Oxidation of pyridoxine by hexacyanoferrate (III) in aqueous alkaline medium:

A kinetic and mechanistic study

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- ## Novelty and Highlights:

1 – Pyridoxine is Vitamin $B_6.$ Its oxidation study is carried out using hexacyanoferrate as oxidant

2 – Kinetic and mechanistic approach is used to understand the oxidative degradation of the substrate.

3 – The study of degradation of vitamin B_6 along with oxidant in aqueous medium is helpful in understanding its biological metabolism.

Graphical Abstract:
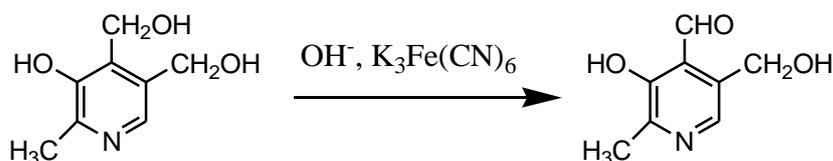
The kinetic study of oxidation of pyridoxine (PYD) by hexacyanoferrate (abbreviated as HCF) (III) in aqueous alkaline medium at constant ionic strength $0.005 mol/dm^3$ and temperature $298°K$.. in which pyridoxine is converted to pyridoxal.

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ABSTRACT: The kinetics of oxidation of pyridoxine (PYD) by hexacyanoferrate (abbreviated as HCF) (III) in aqueous alkaline medium at constant ionic strength $0.005 mol/dm^3$ and temperature $298°K$ has been studied spectrophotometrically. The reaction exhibit 1:2 stoichiometry of substrate to oxidant and follows fractional order kinetics in [HCF (III)] and first order in [alkali]. The dependence of the rate on substrate 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 $283°K$ to $333°K$. Mechanism involving formation of complex between HCF and PYD has been proposed. Pyridoxal has been identified chromatographically and spectroscopically as the final product of oxidation of PYD. Based on the kinetic data and product analysis a reaction mechanism is proposed.

Keywords: Oxidation, Mechanism, Hexacyanoferrate (III), Pyridoxine

INTRODUCTION

Iron (III) complexes as oxidant 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. Also one of the form of Iron (VI) is an environment friendly oxidant and used as coagulant for water and waste water treatment[1,2]. It is possible to use HCF (III) as a moderate oxidant because the oxidation potential of the couple $[Fe(CN)_6]^{3-}/[Fe(CN)_6]^{4-}$ (0.36V).

In modern day's PYD (also called vitamin B_6) has become a center of interest of research relating the significant role of its compounds in cellular metabolism. PYD plays important role in biological activities in the course of its transformation into a coenzyme for amino acid decarboxylase[3] pyridoxal phosphate. The vitamin B_6 shows six interconvertible forms; pyridoxine, pyridoxal and pyridoxamine each one has a corresponding 5-phosphate. The metabolic path of degradation of vitamin B_6 is its enzymatic oxidative[4] transformation into pyridoxal, 4-pyridoxo-lactone and 4-pyridoxic acid. The most significant excreted catabolite is 4-pyridoxic acid which is found in urine. Vitamin B_6 is usually found in food in free and bound forms and it has extensive applications in pharmaceutical industry. Therefore, the study of degradation vitamin B_6 along with oxidant in aqueous medium is helpful in understanding its biological metabolism. The oxidation of Vitamin B_6 was accounted by using chloramine-T [5], Mn (III) in acidic medium[6] and by $KMnO_4$ in basic medium[7]. Pyridoxal was found to be the major product of reaction. The oxidant potassium HCF (III) contains Fe (III) surrounded by six CN^- octahedral arrangements. Some researchers [8-11] carried out oxidation of vitamin B_6 in order to identify the mechanism of oxidative transformation of PYD, the nature of interaction and the possible intermediates. Due to some synthetic utility ferricyanide oxidation has become known as Decker oxidation[12]

A survey on earlier literature indicates that no attention was paid to the oxidation of PYD by this oxidant. The present work has been undertaken with a view to shed 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 give some information on the chemistry of PYD in aqueous solutions. HCF (III) has been widely used to oxidise numerous organic and inorganic compounds in alkaline media. Researchers[13] have suggested that alkaline HCF (III) ion simply acts as an electron abstracting reagent in redox reactions. Though, Speakman and Waters[14] have recommended different paths of oxidation of aldehydes, ketones and nitroparaffins. While, Singh and co-workers[15,16] 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. In view of the lack of literature on the oxidation of PYD by HCF (III), and in order to explore the mechanistic aspects of HCF (III) oxidation in alkaline medium, we have chosen PYD as a substrate. In continuation of our earlier work[17,18] the present study deals with the title reaction to investigate the redox chemistry of HCF (III) in such media, and to reach a suitable mechanism for the oxidation of PYD by alkaline HCF (III) 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. PYD is soluble in aqueous bases. The solution of PYD (Himedia) 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
A double beam bio-spectrophotometer BL-198 Elico was used for scanning. Thermostat used was of 'Toshniwal' Instrument. The constancy of the temperature maintained was to an accuracy of ±0.5 ℃
Kinetic Procedure: Stoichiometry and Product Analysis:
Reaction mixture containing various ratios of HCF (III) to PYD in presence of 6×10^{-2} mol dm^{-3} NaOH at 298K, under the condition [PYD]>>[HCF], were equilibrated for 24h. Determination of unreacted HCF showed 1:2 stoichiometry of substrate to oxidant. Oxidation product Pyridoxal was detected by thin layer chromatography. Further it was confirmed by its MP, IR and NMR spectra. Strong peak for

$-\overset{\displaystyle O}{\underset{\displaystyle \|}{C}}H$ group was observed at 1720 cm^{-1}.

Results and Discussion:
The λ_{max} for potassium hexacyanoferrate $(1\times10^{-4}M)$ determined spectrophotometrically using bio-

spectrophotometer BL-198 Elico and found to be 420nm.(Figure.1)

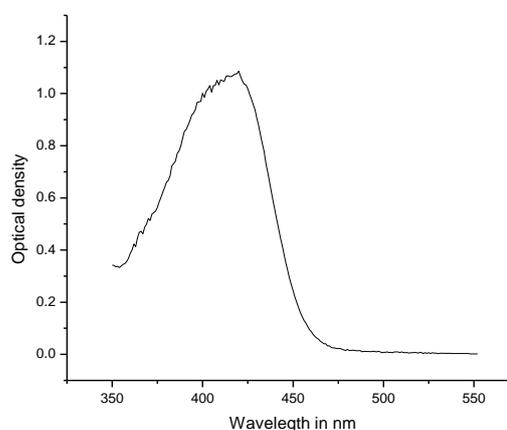Figure1. Spectral scan of potassium hexacyanoferrate (III) 1×10^{-4}M in alkaline medium at [OH$^-$] = 6×10^{-2} M and 298K

1. Reaction orders
The reaction orders were determined from the slope of log k_{obs} versus log concentration plots, by varying the concentration of each substrate, oxidant and alkali while keeping others constant.
2. Effect of Reactants on the Reaction Rate
With substrate in excess, at constant [HCF], [OH$^-$] [NaNO$_3$] and temperature, plots of log [HCF] Vs time were linear indicating fractional order dependence of rate on [HCF]. Plot of log[HCF] Vs logk_{obs} was found to be linear (Table.1) with slope 0.354 confirming fractional order dependence on [HCF]. At constant [HCF], [NaOH], [NaNO$_3$] and temperature (Table.1) Plot of log[PYD] Vs logk_{obs} (Figure.2) was linear with a slope of 0.50 indicating fractional order dependence on [PYD]. The rate increases with increase in [NaOH] (Table.1) and plot of log[NaOH] Vs logk_{obs} (Figure 3) was linear with slope of 0.994, showing first order dependence on [OH$^-$]

3. Effect of salts on the rate constant of the reaction
To study the effect of variation of salts, the concentration of salts were varied from 1 x 10^{-2} to 9 x 10^{-2} M, keeping constant concentration of other reaction ingredients such as [HCF]=7x10^{-4} M, [PYD]=7x10^{-3}M, [NaOH] =6x10^{-2}M and [NaNO$_3$] =4x10^{-2}M. These results are given in the table.6. From the obtained results, it is clear that pseudo observed first order rate constant k_{obs} increased with increase in concentration for K$_2$SO$_4$, NaCl and NH$_4$Cl. A plot of log k_{obs} vs √μ according to extended Bronsted-Debye-Huckel equation was found to be linear with positive slopes indicating positive salt effect.
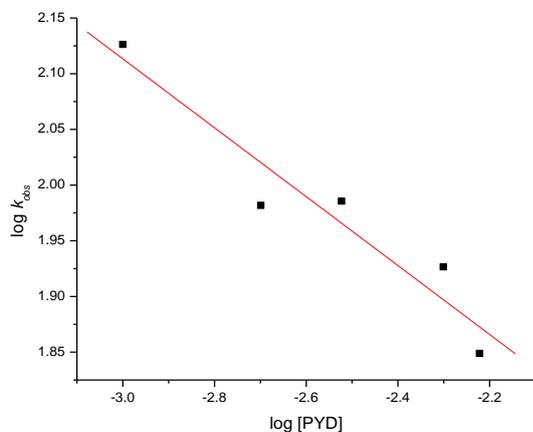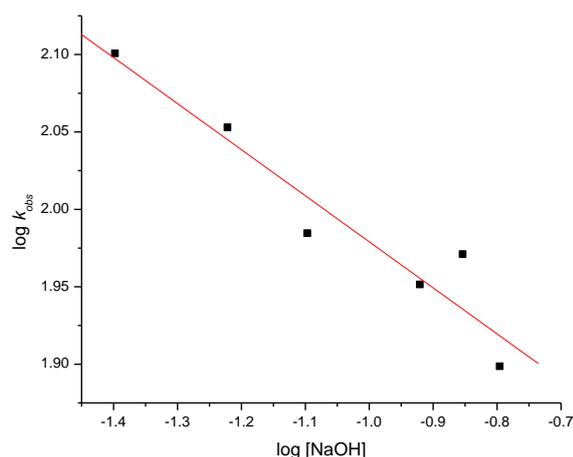
Figure 2. Plot of log[PYD] Vs log k_{obs}

Figure3. Plot of log [NaOH] Vs log k_{obs}

On the other hand pseudo first order rate constant decreased with increase in concentration for KCl, KBr, KI, KNO$_3$, NaHCO$_3$, NH$_4$Br and Na$_2$CO$_3$. A plot of log k_{obs} vs √μ was found to be linear with negative slopes indicating negative salt effect (Table.6).

4. Effect of Ionic Strength and Dielectric Constant on the rate constant of the reaction

Variation in ionic strength using NaNO$_3$ solution (2x10^{-2} mol dm^{-3} to 18x10^{-2} mol dm^{-3}) affect (Table.2) the rate of the reaction indicating that species are involved in the rate limiting step. Dielectric constant (D) of the medium was varied by adding methanol, ethanol, acetonitrile, DMSO and 1,4-dioxane (Table.3). It was found that rate constant increased on decreasing the dielectric constant of acetonitrile, DMSO and 1,4-dioxane, while rate constant decreased on decreasing the dielectric constant of methanol 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[19]. Plot of (1/D) Vs logk_{obs} was found to be linear.

5. Effect of Temperature on the Reaction Rate

Reaction was studied over a range of temperature 283K to 333K by varying the concentration of PYD keeping other experimental conditions constant. It was found that the rate increased with increase in temperature (Table.5)

From the Arrhenius plot (Figure.4), activation parameters like energy of activation (Ea), enthalpy of activation (ΔH$^{#}$), entropy of activation (ΔS$^{#}$), energy of activation (ΔG$^{#}$), and logA were computed (Table.5).

6. Test of Free Radicals

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

Table1 Effect of reactant concentrations on the rate constant of the reaction at 298K.

10^4[HCF]	10^3[PYD]	10^2[NaOH]	10^2[NaNO$_3$]	10^4 k_{obs}
Mol dm^{-3}	Mol dm^{-3}	Mol dm^{-3}	Mol dm^{-3}	s^{-1}
2.0	10	20	20	7.277
4.0	10	20	20	6.985
7.0	10	20	20	6.802
9.0	10	20	20	6.259
7.0	4.0	20	20	7.592
7.0	5.0	20	20	6.827
7.0	7.0	20	20	6.569
7.0	9.0	20	20	6.419
7.0	7.0	4	20	6.609
7.0	7.0	8	20	6.679
7.0	7.0	16	20	6.982
7.0	7.0	18	20	7.236

Table 2 Effect of ionic strength on the reaction rate at 298K.

10^4[HCF]	10^3[PYD]	10^2 [NaOH]	10^2 [NaNO$_3$]	10^4 k_{obs}
Mol dm^{-3}	Mol dm^{-3}	Mol dm^{-3}	Mol dm^{-3}	s^{-1}
7.0	7.0	6.0	4	6.427
7.0	7.0	6.0	10	6.547
7.0	7.0	6.0	14	6.744

DISCUSSION

Variation of the concentration of each of the oxidant HCF (III), substrate (PYD) 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 PYD 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.

Table.3. Effect of Variation of Solvents on oxidation of PYD in basic media.
$K_3[Fe(CN)_6]=7x10^{-4}$ M   [PYD]= $7x10^{-3}$ M [NaOH]=$6x10^{-2}$M [NaNO_3]=$4x10^{-2}$M

Variation of solvents (k_{obs}), s^{-1}									
Conc. %	Methanol	Conc. %	Ethanol	Conc. %	Acetonitrile	Conc. %	DMSO	Conc. %	1,4-dioxane
10	0.0710	30	0.0768	10	0.0774	20	0.0738	30	0.0791
30	0.0753	40	0.0794	20	0.0747	40	0.0764	40	0.0708
40	0.0788	50	0.0896	40	0.0740	50	0.0824	50	0.0674
50	0.0806			50	0.0682			60	0.0645
60	0.0830								

Table.4-Effect of Temperature on Oxidation of PYD in basic media.
$K_3[Fe(CN)_6]=7x10^{-4}$ M   [PYD]= $7x10^{-3}$ M
[NaOH]=$6x10^{-2}$M [NaNO_3]=$4x10^{-2}$M,
Activation Energy = -6.3759 KJ/mole

temp °K	$\Delta H^{\#}$ (KJ/mole)	$\Delta S^{\#}$ (KJ/mole)	$\Delta G^{\#}$ (KJ/mole)
283	-8.7288	-0.1303	28.1465
293	-8.8120	-0.1298	29.2307
303	-8.8951	-0.1293	30.2994
313	-8.9782	-0.1289	31.3863
323	-9.0614	-0.1283	32.4012
333	-9.1445	-0.1279	33.4689

Table 5 Effect of Temperature on the observed first order rate constant and Activation parameters.

Temperature (K)	$10^4 k_2$ (s^{-1})	Activation parameters	
		Parameter	Value
283	7.3143	Ea(J mol^{-1})	6375.9
293	7.8429	$\Delta H^{\#}$(J mol^{-1})	-8936.7
303	8.5143	$\Delta G^{\#}$(J mol^{-1})	30822.2
313	9.0429	$\Delta S^{\#}$ (J K^{-1}mol^{-1})	-129.1
323	10.2000	logA	-333.0
333	10.9286		

The kinetic aspects and the mechanism proposed are similar to those of phenols[20] first-order in oxidant, substrate and base concentrations. The formation of an alkyloxy radical occurs in the rate-determining step by oxidation of the substrate anionic form, followed by rapid oxidation to generate more unsaturated species. The oxidation of aminoalcohols, diols and glycols does not occur via free radicals, but to a certain extent through an intermediate complex between the oxidant and the anionic substrate[21–23].

Table.6 Effect of added Salt on observed first order rate constant
$K_3[Fe(CN)_6]=7x10^{-4}$ M [PYD]= $7x10^{-3}$ M
[NaOH]=$8x10^{-2}$ M [NaNO3]=$8x10^{-2}$M

Observed first order rate constant (k_{obs}), s^{-1}						
Salt Conc./M	0.01	0.03	0.04	0.06		
KCl	0.0796	0.0743	0.0729	0.0709		
Salt Conc./M	0.02	0.04	0.06	0.09		
KBr	0.0812	0.0807	0.0805	0.0802		
Salt Conc./M	0.02	0.03	0.06			
KI	0.0798	0.0762	0.0759			
Salt Conc./M	0.03	0.06	0.07			
KNO_3	0.0830	0.0790	0.0774			
Salt Conc./M	0.01	0.05	0.06	0.07	0.09	
K_2SO_4	0.0771	0.0779	0.0799	0.0806	0.0837	
Salt Conc./M	0.01	0.03	0.05	0.06		
NaCl	0.0786	0.0793	0.0795	0.0841		
Salt Conc./M	0.06	0.07	0.08	0.09		
NaHCO_3	0.0837	0.0814	0.0810	0.0778		
Salt Conc./M	0.02	0.04	0.06	0.07	0.08	0.09
Na_2CO_3	0.0856	0.0842	0.0830	0.0817	0.0792	0.0787
Salt Conc./M	0.02	0.04	0.07			
NH_4Cl	0.0785	0.0805	0.0829			
Salt Conc./M	0.02	0.04	0.05	0.06	0.08	
NH_4Br	0.0812	0.0807	0.0786	0.0805	0.0767	

Phenoxy radicals are more stable than alkyloxy radicals and alcohol oxidations usually require a catalyst. This oxidation follows Michaelis–Menten-type plots: the substrate–catalyst complex disproportionates to give the products. The role of HCF (III) consists of regenerating a hydride catalyst by oxidizing its reduced form, hence the majority reactions are zero-order in oxidant, accordingly as in the Ru (VIII)-catalyzed oxidation of alcohols[24], the Ru(VI)-catalysed oxidations of *n*-alkanols[25,26], unsaturated alcohols[27], the cycloalcohols[28], glycols[29], benzyl alcohol[30] and ethylene glycols[31]; a similar pattern follows the Ru(VIII)-catalyzed oxidations of butanediols and cyclopentanol[32]; The Os(VIII)-catalysed oxidations of 1- and 2-propanol[33], butylglycol[34] and allyl alcohol[35] the catalytic species being $OsO_4(OH)_2^{2-}$, as do the Rh(III)-catalysed

oxidations of 2-propanol and 2-butanol[36]. These reactions generate the corresponding carboxylic acids or a mixture of organic acids for secondary alcohols; cyclic alcohols produce mainly ketones. A rather unusual behaviour is shown by the alkaline Os (VIII) -catalysed oxidation of 2-aminoethanol and 3-aminoethanol[37].

During the oxidation of PYD using HCF (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 (-6.3759 kJ mol^{-1}) and the negative entropy (-0.1291 KJ K^{-1} mol^{-1}) for PYD, is consistent with a rate-determining step involving ions having charges of same sign, consistent with the following mechanism.
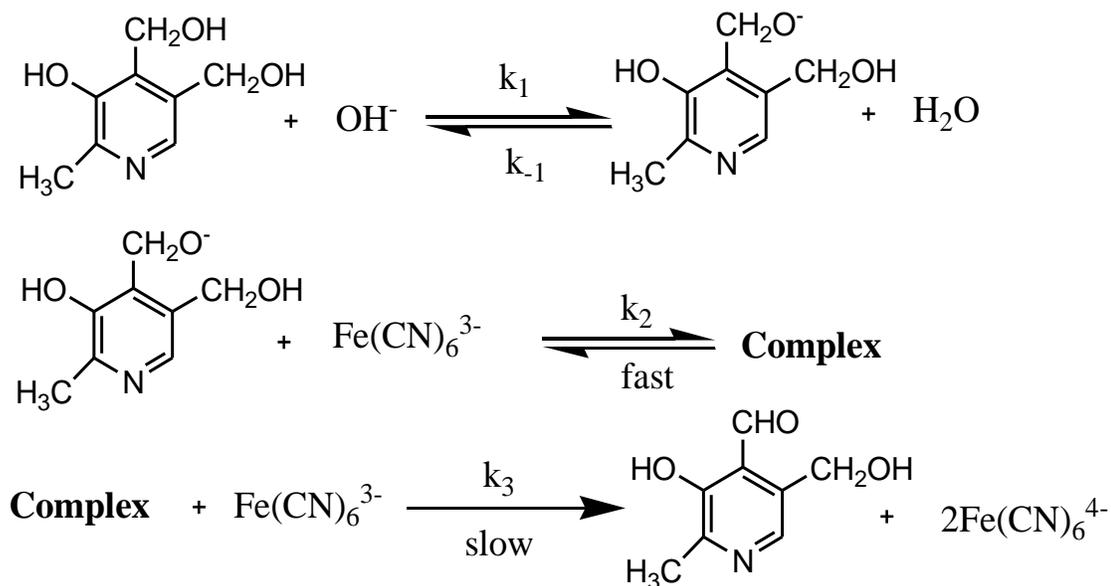
Scheme.1

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 (0.354) in [oxidant]. The pseudo-first-order rate constants were found to increase as [PYD] increases from 1.0×10^{-3} to 9.0×10^{-3} mol dm^{-3} at a constant [oxidant] of 7×10^{-4} mol dm^{-3}. The order in [PYD] was found to be 0.480 as determined from the log k_{obs} against log [PYD]. Since, the order in [PYD] was fractional which indicates the formation of a complex therefore, the kinetic data were used to obtain plot of $1/k_{obs}$ against $1/$[PYD]. 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 [PYD] 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 0.994. The effects of ionic strength and solvent polarity were studied keeping concentration of [HCF], [PYD] and sodium hydroxide constant at 7×10^{-4} mol dm^{-3}, 7×10^{-3} mol dm^{-3} and 6×10^{-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 methanol 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, DMSO and 1,4-dioxane 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 1. According to Scheme 1 the reaction proceeds with the formation of a complex between oxidant and anion of PYD 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 pyridoxal. The rate law explains that the fractional orders with respect to the [PYD] and the plots of $1/k_{obs}$ against $1/$[PYD] were found to be linear. (Figure.6)

From the slope and intercept of Figure.6 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 -8.9367 and 30.8222 kJ mol^{-1} respectively were

favourable 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 neutral and decrease in the rate with decrease in the dielectric constant is in conformity with Amis concept for ion–dipole interactions [38].

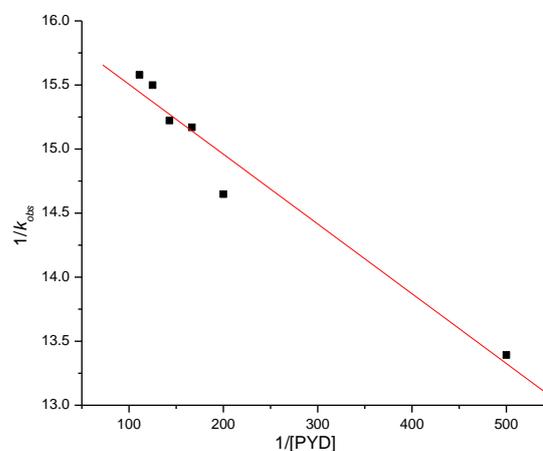$$rate = \frac{k_1[PYD][OH^-]}{1 + k_2[PYD] + k_3[OH^-]}$$

Figure6. Plot of $1/$[PYD] vs $1/k_{obs}$

Conclusion The oxidation of PYD with HCF (III) in alkaline medium involves an outer-sphere mechanism and oxidations taking place in sequences of one electron steps. The overall mechanistic sequence described here is consistent with product, mechanistic and kinetic studies.

References

1. J. Q. Jiang, B. Lloyd, *Water Res.,* 2002, **36**, 1397.
2. V. K. Sharma, *Adv. Environ. Res., 2002,* **6**, 143.
3. R. G. Kallen, T. Korpela, A.E. Martell, Y. Matsushima, C.M. Metzler, D.E. Metzler, Y.V.Morozov, I.M. Ralston, F.A. Savin, Y.M. Torchinsky, Y. Ueno, Transaminases, in: P. Christen, D.E. Metzler (Eds.), John Wiley & Sons, New York, 1986.
4. G.F. Combs, the Vitamins: *Fundamental Aspects in Nutrition and Health*, Elsevier, San Diego, 2008.
5. V. Shukla, N. Kambo, S.K. Upadhyay, *J. Dispersion Sci. Technol.* 2008, **29**, 848.
6. I. K. Bhat, *Transition Met. Chem*. 19 (1994) 178.
7. H.A. Harris, D. Heyl, K. Folkes, *J. Am. Chem. Soc.,* 1944, **66**, 2088.

8. S.D. Kadam, A.R. Supale, G.S. Gokavi, *Z. Phys. Chem.,* 2008, **222** 635.

9. S.D. Kadam, A.R. Supale, G.S. Gokavi, *Transition Met. Chem.* 2008, **33** 989.

10. V. M. Gurame, A. R. Supale, G. S. Gokavi, *Amino Acids*, 2010, **38** 789.

11. V.M. Gurame, G.S. Gokavi, *Polyhedron*, 2008, **27**, 1905.

12. E.A. Prill and S.M. Mcelvain, *Org. Synth. Coll.* 1943, **2**, 419.

13. A. I. Vovk, I. V. Muraveva, V. P. Kukhar, V. F. Baklan, *Russ. J. Gen. Chem.* 2000, **70**, 1108–1112.

14. P. T. Speakman, W. A. Waters, **J. Chem. Soc.,** 1955, 40–45.

15. V. N. Singh, M. C. Gangwar, B. B. L. Saxena, M. P. Singh, *Can. J. Chem.* 1969, **47**, 1051–1056.

16. V. N. Singh, M. P. Singh, B. B. L. Saxena, *Indian J. Chem., 1970*, **8**, 529–532.

17. S. R. Gour, B. S. Dobhal, Sayyad Hussain, Mazahar Farooqui, Oxidation of chemical compounds: Kinetics and mechanistic approach, *J. Chem. Pharma Res.,* 2011, **3(5)**, 750-761; (ISSN No 0975-7384)

18. Sandipsing Gour, Bhagwansing Dobhal, Mazahar Farooqui; Kinetics and Mechanistic Study of Permaganatic Oxidation of Ranitidine in Acidic Medium; *Elixir Apl. Chemistry*, 40(2011) 5568-5572; (ISSN:2229-712X)

19. *Hand Book of Chemistry and Physics* 73 rd ed. Lide, D.R., Chemical Rubber Publishing Company: London, 1992; pp 8-51.

20. H.S. Singh, V.P. Singh, D.P. Pandey, *Monatsh. Chem.*, 1979, **110** 1455.

21. S. Gupta, S.K. Upadhyay, *Asian J. Chem.,* 1992, **4**, 229.

22. H.S. Singh, S.M. Singh, P. Singh, K.K. Singh, Proc. Indian Natn. Sci. Acad. 49A (1983) 173.

23. M.P.K. Tandon, B. Krishna, *Z. Phys. Chem. Leipzig*, 1985, **266**, 1153.

24. T.V. Latitha, B. Sethuram, *Trans. Met. Chem.,* 1992, **17**, 29.

25. M.N. Pandey, H. Narayan, R.S. Shukla, K. Behari, *Z. Phys. Chem. Leipzig*, 1982, **263**, 1055.

26. H.S. Singh, J.K. Singh, *Indian J. Chem.,* 1990, **29**, 1068.

27. R.K. Dwivedi, M. Verma, P. Kumar, K. Behari, *Tetrahedron*, 1983, **39** 815.

28. K. Behari, H. Narayan, R.S. Shukla, K.C. Gupta, *Int. J. Chem. Kinet.,* 1984, **16**, 195.

29. T.V. Lalitha, M.P. Rao, B. Sethuram, *Indian J. Chem.*, 1992, **31A**, 309.

30. N. Nath, L.P. Singh, R.P. Singh, *J. Indian Chem. Soc.*, 1981, **58** 1204.

31. H.S. Singh, K.C. Tiwari, S.M. Singh, *Indian J. Chem.,* 1982, **21A** 520.

32. M.K. Verma, P.K. Tandon, H.S. Singh, M.P. Singh, *Z. Phys. Chem. Leipzig,* 1986, **267** 1219.

33. H.S. Singh, S.P. Singh, S.M. Singh, R.K. Singh, A.K. Sisodia, *J. Phys. Chem.,* 1975, **79** 1920.

34. H.S. Singh, P. Singh, *Ann. Soc. Sci. Bruxelles,* 1983, **97**, 21.

35. V.A. Morab, S.M. Tuwar, S.T. Nandibewoor, J.R. Raju, *J. Indian Chem. Soc.,* 1992, **69** 862.

36. H.S. Singh, K.K. Singh, S.M. Singh, P. Singh, P. Thakur, *Indian J. Chem.*, 1982, **21A**, 816.

37. S. Gupta, S. K. Upadhyay, *Asian J. Chem.*, 1992, **4**, 229.

38. R. G. Panari, R. B. Chougule, S. T. Nandibewoor, *J. Phys. Org. Chem.*, 1998, **11**, 44.