CHAPTER II

MATERIALS & METHODS
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In the kinetic oxidation of ketones by vanadium (V) in the aqueous and micellar media, different chemicals were used in form of solution. The procedure employed for the preparation of these solutions and the kinetic studies have been described in this chapter.

Solution Preparation

Oxidant Solution

Ammonium Meta vanadate (Loba chime) is used as a primary standard. The solution of oxidant was prepared by suspending weighed amount of ammonium meta vanadate in distilled water in a standard measuring flask and by adding a known volume of standard sulphuric acid (AR, BDH) to it, till a clear solution was obtained. The solution was made upto the required volume. The solution so prepared remains stable for months [197] and hence such solution was used as stock solution. The concentration of stock solution was determined by titrating it ferrometrically. The known volume of stock solution of oxidant and excess known volume of standard ferrous ammonium sulphate (0.01M) was taken and titrated against potassium dichromate (0.01M) using N-phenyl anthranilic acid as a reversible redox indicator. The acidity of the solution was calculated after allowance for hydrogen ion used for VO$_2^+$ formation as following equation.

\[ \text{VO}_3^+ + 2\text{H}^+ \rightarrow \text{VO}_2^+ + \text{H}_2\text{O} \]

Substrate Solution

Ketones of (AR grade) were used. Actone (Loba-chime), cyclohexanone (BDH), acetophenone, benzophenone and ethylmethyl ketone (Loba-chime) were chosen as reductant in the present investigation. The stock solutions of ketones were prepared by weighing and dissolving the required quantity of the doubly distilled water and keeping in dark place.

Acetone and ethyl methyl ketones of A.R. (Loba chieme) were used for preparing the substrate solution. Both are quite soluble in water and hence the stock solution of
substrate was prepared directly by dissolving the required amount of acetone and ethylmethyl ketone in doubly distilled water. Cyclohexanone, actophenone, and benzophenone were used for preparing the substrate solution these are soluble in v/v distilled water and acetic acid.

**Sulphuric Acid Solution**

Stock solution of sulphuric acid (AR, BDH) was prepared by diluting its appropriate volume with distilled water. The concentration of acid was determined by titrating it against standard alkali solution [198].

**Indicator Solution**

The indicator solution was prepared by dissolving 0.107 g of N-phenylantranilic acid in 2 ml of 5% sodium carbonate (S. MERCK) solution and was diluted to 100 ml by adding distilled water [199]. Three to four drops of indicator solution were used in each titration. The rate of colour change of indicator was not very clear in the medium containing more than 6.0 M sulphuric acid. However, below that 5.0 M sulphuric acid medium the colour change was sharp, hence in each titration the overall concentration of sulphuric acid was maintained at below 5.0 M the colour of indicator in the oxidized form is purple, while it was brown colour in the reduced state.

**Sodium Lauryl Sulphate Solution**

The solution of sodium lauryl sulfate (Loba-chemie) was prepared in double distilled water.

**Other Solution**

The solution of sodium carbonate was prepared in double distilled water dissolving accurately weighed required quantity. The standard solution of potassium dichromate (BDH) was prepared by dissolving the appropriate amounts in distilled water. The solution of ferrous ammonium sulphate (BDH) was prepared by dissolving its calculated
weight in distilled water and was standardized by titrating it against standard potassium dichromate (BDH) solution using N-phenyl anthranilic acid as an indicator. Glacial acetic acid (BDH) was used for preparing composition of binary mixtures of acetic acid-water.

Determination of Critical Micelles Concentration (CMC)

CMC of micelles was determined for each ketones separately by adding varying concentrations of micelle in the reaction mixture and the kinetics of the reaction were followed by the procedure given below. The pseudo first rate constant was determined at each concentration of micelle. A plot between $k_w$ and [micelle] was drawn and from the maximum value of the rate constant, CMC is evaluated. $k_w$ represents the rate constant at different [micelles].

Kinetic Methods

All the standard flasks and reaction bottles were of Pyrex glass with well ground stoppers. The volumetric apparatus, the pipettes, burettes and flasks were standardized by the usual methods. The glassware used was pretreated with chromic acid and rinsed with redistilled water.

An electrically operated thermostatic waterbath was used. As usual, it was provided with sufficient thermal logging with suitable stirrers for the work. Contact German thermometer worked in conjunction with an electric relay maintained the required temperature accurately with fluctuation of not more than $\pm 0.1^\circ$C. The temperature was recorded by means of an accurate and sensitive thermometer, reading to tenths of a degree.

Rate Measurements

In rate measurements, following procedure was adopted. The kinetic studied were made by taking a large amount of ketones and acid concentration over the oxidant concentration at constant ionic strength. The reaction mixture, containing appropriate quantity of oxidant solution, acid and water were taken in 100ml conical flask. The
substrate solution was taken in another flask. These two flasks were kept in a thermostat maintained at required temperature. The total volume of reaction mixtures was 50 ml. After allowing sufficient time for the reactants to attain the temperature of the waterbath, they were mixed to each other. The progress of reaction was monitored by withdrawing aliquot at definite time intervals in another conical flask containing unreacted ferrous ammonium sulphate solution was titrated against potassium dichromate solution using N-phenyl anthranilic acid as an indicator. The same procedure is performed with surfactant. The surfactant was kept with substrate solution before final mixing in thermostat. The experimental data were fed into various integrated rate equations.

**Kinetic Studies**

It was found that in each oxidation under study, the values of pseudo first order rate constant obtained from the rate equation were constant within the experimental error suggesting that each reaction obeys first order kinetics.

\[ k = \frac{2.303}{t} \log \frac{a}{(a-x)} \]

**Typical Kinetic Runs**

In the oxidation studies for each substrate some typical runs shall be carried out to investigate the general behaviour of the reaction under different experimental conditions. These studies are effect of concentration of the oxidant, substrate, sulphuric acid and anionic surfactant (sodium lauryl sulphate) and the variation of temperature. The effect of solvent was also carried out.

**Order of the Reaction**

The order of the reaction with respect to oxidant and substrate shall be determined by Ostwald’s isolation method. Kinetic studies shall be carried out at varying concentration of oxidant keeping the other conditions constant to obtain the order with
respect to oxidant. The reaction order has also been found from log-log plots of initial rates versus concentration. The validity of plot shall be examined.

**The Effect of Temperature**

The effect of temperature was studied at four different temperatures at constant [Vanadium (V)], [Ketones], [H+] and [surfactant].

**THERMODYNAMIC PARAMETERS**

The activation parameters such as temperature co-efficient, energy of activation, frequency factor, entropy of activation, heat of reaction and free energy of activation from temperature dependent rate data, have been evaluated in this section. The following method has been applied.

**Energy of Activation (E_a)**

Empirically, the activation energy is the parameter which expresses the temperature dependence of the rate constant.

\[ k = A \cdot e^{-\frac{E_a}{RT}} \]

The standard method for obtaining \( E_a \) is either to evaluate from Arrhenius equation or from Arrhenius plot. Both the method has been applied as detailed below.

**Arrhenius Equation**

The activation energy can be calculated by appropriately filling Arrhenius equation.

\[ E_a = 2.303 \cdot R \times \frac{T_2 \times T_1}{T_2 - T_1} \log_{10} \frac{k_2}{k_1} \]
**Graphical Method**

The energy of activation was also obtained by plotting $\log k_0$ (and $k_m$) against $1/T$. An Arrhenius plot was found to be linear one for the data recorded.

Gradient = \[- \frac{E_a}{2.303 \, R} \]

\[ E_a = - \text{Slope} \times 2.303 \, R \]

**Frequency Factor ($A$)**

The frequency factor ($A$) which represents the total frequency of the encounters between the two reactant molecules, irrespective of whether they possess sufficient energy or not, is given by

\[ \log A = \log k_1 + \frac{E_a}{2.303 \, R \, T} \]

**Heat of Reaction**

Thermodynamically the equation for the enthalpy of activation or heat of reaction is as follows.

\[ \Delta H^* = E_a - RT \]

**Entropy of Activation ($\Delta S^*$)**

The entropy of activation is evaluated by employing equation

\[ \Delta S = 2.303 \, R \left( \log_{10} A - \log_{10} \frac{e \, k \, T}{h} \right) \]

Where:

$K = $ Boltzmann constant $= 1.38 \times 10^{-23}$ JK$^{-1}$
T = Absolute Temperature
H = Plank's Constant = $6.626 \times 10^{-34}$ J Sec.
e = 2.718
R = Universal gas constant = 8.3144 Jk$^{-1}$mol$^{-1}$

**Free Energy of Activation**

The change in free energy ($\Delta G^*$), gives the extent to which a reaction goes to completion. It is determined from the following relationship

$$\Delta G^* = \Delta H^* - T\Delta S^*$$

where $\Delta H^*$ and $\Delta G^*$ are the change in enthalpy and entropy and $T$ is the absolute temperature. The calculated values of all the activation parameters have been recorded.