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OXIDATION OF THIAMINE: KINETIC AND MECHANISTIC STUDY BY HEXACYANOFERRATE (III) IN AQUEOUS ALKALINE MEDIA

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ABSTRACT

The kinetics of oxidation of thiamine by hexacyanoferrate (abbreviated as HCF) (III) ions in aqueous alkaline medium at constant ionic strength 0.0016 mol/dm^3 and temperature 298K has been studied spectrophotometrically. The reaction shows 1:2substrate to oxidant stoichiometry and follows first order kinetics in [alkali]. The dependence of the rate on substrate and [HCF (III)] concentration has been found to be of fractional order type. The ionic strength of the reaction mixture shows positive salt effect on the reaction rate. To calculate thermodynamic parameters the reaction has been studied at six different temperatures from 283K to 333K. Mechanism involving formation of complex between hexacyanoferrate and thiamine has been proposed. 2-[3-[(4-Amino-2-methyl-pyrimidin-5-yl) methyl]-4-methyl-thiazol-5-yl] ethanol have been identified chromatographically and spectroscopically as the final product of oxidation of thiamine. Based on the kinetic data and product analysis a reaction mechanism is proposed.

KEYWORDS

Oxidation, Mechanism, Hexacyanoferrate (III) and Thiamine.

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INTRODUCTION

Iron (III) in the form of different complexes in oxidation of different compounds has acknowledged great interest due to cost-effective availability, less difficulty involved in the estimation and its capability to act in both acidic and alkaline medium. Iron (VI) is an environment friendly oxidant and also used as coagulant for water and waste water treatment[1,2]. It is possible to use hexacyanoferrate (III) as a moderate oxidant because of oxidation potential of the couple $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$

(0.36V). Hexacyanoferrate (III), (HCF) has been widely used to oxidise numerous organic and inorganic compounds in alkaline media. Researchers[3] have suggested that alkaline hexacyanoferrate (III) ion simply acts as an electron abstracting reagent in redox reactions. Though, Speakman and Waters[4] have recommended different paths of oxidation of aldehydes, ketones and nitro paraffins. While, Singh and co-workers[5,6] during discussion of the oxidations of formaldehyde, acetone and ethyl methyl ketone have suggested that the oxidation takes place through an electron transfer process resulting in the formation of a free radical intermediate.

Thiamine hydrochloride (THIA) or vitamin B_1 is-2-[3-[(4-Amino-2-methyl-pyrimidin-5-yl) methyl]-4-methyl-thiazol-5-yl] ethanol which belongs to thiazolium group is biologically very important. Thiamine derivatives and thiamine-dependent enzymes are present in all cells of the body, thus a thiamine deficiency would seem to adversely affect all of the organ systems. However, the nervous system is particularly sensitive to thiamine deficiency; because of its dependence on oxidative metabolism. Thiamine deficiency commonly presents sub acutely and can lead to metabolic coma and death. A lack of thiamine can be caused by malnutrition, a diet high in thiaminase-rich foods (raw freshwater fish, raw shellfish, ferns) and/or foods high in anti-thiamine factors (tea, coffee, betel nuts) and by grossly impaired nutritional status associated with chronic diseases, such as alcoholism, gastrointestinal diseases, HIV-AIDS and persistent vomiting[7] It is thought that many people with diabetes have a deficiency of thiamine and that this may be linked to some of the complications that can occur. Well-known syndromes caused by thiamine deficiency include beriberi, optic neuropathy and polyneutrics in birds[8,9]. Kinetics of oxidation of thiamine by other oxidants has been carried out[10-14]. Hence Kinetics of oxidation of thiamine hydrochloride(2-[3-[(4-Amino-2-methylpyrimidin-5-yl) methyl]-4 methyl-thiazol-5-yl] ethanol) with HCF in basic medium at 298K have been studied.

Due to some synthetic utility ferricyanide oxidation has become known as Decker oxidation[15].

A survey on earlier literature indicates that no attention was paid to the oxidation of thiamine by this oxidant. The present work has been undertaken with a view at shedding some light on the influence of the nature of both the oxidant and the media on the kinetics and mechanistic of the redox reactions as well as on the nature of oxidation products. Moreover, the results obtained may gain some information on the chemistry of thiamine in aqueous solutions.

Literature survey reveals no study on oxidation of thiamine by HCF (III) but several studies have been reported on the oxidation of thiamine by other oxidants. Different workers have identified different products by different oxidants for thiamine. In view of the lack of literature on the oxidation of thiamine by HCF(III) and in order to explore the mechanistic aspects of HCF(III) oxidation in alkaline medium, we have chosen thiamine as a substrate. In continuation of our earlier work[16,17] the present study deals with the title reaction to investigate the redox chemistry of HCF(III) in such media and to arrive at a suitable mechanism for the oxidation of thiamine by alkaline hexacyanoferrate (III) ions on the basis of kinetic results.

EXPERIMENTAL
Materials and methods
Reagent grade chemicals and doubly distilled water were used throughout. A solution of $Fe(CN)_6^{3-}$ was prepared by dissolving $K_3Fe(CN)_6$ (SD fine chem.) in H_2O and was standardized iodometrically. Thiamine is soluble in aqueous bases. The solution of thiamine (Hi-media) was prepared by dissolving appropriate amount of sample in very dilute alkaline solution. Sodium hydroxide (Merck) and sodium nitrate (SD fine chem.) were used to provide the required alkalinity and to maintain the ionic strength respectively.

Instruments used
A sophisticated double beam bio-spectrophotometer BL-198 was used is a microprocessor based scanning UV-visible spectrophotometer with PC compatabity

and with RS232C interface; MS Windows based software used for data acquisition, processing, storage and interpretation of data. This spectrophotometer has automatic wavelength calibration system, Lamp selection; auto focusing, programmable wavelength and thermoelectrically temperature controller. Thermostat used was of 'Toshniwal' Instrument. The constancy of the temperature maintained was to an accuracy of ±0.5 ºC.

Kinetic Procedure
Stoichiometry and Product Analysis
Reaction mixture containing various ratios of hexacyanoferrate (III) to thiamine in presence of 1×10^{-2} mol dm^{-3} of sodium hydroxide at 307K, under the condition [THIA]>>[HCF], were equilibrated for 24h. Determination of unreacted HCF showed 1:2 stoichiometry of substrate to oxidant. Oxidation product 2-[3-[(4-Amino-2-methyl-pyrimidin-5-yl) methyl]-4-methyl-thiazol-5-yl] ethanol was detected by thin layer chromatography. Further it was confirmed by its MP, IR and NMR spectra. Strong peak for $-\overset{O}{\overset{\|}{C}}-H$ group was observed at 2710 cm^{-1}.

RESULTS
λ_{max} for potassium hexacyanoferrate(1×10^{-4}M) determined spectrophotometrically using bio-spectrophotometer BL-198 Elico make and found to be 420nm (Figure No.1).

Effect of Reactants on the Reaction Rate
With substrate in excess, at constant [THIA], [OH$^-$] and temperature, plots of log [HCF] Vs time were linear indicating fractional order dependence of rate on [HCF]. Rate constant k decreases with increase in [HCF] (Table No.1) confirming fractional order dependence on [HCF]. Increase [THIA] lead to decreases in rate of reaction (Table No.1) at constant [HCF], [NaOH], [NaNO$_3$] and temperature. Plot of log [THIA]Vslogk_{obs} (Figure No.2) was linear with a slope of 0.366 indicating fractional order dependence on [THIA]. The rate increases with increase in [NaOH] (Table No.1). Plot of log [NaOH]Vslogk_{obs} (Figure No.3) was linear with slope of 1.06, showing first order dependence on [OH$^-$].

Effect of salts on the Rate
To study the effect of variation of salts, the concentration of salts were varied from 1×10^{-2} to 9×10^{-2} M, keeping constant concentration of other reaction ingredients such as [HCF]=1×10^{-3}M, [THIA]=9×10^{-4} M, [NaOH]=10×10^{-2}M and [NaNO$_3$]=14×10^{-2}M (Table No.6). From the obtained results, it is clear that pseudo first order rate constant k_{obs} increased with increase in concentration for KBr, NH$_4$Cl and K$_2$SO$_4$. A plot of log k_{obs}vs$\sqrt{\mu}$ according to extended Bronsted-Debye-Huckel equation was found to be linear with positive slopes indicating positive salt effect. On the other hand pseudo first order rate constant decreased with increase in concentration for KCl, KI, KNO$_3$, NaHCO$_3$, NH$_4$Br, NaCl and Na$_2$CO$_3$. A plot of log k_{obs}vs$\sqrt{\mu}$ was found to be linear with negative slopes indicating negative salt effect.

Effect of Ionic Strength and Dielectric Constant on the Rate
Variation in ionic strength using NaNO$_3$ solution (2×10^{-2} mol dm^{-3} to 18×10^{-2} mol dm^{-3}) affect (Table No.2) the rate of the reaction indicating that ionic species are involved in the rate limiting step. Dielectric constant (*D*) of the medium was varied by adding methanol, ethanol, DMSO, 1,4-dioxane and acetonitrile (Table No.3). It was found that rate constant increased on decreasing the dielectric constant of acetonitrile and methanol, while rate constant decreased on decreasing the dielectric constant of DMSO, 1,4-dioxane and ethanol. The relative permittivity (*D*) effect was studied by varying solvent-water content in the reaction mixture with all other conditions being constant. Attempts to measure the relative permittivity were not successful. However, they were computed from the values of pure liquids[18]. Plot of (1/*D*) Vslogk_{obs} was found to be linear.

Effect of Temperature on the Reaction Rate
Reaction was studied over a range of temperature 283 to 333K by varying the concentration of sulfanilamide (Figure No.4), keeping other experimental conditions constant. It was found that the rate increased with increase in temperature

(Table No.5). From the Arrhenius plot (Figure No.5), activation parameters like energy of activation (Ea), enthalpy of activation ($\Delta H^{\#}$), entropy of activation ($\Delta S^{\#}$), free energy of activation ($\Delta G^{\#}$), and logA were computed (Table No.5).

Test of Free Radicals

Addition of reaction mixture to aqueous acrylonitrile solution did not initiate polymerization, showing absence of free radical species.

DISCUSSION

During the oxidation of thiamine using hexacyanoferrate (III) the reaction is found to be fractional order with respect to oxidant, substrate and first order with respect to base (OH⁻) and ionic strength (NO_3^-). The effect of solvent relative permittivity on the rate constants, the activation energy (-8.9750 kJ mol⁻¹) and the negative entropy (-0.1291 KJ K⁻¹ mol⁻¹) for thiamine, is consistent with a rate-determining step involving ions having charges of same sign, consistent with the following mechanism (Scheme-D). X represents complex intermediate.
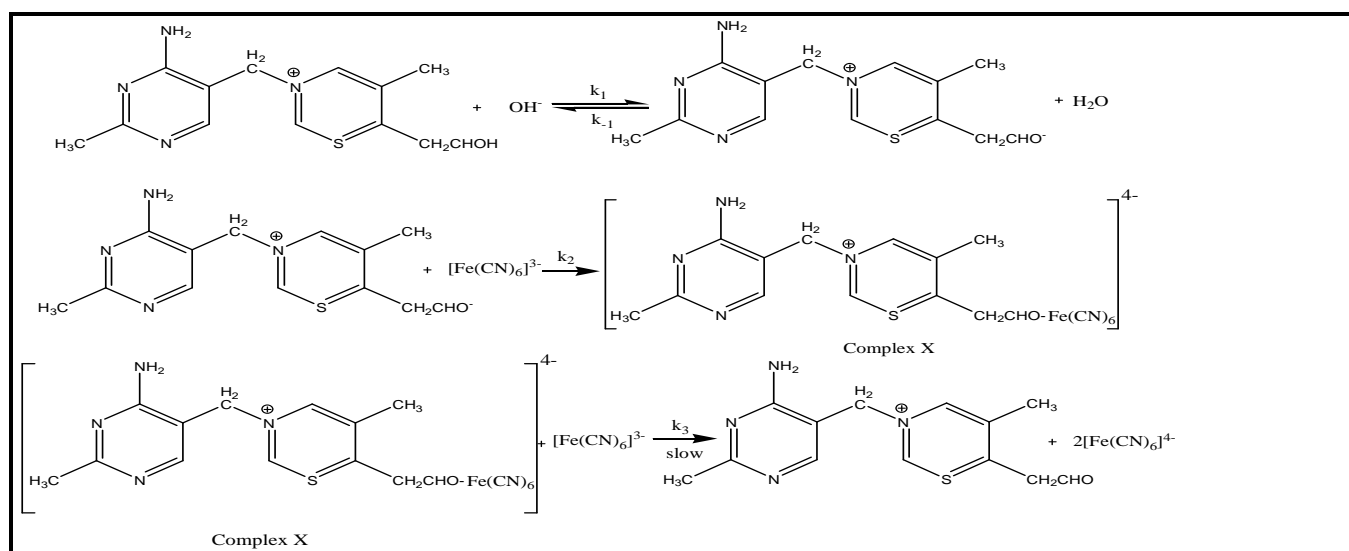
Scheme-D

$$Rate = \frac{-d[\text{HCF}]}{dt} = k_3[X]$$

$$[X] = \frac{k_1 k_2 [HCF][THIA]}{[OH^-] + k_1(1 + k_2[THIA])}$$

$$Rate = \frac{-d[HCF]}{dt} = \frac{k_1 k_2 k_3 [HCF][THIA]}{[OH^-] + k_1(1 + k_2[THIA]}$$

$$k' = \frac{k_1 k_2 k_3 [THIA]}{[OH^-] + k_1 + k_1 k_2 [THIA]}$$

$$\frac{1}{k'} = \frac{[OH^-]}{k_1 k_2 k_3 [THIA]} + \frac{1}{k_2 k_3 [THIA]} + \frac{1}{k_3}$$

Variation of the concentration of each of the oxidant HCF (III), substrate (THIA) base and ionic strength, while maintaining the others concentration constant showed that the reaction is fractional order in oxidant and substrate while first order in base (OH⁻) and with respect to NO_3^- ion. The stoichiometry of the reaction between THIA and HCF (III) is 1:2. Due to higher oxidation potential of $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ (0.36V) in alkaline medium suggests better possibility of rapid oxidation of the free radical might completely mask the polymerization. The kinetic aspects and the mechanism proposed are similar to those of oxidation of amino alcohols, diols and glycol does not occur via free radicals, but to a certain extent through an intermediate complex between the oxidant and the anionic substrate.

During the oxidation of diols[19] substrate-catalyst complex formed which decomposes to give the product. Complex formation between substrate and oxidant reported which subsequently decomposes to give the product aldehyde and reduced form of oxidant[13, 14, 20]. Oxidation of benzyl alcohol to benzaldehyde by benzimidazolium fluorochromate suggests participation of an ion and a neutral molecule to form intermediate complex in the mechanistic step[21].

Oxidation of mephenesin and guaifenesin derivatives of propanediol to corresponding aldehydes involves formation intermediate complex species which decomposes in rate limiting step[22]. In Ru(III) catalysed and uncatalysed oxidation of atenolol by CAT in perchloric acid medium suggest formation of intermediate complex which decomposes into carbonyl compound[23]. Cetyltrimethyl ammonium bromide catalysed oxidation of diethylene glycol by CAT in acidic medium suggests formation of complex between substrate and the oxidant[24]. Phosphotungstic acid catalysed oxidation of cyclic alcohols by N-bromo phthalimide suggests formation of complex between catalyst, oxidant and substrate[25]. Oxidation of 2-amino-1-butanol and 3-amino-1-propanol by potassium ferrate were completed by double electron transfer with formation of complex between oxidant and substrate[26]. Ru(III) catalysed oxidation of amino alcohol by alkaline hexacyanoferrate(III) has been shown to proceed via formation of intermediate complex which decomposes to yield corresponding aldehyde[27]. Oxidation of xylitol and galactitol by hexacyanoferrate (III) ion in aqueous alkaline medium proceeds via formation of anions of substrate which forms complex with the oxidant[28].

The reaction was also studied in presence of added acrylonitrile to understand the involvement of free radicals. There was no effect of added acrylonitrile on the reaction and also no precipitate due to the polymerization of the added acrylonitrile was observed thus verifying the absence of any free radical formation in the reaction. The reaction was carried out under pseudo-first-order conditions and the plots of log [oxidant] against time were found to be linear and the fractional order (0.300) in [oxidant]. The pseudo-first-order rate constants were found to increase as [THIA] increases from 1.0×10^{-4} to 9.0×10^{-4} mol dm^{-3} at a constant [oxidant] of 1×10^{-3} mol dm^{-3}. The order in [THIA] was found to be 0.366 as determined from the log k_{obs} against log [THIA]. Since, the order in [THIA] was fractional which indicates the formation of a complex therefore, the kinetic data were used to obtain plot of $1/k_{obs}$ against 1/ [THIA]. Such a plot was found to be linear with an intercept supporting the formation of a complex between the reactants. In order to evaluate thermodynamic parameters the effect of [THIA] was studied at six different temperatures. The effect of [OH⁻] on the reaction was studied by varying the sodium hydroxide concentration between 0.02 and 0.18 mol dm^{-3} at a constant ionic strength of 0.2 mol dm^{-3}. The rate of reaction is accelerated by increase in [OH⁻] and the order in [OH⁻] was found to be 1.06. The effects of ionic strength and solvent polarity were studied keeping concentration of [HCF], [THIA] and sodium hydroxide constant at 1×10^{-3} mol dm^{-3}, 9×10^{-4} mol dm^{-3} and 14×10^{-2} mol dm^{-3} respectively at 25 °C. Sodium nitrate was used to vary the ionic strength. The rate of the reaction increases with varying ionic strength and the rate of reaction decreases as percentage of DMSO, 1,4-dioxane and ethanol increases from 0 to 60% v/v. The plot of log k_{obs} vs. (1/D) is linear with a negative slope. The rate of reaction increases as percentage of acetonitrile and methanol increases from 0 to 60%

v/v. The plot of log k_{obs} vs. (1/D) is linear with a positive slope.

The mechanism of the reaction, based on the kinetic results and spectrophotometric examination of the reactants and the reaction mixture can be represented as in Scheme 2. According to Scheme 2the reaction proceeds with the formation of a complex between oxidant and anion of thiamine to form a complex in a prior equilibrium with a constant k_2. The complex so formed will decompose in a slow second step with rate constant k_3 to form 2-[3-[(4-Amino-2-methyl-pyrimidin-5-yl) methyl]-4-methyl-thiazol-5-yl] ethanol. The rate law explains that the fractional orders with respect to the [THIA] and the plots of $1/k_{obs}$ against 1/[THIA] were found to be linear (Figure No.6). The rate law explains that the first order with respect to the [NaOH] and the plots of $1/k_{obs}$ against [OH⁻] were found to be linear (Figure No.7).

From the slope and intercept of Figure No.D 4.18 the values of rate constant for the slow step, k_3 and formation constant of complex, k_2, were calculated along with the activation parameters. The moderate values of $\Delta H^{\#}$ and $\Delta G^{\#}$ of -8.9750 and 30.8005 kJ mol^{-1} respectively were favorable for electron transfer processes. The negative value of $\Delta S^{\#}$ can be attributed to the nature of electron pairing and unpairing processes and to the loss of degrees of freedom formerly available to the reactants upon the formation of transition state. The effect of ionic strength indicates that one of the reactant is ionic in nature and decrease in the rate with decrease in the dielectric constant is in conformity with Amis concept for ion-dipole interactions.

Table No.1: Effect of Reactant Concentrations on the Reaction Rate at 307 K

S.No	10^3[HCF] Mol dm^{-3}	10^4[THIA] Mol dm^{-3}	10^2[NaOH] Mol dm^{-3}	10^2[NaNO$_3$] Mol dm^{-3}	10^4 k Mol dm^{-3}
1	0.1	100	20	20	3.33
2	0.2	100	20	20	3.00
3	0.4	100	20	20	2.32
4	0.7	100	20	20	2.09
5	0.8	100	20	20	2.06
6	0.9	100	20	20	2.01
7	1.0	1	20	20	2.18
8	1.0	2	20	20	2.11
9	1.0	6	20	20	2.08
10	1.0	8	20	20	2.04
11	1.0	9	20	20	2.02

Table No.2: Effect of Ionic strength on the Reaction Rate at 307K

S.No	10^3[HCF] Mol dm^{-3}	10^4[THIA] Mol dm^{-3}	10^2 [NaOH] Mol dm^{-3}	10^2 [NaNO$_3$] Mol dm^{-3}	10^4 k Mol dm^{-3}
1	1.0	9	14	4	2.09
2	1.0	9	14	6	2.11
3	1.0	9	14	14	2.18
4	1.0	9	14	18	2.24

Table No.3: Effect of Variation of Solvents on kinetics of ferrate oxidation of Thiamine (THIA) in basic media, $K_3[Fe(CN)_6]=1\times10^{-3}$ M[THIA]= 9×10^{-4} M [NaOH]=14×10^{-2}M[NaNO$_3$]=10×10^{-2}M

S.No	Conc. %	Variation of solvents									
		Methanol		Ethanol		Acetonitrile		DMSO		1,4-dioxane	
		I.R.	k	I.R.	k	I.R.	K	I.R.	K	I.R.	k
1	10	5.6713	0.0451	5.1446	0.0465	5.6713	0.0449	5.1446	0.0446	4.7046	0.0445
2	20	4.7046	0.0446	5.1446	0.0454	5.1446	0.0462	5.6713	0.0447	5.6713	0.0445
3	30	1.7321	0.0449	6.3138	0.0442	4.7046	0.0443	4.7046	0.0451	1.4826	0.0449
4	40	4.7046	0.0431	5.6713	0.0439	5.6713	0.0426	5.6713	0.0435	5.1446	0.0440
5	50	6.3138	0.0452	4.3315	0.0460	5.1446	0.0423	5.6713	0.0443	5.1446	0.0464
6	60	6.3138	0.0441	6.3138	0.0469	5.1446	0.0442	5.6713	0.0452	4.7046	0.0479

Table No.4: Effect of temperature oxidation of Thiamine (THIA) in basic media, Activation Energy Ea = -6414.2926 Jmole^{-1}

S.No	Temp.(K)	$\Delta H^{\#}$ (Jmole^{-1})	$\Delta S^{\#}$ (Jmole^{-1})	$\Delta G^{\#}$ (Jmole^{-1})
1	283	-8767.1546	-130.3607	28124.9184
2	293	-8850.2946	-129.8955	29209.0793
3	303	-8933.4346	-129.4100	30277.8068
4	313	-9016.5746	-129.0137	31364.7045
5	323	-9099.7146	-128.4189	32379.6055
6	333	-9182.8546	-128.0185	33447.2904
	Average	-8975.0046	-129.1862	30800.5675

Table No.5: Effect of Temperature on the Reaction Rate and Activation parameters

S.No	Temperature(K)	10^4 k(s^{-1})	Activation parameters	
			Parameter	Value
1	283 293 303 313 323 333	0.0401 0.0436 0.0405 0.0494 0.0544 0.0604	Ea(J mol^{-1}) $\Delta H^{\#}$(J mol^{-1}) $\Delta G^{\#}$(J mol^{-1}) $\Delta S^{\#}$ (J K^{-1}mol^{-1}) logA	6414.2 -8975.0 30800.5 -129.1 -335.0

Table No.6: Effect of added Salt on first order rate constant $K_3[Fe(CN)_6]=1\times10^{-3}$ M [THIA]= 9×10^{-4} M [NaOH]=10×10^{-2}M [NaNO$_3$]=14×10^{-2}M

| S.No	Conc. of salts(M)	Rate constant (k), S^{-1}									
		KCl	KBr	KI	KNO$_3$	K$_2$SO$_4$	NaCl	NaHCO$_3$	Na$_2$CO$_3$	NH$_4$Cl	NH$_4$Br
1	0.01	0.0428	0.0462	0.0446	0.0427	0.0443	0.0443	0.0373	0.0491	0.0565	0.0633
2	0.02	0.0442	0.0472	0.0447	0.0436	0.0482	0.0430	0.0386	0.0514	0.0682	0.0762
3	0.03	0.0446	0.0478	0.0452	0.0446	0.0464	0.0448	0.0375	0.0548	0.0606	0.0677
4	0.04	0.0447	0.0465	0.0449	0.0441	0.0430	0.0426	0.0423	0.0554	0.0628	0.0683
5	0.05	0.0434	0.0456	0.0500	0.0456	0.0455	0.0511	0.0409	0.0559	0.0778	0.0645
6	0.06	0.0467	0.0453	0.0481	0.0529	0.0443	0.0434	0.0425	0.0532	0.0744	0.0708
7	0.07	0.0453	0.0415	0.0449	0.0466	0.0456	0.0438	0.0438	0.0544	0.0714	0.0750
8	0.08	0.0486	0.0432	0.0429	0.0441	0.0449	0.0436	0.0456	0.0558	0.0692	0.0713
9	0.09	0.0423	0.0428	0.0457	0.0455	0.0448	0.0451	0.0463	0.0538	0.0680	0.0720
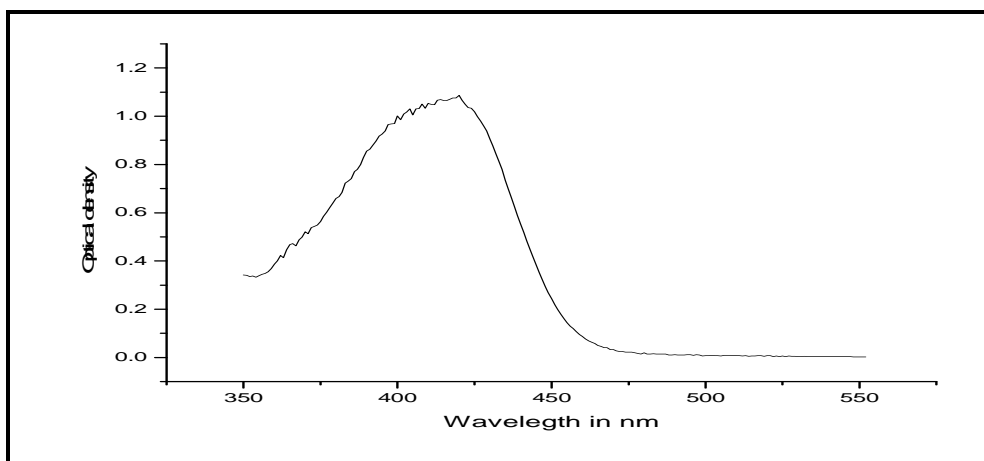
Figure No.1: Determination of max. wavelength of potassium hexacyanoferrate(III) $1 \times 10^{-4}M$
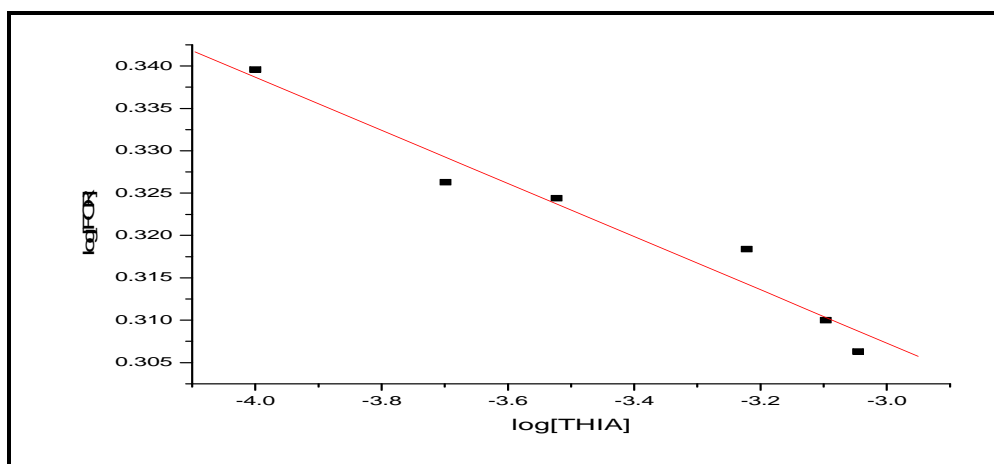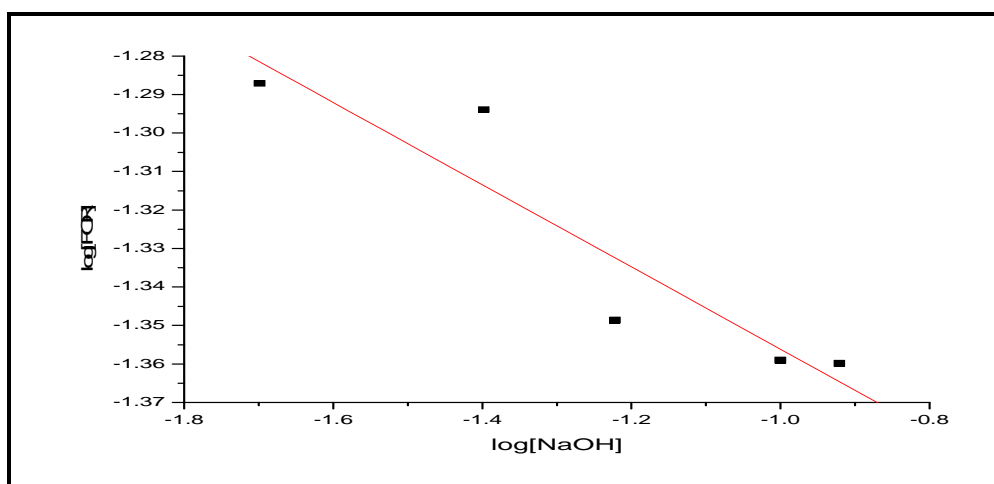

Figure No.2: Plot of log [THIA] vs log kobs
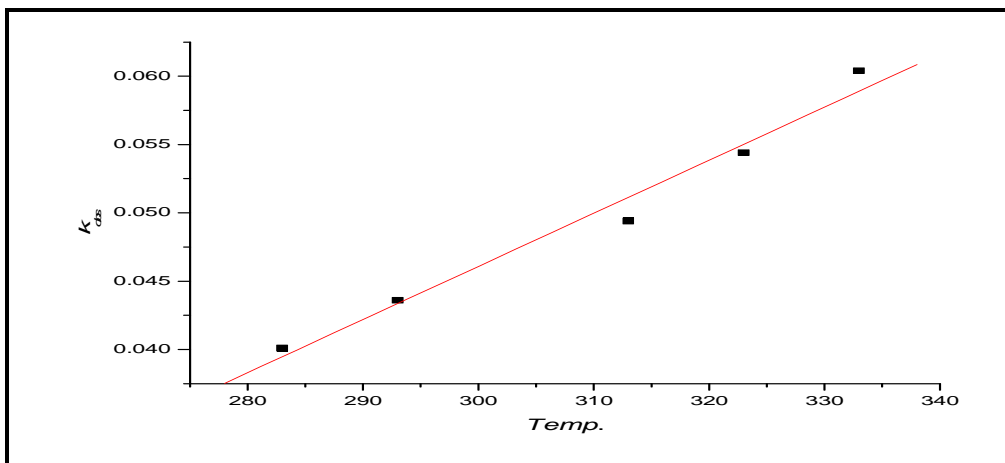

Figure No.3: Plot of log [NaOH] vs log kobs

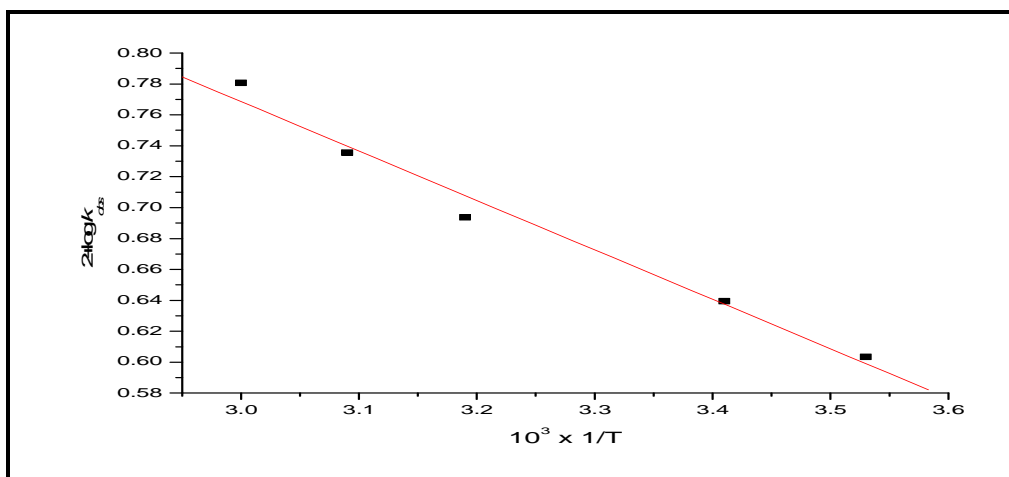**Figure No.4: Plot of temp. Vs k_{obs}**
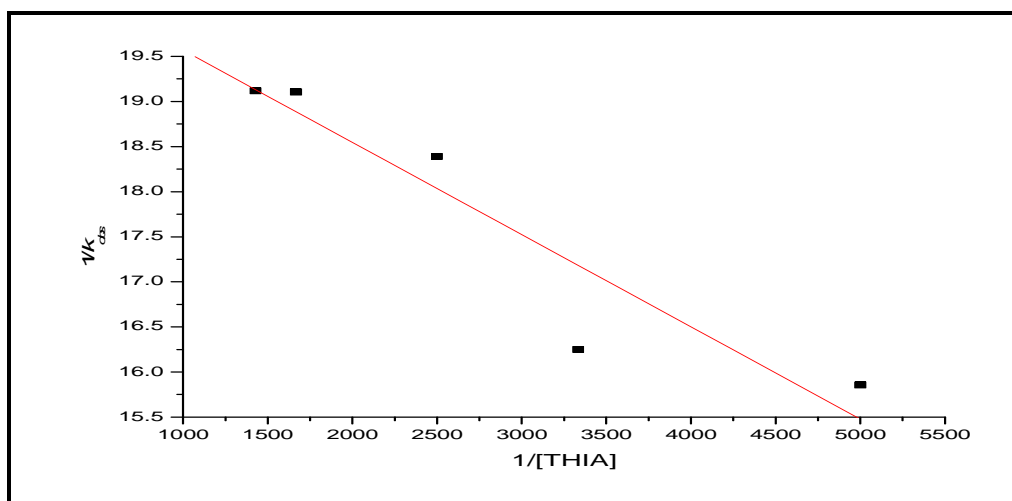

Figure No.5: Arrhenius plot

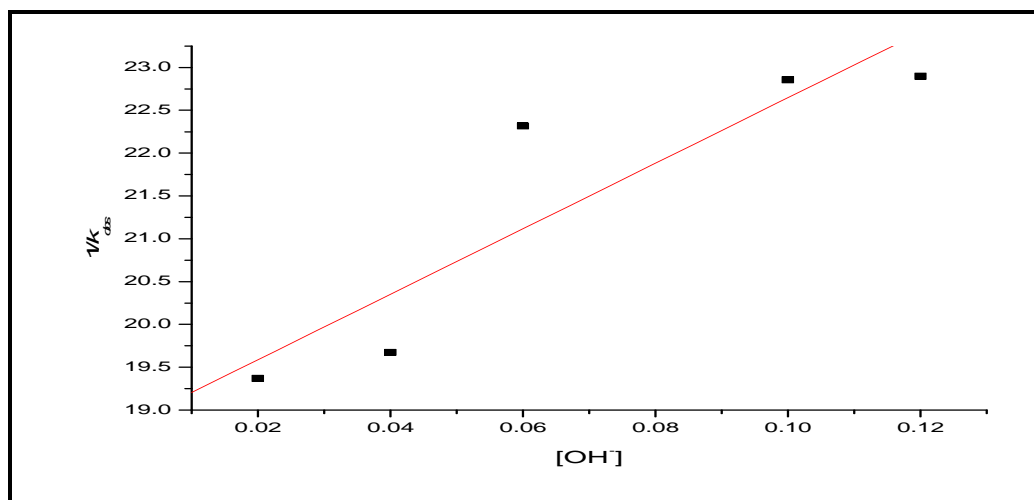**Figure No.6: Plot of 1[THIA] vs $1/k_{obs}$**

Figure No.7: Plot of [OH⁻] Vs 1/K_{obs}

CONCLUSION

The oxidation of THIA with HCF (III) in alkaline medium involves formation of a complex between anion of thiamine with oxidant which decomposes to yield corresponding aldehyde. The overall mechanistic sequence described here is consistent with product, mechanistic and kinetic studies.

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CONFLICT OF INTEREST

We declare that we have no conflict of interest.

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