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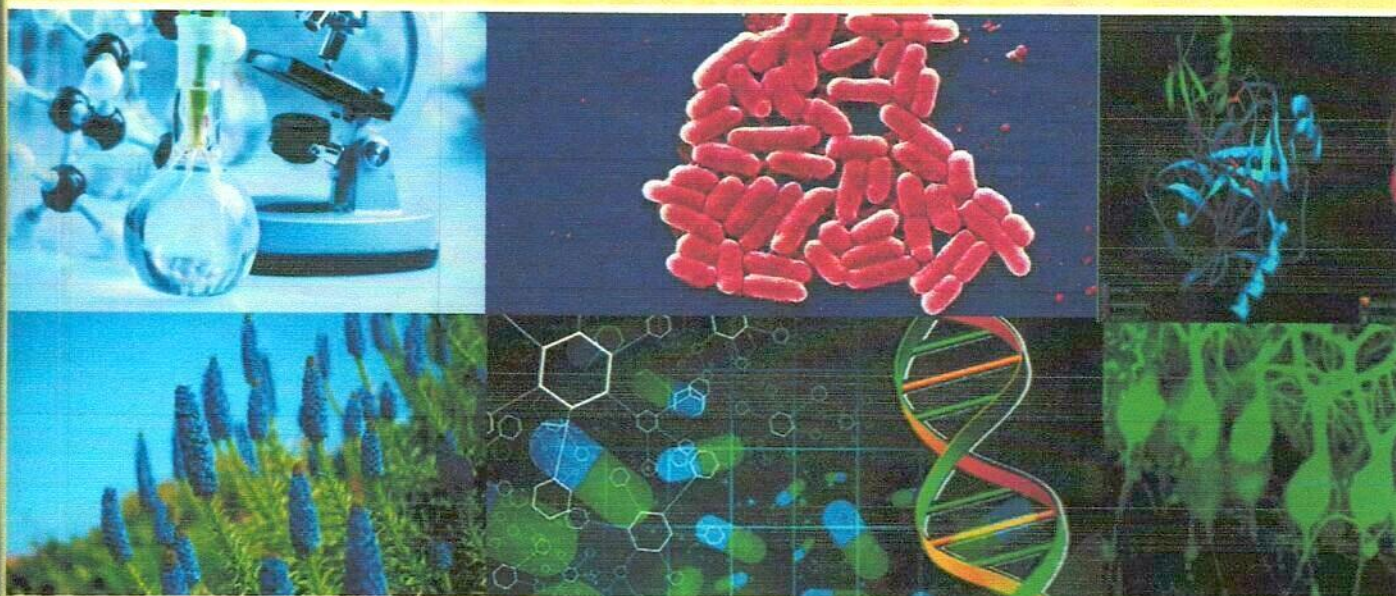
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Contemporary Research in Chemical and Life Sciences - 2015

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22nd and 23rd April, 2015



Organized by

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REDOX REACTION OF ISO-NICOTINIC ACID HYDRAZIDE BY HEXACYANOFERRATE(III) A KINETICS AND MECHANISTIC APPROACH

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ABSTRACT :

The Spectrophotometric study of oxidation of reaction between hexacyanoferrate (III) and iso-Nicotinic acid hydrazide (NAH) was carried out kinetically for determination of its mechanism in sodium hydroxide medium under pseudo first order condition. The formation of complex takes place between the reactants, which on decomposition in the subsequent step gives the products. The reaction proceeds by direct one electron transfer with intervention of free radical and the order of reaction was found to be one with respect to hydrazide and hexacyanoferrate (III). The specific rate increases with an increase in the concentration of hydrazide and hexacyanoferrate (III). The salt that is ionic strength effect is positive i.e. addition of potassium chloride increases the rate of reaction; hence the reaction must be between species of the same charges. Increase in sodium hydroxide concentration increases the reaction rate and decreases with decrease in dielectric constant. The effect of temperature was studied between 25 to 45 °C. The activation parameters were determined and the values support the proposed mechanism as evidenced by considerable decrease in entropy of activation. ($-\Delta S^\ddagger = 24.37 \text{ J K}^{-1} \text{ mol}^{-1}$) The progress of the reaction was followed by measuring the absorbance (A) of the hexacyanoferrate (III) at 420 nm.

Keywords : hexacyanoferrate (III) , NAH, hydrazides, kinetics, oxidation, absorbance, redox reaction

INTRODUCTION :

Hydrazides are physiologically active tested for their anti bacterial^{16, 23} biological activity⁷, anti inflammatory properties¹³, anti leprosy⁸, anti-convulsive action¹⁸, anti-thelminities¹, to regulate and inhibit the growth of the plants²⁴, anti oxidants for poly olefins and polyurethanes. They have been extensively studied as a strong antituberculostatic agent.¹¹ Some hydrazides are used in synthesis of certain amines, aldehydes and heterocyclic compounds. The applications of hydrazides and their derivatives in heat and corrosive stabilization of cellulose, applicability in plastics and cable insulation⁴, in sensitizing electrographic layers of polyvinyl carbazole⁷, dihydrazides also used in cigarette filters for the removal of aldehydes from tobacco smoke. According to Haber and weiss⁹ 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 done¹⁵. The kinetics of oxidation of nicotinoyl and iso-nicotinoyl hydrazides by Iron(III) in the presence of 1:10 phenanthroline⁵ and the kinetics of Ag⁺ catalysed oxidation of nicotinic and iso-nicotinic acid hydrazides¹² has been investigated. The study of the effect of position of Nicotinic acid hydrazide group on rate and mechanism of oxidation reaction, by HCF(III) is done in alkaline medium.

MATERIAL AND METHOD :

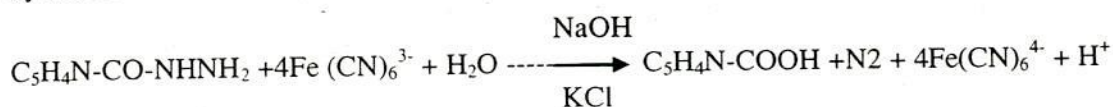
The iso-Nicotinic acid hydrazide (NAH) was prepared by reported procedure²⁰ and stored in amber colored bottles kept in dark place. K₃Fe(CN)₆, sodium hydroxide ,Potassium chloride and methanol used were of AR grade. The double distilled water was used throughout the experiment. All possible precautions were taken to avoid the impurities. Their purity was checked after recrystallisation and from physical Constant 161°C.

Kinetic Procedure: λ Max for HCF(III) is Determined by measuring Absorbance of 5.0×10^{-4} M Solution of HCF(III) 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 nm³. Reaction were performed

under pseudo-first order conditions: $[\text{hydrazide}] \geq [\text{hexacyanoferrate (III)}]$ in a conical Pyrex glass (coated black), thermostated at 35°C . The oxidation was initiated by adding a thermostated solution of hydrazide to a thermostated solution of HCF(III) containing the required quantities of NaOH. The progress of the reaction was followed by measuring the absorbance (A) of hexacyanoferrate (III) at 420 nm ($\epsilon = 1015 \text{ dm}^3 \text{ mol}^{-1} \text{ cm}^{-1}$) employing Spectronic 20 (Milton Roy Company) and 1 cm path length cells. Pseudo-first order rate constants (k) were evaluated using equation 1(3), which was valid to well over 70% disappearance of HCF(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 t, respectively. The k values were in good agreement with those obtained from linear plots of $\log A$ versus time. The second order k_2 was calculated from the relationship $k_2 = k_1 / [\text{hydrazide}]_0$

Stoichiometry and products :

The Stoichiometry of the reaction was determined using known excess of HCF(III) over hydrazide concentration and results consistent with following equation



The iso-Nicotinic acid was detected by paper chromatography³. The nitrogen was detected by lime tests²¹. The resultant mixture at the end of the reaction was rendered neutral after removal of $\text{Fe}(\text{CN})_6^{4-}$. 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 hydrazides¹⁰ is well documented in chemical literature. The formation of ammonia also takes place in addition to the formation of respective aryloxy acetic acid and nitrogen¹⁷.

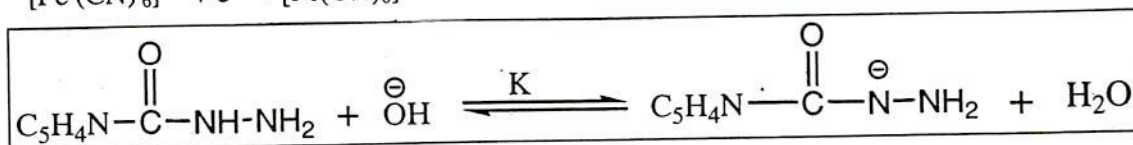
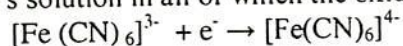
Reaction Intermediates: The formation of free radical during the reaction was confirmed via neither induced polymerization of acrylonitrile nor reduction of HgCl_2 occurred in the absence of one of the two reactants.

RESULT AND DISCUSSION :

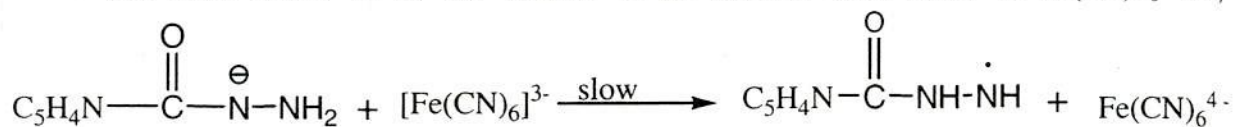
The reaction proceeds with measurable velocity and shows the first order rate constant goes on slightly decreasing with the time. The plot of time in minute against optical density. (Fig. 1)

The Effect of concentration of reactants [hexacyanoferrate (III)] show that the order of reaction with respect to HCF(III) is one. The Effect of concentration of reactants [hydrazide] confirmed the first order behavior of the reaction w.r.t. iso-Nicotinic acid hydrazide. The Effect of concentration of alkali [NaOH] was found to be directly proportional to the concentration of sodium hydroxide. The effect of temperature used to calculate activation parameters for the overall reaction evaluated from the Arrhenius and Eyring linear plots, are listed in Table 1. There was no effect of concentration of Salt [KCl] on the reaction rate. Effect of Dielectric Constant of the Medium [CH_3OH] was negligible.

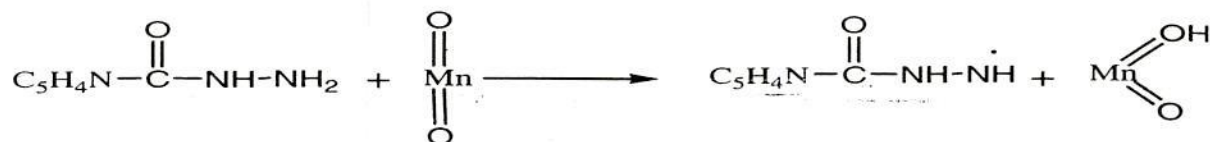
According to Haber and Weiss⁹ is the stepwise transfer of an electron from reductant to oxidant. Thus Traube and King¹⁹ while studying the reaction of $\text{CO}(\text{NH}_3)_5\text{Cl}^{2+}$ and Cr^{2+} in HClO_4 solution, suggested the formation of Cr^{3+} which was found in the form of CrCl^{2+} . They also obtained similar results for the very fast exchange of Cr^{2+} with $\text{Cr}(\text{H}_2\text{O})_5\text{Cl}^{2+}$ 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.



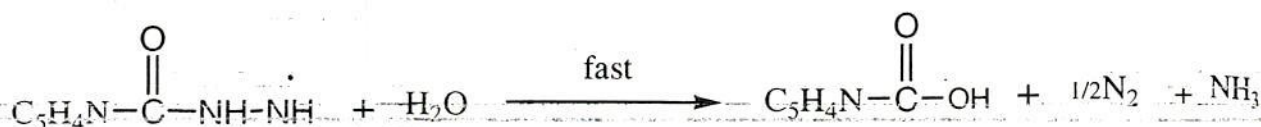
The RDS seems to be the transfer of an electron from anion to $\text{Fe}(\text{CN})_6^{3-}$ ion,



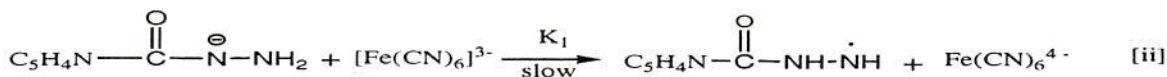
Frank and Krishna Rao⁵ have shown the formation of free radical in the oxidation of hydrazides by other reagents. The formation of free radical by electron transfer has shown by Haskar, Mehrotra and Ramachandra¹⁰



The mole ratio for this reaction is 1:1, The free radicals formed from the substrate undergo hydrolysis to produce carboxylic acid, ammonia and nitrogen.¹⁴



Scheme



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

$$-\frac{d[\text{Fe}(\text{CN})_6]^{3-}}{dt} = K_1 [\text{C}_5\text{H}_4\text{N}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\ominus}{\text{N}}-\text{NH}_2] [\text{Fe}(\text{CN})_6]^{3-} \quad \text{[iv]}$$

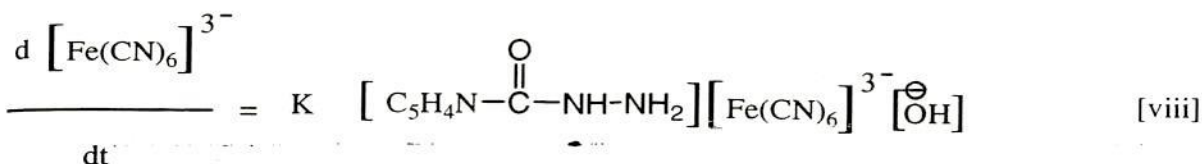
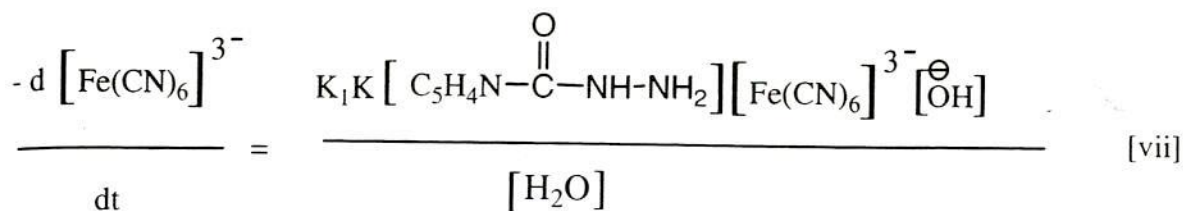
However, the equilibrium constant k for the first reaction can be written as:

$$K = \frac{[\text{C}_5\text{H}_4\text{N}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\ominus}{\text{N}}-\text{NH}_2] [\text{H}_2\text{O}]}{[\text{C}_5\text{H}_4\text{N}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}-\overset{\ominus}{\text{N}}\text{H}_2] [\overset{\ominus}{\text{O}}\text{H}]} \quad \text{[v]}$$

On rearrangement,

$$[\text{C}_5\text{H}_4\text{N}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\ominus}{\text{N}}-\text{NH}_2] = K \frac{[\text{C}_5\text{H}_4\text{N}-\overset{\text{O}}{\parallel}{\text{C}}-\text{NH}-\overset{\ominus}{\text{N}}\text{H}_2] [\overset{\ominus}{\text{O}}\text{H}]}{[\text{H}_2\text{O}]} \quad \text{[vi]}$$

Substituting these values for $[\text{C}_5\text{H}_4\text{N}-\overset{\text{O}}{\parallel}{\text{C}}-\overset{\ominus}{\text{N}}-\text{NH}_2]$ into equation we get



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

CONCLUSION:

The reaction is first order in substrate and oxidant. The specific rate is directly proportional to $[\text{NaOH}]$. The large negative entropy ΔS^\ddagger , suggests the formation of a rigid transition state. While fairly high positive values of free energy of activation state is highly solvated. The effect of chloride ion concentration was found to be concentration dependent, indicates the reaction must be between species of the same charge. Allyl acetate²² 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 is oxidant to substrate was found to be 1: 1,

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Table No.1 : Effect of Temperature :

Temp in °C	25	30	35	40	45	
$K \times 10^2 \text{ min}^{-1}$	0.601	0.780	1.19	1.56	2.36	
Temp in T(k°)	298	303	308	313	318	
$1/T \times 10^3$	3.35	3.30	3.25	3.20	3.15	
$K_r \times 10^2 \text{ min}^{-1}$	0.601	0.780	1.19	1.56	2.36	
log K_r	-2.2211	-2.1079	-1.9244	-1.8069	-1.6270	
log $K_r/kT/h$	-15.0134	-14.9074	-14.7310	-14.6205	-14.4475	Mean
Temp Coefficient per 10 °C	-	1.98	1.96	1.98	-	1.97
$E_a \text{ kcal/mol}^{-1}$ by Graph	-	-	12.20	-	-	12.20
$E_a \text{ kcal/mol}^{-1}$ by calculation	-	12.46	12.70	12.30	-	12.82
$\Delta H^\ddagger \text{ kcal/mol}^{-1}$	-	-	13.27	-	-	13.27
$A \times 10^5 \text{ sec}^{-1}$	2.51	2.28	2.46	2.27	2.53	2.41
$\Delta S^\ddagger \text{ e.u.}$	-24.17	-24.42	-24.33	-24.55	-24.38	-24.37
$\Delta G^\ddagger \text{ kcal/mol}^{-1}$	20.47	20.67	20.76	20.95	21.02	20.77

