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CHAPTER - I

INTRODUCTION

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INTRODUCTION

The study of reaction rates is called kinetics and is
a very widely practiced specially in organic chemistry at
present, since it is most powerful tool for illuminating
reaction mechanism. Basically, the investigator must mix
reactants of known concentrations at constant temperature and
then determine the rate of decrease of these concentrations
with time, thus measuring in fact the rate of reaction i.e.
rate of disappearance of starting material. He has to observe
these concentrations at specific time interval either by taking
spectra of the mixture or by removing a measured sample(aliquot),
stopping its reaction, and determing the concentration in the
arrested sample by titration. Spectroscopic observation of
reactions is easiest as in the example of monitoring the
reaction of a diene with bromine by observing rate of decrease
of the ultraviolet absorption of the diene with time, the
intensity of absorption being a function of diene concentration.
Further these measurements are carried out in such a way that
effects of temperature, pressure, catalyst, isotope, salt etc.
on the rate of reaction can be assessed.

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

The mechanism of chemical reactions may be considered as a hypothetical motion picture of the behaviour of the participating atoms. Such a picture would begine at some time before the reacting species approach each other, then go on to record the continuous paths of the atoms during the course of the reaction. Thus 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 rate of each step and similar important points.

In a reactions, when reactants are converted into products, they pass through some intermediates. So, to establish the mechanism of perticular reaction, it must fulfil following conditions.
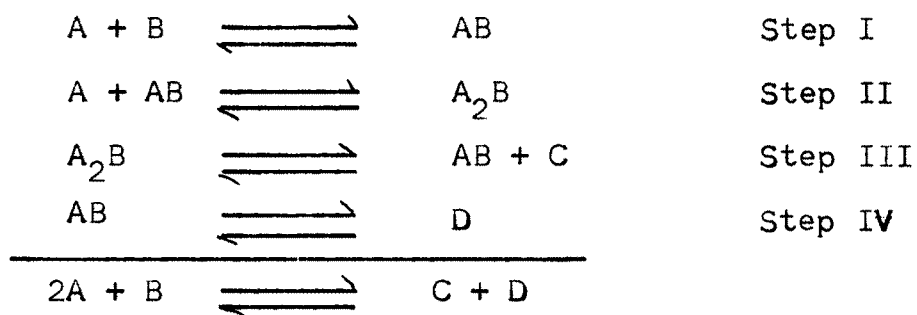
1) The proposed mechanism should be as simple as possible, while accounting for the experimental facts

2) The proposed mechanism should, if possible suggest tests of its correctness

3) The proposed mechanism would specify the molecularity of reaction

4) The proposed mechanism should not violate the principle of microscopic reversibility

5) The proposed reactions should be chemically reasonable

6) The proposed reactions 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 effect them and with the explanation in terms of reaction mechanism. All chemical reactions take place at some finite rate which is dependant on conditions such as temperature, pressure, concentration and presence of catalyst or inhibitors. The chemical kinetics is of considerable importance to analytical and industrial chemists. The knowledge of the kinetics of a system is useful to bring the reaction to desired stage by changing the conditions.

The rate of reaction is determined from the mathematical expression showing the dependance 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, in complex reactions substances undergoes series of stepwise changes. Then the overall mechanism is made up of contributions from all such reactions. For example

$$2A + B \longrightarrow C + D$$

may takes place as follows

$$A + B \rightleftharpoons AB \qquad \text{Step I}$$

$$A + AB \rightleftharpoons A_2B \qquad \text{Step II}$$

$$A_2B \rightleftharpoons AB + C \qquad \text{Step III}$$

$$AB \rightleftharpoons D \qquad \text{Step IV}$$

$$\overline{2A + B \rightleftharpoons C + D}$$

The slowest step controls the rate of the reaction.
The mechanism rather than rate equation is important to
theoretical chemists.

Thermodynamics of Reaction rates

There are two main theoretical approaches for dealing with
problems 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 a model, the vertical
co-ordinate indicate energy changes. The transition state theory
is generally more useful of the two, particularly for organic
reactions. The collision theory is of historical importance
because of the influence it has made on thinking about reaction
mechanism.

The Collision Theory

This theory is based upon the idea that if two molecules
are to combine chemically, an essential first step is that they
should collbid with each other. Only those collisions are
effective in which collçiding molecules have more than average
energy content. The excess of energy required for reaction is
called as activation energy. However, even collisions between
molecules having the requisite energy content do not often result
in reaction. Unfruitful collisions result if the molecules
collside in wrong way or if the excess energy in the molecule is
not associated with the appropriate internal motions of the

molecule. The probability of reaction occuring even in collision between activated molecules may be rather small if the stereo-electronic requirements of the reaction are stringent. Therefore, the collision theory may be expressed as the rate of reaction is equal to the number of activated collisions per unit time. The rate constant (k) at unit concentration of the reagent is given by the equation

$$k = P.z.e^{-Ea/RT} \qquad \ldots \qquad (1.1)$$

where k = Rate constant
P = Probability factor
z = Frequency of collision at unit concentration
E_a= Energy of activation
T - Absolute temperature
R - Gas constant

'z' may be calculated from the kinetic theory. The equation (1.1) is therefore similar to Arrhenius equation

$$k = A.e^{-Ea/RT} \qquad \ldots \qquad (1.2)$$

where A is Frequency factor.

The basic idea of the theory is that the rate of reaction equals the number of activated collisions per unit time.

The Transition State Theory

The main assumption of the theory is that all reactions proceed through formation of transition state, which is with higher potential energy than average potential energies of reactants. The transition state is a molecular complex in

which reactants have been forced together in such a way that they have paid the price (in the form of energy) required for the reaction and are ready to collapse into products. According to transition state theory, molecules undergoing reaction must form an activated complex in equilibrium with the reactants and then pass into products. So, the rate of the reaction is given by the rates of decomposition of the complex to form the reaction products. This may be represented as follows

$$A + B \rightleftharpoons [A B]^* \longrightarrow Products.$$
Reactants   Activated complex

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

$$k = \frac{RTK^*}{Nh} \qquad \qquad ... \qquad (1.3)$$

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} erg sec.

T - Absolute Temperature

K^*- Equilibrium constant for the activated complex from the reactants.

The factor RT/Nh is constant for molecules irrespective of their chemical properties. The equation is not directly useful, since K^* cannot be measured experimentaly. However, assuming that the transition state is in thermodynamic equilibrium with reactants we may write for K^*

$$\ln K^* = \frac{-\Delta F}{RT} = -\left[\frac{\Delta H^* - T\Delta S^*}{RT}\right] \quad \cdots \quad (1.4)$$

where ΔF^* - free energy of activation

ΔH^* - Enthalpy of activation

ΔS^* - Entropy of activation

Introducing equation (1.4) into equation (1.3) we can write

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

$$\ln k = \frac{RT}{Nh} + \frac{\Delta S^*}{R} - \frac{\Delta H^*}{RT} \quad \cdots \quad (1.5)$$

when k and ΔH^* of the reaction are known at given temperature, ΔS^* may be calculated.

Equation (1.5) is the fundamental relation of the transition state theory.
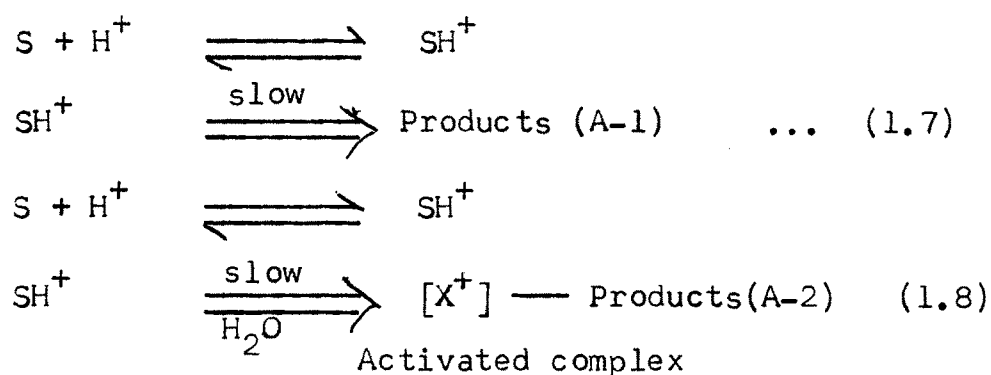
Entropy of Activation

Entropy is the measurement of randomness of a system. If a reaction occurs with an increase in entropy, there is more disorder possible among the products than among the reactants. That is, there is more restrictions to the motion of the reactant molecules than to the motion of the product molecules. The entropy of activation which may be calculated by equation

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

It is a measure of the freedom from restraint of motion among the reactants.[3]

Long et.al(1957)[4] amplifying a suggestion of Taft[5] and coworkers (1955) have proposed the use of $\triangle S^*$ as a criteria of the mechanism of hydrolysis reaction. The reactions are usually classified unimolecular (A-1, SN_1) or bimolecular (A-2, SN_2). In the former case a water molecule does not participate in the rate determining step. The A-1 and A-2 process involve specific hydronium ion catalysis and may be represented as follows[6]

$$S + H^+ \rightleftharpoons SH^+$$

$$SH^+ \xrightarrow{\text{slow}} \text{Products (A-1)} \qquad \dots \quad (1.7)$$

$$S + H^+ \rightleftharpoons SH^+$$

$$SH^+ \xrightarrow[H_2O]{\text{slow}} [X^+] \text{ — Products(A-2)} \quad (1.8)$$
$$\text{Activated complex}$$

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

Solvent Effect

The medium in which chemical reaction takes place has also got importance. The change in solvent will affect both the rate and mechanism of reaction. Some times the solvent alters the rate without affecting the mechanism and rarely changes the mechanism without altering the rate. A solvent can change the rate 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 theory[7] of solvent effect put forwarded by Hughes and Ingold, could be used as criteria for mechanism. It postulates that increase in ionization powder of solvent will be favourable to an increase in the magnitude of charge but unfavourable to decrease in the magnitude of charge to small extent, to a dispersion of a given charge.

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 is found that the rate constant of the reaction is altered by the isotope substitution. Such a change in rate is referred to as the kinetic isotope effect.

The existance of this effect suggests that the bond abnormally stretched in the transition state involves one or more of the isotopically substituted atoms. Thus from kinetic isotope effect, information regarding particular bond involved in the rate determining step can be understood.

Large changes in rate have been observed in many reactions[8-10] following isotopic substitution of hydrogen by deuterium. Since the relative change in mass, the change in rate of the reaction is observed. So use of deuterium substitution has been suggested for the slowing of unwanted reactions, such as the oxidative deuterioration of engine lubricants. In the oxidation of benzaldehyde to benzoic acid by acidic permanganate, replacing the the aldehydic hydrogen by deuterium reduces the reaction rate at room temperature by a factor of seven.

The Reverse Kinetic Isotope Effect

If reactions are carried out using heavy water (D_2O) as a solvent, in some cases the reaction rate is found to be higher 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 such effect.

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 greately

affected by the other ionic species which are present in addition to the reactants. The variables that determine the effect of ion on the equilibrium is the ionic strength (μ), defined by equation

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

where   mi = molarity and

zi = 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 emphirical equation of Debye-Huckel and can be compared with observed rates as has been done for the hydrolysis of propiondimide[14].

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