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Kinetics And Mechanism of Oxidation of 1-(Isopropylamino)-3(P-2-Methoxyethyl Phenoxyl)-2-Propanol In Aqueous Alkaline Medium By Hexacyanoferrate (Iii)Ion.

Dr. S. N. Yadav[1], Dr. S. A. Afsah[2]
[1]*Department of physics R. K. College Madhubani*
[2]*Department of Chemistry, R. K. College, Madhubani*

Abstract
Kinetics and mechanism of oxidation of 1-(isopropylamino)-3(p-2-methoxyethyl)phenoxy)-2-propanol commonly known as Metropolol(MET) by hexacyanoferrate (III) ion has been studied in aqueous alkaline medium at 300 K . The rate of reaction were found to be directly proportional to the organic substrate and hydroxide ion concentration and fractional order in $(OH)^-$. The oxidation products of the reaction were found to be propane-2-amine, 2(4-oxypentyle phenoxy) etnanal and formaldehyde. A probable reaction mechanism has been suggested. The activation parameters were computed and some significant generalisation drawn.

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I. Introduction

Metoprolol. Is an andergenic antagonist which fids its uses i the treatment of several diseases like high blood pressure , hypertension, angina . Although there were recent studies involving the oxidation of β blockers over the past few years but the detailed investigation on the kinetics and mechanism of oxidation of Metprolol a potent drug for the regulation of blood pressure drawn limited attention. Literature survey reveals relatively less information about their oxidation kinetics . As hexacyaoferrate(III) ion widely used as an oxidising agent in alkaline medium for numerous organaic and inorganic compounds . Keeping in view a detailed investigation is carried out on the kinetics and mechanism of oxidation of Metoprolol by hexacyanoferrate (iii) in alkaline medium.

II. Experimental And Apparatus

The absorbance measurement were made by using Systronics uv visible double beam spectrophotometer 2203 with 1cm. Glass cell. The temperature was maintained constant using constant temperature water bath with shaker.

III. Materials and Reagents

Analytical grade chemicals and doubly distilled water were used throughout the experiment and investigation. A 0.0109 mol dm^{-3}. Solution of Metoprolol were prepared by dissolving requisite amount of Metoprol i n distilled water. A 0.015 mol.dm^{-3}. Solution of HCF (III) ion was prepared by dissolving required amount of potassium hexacyanoferrate (III) in double distilled water and standardised by measuring absorbance using systronics uv visible double beam spectrophotometer 2203 at 420 nm (€1060 I 50 dm^{-3} mol^{-1} cm^{-1}) sodium hydroxide stock solution of desired concentration with suitable dilution .Ionic strength were maintained using sodium perchlorate solution.

A calculated amount of HCF(III) ion is added to a mixture of Metoprolol (MET) sodium hydroxide and sodium perchlorate solution at constant temperature of 300K 0,,1 C .The progress of the reaction was followed by measuring the absorbance of HCF(III) ion at 420 nm. Using systronics uv visible double beam Spectrophotometer.

IV. Results and discussion

A known excess of HCF(III) ion was allowed to react completely with a known amount of Metoprolol solution at 300 K and in 0.01 mol s/dm^3. Of Sodium hydroxide solution. After 24 hrs. the residual HCF(III) ion in each case was determined spectrophotometrically at 420 nm. The stoichiometry of the reaction corresponds to the equation:

The products were analysed and found to be 2(4-oxopentyllphenylloxy) ethanal , dimethylamines and formaldehyde .This were confirmed by i.r. spectrum,

$$C_{12}H_{25}NO_3 \longrightarrow C_3H_9N + C_{11}H_{14}O_3 + CH_2O$$

Main i.r. bands – 3358(s) N-H,2920-2852 (s) ,1650 C=O 1605 C=C,1455-1155(b)C-H Ch-1230-1010(s) c-n;840-822 substituted benzene. The i.r. spectra lack of o-h stretching which explains the oxidation of alcohol . the pick at 1650 conforms this oxidation the bands 3357,2920,2850 crrosponds to stretching viveration N-H in anime and C-H in alcile group. The region 1450-1150 and 1230-1010 deceives the bending viveration of C-H in alkyl and C-N stretch.

HCF(III) ion concentration varies from 1.0 to 6.0x10 moldm^{-3} . By keeping the concentration of all other species constat, the log. Vs time plot at different concentration of HCF(III) ion were found to be in good agreement as appears a straight line plot.

The pseudo first order rate constant k determined from the slope were found to be invariable indicating the Ist. Order with respect to HCF(III) ion concentration. I n order to find out the dependence of rate on MET kinetic run were carried out by varying the concentration of MET from 1.0x10 to 6.0x 10^{-3} .Keeping the concentration of all other three species constant . The result so obtaianed are tabulated below :

Table 1 Effect of $[HCF(III)], [MET][OH]$ and μ on the pseuso first order rate constant, K at 300 K.

$[HCF(III)]$ $\times 10^{-4}(mol\ dm^{-3})$	$[MET]$ $\times 10^{-3}(mol\ dm^{-3})$	$[NaClO_4]$ $\times 10^{-2}(mol\ dm^{-3})$	$[OH] \times 10^{-2}(mol\ dm^{-3})$	$[K^1]$ $\times 10^{-4}(S^{-1})$
1.00	4.00	2.00	1.00	10.262
2.00	4.00	2.00	1.00	10.453
3.00	4.00	2.00	1.00	10.860
4.00	4.00	2.00	1.00	9.011
5.00	4.00	2.00	1.00	8.022
6.00	4.00	2.00	1.00	8.565
4.00	1.00	2.00	1.00	2.849
4.00	2.00	2.00	1.00	4.220
4.00	3.00	2.00	1.00	6.551
4.00	4.00	2.00	1.00	9.011
4.00	5.00	2.00	1.00	13.21
4.00	6.00	2.00	1.00	15.79
4.00	4.00	1.50	1.00	9.011
4.00	4.00	2.00	1.00	9.012
4.00	4.00	2.50	1.00	9.025
4.00	4.00	3.00	1.00	9.032
4.00	4.00	3.50	1.00	9.035
4.00	4.00	4.00	1.00	8.99
4.00	4.00	2.00	0.50	5.222
4.00	4.00	2.00	0.70	6.510
4.00	4.00	2.00	1.00	9.012
4.00	4.00	2.00	2.00	19.00
4.00	4.00	2.00	3.00	25.23
4.00	4.00	2.00	4.00	26.98

Again kinetic run were carried out by keeping the concentration of other reactants constants and varying the OH ion concentration by keeping the concentration of Na (OH) from 0.5 to 4.0x10 mol dm^{-3} .The data in table 1 reveals that the rate of reaction increases with the increase in the concentration of OH ion .The plot of log K vs log $(OH)^-$ were found to be straight line (fig.2) This indicates fractional order dependence of reaction rate with respect to OH ion concentration. The variation in ionic strength were carried out by varying the concentration of $NaClO_4$ and keeping the concentration of other species constant. It was found that ionic strength produces negligible effect on the rate of reaction.

Based on the experimental observations and the data available in table 1 , the following conclusion were drawn.

1. The reaction is first order dependence on HCF(III) ion concentration
2. The reaction follows first order kinetic with respect to metropolol concentration.
3. The reaction is fraction order dependence on hydroxyl ion concentration

On the basis of aforementioned observation the following mechanisms has been proposed.

$$MET_x + OH^- \underset{}{\overset{K}{\rightleftharpoons}} [MET(OH)]_x \longrightarrow (1)$$

$$[MET(OH)]_x + HCF \xrightarrow[Slow]{k} \text{Intermediate (I)} \rightarrow (2)$$

$$I + [MET(OH)]_x \xrightarrow[fast]{} \text{Products} \rightarrow (3)$$

$$\text{Rate}, r = k [MET(OH)_x][HCF(III)] \quad \cdots \rightarrow (4)$$

Rate equation becomes

$$r = \frac{Kk [MET].[OH^-][HCF(III)}{1 + K[OH^-]} \rightarrow (5)$$

Further

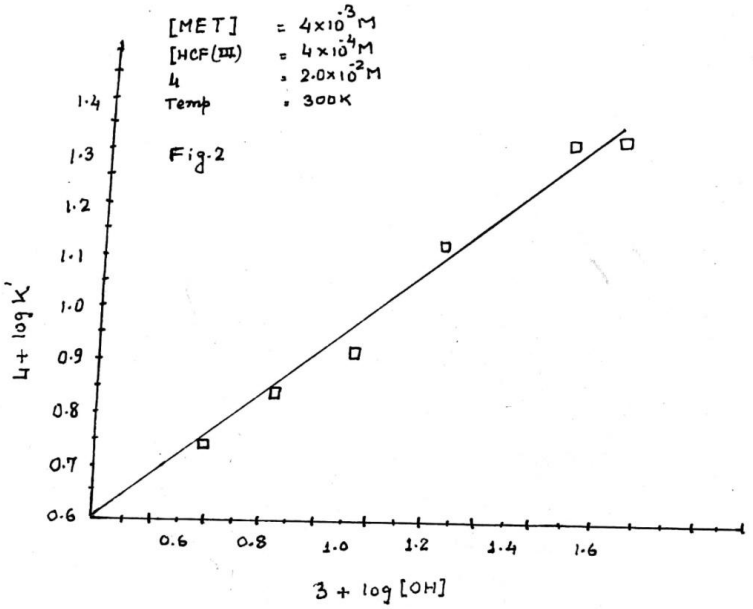
$$\frac{\text{rate}}{[HCF(III)} = \frac{Kk [MET].[OH^-]}{1 + K[OH^-]} \longrightarrow (6)$$

Taking reciprocal of eq. (6)

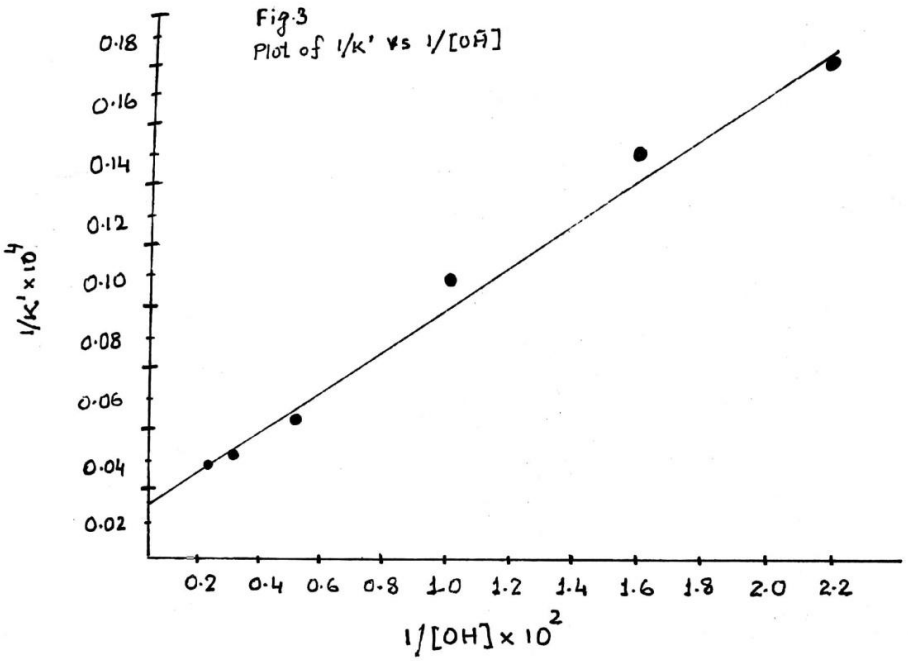
$$\frac{1}{k'} = \frac{1}{Kk [MET][OH^-]} + \frac{1}{k[MET]} - (7)$$

This predicts the plot $\frac{1}{k'}$ Vs $\frac{1}{[OH^-]}$

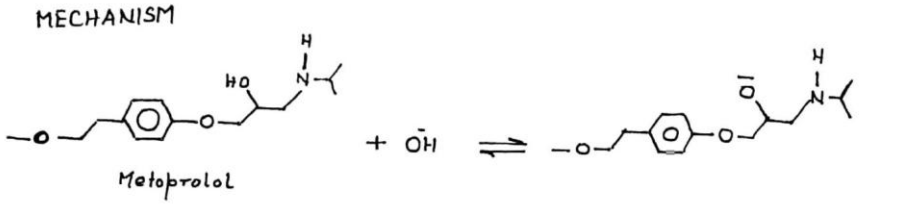
Exactly similar plot were obtained experimentally supporting the proposed mechanism



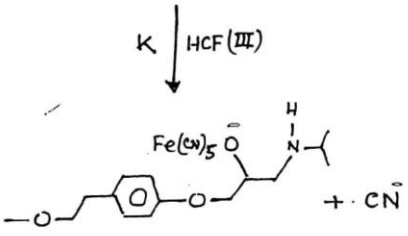
K and K values were calculated from the intercept of the plot

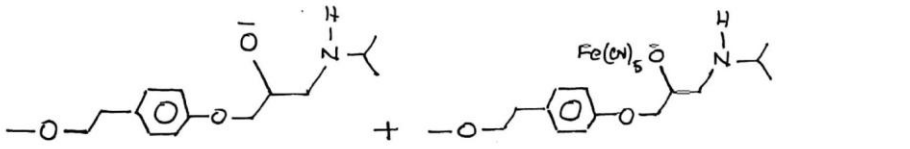


MECHANISM

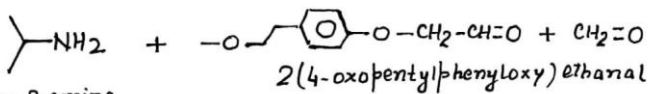


Metoprolol





Fast



Propan-2-amine

2(4-oxopentylphenyloxy) ethanal

+ Fe(III) + $[Fe(CN)_5]^{3-}$

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