

CHAPTER IV

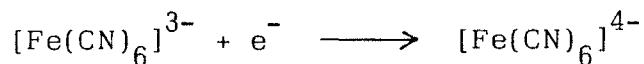
CHAPTER-IV

DISCUSSION

A knowledge of the mechanism of chemical reaction has advanced, it has become increasingly clear that, the formation of final product from the initial reactants, generally takes place by a number of relatively simple steps in each of which the amount of atomic rearrangement is at maximum. The most rational approach of Arrhenius¹ for explaining the occurrence of chemical reaction is a placing the concept of molecular activation as a pre-requisite to chemical reaction. This concept of activation is now universally accepted and forms the basis of all subsequent theories of chemical reactions.

Since, the present work is concerned with the redox reaction involving $\text{Fe}(\text{CN})_6^{-3}$ ion. It is rather necessary to state the present views on mechanism of redox reaction in general. For the oxidation reduction reactions, a number of mechanisms have been proposed. The simple process according to Haber and Weiss² 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 King,³ 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 oxidising agents comprising ceric sulfate, ammonical silver nitrate and Fehling's solution in all of which the oxidising species is an electron abstracting ion.





Consequently, ferricyanide has been used in systems obviously favoured for oxidation in this manner, that is extraction of an electron from an electron rich site. Similar oxidations are also encountered in biological systems of the cytochrome type, where, a "one electron transfer" is involved. However, there are innumerable instances where the reagent has also been utilised with considerable success even though it's capability was not originally apparent. The various types of oxidations, where alkaline ferricyanide has been successfully employed are reported.

In order to discuss the possible mechanism for oxidation of iso-Nicotinic and Nicotinic acid hydrazides by alkaline hexacyanoferrate (III) ion, it is necessary to summarise the results obtained in the present investigation.

1. The oxidation of iso-Nicotinic and Nicotinic acid hydrazides is first order w.r.t. hexacyanoferrate (III) ion.
2. Both these reactions are first order w.r.t. organic substrate (hydrazide), specific rate increases with an increase in the concentration of organic substrate (hydrazide).
3. The specific rate of the reaction is directly proportional to sodium hydroxide concentration in both the hydrazides studied.
4. The salt effect is positive ie addition of neutral salt; increases the rate of reaction, hence the reaction must be between species of the same charge.

5. The various activation parameters determined are as follows

Reaction	Temp co-efficient Per10°C	Ea Kcal mole ⁻¹	A x10 ⁵ Sec ⁻¹	ΔG^\ddagger Kcal mole ⁻¹	ΔS^\ddagger (e.u)	ΔH^\ddagger Kcal mole ⁻¹
iso-Nicotinic acid hydrazide	1.97	12.20	2.410	20.77	-24.37	13.27
Nicotinic acid hydrazide	1.98	12.81	3.021	20.72	-26.45	12.58

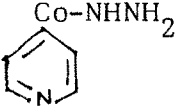
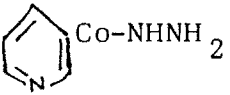
Both the reactions were characterised by large negative entropy of activation ΔS^\ddagger , suggests the formation of a rigid transition state. While fairly high positive values of free energy of activation ΔG^\ddagger and enthalpy of activation ΔH^\ddagger indicate that, the transition state is highly solvated.

6. The rate of oxidation of Nicotinic acid hydrazide is slightly more than that of iso-Nicotinic acid hydrazide.
7. The effect of variation of chloride ion concentration on the rate of oxidation of hydrazides is found to be concentration dependent.
8. The rate is dependent on ionic strength and increases with increase in ionic strength of the reaction mixture, indicating that the reaction must be between species of the same charge.
9. Allyl acetate⁴ 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.

10. The mole ratio is oxidant to substrate was found to be 1:1, which indicates that, one mole of oxidant is required to oxidise one mole of the substrate.
11. The oxidation products identified in these reactions are as follows :
- i) iso-Nicotinic acid hydrazide \longrightarrow iso-Nicotinic acid.
 - ii) Nicotinic acid hydrazide \longrightarrow Nicotinic acid.
12. In addition to these products Nitrogen is detected by lime test⁶ and Ammonia by Nessler's reagent.⁷

The kinetic data of two hydrazides of iso-Nicotinic and Nicotinic acids shows the following order of reactivity.

- | | | |
|-----|---|---------------------------------------|
| i) | iso-Nicotinic acid hydrazide | Mean $k \times 10^2 \text{ min}^{-1}$ |
| |  | = 1.19 |
| ii) | Nicotinic acid hydrazide | |
| |  | = 1.26 |

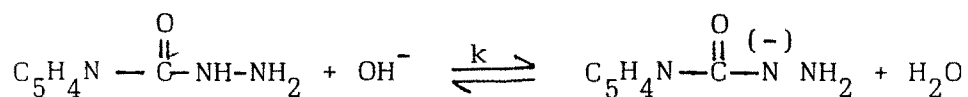
Persual of the above order of reactivity indicates that, the overall rates of oxidation of both the compounds studied are found to be similar.

There is no considerable difference in the rate of oxidation but due to the change in position of carboxylic group in the pyridine, the Nicotinic acid is slightly more reactive than that of iso-Nicotinic acid.

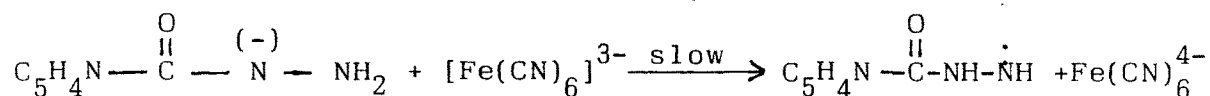
This may be attributed to the presence of carboxylic group at position No.4 to the nitrogen from pyridine ring lowers the oxidation rate than that of presence of it to the position ^{No.3} to the nitrogen from pyridine ring.

The fact that, the oxidation reaction in the present case, rate determining step between two anions and free radical is also involved. It is found that OH^- ion which seems to act as a catalyst attacks the substrate hydrazide molecule to form a negative ion and this negative ion is involved in rate determining step. The attack of OH^- ion on the substrate molecule should take place at the nitrogen adjacent to carbonyl group.

It seems that OH^- ion abstracts a proton from nitrogen and produces negative ion. The reaction may be written as

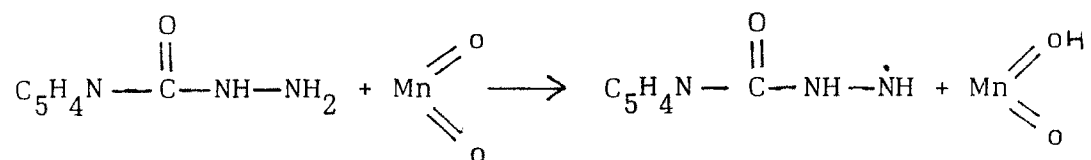


The rate determining step seems to be the transfer of an electron from this anion to $[\text{Fe}(\text{CN})_6]^{3-}$ ion, hence we can write,

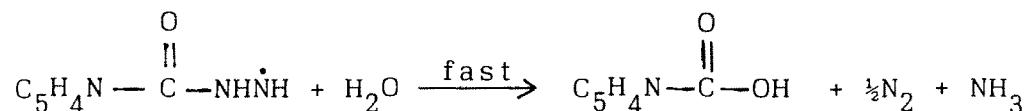


Frank and Krishna Rao⁸ have shown the formation of

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 Ramachandra⁹ as :

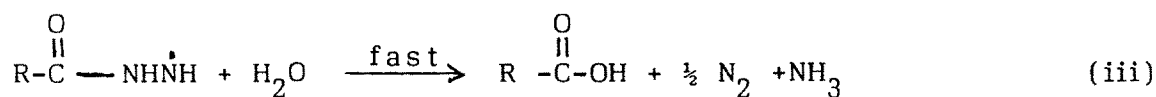
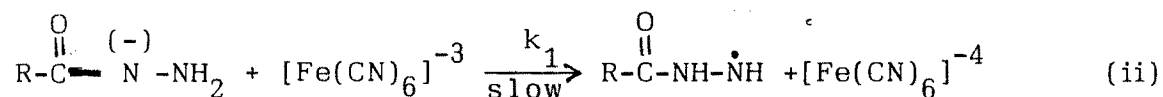
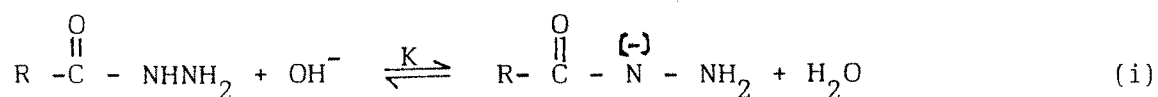


As per our observation the mole ratio for this reaction is 1:1, it seems probable that the free radicals formed from the substrate undergo hydrolysis to produce carboxylic acid, ammonia and nitrogen.¹⁰



As the reaction is first order w.r.t. oxidant, substrate as well as OH^- ion concentration. The first step has been shown as an equilibrium reaction, while second step seems to be the rate determining step. Thus, the overall mechanism for the oxidation reaction between hexacyanoferrate (III) and hydrazide in alkaline medium can be represented taking into consideration the close similarity in the kinetic behaviour of the oxidation of the two hydrazides, iso-Nicotinic and Nicotinic acid hydrazides respectively.

Thus, on the basis of the foregoing kinetic evidence following sequence of reactions for the oxidation of iso-Nicotinic acid and Nicotinic acid hydrazides is suggested.



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

$$\frac{-d [\text{Fe}(\text{CN})_6]^{3-}}{dt} = k_1 [R-\overset{\text{O}}{\parallel}{\text{C}}-\overset{(-)}{\text{N}}-\text{NH}_2] [\text{Fe}(\text{CN})_6]^{-3} \quad (\text{iv})$$

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

$$K = \frac{[R-\overset{\text{O}}{\parallel}{\text{C}}-\overset{(-)}{\text{N}}-\text{NH}_2][\text{H}_2\text{O}]}{[R-\overset{\text{O}}{\parallel}{\text{C}}-\text{NHNH}_2][\text{OH}^-]} \quad (\text{v})$$

Re-arrangement gives,

$$[R-\overset{\text{O}}{\parallel}{\text{C}}-\overset{(-)}{\text{N}}-\text{NH}_2] = k \frac{[R-\overset{\text{O}}{\parallel}{\text{C}}-\text{NHNH}_2][\text{OH}^-]}{[\text{H}_2\text{O}]} \quad (\text{vi})$$

Substituting these values for $[R-\overset{\text{O}}{\parallel}{\text{C}}-\overset{(-)}{\text{N}}-\text{NH}_2]$ into equation (iv) we get :

$$\frac{-d [\text{Fe}(\text{CN})_6]^{3-}}{dt} = \frac{k_1 K [R-\overset{\text{O}}{\parallel}{\text{C}}-\text{NHNH}_2] [\text{Fe}(\text{CN})_6]^{3-} [\text{OH}^-]}{[\text{H}_2\text{O}]} \quad (\text{vii})$$

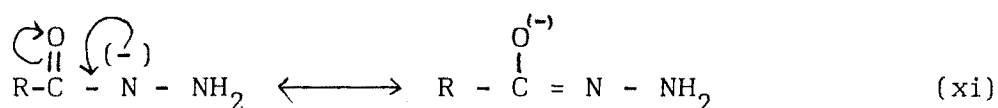
$$\frac{d[\text{Fe}(\text{CN})_6]^{3-}}{dt} = k [R-\overset{\text{O}}{\parallel}{\text{C}}-\text{NHNH}_2] [\text{Fe}(\text{CN})_6]^{3-} [\text{OH}^-] \quad (\text{viii})$$

where $k = k_1 K / [\text{H}_2\text{O}]$

This shows that the reaction should be first order in substrate, oxidant as well as OH^- ion concentration as has been observed experimentally. Same mechanism has shown in the third step which has been suggested by Ladbury and Cullis.¹⁰

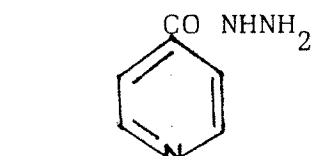
This mechanism is also in accordance with the other observations namely :

1. Ionic strength effect and dielectric constant effect show that the reaction is between ions of similar charge as has been suggested in step (II).
2. Nitrogen and ammonia have been detected as final products of the reaction.
3. The reaction proceeds via free radical formation.
4. Both the reactions are characterized by large negative entropy of activation ΔS^\ddagger suggests the formation of a rigid transition state. The negative ion of $\text{R}-\overset{\overset{\text{O}}{\parallel}}{\text{C}}-\overset{\ominus}{\text{N}}-\text{NH}_2$ seems to be stabilised through resonance interaction as



5. The hydrazides undergo oxidation through the formation of free radical which is further decomposed to corresponding acid and Nitrogen, this is according to Haskar et.al.⁹ Which is further supported by the observation of Kelly et.al.¹¹
6. A large negative entropy of activation exhibited by this oxidation indicates the reaction may involve the species of same charge or charged species and neutral molecule.^{12,13}

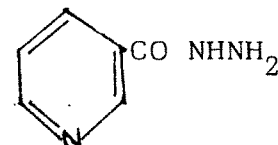
To find out, the order of reactivity in heterocyclic hydrazides, their first order rate constants are compared under the same reaction conditions



iso-Nicotinic acid

hydrazide (I)

$$K = 1.19 \times 10^2 \text{ min}^{-1}$$



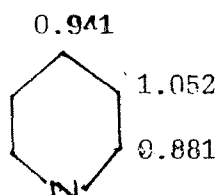
Nicotinic acid hydrazide

(II)

$$k = 1.26 \times 10^2 \text{ min}^{-1}$$

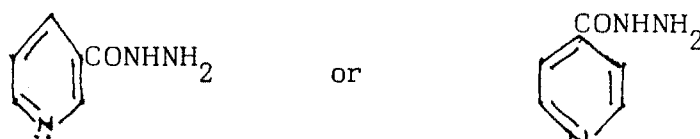
The kinetic data for these two hydrazides of pyridine carboxylic acid (or heterocyclic hydrazides) shows that they are reacting almost with the same rate.

The slight variation in the rates of oxidation in these hydrazides may be explained on the basis of molecular orbital calculations which show that the π electron density at Position 3 of the pyridine ring is higher than that of position 2 or 4. This is a consequence of nitrogen being more electronegative than carbon, and the nitrogen atom therefore causes a drift of electrons in it's direction. This drift denudes the 2 and 4 positions of electrons by a resonance interaction (I) and the effect is very strong.



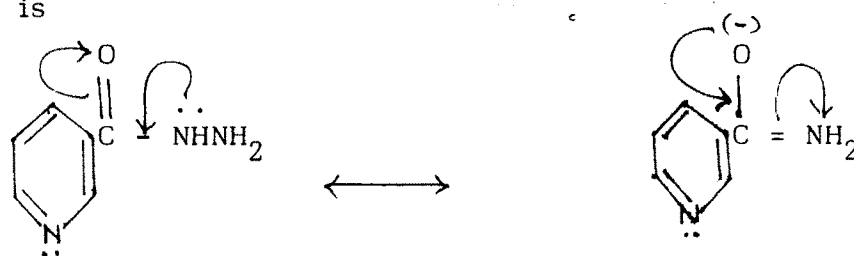
The π electron densities at the various positions of the pyridine ring have been calculated by a self consistent field method¹⁴ and are reported here (II).

Rates of oxidation of pyridine β and γ hydrazides correlate well with the electron densities at β and γ positions of pyridine. This slight variation in the electron densities at β and γ positions of pyridine may affect the rate of formation of the radical ion by hydride abstraction to a some extent.



Thus causing oxidation of β isomer slightly faster than γ isomer.

Though the possible resonance in the case of these hydrazides is



This effect is more powerful in the case of β isomer than the γ isomer. Since, carbonyl carbon withdraws electron density from the adjacent ring carbon by induction, thus makes the resonance stronger and therefore increases the rate of formation of radical ion.

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