CHAPTER–IV

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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 Arrhenius[1] 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 $Fe\ (CN)_6^{-3}$ 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 simpler process according to Haber and Weiss[2] 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 reactions 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 $CrCl^{2+}$ complex. 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 oxidising agents comprising ceric sulfate, ammonical silver nitrate and Fehling's solution in all of which the oxidising species is an electron abstracting ion.

$$[Fe(CN)_6]^{3-} + e^- \longrightarrow [Fe(CN)_6]^{4-}$$

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 utilized with considerable success even though its 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 n-butyric and iso-butyric acid hydrazides by alkaline hexacyanoferrate(III) ion, it is necessary to summarise the results obtained in the present investigation.

1) The oxidation of n-butyric and iso-butyric 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 various activation parameters determined are as follows :

Reaction oxidation	Temp. co-efficient per 10°C	E_a K cal. $mole^{-1}$	$A\times10^{-4}$ sec^{-1}	$\Delta G^{\neq}$ K cal $mole^{-1}$	$\Delta S^{\neq}$ (E.U.)	$\Delta H^{\neq}$ K cal $mole^{-1}$
n-Butyric acid hydrazide	1.98	13.57	0.58	21.85	-32.26	11.76
iso-butyric acid hydrazide	1.84	11.28	1.30	25.14	-39.76	12.70

Both the reactions were characterized by large negative entropy of activation $\Delta S^{\neq}$, suggests the formation of a rigid transition state. while fairly high positive values of free energy of activation $\Delta G^{\neq}$ and enthalpy of activation $\Delta H^{\neq}$ indicate that, the transition state is highly solvated.

5) The rate of oxidation of n-butyric acid hydrazide is slightly more than that of iso-butyric acid hydrazide.

6) The effect of variation of chloride ion concentration on the rate of oxidation of hydrazides is found to be concentration dependent

7) 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.

8) Allylacetate[4] exerted an appreciable inhibitory effect on the reaction rate indicates the free radical intermediate formatior during the reaction and free radical is detected by acrylonitrile test.[5]

9) The mole ratio i.e. 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.

10) The oxidation products identified in these reactions are as follows :

i) n-butyric acid hydrazide ——> n-butyric acid

ii) iso-butyric acid hydrazide ———> iso-butyric acid.

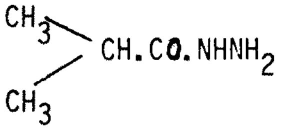
11) In addition to these products Nitrogen is detected by lime test[6] and Ammonia by Nesseler's reagent.[7]

The kinetic data of two isomers of butyric acid hydrazide show the following order of reactivity :

i) n-butyric acidhydrazide Mean k x 10^2 min^{-1}

$CH_3CH_2-CH_2CO.NHNH_2$ = 1.17

ii) iso-butyric acidhydrazide



= 1.00

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

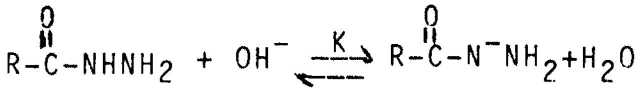
There is no considerable difference in the rate of their oxidation, but the presence of branched chain in the iso-butyric acid hydrazide has made the molecule less reactive than the n-butyric acid hydrazide.

This may be attributed to the presence of bulky methyl groups exerting steric hindrance to the attacking reagent.

Therefore, specific rate of oxidation of iso-butyric acid hydrazide is slightly slow as compare to its straight chain isomer. Similar, observations have been reported by Swami and Jagdale[8] in their investigation of oxidation of n-butyric and iso-butyric acid hydrazides by Chloramine-T.

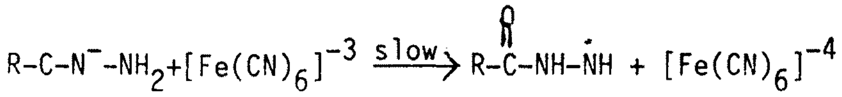
The fact that, the oxidation reaction in the present case involves rate determining between two anions and free radical is also involved. It seems probable that $\overline{OH}$ ion which seems to act as a catalyst attacks the substrate hydrazide molecule to form a negative ion and this negative ion is involved in the 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 in :



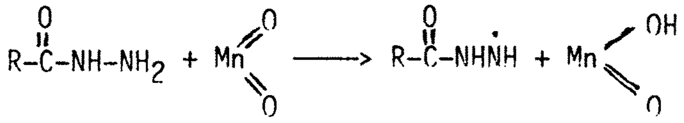
$$R-\overset{O}{\overset{\|}{C}}-NHNH_2 + OH^- \underset{}{\overset{K}{\rightleftharpoons}} R-\overset{O}{\overset{\|}{C}}-N^-NH_2+H_2O$$

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

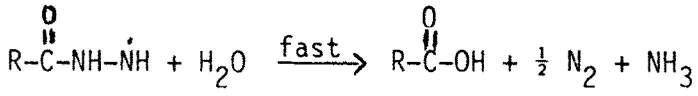


$$R-C-N^--NH_2+[Fe(CN)_6]^{-3} \xrightarrow{slow} R-\overset{O}{\overset{\|}{C}}-NH-\dot{N}H + [Fe(CN)_6]^{-4}$$

The formation of free radical by electron transfer has also been shown by Hasker, Mehrotra and Ramchandra[9] as



As the observed mole ratio for the present reaction is found to be 1:1, it seems probable that the free radical formed from the substrate undergoes hydrolysis to produce carboxylic acid, ammonia and nitrogen.[10]

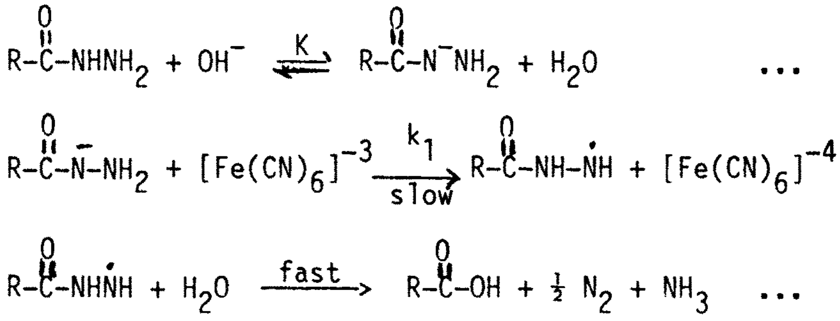


$$R-\overset{O}{\overset{\|}{C}}-NH-\dot{N}H + H_2O \xrightarrow{fast} R-\overset{O}{\overset{\|}{C}}-OH + \tfrac{1}{2}\,N_2 + NH_3$$

As the reaction has been observed to be first order w.r.t. oxidant, substrate as well as OH^- 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 n-butyric and isobutyric acid hydrazides oxidation.

I am led to believe that, the alkaline oxidation of these hydrazides by hexacyanoferrate(III) ion follows an identical reaction mechanism.

Thus, on the basis of the foregoing kinetic evidance, I propose following sequence of reactions for the oxidation of n-butyric and iso-butyric acid hydrazides.

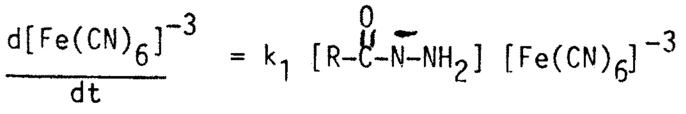


$$\mathrm{R\!-\!\overset{O}{\overset{\|}{C}}\!-\!NHNH_2 + OH^- \overset{K}{\rightleftharpoons} R\!-\!\overset{O}{\overset{\|}{C}}\!-\!N^-NH_2 + H_2O} \quad \ldots \quad (i)$$

$$\mathrm{R\!-\!\overset{O}{\overset{\|}{C}}\!-\!\bar{N}\!-\!NH_2 + [Fe(CN)_6]^{-3} \xrightarrow[slow]{k_1} R\!-\!\overset{O}{\overset{\|}{C}}\!-\!NH\!-\!\dot{N}H + [Fe(CN)_6]^{-4}} \quad (ii)$$

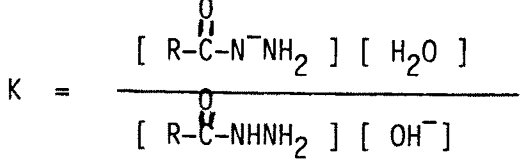
$$\mathrm{R\!-\!\overset{O}{\overset{\|}{C}}\!-\!NH\dot{N}H + H_2O \xrightarrow{fast} R\!-\!\overset{O}{\overset{\|}{C}}\!-\!OH + \tfrac{1}{2}\,N_2 + NH_3} \quad \ldots \quad (iii)$$

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



$$\frac{d[\mathrm{Fe(CN)_6}]^{-3}}{dt} = k_1\ [\mathrm{R\!-\!\overset{O}{\overset{\|}{C}}\!-\!\bar{N}\!-\!NH_2}]\ [\mathrm{Fe(CN)_6}]^{-3} \quad \ldots \quad (iv)$$

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



$$K = \frac{[\ \mathrm{R\!-\!\overset{O}{\overset{\|}{C}}\!-\!N^-NH_2}\ ]\ [\ \mathrm{H_2O}\ ]}{[\ \mathrm{R\!-\!\overset{O}{\overset{\|}{C}}\!-\!NHNH_2}\ ]\ [\ \mathrm{OH^-}]} \quad \ldots \quad (v)$$

Rearrangement gives

$$[R-\overset{O}{\overset{\|}{C}}-N^{-}NH_2] = K\,\frac{[R-\overset{O}{\overset{\|}{C}}-NHNH_2]\,[OH^{-}]}{[\,H_2O\,]} \quad \ldots \quad (vi)$$

Substituting these values for $[R-\overset{O}{\overset{\|}{C}}-N^{-}-NH_2]$ into equation (iv) we get :

$$\frac{d[Fe(CN)_6]^{-3}}{dt} = \frac{k_1K\,[R-\overset{O}{\overset{\|}{C}}-NHNH_2][Fe(CN)_6]^{-3}[OH^{-}]}{[\,H_2O\,]} \quad \ldots \text{ (vii)}$$

$$\therefore \quad \frac{d[Fe(CN)_6]^{-3}}{dt} = \frac{k_1K[R-\overset{O}{\overset{\|}{C}}-NHNH_2][Fe(CN)^{-3}[OH^{-}]}{[\,H_2O\,]} \quad \ldots \quad (viii)$$

$$\therefore \quad \frac{d\,[Fe(CN)_6]^{-3}}{dt} = k\,[R-\overset{O}{\overset{\|}{C}}-NHNH_2]\,[Fe(CN)_6]^{-3}\,[OH^{-}] \ldots \quad (ix)$$

$$\text{where} \quad k = \frac{k_1K}{[H_2O]}$$

$$\therefore \quad \frac{d[Fe(CN)_6]^{-3}}{dt} = k\,[R-\overset{O}{\overset{\|}{C}}-NHNH_2]\,[Fe(CN)_6]^{-3}\,[OH^{-}] \ \ldots \quad (x)$$

This suggests that, the reaction should be first order in substrate, oxidant as well as OH^{-} ion concentration as has been observed experimentally. Similar mechanism shown in the third step has been suggested by Ladbury and Cullis.[10]

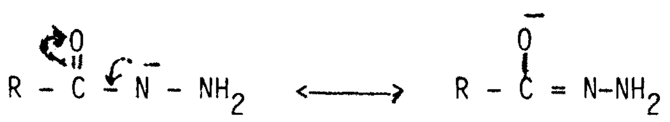
This mechanism is also in accordance with the other observations namely :

1) Ionic strength effect and dielectric constant effect show that the reaction is between ions of similar charges as has been suggested in step (11).

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 $\Delta S^{\neq}$ suggests the formation of a rigid transition state. The negative ion of $R-\overset{O}{\overset{\|}{C}}-\bar{N}-NH_2$ seems to be stabilized through resonance as :



$$R-\overset{O}{\overset{\|}{C}}-\bar{N}-NH_2 \longleftrightarrow R-\overset{\bar{O}}{\overset{|}{C}}=N-NH_2 \quad \ldots \quad (xi)$$

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