



## **CHAPTER – I I**

# **EXPERIMENTAL TECHNIQUE**



## CHAPTER – II

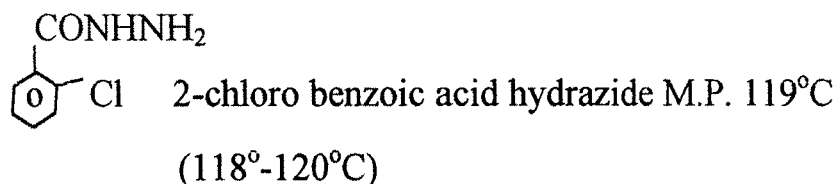
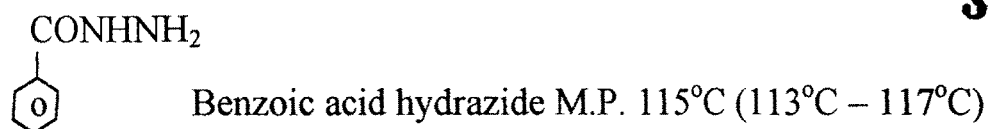
### EXPERIMENTAL TECHNIQUES

The oxidation of Benzoic and 2-chlorobenzoic acid hydrazides by thallium(III) is carried out in water alcohol mixture (50% v/v). To ensure that the oxidation of ethanol with thallium(III) under these experimental conditions is carried out without taking hydrazide. Repeated experiments were performed. But it is confirmed that ethanol does not undergo oxidation with thallium(III).

The oxidation by thallium(III) ion takes place slowly but proceeds with a measurable velocity in HCl medium.

#### **Purity of chemicals**

All the chemicals used during the investigation were of AR/AG quality. The impurities present in the reagents generally influences the rate of chemical reaction, hence all possible precautions were taken to avoid the impurities in the reaction system. Benzoic and 2-chloro benzoic acid hydrazides were prepared in the laboratory.<sup>3</sup> Their purity was checked after recrystallisation by determining their physical constants and by TLC.



The other chemicals used are Thallium(III), sodium thiosulphate, perchloric acid, hydrochloric acid, starch, ethanol were of AR or BDH grade.

### Preparation of Hydrazides

The following procedure was followed for the preparation of hydrazides.<sup>3</sup> A mixture of equimolecular quantities of methyl esters of corresponding carboxylic acids and hydrazine hydrate (BDH 99%) was refluxed on a water bath for more than three hours till the two layers disappeared and a homogenous 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 quantities of hydrazides and dissolving them in double distilled water in standard pyrex glass measuring flask.

### Preparation of solutions

Stock solutions of Benzoic and 2-chloro benzoic acid hydrazides were prepared by weighing calculated quantities of the hydrazides and dissolving in water-ethanol mixture. The solutions were stored in dark place. The glass used for the preparation and for storing the solution was of pyrex glass. The stock solution of hydrazides were kept in amber coloured bottle and bottle was always kept in dark place.

The standard thallium solution was prepared by exactly weighing the calculated amount of Thallium oxide and dissolving it in concentrated hydrochloric acid and then diluted with distilled water using standard pyrex glass measuring flask.

Similarly, a stock solution of sodium thiosulphate was prepared and standardisation is done for every set of experiment.

Stock solutions of perchloric acid, hydrochloric acid, potassium dichromate etc. were prepared.

### Standardisation of sodium thiosulphate

Burette is filled with 0.002 N  $\text{Na}_2\text{S}_2\text{O}_3$  solution. 5 ml  $\text{K}_2\text{Cr}_2\text{O}_7$  solution of 0.001 N is taken in a iodine flask, 5 ml of 2 M  $\text{H}_2\text{SO}_4$  and 5 ml of 5% KI are added to it. By using starch indicator, the liberated iodine was titrated against  $\text{Na}_2\text{S}_2\text{O}_3$  till colour changes from violet to colourless [Iodometric titration].

### Following the kinetics

All the reactions were carried out in a thermostated water bath adjusted to the desired temperature. The calculated quantities of standard

solutions of thallium(III), 1 M HCl solution, 1 M perchloric acid were taken in one conical flask by using graduated pipette. The volume 25 ml was adjusted by adding required amount of distilled water alcohol mixture using graduated pipette.

The calculated quantity of standard solution of hydrazide was taken in another flask by using graduated pipette. 1M perchloric acid solution is added by graduated pipette. The volume 25 ml was adjusted by adding required amount of distilled water alcohol mixture by graduated pipette.

Both the flasks were thermostated at least for 20 minutes.

The reaction was initiated by adding the thermostated solution of hydrazide to the thermostated solution of Thallium(III) containing HCl and HClO<sub>4</sub> mixture. The time of mixing of the two solutions was recorded as zero time.

At zero time 5 ml of reaction mixture is pipetted out and added in a clean conical flask. Then 5 ml of 2 M H<sub>2</sub>SO<sub>4</sub> solution and 5 ml of 5% KI solution is added to the reaction mixture. Starch solution is then added and the reaction mixture is titrated with standard Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution till colour changes from violet to colourless. Similarly the reaction mixture was pipetted out at different intervals of time and Burette reading is noted down. Then the graph of  $-\log(a-x)$  against time is plotted and slope is calculated. Then  $k$  is calculated by using the equation  $k = 2.303 \times \text{slope}$ .

**REFERENCES**

1. Vogel A.I. : A Text Book of Practical organic chemistry including qualitative Organic Analysis, 3<sup>rd</sup> Ed. (E.L.B.S. and Longman Group Ltd.) 1975.
2. Vogel A.I. : A Text Book of Quantitative Inorganic analysis IV Edn. [E.L.B.S. and Longman's Press] 385.
3. Datta, Ahmed, A. and Ray Chaudhari, N. J. Ind. Chem. Soc. 1971, 48, 747.