Molecularity of a reaction:-

The molecularity of a reaction is defined as the number of molecules involved in a step leading to chemical reaction. If only one molecule is involved, the reaction is said to be unimolecular

Order and molecularity of simple reaction:

For simple reactions order and molecularity are almost same. The rate of the reaction varies only with the concentration of ester for the reaction in the reaction

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+} CH_3COOH + C_2H_5OH$$

The molecularity of this reaction is two but the order is one. Since the water is in large excess its concentration is assumed to be unity.

Such reaction are termed as pseudo unimolecular reactions

For a multistep reaction the slow step is the rate determining step of the reaction.

Mechanism of complex reactions:-

Most of the elementary reactions are either unimolecular or bimolecular. This is mainly for gaseous reactions only. Complex reaction proceeds in a number of steps, each step having its own molecularity.

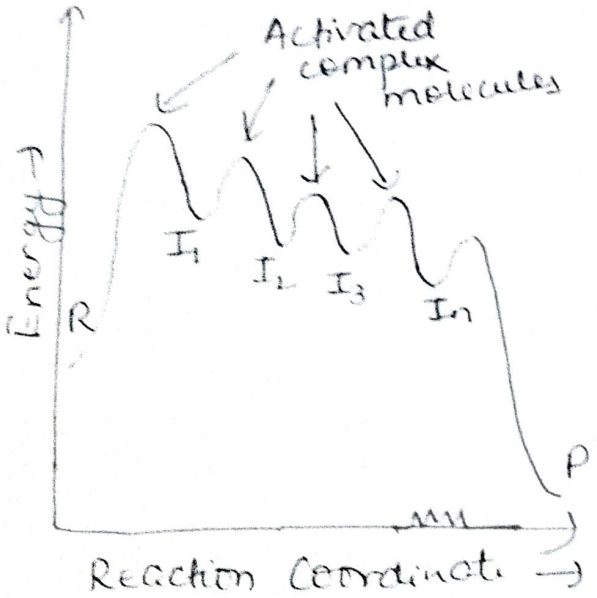
Two approximations are generally used for elucidating the mechanism of a complex reaction

These are

① Equilibrium Approximation : Consider a reaction in which reactant R gives rise to product P through the formation of series of consecutive intermediates I_1, I_2, I_3

$$R \xrightarrow{k_0} I_1 \xrightarrow{k_1} I_2 \underset{}{\overset{k_2}{\rightleftharpoons}} I_3 \xrightarrow{k_3} \cdots \xrightarrow{k_{n-1}} I_n \xrightarrow{k_n} P$$

The whole reaction sequence may be described in terms of a single coordinate composing of coordinates of individual step.



The intermediates are supposed to be stable occupying points on energy valley.

In order to derive a rate equation for the reaction, we assume that rate determining steps exists. This rate determining step is slowest in a sequence of steps.

It is further assumed that all the steps preceding the rate determing steps are in equilibrium.

$$R \underset{}{\overset{K_0}{\rightleftharpoons}} I_1 \underset{}{\overset{K_1}{\rightleftharpoons}} I_2 \underset{}{\overset{K_2}{\rightleftharpoons}} I_3 \cdots \underset{}{\overset{K_{n-1}}{\rightleftharpoons}} I_n \underset{}{\overset{K_n}{\rightleftharpoons}} P$$

② The steady state Approximation:

In a case where the reactions are investigate under such condition that the slowest step is rate determing step does not exist, one assume the steady state approximation (s.s.a.) for the transient i.e. short-lived, intermediate. In such a way.

$$R \xrightarrow{k_0} I_1 \xrightarrow{k_1} I_2 \xrightarrow{k_2} I_3 \xrightarrow{k_3} \cdots\cdots \xrightarrow{k_{n-1}} I_n \xrightarrow{k_n} P$$

The rate of formation of intermediate is equal to the rate of decomposition of it

$$\frac{d[I_1]}{dt} = \frac{d[I_2]}{dt} \cdots\cdots = \frac{d[I_n]}{dt} = 0$$

Collisions and Encounters :- In a reaction occuring between liquid and solid, a molecule A in a condensed equilibrium medium is surrounded by a cage of other molecules, usually the solvent molecules continually bumps into other molecules which constitute the wall of the cage. This is known as cage-effect or Franck-Rabinovich effect.

Q// The gaseous decomposition of ozone $2O_3 \rightarrow 3O_2$ obeys the rate law, $r = -d[O_3]/dt = k[O_3]^2[O_2]$. Prove that the mechanism is consistent with rate law.

$$O_3 \overset{K}{\rightleftharpoons} O_2 + O \qquad \text{(fast eqm)}$$

$$O + O_3 \xrightarrow{k_1} 2O_2 \qquad \text{(slow)}$$

Effect of temperature on reaction rates :-

Increase in temperature has marked effect on the rate of reaction. The ratio of rate constant of a reaction at two temperatures differing by 10°C is known as temperature coefficient of the reaction.

The temperature mainly selected is 25°C and 35°C.

Thus,

$$\text{Temperature coefficient} = \frac{\text{Rate constant at } 35^\circ C}{\text{Rate constant at } 25^\circ C}$$

$$= \frac{k_{35}}{k_{25}}$$

The value of temperature coefficient is mainly close to 2 and sometimes approaches 3.

All M.Sc. Sem (II) students

Notice: Please contact ankitaojha226@gmail.com for the commencement of online classes.