
CHAPTER - I V

DISCUSSION

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It has already been mentioned that the aim of the present study is not only to formulate the mechanism of the reaction under investigation but also to explain the relative reactivities of o-chloro and p-chloro benzoic acid hydrazides. Hence it is necessary to review the various mechanistic criteria usually employed in the determination of reaction mechanism and to suggest possible mechanism on the basis of experimental facts.

A 'mechanism of reaction' is a concept which explains the transformation of reactant(s) into product(s). Chemical reactions often occur in a number of relatively simple steps in which there is always a slowest of all other steps. The overall rate of reaction is governed by slowest step which is conveniently called the rate determining step. All the species which occur in steps preceding the rate determining step appear in the rate law but those which react after the slowest step do not appear in the rate expression.

The most rational approach of Arrhenius¹ for explaining the chemical reaction is replacing the concept of molecular activation as a pre-requisite for chemical reaction. This concept of activation is now universally

accepted and forms the basis of all subsequent theories of chemical reaction. Evans, Polanyi² and Eyring³ have postulated that molecular collisions between energised molecules result in the formation of activated complex.

The present work is concerned with the redox reaction involving $\text{Fe}(\text{CN})_6^{3-}$ ion, so it is necessary to state the present views on mechanism of redox process in general. For oxidation reduction reactions, a number of mechanisms have been proposed. According to Haber and Weiss⁴, it is simple process which involves the stepwise transfer of an electron from reductant to oxidant. Oxidation-reduction reaction may take place via simple electron transfer or through the agency of the atom or ion transfer. Trube and King⁵, in the study of reaction of $\text{Co}(\text{NH}_3)_5\text{Cl}^{2+}$ and Cr^{2+} in HClO_4 solution, have put forth the formation of Cr^{3+} which was found in the form of CrCl^{2+} complex. They have 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 .

Hexacyanoferrate(III) belongs to the class of oxidising agents comprising ceric sulphate, ammonical silver nitrate and Fehling's solution. All these oxidising species are electron abstracting ions



Consequently, ferricyanide has been used in systems obviously favoured for oxidation. That is in this manner an electron from an electron rich site is extracted.

In order to suggest the possible mechanism for oxidation of o-ClBAH and p-ClBAH by alkaline hexacyano-ferrate(III) ion, it is essential to summarize the results obtained in the present study.

1. The oxidation of o-chlorobenzoic acid hydrazide and p-chlorobenzoic acid hydrazide is first order w.r.t. hexacyanoferrate ion.

The psuedo first order rate constant (k) of both oxidation reactions is found to be constant at different initial concentrations of hexacyano-ferrate(III).

2. Both the reactions : oxidation of o-Cl BAH and p-Cl BAH are first order w.r.t. substrate (hydrazide). Specific rate increases with an increase in the concentration of hydrazide.
3. The rate constant increases with increase in NaOH concentration in both the studied hydrazides. This shows that the reactive species may be probably the anion of hydrazide,



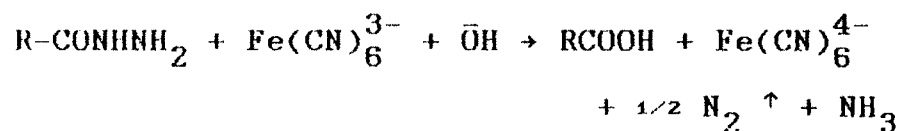
4. The rate is dependent on ionic strength and increases with increase in ionic strength of the reaction mixture; however, increase in reaction rate is marginal. This indicates that the reaction must be between species of the same charge.
5. Specific rate of reaction under study decreases with increase in dioxane content of the mixture. Hence, according to Amis⁶ concept, the positive dielectric effect observed in the present study clearly suggests the negative ion-dipole interaction in rate determining step. Since the reaction is favoured by increase in water content of mixture having high dielectric constant, it appears that transition state is more solvated than reactant.
6. The various activation parameters calculated are as follows :

Oxidation reaction	Temp. coefficient per 10 ⁰ C	E _a K ^a cal mole ⁻¹	Frequency factor A sec ⁻¹	ΔG [‡] K cal mole ⁻¹	ΔS [‡] (e.u.)	ΔH [‡] K cal mole ⁻¹
o-CIBAH	1.82	12.48	6.18x10 ⁴	25.67	-26.66	11.44
p-CIBAH	1.88	13.05	1.94x10 ⁵	24.19	-26.20	13.23

The high negative value of ΔS^\ddagger and low frequency factor in both the cases indicate the formation of rigid transition state. It is good proof to say that the rate determining step involves the interaction between two negatively charged ions or between a negatively charged ion and a polar molecule.^{7,8}

Fairly high positive values of free energy of activation and enthalpy of activation indicate that the transition state is highly solvated. The free energy of activation for both the reactions is almost the same. It suggests that probably both the reactions proceed with same mechanism.

7. The addition of acrylonitrile⁹ and HgCl_2 ¹⁰ retarded the rate of oxidation, indicating the free radical intermediate formation during the reaction.
8. The mole ratio [hydrazide : fericyanide] is found to be 1:1. This makes it clear that for the oxidation of one mole of aryl hydrazide one mole of hexacyanoferrate(III) is required.



9. The intermediate product of the reaction is the anion of hydrazide which is further oxidised to

corresponding acid, nitrogen and ammonia. Nitrogen is detected by lime test¹¹ and ammonia by Nessler's reagent.¹²

10. The oxidation products identified in these reactions are

i) o-chloro benzoic acid hydrazide →

o-chloro benzoic acid - M.P. - 140° (138-140°C)

ii) p-chloro benzoic acid hydrazide →

p-chloro benzoic acid - M.P. 238° (239-241°C)

11. The pseudo-first order rate constant (k) of the reactions of o-CIBAH and p-CIBAH under identical experimental conditions are as follows :

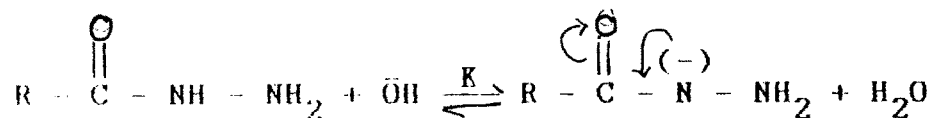
Hydrazide	k x 10 ² min ⁻¹
o-Chloro benzoic acid hydrazide	1.32
p-chloro benzoic acid hydrazide	1.64

This shows that the rate of oxidation of p-chlorobenzoic acid hydrazide is somewhat higher than that of o-chloro benzoic acid hydrazide.

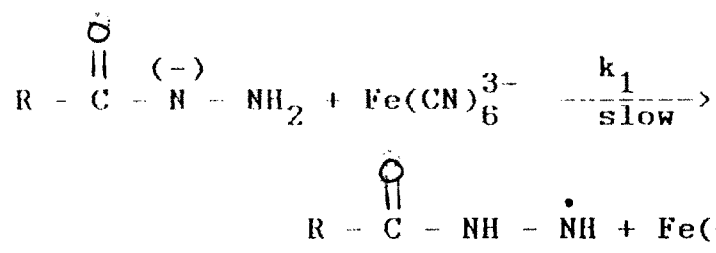
On the basis of observed kinetics, reaction intermediate, oxidation products and stoichiometry of the reaction following probable mechanism is suggested.

It is observed that $\bar{O}H$ ion which catalyses the reaction resulting in the formation of negatively charged species. This species is involved in rate determining step. The abstraction of proton by $\bar{O}H$ is from the nitrogen atom

adjacent to carbonyl group which may be represented as follows

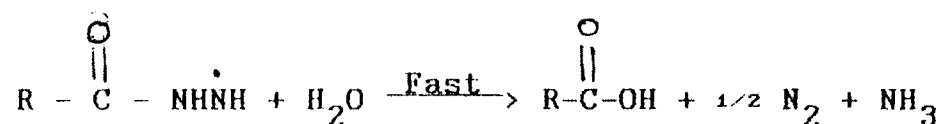


The rate determining step seems to be the transfer of an electron from above anion to $Fe(CN)_6^{3-}$ ion, which can be shown as,



Frank and Krishna Rao¹³ reported the formation of free radical in the oxidation of hydrazides by other reagent.

According to our observation the mole ratio [hydrazide : oxidant] is 1:1. So probably it seems that the free radical formed from the substrate undergoes hydrolysis to produce carboxylic acid, ammonia and nitrogen¹⁴

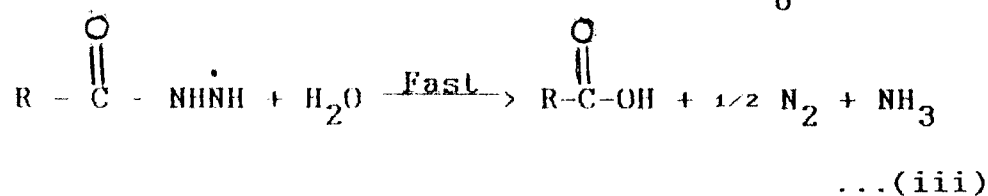
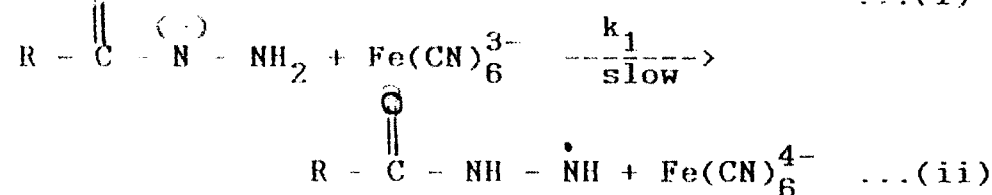
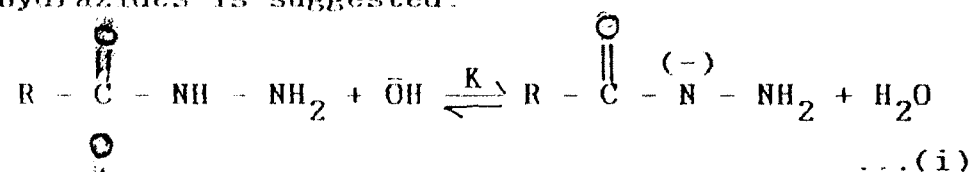


The first step has been shown as an equilibrium reaction, while second step seems to be the rate determining step.

Thus, overall mechanism for the oxidation of o-chloro and p-chloro benzoic acid hydrazides by alkaline

hexacyanoferrate can be represented taking into consideration the close similarity in the kinetic behaviour.

Thus, on the basis of the foregoing kinetic evidences, following sequence of reactions for the oxidation of these hydrazides is suggested.



where,



From step (ii) the rate of disappearance of hexacyanoferrate(III) is given by,

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

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

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

On rearrangement :



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

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

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

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

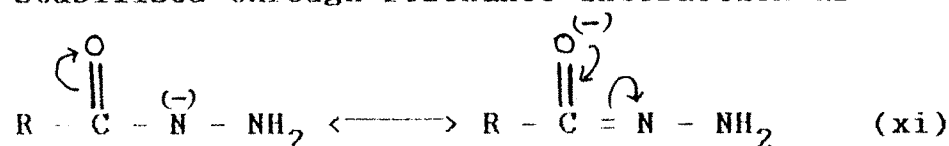
Above expression (viii) explains the order of the reaction w.r.t. hydrazide, hexacyanoferrate and alkali is one in each.

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 (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. This suggests the formation of a rigid transition state.

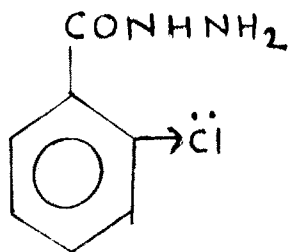
The negative ion $\text{R}-\overset{\text{O}}{\parallel}(\ominus)\text{N}-\text{NH}_2$ seems to be stabilised through resonance interaction as :



- (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.¹⁵ which is further supported by the observation of Kelly et al.¹⁶
- (6) A large negative entropy of activation exhibited by this oxidation indicates that the reaction may involve the species of same charge or charged species and neutral molecule.

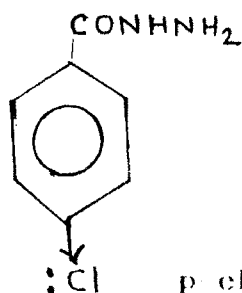
Order of reactivity :

The overall rate of oxidation of these two hydrazides are found to be similar but p-Cl BAH undergoes oxidation at slightly faster rate than o-Cl BAH which can be explained by comparing their first order rate constants.



$$k = 1.32 \times 10^{-2} \text{ min}^{-1}$$

o-Chlorobenzamide



$$k = 1.64 \times 10^{-2} \text{ min}^{-1}$$

p-chlorobenzamide

i.e. rate of oxidation of p-Cl BAH > o-Cl BAH

This order of reactivity can be explained on the basis of following points.

Chlorine being more electronegative than carbon, it exerts electron-withdrawing inductive effect. This effect will tend to decrease with distance from the chlorine atom, being exerted somewhat less strongly on the distant 'p'-position compared with the adjacent 'o'-position.

This effect, when the chlorine is in the o-position, is due to the short distance over which its inductive effect is operating. When the chlorine is in p-position same effect is not operating due to greater distance.

However, chlorine atom, adjacent to the nucleus (aryl group), that carries an electron pair exerts electron-donating mesomeric effect. so in p-ClBAH, only electron

donating mesomeric effect is operating whereas in o-ClBAH both the effects [inductive as well as mesomeric] are operating making nitrogen atom adjacent to carbonyl group in the hydrazide less basic compared with its p-isomer. Therefore p-Cl BAH undergoes oxidation by alkaline hexacyanoferrate (III) at somewhat faster rate than the o-Cl BAH.

REFERENCES

1. Arrhenius, S : Z. Physik., Chem., 4, 226 (1889).
2. Evan, M.C. and Polanyi, M : Trans. Far Soc., 31, 875 (1935), *Ibid.*, 448 (1937).
3. Eyring, H. : J. Chem. Phys., 3, 107 (1935).
4. Haber, F. and Weiss, J. : Proc. Roy. Soc., 147, 322 (1934).
5. Traube, H. and King, E.L. : J. Am. Chem. Soc., 76, 4053 (1954).
6. Amis, E.S. : J. Chem. Educ., 30, 351 (1953); Anal. Chem., 27, 1672 (1955); Solvent Effects on Reaction Rates and Mechanism (Academic Press, New York) 1966.
7. Garrison, A.W. and Boozer, C.E. : J. Am. Chem. Soc., 90, 3486 (1968).
8. Lal, V., Singh, U.N., Singh, H.S. and Singh, M.P. : Ind. J. Chem., 10, 329 (1972).
9. Horner, L. and Podschus : Angew. Chem., 63 (1951).
10. Drummond, A.Y. and Waters, W.A. : J. Chem. Soc., 3119 (1953).
11. Fritz Feigl : "Spot Tests Inorganic Analysis"
Elsevier, Publishing Co. New York, 2nd Ed. (1972).
12. Vogel, A.I. : A Textbook of Qualitative Inorganic Analysis.

13. Frank, M.S. and Krishna Rao, P.V. : Ind. J. Chem., 17-A, 632-34 (1979).
14. Ladbury, J.W. and Cullis, C.F. : Chemical Reviews, Vol.58, 434 (1958).
15. Haskar, C.N., Mehrotra, R.C. and Ramchandran, P.K.: Ind. J. Chem., 178, 191 (1979).
16. Kelly, R.B., Umbreit, G.R. and Liggett, W.F. : J.Org.Chem., 29, 1273 (1964).