CHAPTER -II

EXPERIMENTAL - TECHNIQUES

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An account of the use of potassium bromate as an oxidant has been given in the first chapter. Third chapter contains the present work on the kinetics and mechanism of oxidation of three aromatic amines, namely O-Toluidine, m-Toluidine and p-Toluidine, by potassium bromate, in order to study the effect of structure on the rate of oxidation of amines. Kinetics of oxidation of these three amines by potassium bromate was carried out in aqueous acidic medium with amine concentration in large excess over the potassium bromate 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 potassium bromate concentration.

(3) The order of reaction with respect to hydrogen ion.

(4) Effect of addition of salt.

(5) Effect of change in temperature on the rate of reaction, from which the kinetic and thermodynamic parameters have been calculated.

(6) End product analysis and free radical test.

(7) Stoichiometry.

CHEMICALS :

Chemicals used were AR grade BDH. The source of Br(V) was $KBrO_3$(BDH, AR), sodium thiosulphate (BDH), All Toluidines (BDH,AR), sulphuric acid (A.R), K_2SO_4, $ZnSO_4$ $CdSO_4$ (BDH,AR), double distilled water.

Standard solutions for various experiments were prepared as follows :

(1) Preparation of Toluidines :

All the Toludines (o-Toluidine and m-Toluidine) were first purified by the double distillation. Then these double distilled colourless Toluidines were used to prepare the solutions.

o-Toluidine B.P. = 193°C

m-Toluidine B.P. = 199°C

The p-Toluidine was recrystallised from warmed petrolium ether.

p-Toiuidine m.p. = 45°C

Standard solutions of Toluidines were prepared by dissolving calculated amount of double distilled, recrystallised samples in 1 M sulphuric acid.

(2) Potassium Bromate ($KBrO_3$) :

To prepare (0.1M) stock solution 16.701 gm of potassium bromate (BDH) was accurately weighed on chemical balance and then dissolved in one litre distilled water.

For the various experiments the desired amount of stock solution was taken and was diluted to the required concentration.

(3) Sodium Thiosulphate ($Na_2S_2O_3$) solution :

To prepare (0.1 M) stock solution, 24.818 gms of sodium thiosulphate (BDH) was dissolved in one litre distilled water. Then stock solution was diluted to the required concentration and then used.

(4) Sulphuric Acid (H_2SO_4) :

The 5 M sulphuric acid (AR) was prepared by the standardization method. Then stock solution was used for the various experiments by dilution to the desired concentration.

(5) Potassium iodide (KI) :

The 10 % fresh solution of potassium iodide(BDH) was prepared for every experiment.

(6) Indicator :

A freshly prepared saturated solution of starch.

For studying the kinetics of the reaction, a thermostatic water bath with electronic relay and with an accuracy of $\pm$ 0.1^{o}C was employed.

EXPERIMENTAL PROCEDURE :

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

In a typical experiment, measured quantities of Toluidine and sulphuric acid were taken along with the calculated quantity of double distilled water in the reaction vessels at room temperature. These vessels were placed in the thermostat maintained at the temperature of the experiment and allowing for the period of 10-15 minutes to attain the temperature of the bath. A measured quantity of potassium bromate solution was also thermostated at the same temperature. The solutions of Toluidine, potassium bromate and sulphuric acid were mixed together thoroughly. The process of reaction was monitered by estimating unreacted potassium bromate iodometrically, by pipetting out 5 ml of the reaction mixture at different time intervals. This pipetted out solution was added in the iodine flask containing 10 ml 10 % potassium iodide solution. Then the liberated iodine was estimated by titrating it against a standard solution (0.002 M) of $Na_2S_2O_3$ using freshly prepared starch solution as an indicator. The end point is blue to colourless. Then after every five minutes, 5 ml aliquots of reaction mixture were titrated ddopting above procedure. A semi-micro- burette reading upto 0.05 ml, was employed. Solution of $Na_2S_2O_3$ was previously standardised against a standard solution of arsenious oxide by the usual method. From these titration readings the rate constant k was calculated

$$k = \frac{2.303}{t} \log_{10} \frac{a}{a-x}.$$

where

a = Initial concentration of potassium bromate in terms of 0.002 M $Na_2S_2O_3$

x == The amount of potassium bromate consumed in time interval (t) in terms of $Na_2S_2O_3$

t = time in minutes.

All the calculations were done by using CASIO- fx - 82 Scientific Calculator.

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 $Na_2S_2O_3$ equivalent to the unreacted potassium bromate at any time (t).

(2) 'Co' represents the initial concentration of the reacting species.

(3) 'k' represents the first order rate constant for the total reaction.

(4) 'o-T', 'm-T' and 'p-T' for o-Toluidine, m-Toluidine and p-Toluidine respectively.