CHAPTER - I I

EXPERIMENTAL TECHNIQUE

CHAPTER - II

EXPERIMENTAL TECHNIQUES

The oxidation of o-chloro and p-chloro benzoic acid hydrazides by alkaline hexacyanoferrate(III) is carried out in dioxane-water mixture (50% v/v).

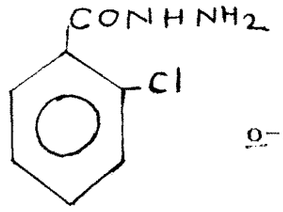
The oxidation by hexacyanoferrate(III) ion takes place slowly but proceeds with a measurable velocity in alkaline medium. The literature survey on oxidation of organic compounds by hexacyanoferrate shows that, impurity present in the reagents generally catalyses[1] or inhibits[2] the rate of chemical reaction. In addition to this, the hexacyanoferrate(III) reacts with ions like Fe(II), Fe(III) and Zn(II)[3]. Hence removal of impurities was essential and all precautions were taken to avoid the presence of impurities in the reaction system.

MATERIALS AND PURITY :

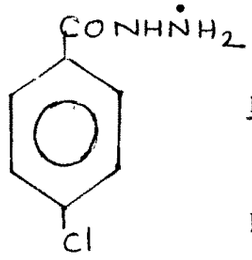
The double distilled water was used throughout the work which was obtained by redistillation of distilled water in the presence of a few crystals of $KMnO_4$ and a few pellets of KOH using corning glass distillation assembly.

o-chloro and p-chloro benzoic acid hydrazides were obtained from Aldrich Chemical Company, Inc. Milwaukee,

Wisconsin, USA. Purity of these hydrazides was checked by taking melting points.



o-chloro benzoic acid hydrazide - 119°C



p-chloro benzoic acid hydrazide - 164°C

Hexacyanoferrate(III), sodium hydroxide, sodium chloride were of A.R. grade.

1,4-dioxane [Qualigene, AR] was purified by the procedure described by Weissberger.[4]

PREPARATION OF SOLUTIONS :

5.0×10^{-3}M stock solution of $K_3Fe(CN)_6$ was always prepared by dissolving accurately weighed, calculated quantity of crystallised salt in double distilled water using standard pyrex glass measuring flask. The exact strength of this stock solution was checked idometrically[5] from time to time. The stock solution of hexacyanoferrate(III) was kept in amber coloured bottle and the bottle was always kept in a dark place.

The 1.0 M stock solution of NaCl was prepared by exactly weighing the calculated amount of salt and dissolving

it in double distilled water using standard purex glass measuring flask.

Similarly, 1.0×10^{-2}M stock solution of NaOH was prepared by using the same above procedure and standardised by using oxalic acid solution.

5.0×10^{-2}M stock solutions of hydrazides were prepared by exactly weighing the calculated amount of hydrazides and dissolving them in dioxane. These standard solutions of hydrazides were always used for the experiments within 12 hours.

DETERMINATION OF λ MAX FOR HEXACYANOFERRATE(III) :

5.0×10^{-4}M solution of hexacyanoferrate was prepared in double distilled water. Absorbance of this solution was measured as a function of wavelength in range of 400-700 nm, water was used as a reference. It was observed that the $K_3Fe(CN)_6$ has strong absorbance at 420 nm[6,7] and hence the wavelength 420 nm was used as λmax for measurement of absorbance of hexacyanoferrate(III) throughout the present investigation.

The absorbance measurements were carried out in 1 cm cell placed in cell compartment of spectronic-20 [Zeiss spectrophotometer, German].

FOLLOWING THE KINETICS :

The main features of the experimental method are as follows :

(i) The reaction was studied under the pseudo-first order condition where [hydrazide] >> [hexacyanoferrate(III)].

(ii) The temperature of the reaction mixture was adjusted and maintained by using auto-thermostated water bath.

(iii) The standard pyrex glasswares were used throughout the experimental work.

(iv) The reaction was carried out in a stoppered standard flask which was coated with black paint from outside to avoid photochemical effects.

(v) The calculated quantities of standard solutions of hexacyanoferrate(III) and NaOH were taken in one conical flask by using graduated pipette. The volume 25 ml was adjusted by adding required amount of double distilled water using graduated pipette.

The calculated quantity of standard solution of hydrazide was taken in another flask by using

graduated pipette. The volume 25 ml was adjusted by adding required amount of distilled 1-4 dioxane by graduated pipette.

Both the flasks were thermostated, atleast, for 15 minutes.

(vi) The reaction was initiated by adding the thermostated solution of hydrazide to the thermostated solution of hexacyanoferrate(III) already containing NaOH. The time of mixing of the two solutions was recorded as zero time.

(vii) At zero time, aliquot of reaction mixture was pipetted out in 1 cm spectrophotometric cell and immediately optical density was measured at 420 nm using double distilled water as a reference solvent. Similarly the aliquots of reaction mixture were pipetted out in the same spectrophotometric cell at definite intervals of time and immediately optical densities were measured at 420 nm.

In this way progress of reaction was followed spectrophotometrically by observing the disappearance of hexacyanoferrate(III).

(viii) The reaction was usually followed upto 70 percent completion or more.

ABBREVIATIONS :

In recording of the observations, calculations of results and plotting of graph following abbreviations are used :

1)	o-Cl BAH	: o-chlorobenzoic acid hydrazide
2)	p-Cl BAH	: p-chlorobenzoic acid hydrazide
3)	HCF(III)	: hexacyanoferrate(III) i.e. $Fe(CN)_6^{3-}$
4)	T	: experimental temperature
5)	λ	: wavelength in nm
6)	M	: Concentration of substance in moles/lit.
7)	D	: dielectric constant of reaction medium.
8)	O.D.	: Optical density i.e. absorbance
9)	k	: observed pseudo- first order rate constant
10)	w.r.t.	: with respect to
11)	$(-d_c/d_t)_o$	: initial rate of reaction
12)	t	: time in minutes
13)	n	: order of reaction
14)	Vs	: versus

REFERENCES

1. Bridgart, G.J., Fuller, M.W. and Wilson, I.R.: J.Chem.Soc.Dalton Trans, 1274 (1973).

2. Kasim A.Y. : Inorganica Chemica Acta, 27, 243 (1978).

3. Welcher, F.J. and Hahn, R.B.: Semimicro Qualitative Analysis (W.D. Ten Broeck for Affiliated East West P.Ltd., New Delhi) 1968.

4. Weissberger, A. and Proskaner, F.S. : "Organic Solvents," Interscience Publishers, New York, Vol.7, 1956, pp. 139.

5. Bassett, J., Jeffery, G.H., Denny, R.C. and Mendham, J. : Textbook of Quantitative Inorganic Analysis Including Elementary Instrumental Analysis, 4th Ed. (The E.L.B.S. and Longman) 1978, by A.I. Vogel.

6. Bhattacharjee, A.K. and Mahanti, M.K. : Ind. J. Chem. 22(B), 74 (1983).

7. Dasgupta, G. and Mahanti, M.K. : React. Kinet. Catal. Lett. 23, 393 (1983).