

CHAPTER - I : GENERAL THEORY

1.1 INTRODUCTION

The subject of reaction kinetics is concerned with the detailed study of the rates of chemical reactions. The experimental part of the subject deals with ways of measuring precisely the variation of the concentrations of reacting substances with time. These measurements are carried out in such a way that effects of temperature, pressure, catalysts, isotopes, radiation, etc. on the rate of reaction can be assessed.

Interpretation of the experimental results leads to a better understanding of the mechanism of a reaction. The combination of the results of a large number of experiments gives rise to general theories of chemical reactivity.

The mechanism of a chemical reaction may be considered as a hypothetical motion picture of the behaviour of the participating atoms. Such a picture would begin at some time before the reacting species approach each other, then go on to record the continuous paths of the atoms during the reaction, and come to an end after the products have emerged. Since it is generally to obtain such an intimate picture, the investigation of a mechanism has come to mean obtaining information that can furnish a picture of the participating species of one or more crucial instants during the course of the reaction. Thus, the mechanism is the actual process by means of which a reaction takes place involving the information such as which bonds are broken, in what order, how many steps are involved,

the relative rates of each step and similar important points.

It is not possible to study the mechanism of a organic reaction directly i.e. while the reactants are converted into products via some intermediate.¹ To establish the mechanism of a particular reaction, it must fulfil the following few conditions.

- a) The proposed mechanism should be as simple as possible, while still accounting for the experimental facts.
- b) The proposed mechanism should, if possible, suggest tests of its correctness.
- c) Individual tests in the proposed mechanism would specify the molecularity of reaction.
- d) The proposed mechanism should not violate the principle of microscopic reversibility.
- e) Individual reactions should be chemically reasonable.
- f) Individual reaction should be energetically reasonable.

Chemical kinetics is the study of system whose properties are a function of time. The field is concerned with the rates of reaction with all the factors that affect them and with the explanation (of both) in terms of the reaction

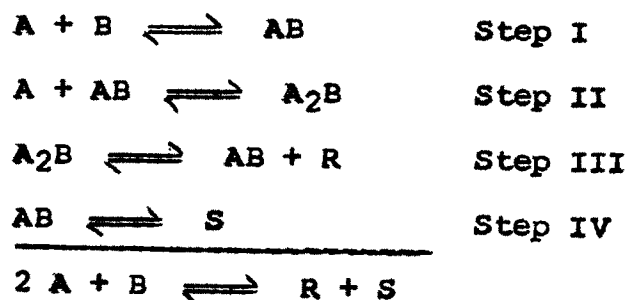
mechanism. All chemical reactions take place at some finite rate which is dependent on conditions such as temperature, pressure, concentration of species and presence of catalyst or inhibitors. The chemical kinetics is of considerable importance to analytical industrial chemists, because through the knowledge of the kinetics of a system, one can increase or decrease the rate of a reaction by varying the conditions employed.

The rate of the reaction is determined from the mathematical expression showing the dependence of rate on the concentration of the reactants and the molecularity.

In some reactions the change occurs directly, which may be represented by an overall stoichiometric equation. However, complex reaction in which the substances undergo a series of stepwise changes, each consists a reaction in its own right and is much more common. The overall mechanism is then made up to contributions from all such reactions. For example, the reaction :



may take place as follows :



4

The slowest step controls the rate of the reaction and may also be determined from the overall rate equation. The mechanism rather than the rate equation is important to theoretical chemist.

1.2 THERMODYNAMICS OF REACTION RATES

There are two main theoretical approaches for dealing with problem of reaction rates. The collision theory is based largely on kinetic theory of gases and uses a mechanical model whereas the transition state theory is based largely on the thermodynamics and uses a three dimensional surface as model, the vertical co-ordinate being energy. Although the transition state theory is the more generally useful of the two, particularly for organic reactions, the collision theory is nevertheless convenient for certain special purposes and is of historical importance because of the influence it has on mode of thinking about reaction mechanism.

1.2.1 The Collision Theory :

This is based upon the idea that if two molecules are to combine chemically an essential first step is that they should meet (i.e. collide) each other. Only those collisions in which molecules acquire energy more than the activation energy will be able to do so. The collision theory may therefore, be expressed in a sentence by saying that the rate of reaction is equal to the number of activated collisions per unit time. The rate constant at unit concentration of the reagent is given by the equation (1.2) :

$$k = PZ \cdot e^{-E/RT} \quad 1.2$$

where k = rate constant, P = probability factor, Z = frequency of collision at unit concentration, E = energy of activation, T = absolute temperature and R = gas constant.

' Z ' may be calculated from the kinetic theory. The equation (1.2) is therefore, like to Arrhenius equation :

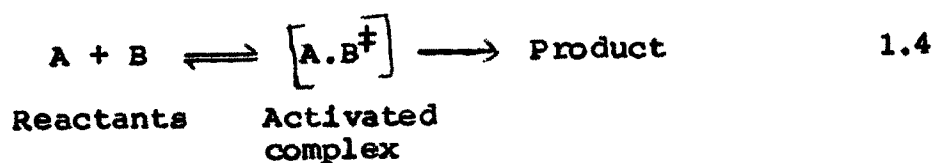
$$k = A \cdot e^{-E/RT} \quad 1.3$$

in which the temperature occurs only as an exponential factor. The basic idea of this theory is that the rate of reaction equals the number of activated collisions per unit time.

1.2.2 The Transition State Theory :

The main assumption of this theory is that all chemical reactions proceed via transition state of potential energy higher than the average potential energies which is in thermodynamic equilibrium with the reactants eventhough of either the reactant or product states, which is in thermodynamic equilibrium with the reactants eventhough overall chemical reaction is irreversible.

This theory postulates that molecules before undergoing reactions must form an activated complex in equilibrium with the reactants, and that the rates of any reaction is given by the rates of decomposition of the complex to form the reaction products. This may be symbolized and given by following equation(1.4) :



where the superscript $A.B^\ddagger$ refers to the activated complex.

The rate constant of any reaction, no matter what the molecularity or order may be given by expression :

$$k = \frac{RT K^\ddagger}{Nh} \quad 1.5$$

where k = rate constant, R = gas constant in ergs mole⁻¹ degree⁻¹, N = Avogadro's number, h = Plank's constant : 6.625×10^{-27} ergs.sec., T = absolute temperature and K^\ddagger = equilibrium constant for the formation of the activated complex from the reactants.

The factor $\frac{RT}{Nh}$ is the same for all molecules irrespective of their chemical properties. This equation is not directly useful since K^\ddagger cannot be measured experimentally. However, assuming that the transition state is in thermodynamic equilibrium with reactants, we may write for K^\ddagger :

$$\ln k^* = \frac{\Delta F^*}{RT} = - \frac{(\Delta H^* - T\Delta S^*)}{RT} \quad 1.6$$

where ΔF^* = standard free energy,
 ΔH^* = enthalpy, and
 ΔS^* = entropy of activation.

Introducing equation (1.6) into equation (1.5) one gets for k

$$k = \frac{RT}{Nh} e^{\Delta S^*/R} e^{-\Delta H^*/RT}$$

$$\text{or } \ln k = \frac{RT}{Nh} + \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT} \quad 1.7$$

Consequently, when k and ΔH^* of a reaction are known at a given temperature ΔS^* may be found :

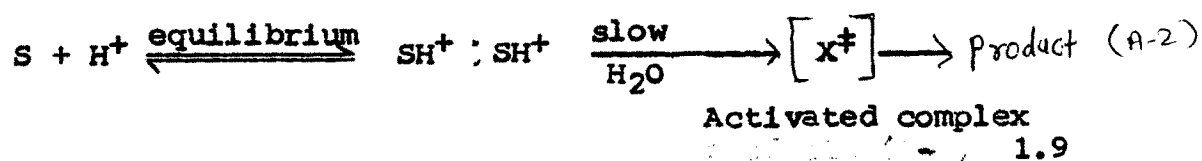
Equation (1.7) is the fundamental relation of the transition state theory.

1.3 ENTROPY OF ACTIVATION

Entropy is the measurement of the randomness of a system. If a reaction occurs with an increase in entropy, there is more disorder, possibly more among the products than among the reactants. That is, there is more restriction to the motion of reactant molecules than to the motion of product molecules. The entropy of activation, which may be calculated from reaction, is a measure of freedom from restraint on motion among the reactants.³

Long et al.⁴ (1957), amplifying a suggestion of Taft⁵ and co-workers (1955), have proposed the use of ΔS^* as a criterion of the mechanism of hydrolysis reaction. These reactions are usually classified as unimolecular (A-1, SN¹) or bimolecular (A-2, SN²). In the former case a water molecule does not

participate in the rate determining step, while a water molecule does not usually considered to be bound in the activated complex in the latter. The A-1 and A-2 processes involve specific hydronium ion catalysis and may be represented as follows⁶ :



It seems quite reasonable that the loss of translational and rotational freedom of water molecule associated with the bimolecular process should lead to lower entropy of activation relative to unimolecular case. It can be said that if the entropy of activation is negative then the mechanism is probably bimolecular. Empirically however, all known bimolecular, specifically acid-catalysed reactions have negative entropies of activation and all known unimolecular acid catalysed reactions have entropies of activation near to zero or have positive values.

1.4 SOLVENT EFFECT

The medium in which chemical reactions take place in solution is an important factor. The change in solvent will affect both the rate and mechanism of reaction. Sometimes the solvent alters the rate without affecting the mechanism and rarely changes the mechanism without altering the rate.

A solvent can change the rate without influencing the mechanism by changing the forces between the reacting particles and hence altering the readiness with which they approach each other. Such a phenomenon is illustrated by the effect of dielectric constant on electrostatic forces among reacting molecules. In diffusion controlled reactions the solvent changes the rate by altering the frequency of collision between the reacting particles by virtue of its viscosity.

The qualitative theory⁷ of solvent effects put forward by Hughes and Ingold could be used as criterion for mechanism. It postulates that increase in ionization power of solvent will be favourable to an increase in the magnitude of charge but unfavourable to decrease in the magnitude of charge to a smaller extent, to a dispersion of a given charge.

1.5 THE KINETIC ISOTOPE EFFECT

Additional insight into reaction mechanism is possible when kinetic studies are carried out with reactant molecules that have been modified by isotope substitution. It may happen that the rate constant of the reaction is altered by the isotopic substitution. Such a change in rate is referred to as the kinetic isotope effect.

The existence of this effect suggests that the bond abnormally stretched in the transition state involves one or more of the isotopically substituted atoms. Thus, kinetic studies, as well as indicating the molecules in rate determining stage can also point to the particular bond involved.

Large changes in rate have been observed in many reactions⁸⁻¹⁰ following isotopic substitution of hydrogen by deuterium since the relative change in mass when this element is involved is very large. Indeed, the rate change is so pronounced that the use of deuterium-substituted compounds has been suggested for the slowing of unwanted reactions, such as the oxidative deterioration of engine lubricants. In the oxidation of benzaldehyde to benzoic acid by acidic permanganate, replacing the aldehydic hydrogen by deuterium reduces the reaction rate, at room temperature, by a factor of 7.

1.6 THE REVERSE KINETIC ISOTOPE EFFECT

If reactions are carried out using heavy water (D₂O) as a solvent, in some cases the reaction rate is greater than that in ordinary water.¹¹⁻¹³ This is known as reverse kinetic isotope effect. The acid-catalysed hydrolysis of aliphatic esters and the bromide-bromate reaction show this effect.

1.7 IONIC STRENGTH EFFECT

The reaction between two ionic species proceeds through transition state complex which is in equilibrium with reactants. The equilibrium properties of such reactions can be greatly effected by other ionic species which are present in addition to the reactants.

The variable that determines the effect of ion on the equilibrium is the ionic strength defined by :

$$\mu = \frac{1}{2} \sum m_i z_i^2$$

where m_i = molarity, and

z_i = charge.

The effect of electrostatic interaction of ionic species can be successfully treated by activity rate theory which was developed by Bronsted, Bjerrum and Debye-Huckel. The theoretical rates can be calculated by applying second empirical equation of Debye-Huckel and can be compared with observed rate as has been done for the hydrolysis of propionamide.¹⁴

REFERENCES

- 1 Richard A. Jackson, "Mechanism and Introduction to the Study of Organic Reactions".
- 2 Grunwald, E. and Leffler John F., "Rates and Equilibria of Organic Reactions", John Wiley & Sons, Inc. New York, London (1963).
- 3 Gold, E.S., "Mechanism and Structure in Organic Chemistry",
- 4 Long, F.A., Pritchard, J.G. and Standford, F.F.,
J. Am. Chem. Soc., 79, 2362 (1957).
- 5 Taft, R.W. Jr., Purlee, E.L., Riesz, P. and De Fazio, C.A.,
J. Am. Chem. Soc., 77, 1584 (1955).
- 6 Hammett, L.P., "Physical Organic Chemistry", McGraw Hill Book Co., Inc. New York, 1940, pp 262 ff.
- 7 Hughes, E.D. and Ingold, C.K.,
J. Chem. Soc., 244 (1935).
- 8 Wiberg, K.B.,
Chem. Rev., 55, 719 (1955).
- 9 Bell, R.P., "Acid-Base Catalysis", Oxford University Press, London, 1941 pp 145.
- 10 Purlee, E.L.,
J. Am. Chem. Soc., 81, 263 (1959).

- 11 Bonhoeffer, K.F. and Reitz, O.,
Z. Physik. Chem., A-179, 135 (1937).
- 12 Moelwyn-Hughes and Bonhoeffer, K.F.,
Z. Electrochem., 40, 469 (1934).
- 13 Pritchard, J G. and Long, F.A.,
J. Am. Chem. Soc., 78, 6008 (1956).
- 14 Jagdale, M.H. and Nimbalkar, A.Y.,
J. Ind. Chem. Soc., 49, No. 3, 269 (1972).