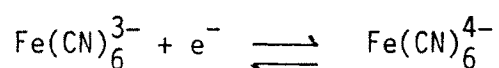


CHAPTER - II
EXPERIMENTAL TECHNIQUE

CHAPTER - I IEXPERIMENTAL TECHNIQUE

The oxidation of n-butyric and iso-butyric acid hydrazides by hexacyanoferrate(III) in alkaline medium is undertaken. In solution Fe(III), accepts electron from anion of the substrate, formed by abstraction of proton due to alkali (NaOH). The reaction under equilibrium can be represented¹ as



The equilibrium can be shifted towards right by using alkaline medium. Hence alkaline medium is used throughout investigation.

During the course of the reaction, Fe(III) reduced to Fe(IV). However, Fe(III) is strongly absorbing species² ($\lambda_{\text{max}} = 420 \text{ nm}, \epsilon = 961 \text{ l mole}^{-1} \text{ cm}^{-1}$) as compared to (IV), which is practically non-absorbing at 420 nm. So the observed absorbance (A) at 420 nm may be safely taken as a measurement of concentration of Fe(III) during the course of reaction. Hence, in the present investigation reaction was followed photo-chemically at 420 nm wave length.

2.1 PURITY OF THE CHEMICALS :

All the chemicals used during the investigation were of AR/GR or equivalent quality. n-butyric and iso-butyric acid hydrazides were



prepared in the laboratory.³ Their purity was checked after recrystallization by determining their physical constants.

n-butyric acid hydrazide, M.P. 43°C [44°C]

iso-butyric acid hydrazide, M.P. 103°C [104°C]

The other chemicals used viz. $K_3Fe(CN)_6$ (AnalaR recrystallized), NaOH, KCl, Ethanol and Acrylonitrile etc., were of AR grade.

2.2 PREPARATION OF HYDRAZIDES :

The n-butyric and iso-butyric acid hydrazides³ were prepared by refluxing equimolar quantities of methyl esters of corresponding carboxylic acids with hydrazine hydrate (B.D.H. 99%), on water bath till the two layers disappeared and homogeneous solution was formed. The excess of hydrazine hydrate and other unreacted material were removed by distilling the solution under reduced pressure. The hydrazides were purified by recrystallization from slightly warmed ethanol. The purity was checked by determining their melting points. Standard solutions were prepared by exactly weighing the calculated quantities of hydrazides and dissolving them in double distilled water in standard pyrex glass measuring flask.

2.3 STANDARDIZATION OF HEXACYANOFERRATE(III) :

The exact molarity of hexacyanoferrate(III) solution was confirmed by standardization method.⁴ In this method 2 ml stock solution of hexacyanoferrate(III) was taken in an Iodine flask,

10 ml of KI (5%) and 2 ml of 0.5% potassium-iodate ~~were~~ added to it. The liberated iodine was titrated against 0.05 N sodium-thio sulphate solution & molarity of hexacyanoferrate(III) was determined.

2.4 PREPARATION OF SOLUTIONS :

Stock solutions of n-butyric and iso-butyric acid hydrazides (0.5 M) were prepared by weighing the required quantities of the hydrazides and dissolved in distilled water. The solutions were stored in dark place. The glassware used for the preparation and storing the solutions was of pyrex glass. The stock solution of hexacyanoferrate(III) (0.05 M) was kept in ambere coloured bottle and the bottle was always kept in dark place. The strength of hexcyanoferrate(III) was checked periodically.⁴ Stock solutions of sodium hydroxide (0.5 M) and potassium chloride (0.5 M) were also prepared by above procedure.

2.5 DETERMINATION OF λ MAX FOR HEXACYANOFERRATE(III) :

5.0×10^{-4} M solution of hexacyanoferrate(III) 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 is observed from the graph of absorbance (A) or optical density (O.D.) versus wavelength (nm) that hexacyanoferrate (III) has a strong absorption at 420 nm^2 .

2.6 FOLLOWING THE KINETICS :

All the kinetic measurements were carried out in pyrex glass-ware which was coated outside with Japan black to avoid photochemical effects. Stock solutions of hexacyanoferrate(III), the organic substrate (n-butyric and iso-butyric acid hydrazides) and sodium hydroxide, were kept in the separate well stoppered bottles and equilibrated to the required temperature in a thermostat with $\pm 0.1^\circ\text{C}$ accuracy for about 10 to 20 minutes. The required volumes of these solutions were mixed in an iodine flask (total volume of the solution 100 ml) and optical density (O.D.) of the reaction mixture at 420 nm was measured at definite time intervals. The reaction mixture was transferred into the spectrophotometer. By using this method minimum errors were observed, reference solution used was water. The reaction was usually followed upto 80% completion. The data was used to calculate $(-dc/dt)$, velocity constants etc. The following variations were studied.

- 1) Variation of concentration of hexacyanoferrate(III).
- 2) Variation of substrate concentration.
- 3) Variation of alkali concentration.
- 4) Variation of temperature of the experiment.
- 5) Effect of salt and dielectric constant of medium.

The observations, graphs and results are given and discussed in Chapters III and IV.

In recording the observations of kinetic runs the following abbreviations have been used :

- 1) HCF(III) represents, Hexacyanoferrate(III).
- 2) [n-BAH] and [iso-BAH] denote n-butyric and iso-butyric acid hydrazides concentration respectively.
- 3) [OH⁻] denotes alkali concentration.
- 4) 'O.D.' denotes the optical density of the HCF(III) soln.
- 5) 'min' denotes the time in minutes.
- 6) 'k' represents the first order rate constant for the total reaction.
- 7) w.r.t. stands for with respect to .

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