

Summary:

The subject of chemical kinetics deals with the quantitative study of the rates of a chemical reaction and various factors upon which it depends, such studies may throw light on the general principles of reactivity or may be useful in arriving at a probable mechanism. Potassium bromate is one of the strong oxidizing agent and has been used for oxidation of various types of organic compounds. The present work deals with the oxidation of anilines namely aniline, o-chloroaniline and p-chloroaniline by potassium bromate in strong sulphuric Acid medium.

In Chapter-1 A brief survey of oxidation reactions of organic compounds by various oxidising agents has been reviewed. Oxidation of various compounds by potassium bromate have been reviewed in detail. In particular, use of potassium bromate in oxidation of carboxylic acids, aldehydes, ketones, Phenols, aminoacides, Diols, alcohols, have been reviewed in detail.

The scope of the present work is also discussed in brief.

Chapter II, deals with the experimental methods adopted for the present study. Preparation of standard solutions and chemicals used is described. Experimental procedure has been given in detail. All calculations are carried out with the help of personal computer PB 100.

Results on the study of oxidation of aniline by potassium bromate are given in Chapter-III. This includes the determination of order of the reaction with-respect to oxidant and the substrate, effect of concentration of sulphuric acid, the effect of temperature variation, effect of salt etc. The reaction is found to be first order with respect of both aniline and potassium bromate. Order of reaction has been calculated by graphical as

well as substitution method. The reaction has been studied at four different temperatures and temperature coefficient and frequency factors have been determined. Thermodynamic parameters such as  $E_a$ ,  $\Delta H^\ddagger$ ,  $\Delta S^\ddagger$  and  $\Delta G^\ddagger$  have also been calculated. Absence of free radical has been shown by acrylonitrile test and the products identified are O-quinone and ammonia.

The results on oxidation of O-chloroaniline are included in Chapter-IV. This includes the parameters which have been sought for aniline in Chapter-III. The reaction seems to be faster as compared to the reaction of aniline. Thermodynamic parameters have been calculated from the study of the temperature effect on the velocity constants of the reaction. The absence of free radical is shown by the acrylonitrile test, and the end products of the reaction have been identified as O-quinone and ammonia.

Chapter-V includes the results for the oxidation of P-chloroaniline. The reaction seems to be faster than aniline and slower than O-chloroaniline.

The reaction is first order with respect to oxidant and substrate. No salt effect. End product are O-quinone and ammonia, absence of free radical is detected by acrylonitrile test.

It seems that all three anilines are oxidized by potassium bromate via the same mechanism. The inductive effect of the chlorine group ( $\text{Cl}^-$ ) has been discussed to explain the difference in velocity constants for the substrates.

The context of the thesis also includes the following :

1. No. of Tables - 25
2. No. of figures - 27
3. Bibliography and References - 67.