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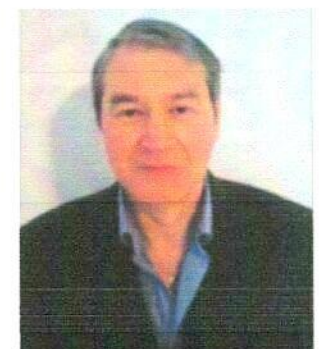


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RESEARCH ARTICLE

OXIDATION OF PICOLINIC ACID HYDRAZIDE BY HEXACYANOFERRATE (III) IN SODIUM HYDROXIDE MEDIUM UNDER PSEUDO FIRST ORDER CONDITION

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ABSTRACT

The objective of the present study is to examine the kinetics and mechanism of Single electron transfer redox reaction of Picolinic acid hydrazide (Pi-AH) by hexacyanoferrate(III) called HCF(III) in Sodium hydroxide medium which involves $Fe(CN)_6^{3-}$. The Spectrophotometric monitoring of oxidation of Pi-AH by HCF(III) was carried out. The kinetic determination of its mechanism in sodium hydroxide medium under pseudo first order condition was done. The formation of complex takes place during the course of the reaction between the reactants, which on decomposition in the subsequent step gives the products. The reaction proceeds by direct Single electron transfer with intervention of free radical and the order of reaction was found to be one with respect to the concentration of hydrazide (Pi-AH) and hexacyanoferrate HCF (III). The specific rate of the reaction increases with an increase in the concentration of hydrazide and hexacyanoferrate HCF (III). The salt effect that is ionic strength effect is positive i.e. addition of KCl increases the rate of reaction: hence the reaction must be between species of the same charges. Increase in the concentration of NaOH increases the rate of reaction and decreases with decrease in dielectric constant of the medium of the Reaction. The effect of temperature was studied between 25°C to 45°C. The activation parameters were determined and the values support the proposed mechanism as evidenced by considerable decrease in entropy of activation. ($-\Delta S^\ddagger = 22.09 \text{ J K}^{-1} \text{ mol}^{-1}$) The progress of the reaction was followed by measuring the absorbance (A) of the HCF(III) at 420 nm.

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INTRODUCTION

Although the hexacyanoferrate (III) is an oxidizing agent in which one electron transfer is involved, no comprehensive summary is available in the literature as an oxidizing agent in Organic Chemistry. However, the Chemistry of hydrazides is very important branch of organic Chemistry because many hydrazides are found to have physiological activities as they are tested for their anti bacterial (Mahzhoyon, 1966; Winterstein *et al.*, 1956) biological activity (Demetrescuet *et al.*, 1963), anti inflammatory properties (Juckeret *et al.*, 1962), anti leprosy (Gradneret *et al.*, 1961), anti-convulsive action (Renzet *et al.*, 1967), anti-thelminities (Cavier and Rips *et al.*, 1955), to regulate and inhibit the growth of the plants (Wood, 1953), anti oxidants for poly olefins and polyurethanes. They have been extensively studied since the discovery of isonicotinic acid hydrazide as a strong antituberculostatic agent (Hervey *et al.*, 1967). In addition to that some hydrazides are important starting materials and intermediates in the synthesis of certain amines, aldehydes and heterocyclic compounds. The applications of hydrazides and their derivatives in heat and corrosive stabilization of cellulose, an incorporation of hydrazide has improved the applicability in plastics and cable insulation (Farben, 1965) and also small amount of hydrazide are useful in sensitizing electrographic layers made up of polyvinyl carbazole (Gavaerst *et al.*, 1966), dihydrazides can also be used in cigarette filters for the selective removal of aldehydes from tobacco smoke. Kinetic study carried out in liquid phase reactions i.e. oxidation reaction of organic compounds have vital importance in synthetic biological fields. According to Haber and weiss (Haber, *et al.*, 1934) oxidation is a simply a transfer of an electrons from reductant to oxidant and by considering number of electrons transferred to the oxidant during oxidative process, classification of the oxidation process as well as oxidants could be done (Lel and Chinn, 1966).

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The kinetics of oxidation of nicotinoyl and iso-nicotinoyl hydrazides by Iron (III) in the presence of 1:10 phenanthroline (Frank and Krishnarao, 1979) and the kinetics of Ag^+ catalyzed oxidation of nicotinic and iso-nicotinic acid hydrazides (Hogale *et al.*, 1984) has been investigated. In present investigation, the study of the Oxidation of heterocyclic acid hydrazide such as Picolinic acid Hydrazide by hexacyanoferrate (III) is done in Sodium hydroxide medium.

MATERIALS AND METHODS

The reported procedure (Vogel, 1975) was adopted for the preparation of the Picolinic acid hydrazide (Pi-AH) and it was stored in amber colored bottles kept in dark place. $K_3Fe(CN)_6$, NaOH, KCl and CH_3OH used were of AR grade. The stock solution of $K_3Fe(CN)_6$ was prepared by dissolving calculated quantity of $K_3Fe(CN)_6$ in hot double distilled water. The exact normality of $K_3Fe(CN)_6$ solution was confirmed by standardization method (Farben, 1965), and used within twelve hours of preparation. The Standard solutions of Pi-AH were prepared by dissolving Pi-AH in distilled water. The impurity present in the reagent generally influence the rate of chemical reaction, hence all possible precautions were taken to avoid the impurities present in the reaction system. The purity of Pi-AH was checked after recrystallisation and by determining their physical Constant $100^\circ C$. The double distilled water was used throughout the experiment.

Determination of λ Max for HCF(III)

Absorbance of 5.0×10^{-4} M Solution of hexacyanoferrate(III) was measured as a function of wavelength in range of 400-700 nm, by using distilled water as reference. From the graph HCF(III) has a strong absorption at 420 nm^3 . The pseudo-first order condition was maintained through the reaction in which concentration of hydrazide was in excess as compared to that of $K_3Fe(CN)_6$. The formation of complex between $K_3Fe(CN)_6$ and hydrazide was found during the course of the reaction. The plot of the log of absorbance at 420 nm against time for each hydrazide was used to calculate the pseudo-first order rate constant k. The reaction was studied spectrophotometrically by measuring the absorbance of the reaction mixture at 420 nm.

Kinetic Procedure

Reaction were performed under pseudo-first order conditions: $[Pi-AH] \geq [HCF(III)]$ in a Pyrex conical glass (coated black), thermo stated at $35^\circ C$. The oxidation was initiated by adding a thermo stated solution of Pi-AH to a thermo stated solution of HCF(III) containing the required quantities of NaOH. The progress of the reaction was followed by measuring the absorbance (A) of HCF(III) at 420 nm ($\epsilon = 1015 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) employing Spectronic 20 (Milton Roy Company) and 1cm path length cells. The Pseudo- first order rate constants (k) were evaluated using equation 1³, which was valid to well over 70% disappearance of hexacyanoferrate(III).

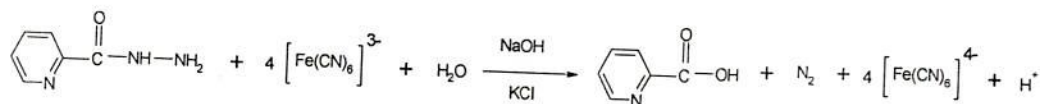
$$K = (2.303 / t) \log A_0/A_t$$

..... (1)

Where A_0 and A_t are the absorbance at time Zero (initial) and at time t, respectively. The k values were in good agreement with those obtained from linear plots of log A verses time. The second order k_2 was calculated from the relationship $k_2 = k_1 / [Pi-AH]_0$.

Stoichiometry and products

The stoichiometry of the reaction was determined using known excess of HCF(III) over Pi-AH concentration and results are consistent with the following equation.



The Picolinic acid was detected by paper chromatography (Edgar, 1957). The nitrogen was detected by lime tests (Vogel, 1975) The resultant mixture at the end of the reaction was rendered neutral after removal of $Fe(CN)_6^{4-}$. A test portion of neutral solution was added to an ignited mixture of lime and manganese dioxide (10:1) in a hard glass tube. The tube was heated and the liberated gas tested with manganese nitrate-silver nitrate paper, which showed grey flecks which turned blue immediately on treatment with a drop of benzidine solution, confirming the presence of nitrogen. The formation of carboxylic acids and N_2 in the oxidation of aliphatic as well as aromatic acid hydrazides (Haskar *et al.*, 1979) is well documented in chemical literature. The study of oxidation of hydrazide by different oxidants indicated that, the formation of ammonia also takes place in addition to the formation of respective aryloxy acetic acid and nitrogen (Ramaiah *et al.*, 1976).

Reaction Intermediates

The first order dependence of reaction rate on HCF(III) concentration indicated the possible formation of free radical (or radical ions) during the course of the reaction. This was also confirmed via neither induced polymerization of acrylonitrile nor reduction of $HgCl_2$ occurred in the absence of one of the two reactants.

RESULTS AND DISCUSSION

It was observed that, in the presence of 5.0×10^{-4} M $K_3Fe(CN)_6$, 7.5×10^{-3} M Pi-AH, 3.0×10^{-4} M NaOH, 4.0×10^{-3} M KCl, λ_{max} 420 nm and at $35^\circ C$ temperature the reaction proceed with measurable velocity, which shows the first order rate constant goes on slightly decreasing with the time.

Table 1. Conditions of the Standard Kinetic Reaction

Substrate	Conc.	Reactant	Conc.	Medium	Conc.	Salt	Conc.	Temp	λ_{max}	$K \times 10^4 \text{Min}^{-1}$
[Pi-AH]	$7.5 \times 10^{-3} M$	[HCF(III)] ₀	$5.0 \times 10^{-4} M$	[NaOH] ₀	$3.0 \times 10^{-4} M$	[KCl] ₀	$4.0 \times 10^{-3} M$	$35^\circ C$	420	1.12

Table 2. Average specific reaction rate constants determined by Calculation & graphical method :

Effect of	[Pi-AH] $\times 10^{-3} M$	5.5	6.5	7.5	8.5	9.5	
[hydrazide]	$K \times 10^2 \text{Min}^{-1}$	0.89	1.01	1.12	1.22	1.31	Increasing order
	$K_1 \times 10^2 \text{Min}^{-1}$	0.89	1.01	1.12	1.22	1.31	
	$K_2 \times 10^2 \text{Min}^{-1}$	1.61	1.56	1.49	1.43	1.39	
	$(-dc/dt) \times 10^6$	3.36	4.00	4.60	5.20	5.80	
	Order of reaction 'n'			1.03			
Effect of [HCF(III)]	[HCF(III)] $\times 10^{-4} M$	3.0	4.0	5.0	6.0	7.0	Increasing order
	$K \times 10^2 \text{Min}^{-1}$	0.94	0.96	1.12	1.24	1.34	
	$(-dc/dt) \times 10^6$	2.41	3.47	4.36	5.23	6.13	
	Order of reaction 'n'			0.99			
Effect of [NaOH]	[NaOH] $\times 10^{-4} M$	2.2	2.6	3.0	3.4	3.8	Increasing order
	$K \times 10^2 \text{Min}^{-1}$	0.98	1.02	1.12	1.19	1.24	
Effect of [KCl]	[KCl] $\times 10^{-3} M$	1.0	2.0	4.0	6.0	8.0	
	$K \times 10^2 \text{Min}^{-1}$	0.90	0.98	1.12	1.13	1.16	
Effect of Dielectric Const.	[Methanol] % V/V	----	---	0.0	5.0	10.0	15.0
	$K \times 10^2 \text{Min}^{-1}$	--	--	1.12	1.23	1.32	1.44
	D			69.82	68.37	66.29	64.81
	$10^2/D$			1.432	1.463	1.509	1.543
Effect of Temperature	$2 + \log k$			2.049	2.090	2.121	2.158
	Temperature $^\circ C$	25	30	35	40	45	
	$K \times 10^2 \text{Min}^{-1}$	0.564	0.700	1.12	1.41	2.23	

Table 3. The various Energy parameters calculated are

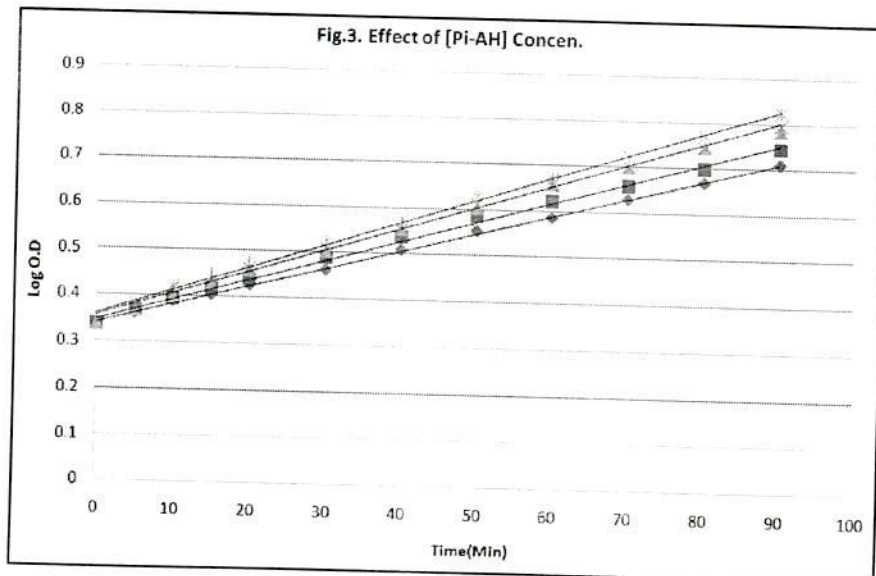
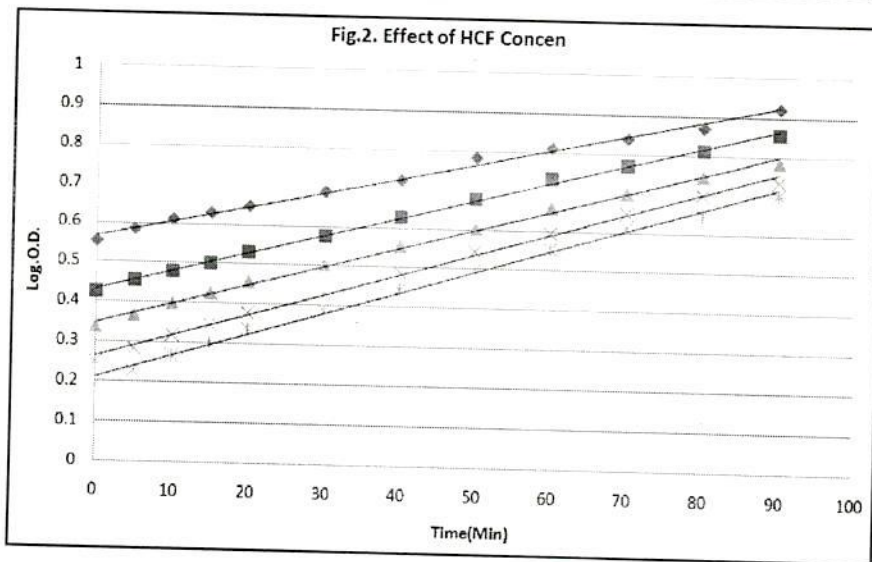
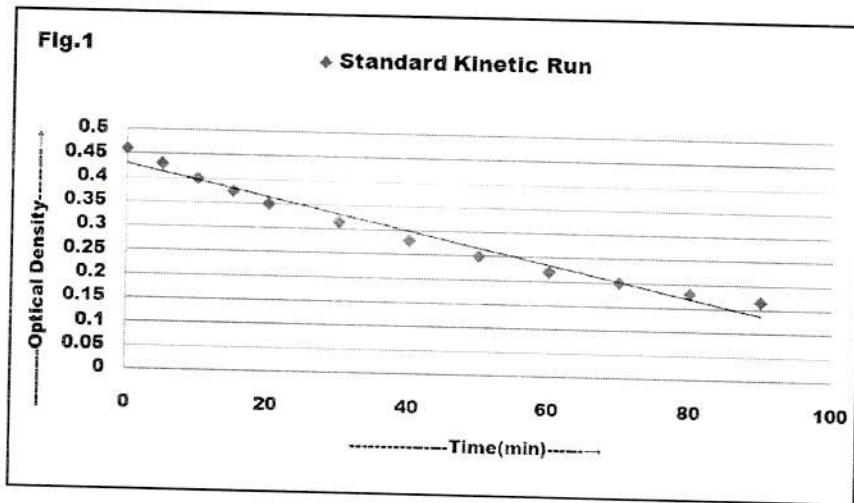
Temp in $^\circ C$	25	30	35	40	45	
$K \times 10^4 \text{min}^{-1}$	0.564	0.700	1.12	1.41	2.23	
Temp in T(k°)	298	303	308	313	318	
$1/T \times 10^3$	3.35	3.30	3.25	3.20	3.15	
$\log K_r$	-2.2487	-2.1549	-1.951	-1.850	-1.6517	
$\log K_r/kT/h$	-13.3533	-13.2308	-13.0720	-13.0536	-13.0091	Mean
Temp Coefficient per $10^\circ C$	-	1.99	1.98	1.99	-	1.99
E_a kcal/mol ¹ by Graph	-	-	11.38	-	-	11.38
E_a kcal/mol ¹ by calculation	-	11.29	11.74	11.23	-	11.42
ΔH^\ddagger kcal/mol ¹	-	-	11.18	-	-	11.18
$A \times 10^5 \text{sec}^{-1}$	2.70	2.60	2.76	2.61	2.76	2.68
ΔS^\ddagger e.u.	-23.44	-23.55	-23.51	-23.59	-23.47	-23.51
ΔG^\ddagger kcal/mol ¹	18.16	18.32	18.42	18.56	18.65	18.42

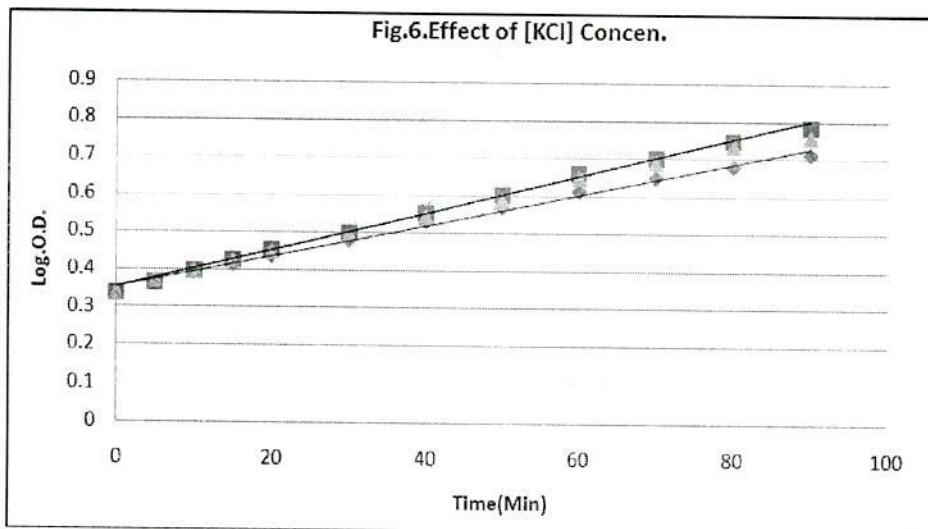
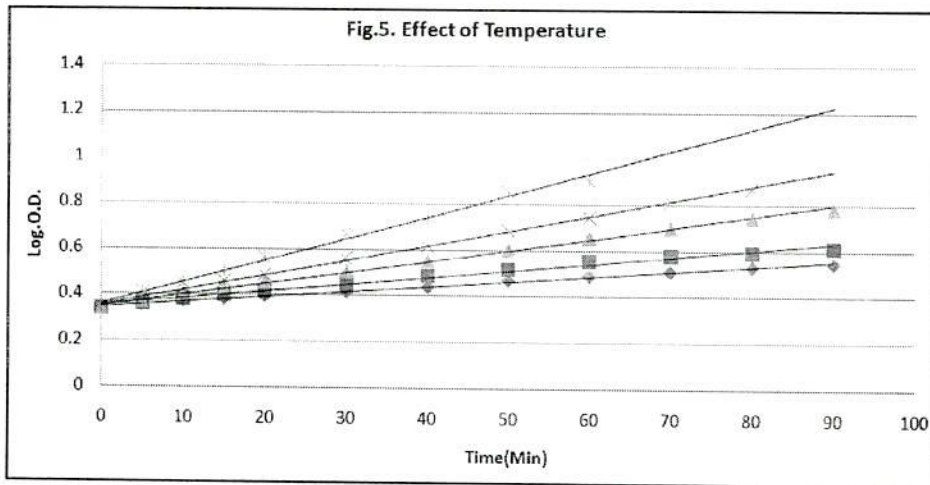
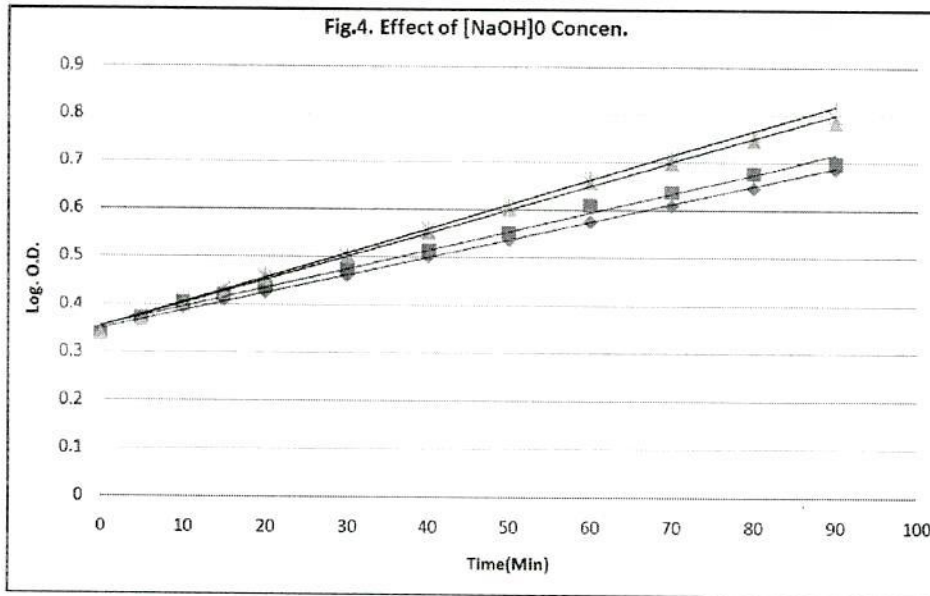
Effect of [HCF(III)]₀: The investigation of the effect of HCF(III) concentration on the specific reaction rate, shows that, when the Pi-AH concentration is in excess, pseudo first order specific rate increases with increase in HCF(III) concentration indicating that the rate of disappearance of HCF(III), obey's the first order kinetics. To confirm the order of the reaction with respect to the HCF(III) the values of $(-dc/dt)$ were determined by plotting the optical density against the time for different initial concentrations of oxidant. From the plot of $\log(-dc/dt)$ vs $\log C_0$, the order of reaction with respect to HCF(III) was found to be one. (Fig.2)

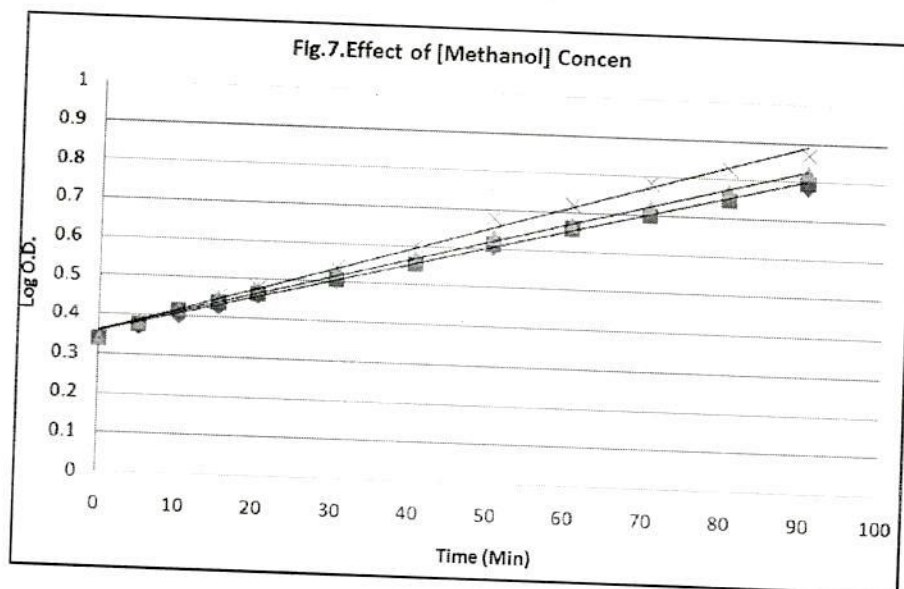
Effect of [Pi-AH]₀: The reaction rate increased with an increase in [Pi-AH]₀ and consequently k_2 remained reasonably constant. From the plot of $\log(-dc/dt)_0$ versus $\log [Pi-AH]_0$ the order of reaction is evaluated which comes out to be nearly one. This confirms the first order behavior of the reaction with respect to Pi-AH. (Fig.3)

Effect of [NaOH]₀: The plot of \log of optical density against the time in minute was plotted. The kinetic study of Pi-AH by HCF(III) was found to be directly proportional to the [NaOH]. (Fig.3)

Effect of Temperature: The reaction was conducted at five different temperatures in the $25-45^\circ C$ range. The plot of \log of optical density against the time in minute was plotted. Activation parameters for the overall reaction evaluated from the Arrhenius and Eyring linear plots, are listed in Table.1, (Fig.4)



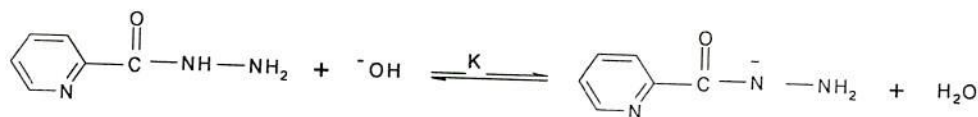




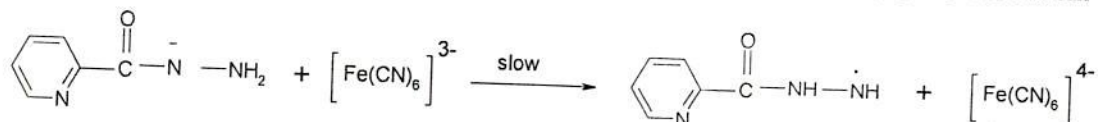
Effect of Salt $[KCl]_0$: The effect of ionic strength (μ) on the reaction rate was studied by varying $[KCl]_0$. The result obtained revealed that the oxidation rate increased as the ionic strength increased that is concentration dependent. In order to observe the effect of foreign ions on the rate, the reaction was carried out using different salts such as $NaNO_3$, $NaCl$, $LiCl$, in place of KCl . The result showed that the oxidation rate was not affected by replacing the salt. Addition of $Fe(CN)_6^{4-}$ (reduction product of oxidant) up to $1.25 \times 10^{-3} \text{ mol dm}^{-3}$ has no effect on the reaction rate. (Fig.6)

Effect of Dielectric Constant of the Medium $[CH_3OH]$: The effect of the solvent dielectric constant (D) on the rate was monitored by conducting the reaction in binary solvent ($H_2O + CH_3OH$). The result of $[CH_3OH]_0$ variations showed that the rate of oxidation of Pi-AH was found to be increased with significant decrease in dielectric constant of the medium, which may be due to the fact that the rate determining step may have involved between the ions of similar charges. The values of dielectric constant of the medium (D) were reported by Gosta-Akerlof. Blank experiment showed that oxidation of CH_3OH by HCF(III) under experimental conditions was negligible (Fig.7). According to (Haber and Weiss, 1934) the simple process is the stepwise transfer of an electron from reductant to oxidant. Redox reaction may take place via simple electron transfer or through the agency of the atom or ion transfer. Thus (Traube and Kind, 1954) while studying the reaction of $CO(NH_3)_5Cl^{2+}$ and Cr^{2+} in $HClO_4$ solution, suggested the formation of Cr^{3+} which was found in the form of $CrCl^{2+}$. They also obtained similar results for the very fast exchange of Cr^{2+} with $Cr(H_2O)_5Cl^{2+}$ in $HClO_4$. Potassium ferricyanide falls into the class of oxidizing agents comprising ceric sulphate, ammonical silver nitrate and felhing's solution in all of which the oxidizing species is an electron abstracting ion. $[Fe(CN)_6]^{3-} + e^- \rightarrow [Fe(CN)_6]^{4-}$

Oxidation reaction in the present case is the rate determining step between two anions and free radical. It is found that $\dot{O}H$ ion which seems to act as a catalyst, attacks the substrate hydrazide in rate determining step. The attack of $\dot{O}H$ ion on the substrate molecule should take place at the nitrogen which is adjacent to carbonyl group. It seems that, $\dot{O}H$ ion abstracts a proton from nitrogen and produces negative ion. The reaction may be written as



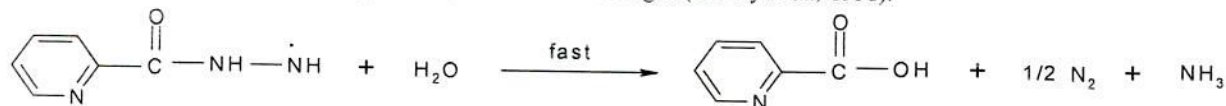
The rate determining step seems to be the transfer of an electron from this anion to $Fe(CN)_6^{3-}$ ion, hence we can write.



(Frank and Krishna Rao, 1979) have shown the formation of free radical in the oxidation of hydrazides by other reagents. The formation of free radical by electron transfer has also been shown by Haskar, Mehrotra and Ramachandra (1979).

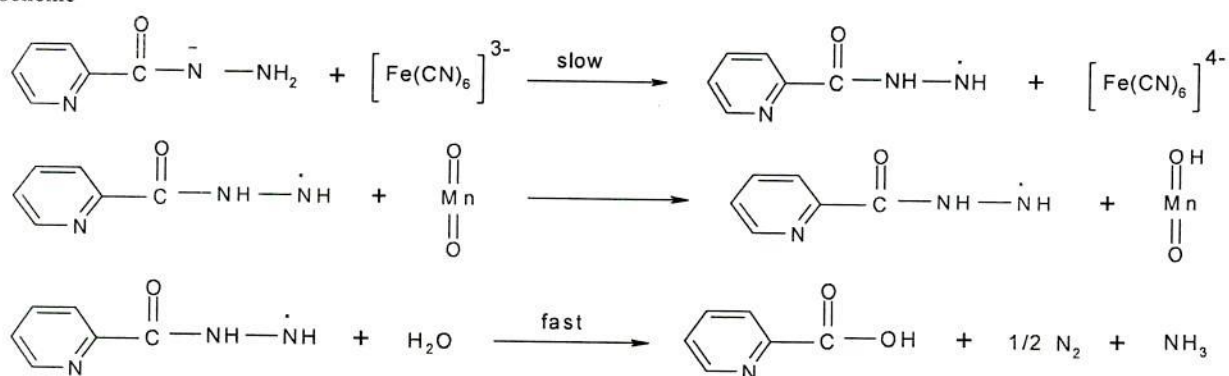


The mole ratio for this reaction was found to be 1:1; it seems to be probable that the free radicals formed from the substrate undergo hydrolysis to produce carboxylic acid, ammonia and nitrogen (Ladury *et al.*, 1958).



As the reaction is first order with respect to the oxidant, substrate as well as OH^- ion concentration. The first step has been shown as an equilibrium step, while second step seems to be rate determining step. Thus, the overall mechanism for the oxidation reaction between HCF(III) and Pi-AH in Sodium hydroxide medium can be represented taking into consideration the kinetic behavior of the oxidation of Pi-AH. Thus, on the basis of the foregoing kinetic evidence following sequence of reactions for the oxidation of Pi-AH is as shown in the scheme as follows.

Scheme



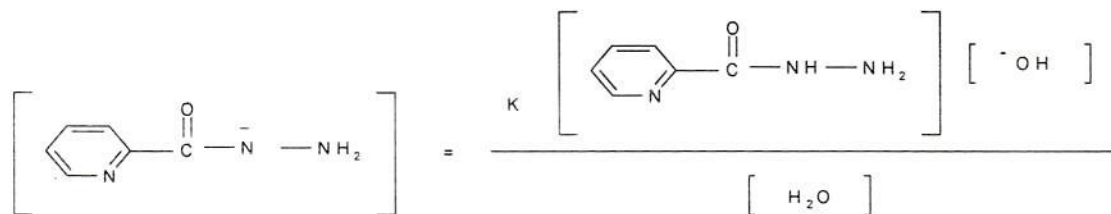
From step (ii) the rate of conversion of $[\text{Fe}(\text{CN})_6]^{3-}$ should be given by

$$\frac{d[\text{Fe}(\text{CN})_6]^{3-}}{dt} = K_1 \left[\text{Pyridine-C(=O)-N}^-\text{-NH}_2 \right] [\text{Fe}(\text{CN})_6]^{3-}$$

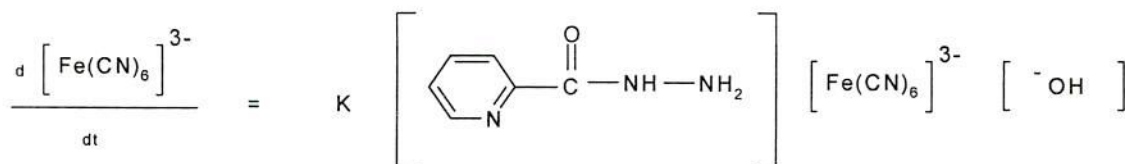
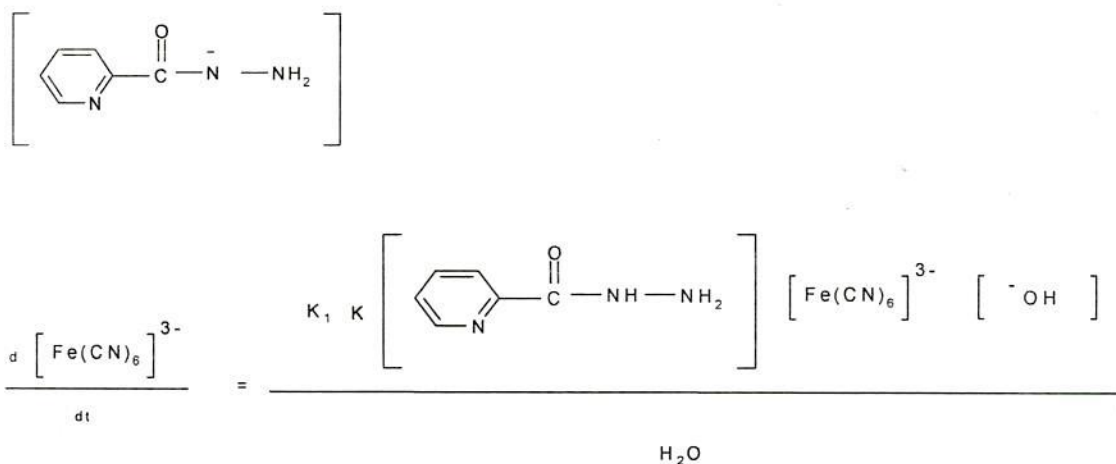
However, the equilibrium constant for the reaction

$$K = \frac{\left[\text{Pyridine-C(=O)-N}^-\text{-NH}_2 \right] [\text{H}_2\text{O}]}{\left[\text{Pyridine-C(=O)-NH-NH}_2 \right] [\text{OH}^-]}$$

On rearrangement



Substituting the values for



$$K = \frac{K_1 K}{\text{H}_2\text{O}}$$

Conclusion

This shows that, the reaction is found to be first order in substrate (Pi-AH) and oxidant as HCF (III). The specific rate of the reaction is directly proportional to sodium hydroxide concentration. The salt effect is positive in addition of neutral salt (ionic strength) increases the rate of reaction, hence the reaction must be between species of the same charge. The reaction was characterized by large negative entropy of activation ΔS^\ddagger which suggests that the formation of a rigid transition state. While fairly high positive values of free energy of activation state is highly solvated. The effect of variation of chloride ion concentration on the rate of oxidation of hydrazides is found to be concentration dependent. Allyl acetate (Weiberg, 1959) exerted an appreciable inhibitory effect on reaction rate indicates the free radical intermediate formation during the reaction and free radical is detected by acrylonitrile test. The mole ratio between oxidant to substrate was found to be 1 : 1, which indicates that, one mole of oxidant is required to oxidize HCF(III) one mole of the substrate (Pi-AH).

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