

CHAPTER : II

Experimental technique

EXPERIMENTAL

A) Chemicals :

Chloramine - T :- Chloramine-T, (Riedel) sample was purified by the method of Morris et al¹²⁸ and 0.01 M solution was prepared in doubled distilled water, and was standardised by the iodometric method.

Hydrazides :- The hydrazides were prepared¹²⁹ by refluxing equimolar quantities of ethyl 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 recrystallisation from slightly warmed ethanol. The purity was checked by determining their melting points. Standard solutions were prepared by exactly weighing the calculated quantity of hydrazides and dissolving them in double distilled water in standard pyrex glass measuring flask.

Sodium perchlorate :- NaClO_4 G.R. grade (Riedel) sample was always used without any purification. A standard solution (1M) of sodium perchlorate was prepared in double distilled water and 10 ml of this solution was always used to keep the ionic strength of the medium constant.

Starch solution :- B.D.H. (A.R.) soluble starch was used. A 1 % starch solution was prepared by dissolving approximately weighed soluble starch in boiling distilled water and adding a pinch of mercurous iodide for greater stability. The starch solution was always prepared fresh.

Sulphuric acid, B.D.H. (Analar) and potassium iodide B.D.H. grade were used for iodometric titrations.

All kinetic runs were carried out in glass stoppered bottles whose outer surface was coated with black Japan to avoid photochemical effect. For studying the kinetics of the reaction, a thermostatic water bath with electronic relay and with an accuracy of $\pm 0.1^{\circ}\text{C}$ was employed.

B) EXPERIMENTAL PROCEDURE :-

The experiments were designed under isolation conditions where the substrate concentration is in excess (~ 10 - 20 times) over the oxidant.

In a typical experiment, measured quantities of hydrazide, alkali and sodium perchlorate solutions were taken along with the calculated quantity of double distilled water in the reaction flasks at room temperature. These flasks were placed in the thermostat maintained at the temperature of the experiment. A measured quantity of chloramine -T solution was also thermostated at the same temperature for the period of 10-15 minutes to attain the temperature of the bath. Just before the start of the experiment, the solutions of hydrazide, chloramine -T, perchlorate and alkali were mixed immediately and shaken properly. The progress of the reaction was monitored at different time intervals by estimating the unreacted chloramine-T iodometrically in the following manner.

A 5 ml of the reaction mixture was pipetted out into an iodine flask containing 10 ml of 5 % KI and 10 ml of 1.N sulphuric acid. The iodine flask was stoppered and allowed to stand for about 10 minutes for complete liberation of iodine. Then the liberated iodine was estimated by titrating it against a standard sodium thiosulfate solution using freshly prepared starch solution as an indicator. A semimicro burette reading upto 0.05 ml, was employed. Solution of sodium thiosulfate was previously standardised against a standard solution of arsenious oxide by the usual method.

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

1. 'C' denotes the volume in ml of the standard solution of $\text{Na}_2\text{S}_2\text{O}_3$ equivalent to the unreacted CAT at any time (t).
2. 'min' denotes the time in minutes and 'conc' denotes the concentration in moles per litre.
3. 'k' represents the first order rate constant for the total reaction.
4. 'CAT' represents Chloramine-T
5. 'NAH' and 'INAH' denote nicotinic acid hydrazide and isonicotinic acid hydrazide respectively.