

CHAPTER —II

EXPERIMENTAL

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An account of the use of Chloramine-T as an oxidant has been given in the first Chapter. This chapter contains the present work on the kinetics and mechanism of oxidation of the two aliphatic acid hydrazides, i.e. n-caproic and n-Heptanoic acid hydrides by Chloramine-T, in order to study the effect of structure on the rate of oxidation of hydrazides. Kinetics of oxidation of these two hydrazides by Chloramine-T was carried out in aqueous alkaline medium with hydrazide concentration in large excess over the Chloramine-T concentration. The experiments were designed to determine -

- (1) The order of reaction with respect to the substrate concentration.
- (2) The order of reaction with respect to the Chloramine-T concentration.
- (3) The order of reaction with respect to hydroxide ion.
- (4) Effect of addition of chloride ion.
- (5) Effect of change in ionic strength of the medium.
- (6) The effect of change in temperature on the rate of reaction, from which the kinetic and thermodynamic parameters have been calculated.

Chloramine-T :

Chloramine-T, (Riedel) sample was purified by the method of Morris et. al.<sup>1</sup> and 0.01 M Solution was prepared in double distilled water, and was standardised by the iodometric method.

Hydrazides :

The hydrazides were prepared<sup>2</sup> by refluxing equimolar quantities of ethyl or methyl esters of corresponding carboxylic acids with hydrazine hydrate (BDH 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 recrystallised from slightly warmed ethanol.

- i) n-Caproic acid Hydrazide - M.P. = 71°C
- ii) n-Heptanoic acid Hydrazide - M.P. = 82°C

Standard solutions of hydrazides were prepared by dissolving calculated amounts of recrystallised samples in double distilled water. Warming on water bath is necessary to dissolve sample completely.

Potassium chloride solution :

KCl G.R. grade (Riedel) sample was always used without any purification. A standard solution (0.5 M) of potassium chloride was prepared in double distilled water and 10 ml of this solution was always used to keep the ionic strength of the reaction medium constant. All kinetic runs were carried out in glass stoppered bottles whose outer surface was coated with black paint 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.

EXPERIMENTAL PROCEDURE :

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

In a typical experiment, measured quantities of hydrazide, alkali and potassium chloride solutions were taken along with calculated quantity of double distilled water, in the reaction flask at room temperature. These flasks were placed in the thermostat maintained at the temperature of

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 experiment, the solutions of hydrazide, Chloramine-T, potassium chloride and alkali were mixed immediately and shaken properly. The progress of the reaction was monitored at different time intervals by estimating unreacted Chloramine-T iodometrically as follows.

A 5 ml of the reaction mixture was pipetted out in to an iodine flask containing 10 ml of 5 % KI, and 10 ml of 2N Sulfuric acid. The iodine flask was allowed to stand for about 10 min; after shaking vigorously, for complete liberation of iodine. Then the liberated iodine was estimated by titrating it against a standard solution of  $\text{Na}_2\text{S}_2\text{O}_3$  using freshly prepared starch solution as an indicator. A semi-micro burette, reading up to 0.05 ml was employed. Solution of  $\text{Na}_2\text{S}_2\text{O}_3$  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 a standard solution of  $\text{Na}_2\text{S}_2\text{O}_3$  equivalent to the unreacted Chloramine-T at any time (t).

- (2) 'k' represents the first order rate constant for the total reaction.
- (3) 'CAT' represents Chloramine-T.
- (4) 'n-CAH' and 'n-HAH' for n-caproic acid hydrazide and n-Heptanoic acid hydrazide respectively.

REFERENCES :

1. Morris, J.C., Salazer, J.A. and Wineman, M.A.,  
J. Am. Chem. Soc., 70, 2036 (1948).
2. Smith, P.A.S. 'Organic Reactions' Vol.III, Ed.  
Roger Adam., John Wiley and Sons. Inc.  
New York, p. 367 (1946).