CHAPTER - V

Summary

Role of Mn(III) in the oxidation of some organic compounds

Kinetics deals with the rate of chemical reactions, with all factors which influence the rate of reaction and with the explaination of the rate in trerms of the reaction mechanism. In the study of chemical kinetics the rate of chemical reaction is studied in different conditions such as temperature variation, change of concentration of reactants, change of solvent use of catalyst etc. Mn(III) is an effective one electron oxidant and has been used for oxidation of various types of organic compounds. The present work deals with the oxidation of Triethylamine and Diethylamine by Mn(III) sulphate in sulphuric acid medium.

In Chapter-I after taking brief survey of how Mn(III) acts as an oxidising agent, oxidising reactions of various types of organic compounds such as alcohols, phenols, amino compounds etc. by Mn(III) in various forms such as acetate, pyrophosphate, oxalate and sulphate have been reviewed. In perticular a detail survey of oxidation of amines by various oxidants Tl(III), Neutral $KMnO_4$, potassium hexa cyanoferrate, chlorine dioxide, cobaltic per chlorate etc. have been taken in this chapter. Scope of the present work is also discussed in brief.

Chapter-II deals with the experimental methods adopted for the present study. Preparation of Mn(III) sulphate from Mn(II) sulphate and its standardization is described. Photometric method has been used to determine the variation of Mn(III) sulphate as a function of time. For this purpose, absorbance of the reaction mixture at 500 nm is measured on a Spectronic 100 spectrophotometer. Experimental procedure with its principle have been given in detail.

Results on the study of oxidation of triethylamine by Mn(III) sulphate are given in Chapter-III. These include the determination of order of the reaction with respect to the oxidant and substrate, effect of change of concentration of sulphuric acid, the effect of Mn(II) sulphate on the rate of oxidation process, the effect of temperature variation etc. The reaction is found to be first order with respect to both Mn(III) sulphate and triethylamine. Order of the reaction has been calculated by graphical method. Presence of Mn(III) sulphate has virtually no effect on the reaction rate but the rate of reaction is decreased with increase in concentration of sulphuric acid. The reaction has been studied at 5 different temperatures and temperature coefficient and frequency factor have been determined. Thermodynamic parameters such as Ea, $\Delta H^{\#}$, $\Delta S^{\#}$ and $\Delta G^{\#}$ have also been calculated. Presence of free radical has been shown by acrylonitrite test and one of the products are identified to be acetaldehyde. A probable mechanism is suggested in which abstraction of electron from end carbon atom producing a carbonium ion radical was suggested. This carbonium ion radical $\overset{+}{C}H_3\text{-}CH_2\text{-}CH_2\text{-}N\begin{matrix}C_2H_5\\ \bullet\\ C_2H_5\end{matrix}$ further looses a proton forming $CH_2\text{-}CH_2\text{-}N\begin{matrix}C_2H_5\\ \bullet\\ C_2H_5\end{matrix}$ + H^+ .This free radical is further looses one electron to Mn(III) to form a carbonium ion. A steady state principle has been applied for the rate determining step and it has been shown further that the given mechanism accords with the observations. The following rate law was proposed

$$\frac{-d\ Mn(III)}{dt} = K\left[Mn(III)\right]\left[TEA\right]$$

Results on the oxidation of diethylamine are included in Chapter-IV. The reaction has been found to be first order with respect to Mn(III) but 2nd order with respect to diethylamine. Effect of concentration of H_2SO_4

was found to be very little. However reaction is seen to proceed much slower as compared to the reaction of triethylamine. Thermodynamic parameters have been calculated from the study of the temperature effect. The reaction has been shown to proceed via free radical formation by acrylonitrite test and the end product of the reaction has been identified as tetraethyl hydrazine. Presence of acetaldehyde was not identified. A probable reaction mechanism is given in which formation of unstable complex of diethylamine with Mn(III) is proposed. Decomposition of this complex into $(C_2H_5)_2\overset{+}{N}H$ is assumed to be rate determining step. The reaction is shown to be proceed via free radical formation.

From the above discussion it is seen that the mechanism of oxidation of triethylamine and diethylamine by Mn(III) sulphate are different. The order of the oxidation of Triethylamine by Mn(III) sulphate is first order with respect to substrate and oxidant. But in case of Diethylamine it is second order with respect to substrate and first order with respect to oxidant..