

CHAPTER III : EXPERIMENTAL

### A) Reagents

- i) Redistilled water from aqueous alkaline permanganate was used as solvent for all the experiments.
- ii) Potassium permanganate was of B.D.H. grade. Potassium permanganate solution was daily standardised by usual oxalate method.
- iii) Sodium hydroxide was of B.D.H. grade. The stock solution of sodium hydroxide was prepared and it was standardised with oxalic acid by using phenolphthalein as an indicator.
- iv) Nicotinamide and iso-Nicotinamide were of B.D.H. grade. (Melting points of these amides were found to be in agree with literature value). The estimation of amide was carried out by Olsen's method.<sup>1</sup>

### B) Apparatus

- i) Absorption measurements were made with an SPEKOL, wavelength 350 nm to 850 nm, CARL ZEISS JENA made in GERMANY DDR.
- ii) Thermostat : Water bath system equipped with relay, heater, stirrer and regulated by a contact thermometer. Water bath temperatures were maintained to  $\pm 0.01^{\circ}\text{C}$ . (German make thermostat.)

### C) Kinetic Measurements

- i) Kinetics of oxidation of nicotinamide and iso-Nicotinamide. Typical initial concentrations for these mixture were

- i)  $2 \times 10^{-3}$  M  $\text{KMnO}_4$ , 5 ml
- ii)  $\text{NaOH}$ , 2 M 5 ml
- iii) Nicotinamide 1 M, 2.5 ml with distilled water 12.5 ml in amide solution. All the above quantities of solution were placed in three different conical flasks (50 ml) and were thermostated at  $35^\circ\text{C}$ . After acquiring constant temperature  $35^\circ\text{C}$ , contents were mixed by proper shaking and <sup>stop</sup> watch was started. The course of the reaction was studied by measuring the optical density of the reaction mixture at  $530 \text{ m}\mu$  at different time intervals, by SPEKOL. The absorption measurements were carried out upto forty (40) minutes after wards  $\text{MnO}_4^{--}$  formed in the reaction retards the rate of chemical change.<sup>2</sup>

By plotting the 'absorption' against 'time' a plot was obtained and the rate was determined from the slope. The rate constant is determined from the slope of the plot of log optical density and time.

It was also observed that there was no considerable change in absorption of the reaction mixture of neutral or acidic potassium permanganate.

#### D) Relative rates of Oxidation of Amides

In order to compare the relative rates of oxidation of amides the equal concentration of the reactants were taken in separate conical flask for the various amides and thermostated at  $25^\circ\text{C}$ .

i) Aliphatic amide = 0.4 M; Aromatic amide = 0.04 M.

ii) NaOH = 0.4 M

iii)  $\text{KMnO}_4 = 4.0 \times 10^{-4}$  M.

After acquiring the constant temperature the reactants were mixed and the absorption was noted at 530 m $\mu$  at different time intervals.

The graphs were plotted for all the amides between optical density and time. From the linear plots the rate of oxidation for each amide was determined from the slope of the straight line.

REFERENCES

- 1 Olsen's Die. Chemi. 56, 202 (1943).
- 2 Wiberg, K.B., "Oxidation in Organic Chemistry", Part A, Academic Press (1965).