CHAPTER - V

SUMMARY

Chemical kinetics deals with the rate of chemical reactions, with the factors which influence the rate and with the explanation of the rate in terms of the reaction mechanism. In the study of chemical kinetics, the rate of chemical reaction is studied in different conditions such as different temperatures, different concentrations of substrate and oxidant etc. The kinetics provides the most general method to determine the mechanism of reaction. To suggest a mechanism for any chemical process by kinetic study, we should get the additional information such as the products of reaction, stereo-chemical evidences, use of isotopes, detection of short lived intermediates and refinement of kinetic methods. In general, analytical procedures may be divided into two broad categories, chemical and physical. It is found that physical methods of analysis are more convenient than chemical methods. Theorotically any property which changes sufficiently could be used to follow the course of a reaction. Oxidation of large number of organic compounds have been studied viz. olefins, phenols, aldehydes, alcohols, amines, esters, carboxylic acids etc., using variety of oxidising agents such as nitric acid, chromic acid, permanganates, ceric sulphate, potassium bromate, potassium persulphate etc.

We had selected Mn(III) as an oxidant and formaldehyde and benzaldehyde as the substrates. Before proceeding to the experimental work, we had done a broad literature survey about the work done on Mn(III) as an oxidant as well as formaldehyde and benzaldehyde as substrates. It is seen that complexes of Mn(III) as acetates, sulphates, pyrophosphates and perchlorates have been largely used as an oxidants. It is seen further that the kinetics of oxidation of formaldehyde has been studied by using nessler's reagent, ammonium nitrate, Co(III), bromamine-T, chloramine-T and peroxydisulphate as an oxidants. Further, it is seen that the kinetics of oxidation of benzaldehyde has been studied by using vanadium(V), permanganate, sodium periodate, chloramine-T, bromamine-T, cerium(IV) and chromic acid as oxidants. Considering the above survey, we decided to study the kinetics of oxidation of formaldehyde and benzaldehyde by Mn(III) sulphate in sulphuric acid medium. The details of the literature survey comprises chapter-I.

The experimental technique is explained in details in Chapter II. Mn(III) is stable in 5 M sulphuric acid so the oxidation of formaldehyde was studied in 5 M H_2SO_4 medium. To increase the solubility of benzaldehyde, a mixture of 3 M sulphuric acid and 4 M acetic acid was used as a medium for the oxidation of benzaldehyde. Mn(III) is reduced to Mn(II) during the course of reaction. Mn(III) is strongly absorbing

species (λ max.= 500 nm. ϵ max = 113.00 M^{-1} cm^{2}) as compared to Mn(II) which is practically non-absorbing at 500 nm. So the observed absorbence (optical density) at 500 nm. was safely taken as a measure of concentration of Mn(III) during the course of the reaction. Hence the reaction was followed spectrophotometrically at 500 nm. wavelength. λ max.for Mn(III) sulphate was determined by using 2.5×10^{-3}M and 5×10^{-3}M solutions of Mn(III) sulphate. Beer-Lambert's law was verified by using Mn(III) sulphate solutions in the range of 1×10^{-3} M to 5×10^{-3}M.

For the oxidation of formaldehyde, following parameters are studied.

For the effect of variation of Mn(III) sulphate, its concentration was varied from 3×10^{-3}M to 8×10^{-3}M

The reaction is first order with respect to Mn(III) sulphate.

For the effect of variation of formaldehyde, its concentration was varied from 0.04 M to 0.1 M. The reaction is first order with respect to formaldehyde.

For the effect of sulphuric acid, it was used in the range from 3 M to 6 M.

For the effect of Mn(II), it was used in the range 0 to 5×10^{-3}M. Both sulphuric acid and Mn(II) have no any effect on the rate of the reaction.

The rate expression from these observations can be written as

$$-\frac{dc}{dt} = k_1 [HCHO] [Mn(III)]$$

For the effect of temperature it was varied from 308°K to 323°K. Temperature coefficient was calculated (2.7) from the values of first order rate constants. The energy of activation is calculated to be 20.00 K cal/mole. Graphically it is found to be 19.740 K cal/mole. ΔH^* is found graphically to be 19.740 K cal/mole. The frequency factor, ΔS^* and ΔG^* are found to be 6.44×10^9 Sec^{-1}, -101.75 e.u. and 51.85 K cal/mole respectively.

From the above observations and literature survey, we have proposed the mechanism of oxidation of formaldehyde by Mn(III) as follow :

(1) $HCHO + Mn(III) \xrightarrow[slow]{k_1} Mn(II) + H^+ + H\dot{C}O$

(2) $H\dot{C}O + H_2O \xrightarrow[fast]{k_2} HCOOH + \dot{H}$

(3) $HCOOH + Mn(III) \xrightarrow[fast]{k_3} Mn(II) + H^+ + HCO\dot{O}$

(4) $H\dot{C}O + H_2O \xrightarrow[fast]{k_4} HCHO + \dot{O}H$

(5) $\dot{O}H + HCO\dot{O} \xrightarrow[fast]{k_5} CO_2 + H_2O$

(6) $\dot{H} + Mn(III) \xrightarrow[fast]{k_6} H^+ + Mn(II)$

The rate expression should be of the form

$$-\frac{dc}{dt} = k_1 [HCHO] [Mn(III)]$$

in accordence with the observed expression.

For the oxidation of benzaldehyde, following parameters are studied.

For the effect of variation of Mn(III), its concentration was varied from 5×10^{-3}M to 8×10^{-3}M. The reaction is first order with respect to Mn(III). For the effect of variation of benzaldehyde, a solution containing 3 M sulphuric acid and 4 M acetic acid was used as a medium for the reaction, to raise the solubility of benzaldehyde. The concentration of benzaldehyde was used in the range 2×10^{-2}M to 8×10^{-2}M. The reaction is independent of benzaldehyde concentration. For the effect of variation of acetic acid, it was used in the range 3 M to 6 M. The reaction is first order with respect to acetic acid.

The variation of sulphuric acid was studied using the range 2 M to 5 M.

The variation of sodium acetate was studied using the range 0.05 M to 0.2 M.

The variation of Mn(II) sulphate was studied by using the range 5×10^{-3}M to 11×10^{-3}M.

It is observed that the concentrations of sulphuric acid, sodium acetate and Mn(II) sulphate have no any effect on the rate of the reaction.

The rate expression can be written as

$$-\frac{dc}{dt} = k_1 [CH_3COOH] [Mn(III)]$$

The temperature was varied from 313°K to 328°K. Temperature coefficient was calculated (2.15) from the values of first order rate constants. The energy of activation is calculated to be 15.73 K cal/mole. Graphically it is found to be 15.35 K cal/mole. Graphically ΔH^* is found to be 13.43 K cal/mole. The frequency factor, ΔS^* and ΔG^* are found to be 4.8×10^6 sec^{-1}, -116.45 e.u. and 50.76 K cal/mole respectively. From the above observations and literature survey, we have proposed the mechanism of oxidation of benzaldehyde by Mn(III) as follow :

(1) $CH_3COOH + Mn(III) \xrightarrow[slow]{k_1} Mn(II) + H^+ + CH_3\dot{C}OO$

(2) $CH_3\dot{C}OO + C_6H_5CHO \xrightarrow[fast]{k_2} C_6H_5\underset{A}{\dot{C}O} + CH_3COOH$

(3) $C_6H_5\underset{A}{\dot{C}O} + H_2O \xrightarrow[fast]{k_3} C_6H_5COOH + \dot{H}$

(4) $\dot{H} + Mn(III) \xrightarrow[fast]{k_4} Mn(II) + H^+$

The rate expression for the reaction should be of the form

$$-\frac{dc}{dt} = k_1 [\, CH_3COOH \,] [\, Mn(III) \,]$$

in accordence with the observed expression.

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