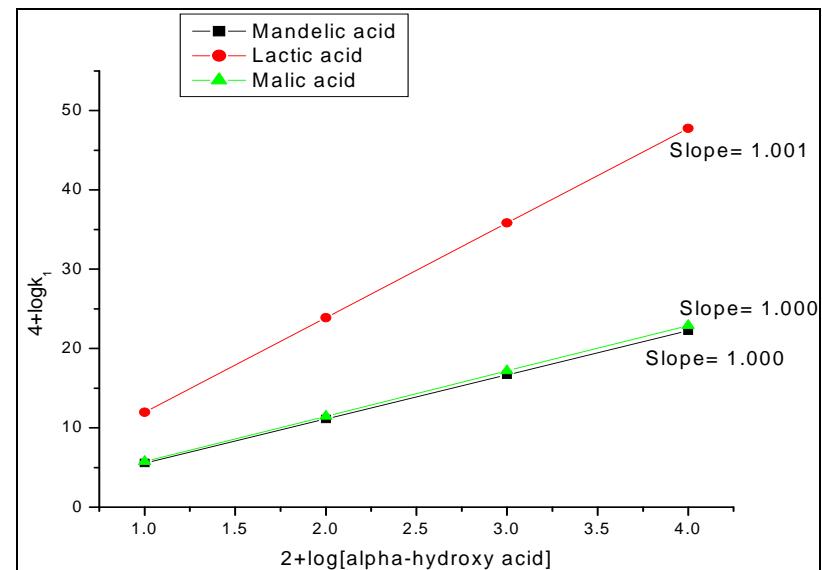
**Fig 2:** Dependence of rate on α -hydroxy acid in NaLES**Fig 3:** Dependence of rate on α -hydroxy acid in BTCl**Fig 4:** Dependence of rate on α -hydroxy acid in Polysorbate 80

Table 3

$10^2 \alpha\text{-hydroxy acids} [\text{mol dm}^{-3}]$	$10^4 k_1 (\text{s}^{-1})$	NaLES	BTCI	POLY SORBATE 80
		$10^4 k_1 (\text{s}^{-1})$	$10^4 k_1 (\text{s}^{-1})$	$10^4 k_1 (\text{s}^{-1})$
Mandelic acid				
0.1	1.0730	1.2308	2.5503	5.5608
0.2	2.1461	2.4616	5.1006	11.1216
0.3	3.2190	3.6924	7.6509	16.6824
0.4	4.2921	4.9232	10.2012	22.2432
Lactic acid				
0.1	1.7107	3.4053	4.6631	11.9421
0.2	3.4214	6.8108	9.3263	23.8842
0.3	5.1321	10.2161	13.9893	35.8236
0.4	6.8428	13.6215	18.6524	47.7684
Malic acid				
0.1	1.1250	2.3732	3.5408	5.7243
0.2	2.2501	4.7465	7.0816	11.4486
0.3	3.3750	7.1196	10.6224	17.1728
0.4	4.5001	9.4929	14.1632	22.8971

IQFC= 0.08 mol dm⁻³, [HClO₄]= 0.25 mol dm⁻³, [Micelles]= 1.00 x 10⁻³ mol dm⁻³, Temperature= 27 ± 0.2 °C

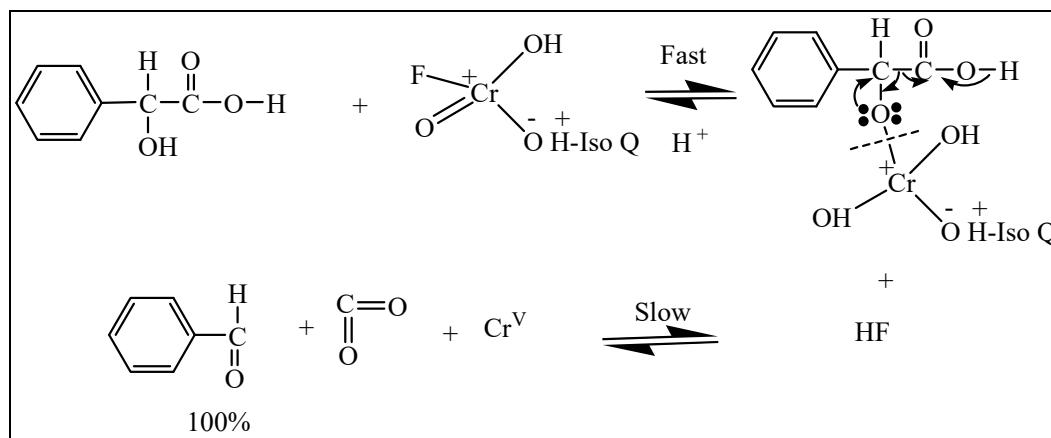
4. Mechanism

4.1 Mechanism of IQFC oxidation of α -hydroxy acids in micellar medium.

IQFC oxidizes OH Centre of the α -hydroxy acids at a rate of comparable to that of the free ligand. There is 100% reduction at the Proton Centre, forms an Isoquinolinium Fluorochromate 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 H₂ gas.

Considering these facts and findings with these results, the following reaction scheme has been proposed for the IQFC oxidation of α -hydroxy acids.



5. Conclusion

An induced electron transfer reaction has been attempted with Isoquinolinium fluorochromate and α -hydroxy acids in the presence of NaLES, BTCI and Polysorbate 80 medium. The reaction exhibits second order kinetics. In these reaction the rate of oxidation shows first order kinetics each in [α -hydroxy acids] and [IQFC]. Product and Stoichiometric analysis were carried out for the oxidation of free ligands in three different (Anionic, Cationic & Neutral) micellar medium with increasing micellar concentration an increase in the rate is observed. IQFC oxidizes α -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 & BTCI. Among three different micelles Polysorbate 80 is react faster than NaLES & BTCI.

A mechanism involving two electron transfer for the ligand was proposed i.e., 1 mole of α -hydroxy acids consumes 1.0 mole of IQFC. The reaction goes by free radical mechanism was proved by acrylonitrile polymerization. The appropriate methodology has been inducted.

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