CHAPTER - VI

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SUMMARY

The subject of chemical kinetics deals with the quantitative study of the rate of a chemical reaction and the 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 reaction mechanism. 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 malonic acid and its esters, namely, dimethyl malonate and diethyl malonate by manganese (III) acetate in acetic acid medium.

In Chapter-I, after taking a brief survey of oxidation reactions of organic compounds by various oxidizing agents, oxidation by Mn(III) in various forms such as sulphate, oxalate, pyrophosphate and acetate has been reviewed. In particular use of Mn(III) acetate in the oxidation of hydrocarbons, aldehydes, ketones, benzaldoximes, amines, carboxylic acids and their esters has been reviewed in detail. A consolidated data on thermodynamic parameters for oxidation reaction of various organic compounds by Mn(III) has been presented in a tabular form. 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) acetate

from Mn(II) acetate and its standardization is described. Photometric method has been used to determine the variation Mn(III) acetate as a function of time. For this, absorbance of the reaction mixture at 420 nm is measured on a spekkol spectrophotometer (Carl Zeisss). Experimental procedure have been given in details.

Results on the study of oxidation of malonic acid by Mn(III) acetate are given in Chapter-III. These include the determination of order of the reaction with respect to the oxidant and the substrate, effects of addition of water to the reaction mixture, the effects of Mn(II) acetate on the reacting rate, the effect of temperature variation etc. The reaction is found to be first order with respect to both malonic acid and Mn(III) acetate. Order of the reaction has been calculated by graphical as well as substitution method. Presence of Mn(II) acetate has virtually no effect on the reaction rate but presence of water is found to enhance the rate. The reaction has been studied at five different temperatures and temperature coefficient and frequency factors have been determined. Thermodynamic parameters such as E_a , $\Delta H^{\neq}$ $\Delta S^{\neq}$and $\Delta G^{\neq}$ have also been calculated. Presence of free radicals has been shown by acrylonitrile test and the end products are indentified to be formaldehyde and carbon dioxide. A probable mechanism is suggested in which direct attack on -COOR group by Mn(III) is assumed to form HOOC $CH_2COO^{\cdot}$radical.

The reaction is shown to follow a further free radical mechanism. Steady state approximation has been applied to solve for the rate determining step and it has been shown further that the given mechanism accords with the observations.

Results on the oxidation of dimethyl malonate are included in Chapter-IV. These include the parameters which have been sought for malonic acid oxidation in Chapter-III. The reaction has been found to be first order with respect to the ester but zero order with respect to Mn(III) acetate. Presence of water is found to increase the rate of the reaction. However reaction is seen to proceed much slow as compared to the reaction of malonic acid. Thermodynamic parameters have been calculated from the study of the temperature effect on the velocity constant of the reaction. The reaction has been shown to proceed via free radical formation by acrylonitirle test and the end products of the reaction have been identified as formaldehyde and carbon dioxide as in case of malonic acid. A probable reaction mechanism is given in which partial hydrolysis of the ester has been assumed to be the rate determining step. The reaction is shown to proceed via free radical formation.

Chapter-V includes the results and mechanism for the oxidation of diethylmalonate. The reaction is seen to proceed in an identical way as that of dimethylmalonate except that it is slower. Thus,

i) The reaction is first order with respect to ester but zero order with respect to oxidant.

ii) Mn(II) has no effect on the rate of the reaction but presence of water has +ve effect.

iii) End products are formaldehyde and carbon dioxide.

iv) Free radical formation is detected by acrylonitrile test.

It seems that both the esters are oxidized by Mn(III) acetate via the same mechanism. The inductive effect of methyl group and ethyl group in the ester has been iscussed to explain the difference in velocity constants for the two substrates. Thermodynamics parameters have also been compared and explained.

The contex of the thesis also includes the following :

1) No. of Table = 34

2) No. of figures = 25

3) Biblography of references = 52