Homogeneous Catalysis

1.1 Catalysis

It is often seen that the speed of a reaction is altered by the presence of a foreign substance which remain unchanged at the end of the reaction. Such substances are called catalysts. A catalyst is defined as a substance which enhances the speed of the reaction itself remaining unaltered in mass and chemical composition. The phenomenon is called catalysis. Thus, H^+ -ion acts as a catalyst in the hydrolysis of esters or sugars and NO acts as a catalyst in the formation SO_3 from SO_2 .

Sometimes a substance slows down the speed of a chemical process or even stops it. These are often called negative catalysts. But such behaviour does not fully satisfy the strict requirement of the definition of catalysts, since the so-called negative catalysts are often used up or changed permanently in the process. Such substances should properly be called inhibitors.

The catalytic reactions are characterised by the following criteria:

(i) *The catalyst remains unchanged in mass and in chemical composition at the end of the reaction.* But its physical form may be modified profoundly.

(ii) *A very minute quantity of a catalyst can produce an appreciable effect on the speed of a reaction.* For example, Titoff found that Cu^{++} at a conc. of 10^{-12}gm-ions/litre would cause an appreciable rise in the rate of oxidation of $NAHSO_3$ –solution in air.

(iii) *A catalyst cannot start a reaction but only increases or decreases its speed.* The catalyst functions as an agent to find out an alternative path for the process.

(iv) *The catalysts do not affect the final state of equilibrium.* This indeed is a thermodynamic requirement. It is known that the free energy change (ΔG) is a perfect differential and is thus independent of the path of transformation. Since the catalyst is reproduced at the end, it does not contribute any energy to the system. The free energy change thus shall be the same whether a catalyst is present or not. Since, under standard state ,

$$-\Delta G^0 = RT\ln K$$

the equilibrium constant will be unaffected by the presence of catalyst.

As the final position of the equilibrium is unchanged and the equilibrium constant $K=k_1/k_2$, the ratio of the velocity constants of the forward and backward reactions would remain constant. Hence the catalyst shall influence the rates of forward and reverse reactions to the same extent. Thus H^+ -ion which accelerates the hydrolysis of an ester is also an accelerator for the esterification of the organic acid.

It is convenient to divide the catalyst reactions into two groups-homogeneous and heterogeneous. In homogeneous catalysis, the catalyst forms a single phase with the reactants, such as nitric oxide in oxidation of SO_2 in the chamber process, or acids catalyzing the hydrolysis of esters. In heterogeneous catalysis, the catalyst and the reactants constitute separate phases and often the surface or interface is responsible for the catalytic effect.

1.2 Homogeneous Catalysis

Many homogeneously catalysed reactions have been studied in the gas –phase and in liquid –phase. Common example of such catalysis in gas –phase are the catalytic effect of nitric oxide in the oxidation of carbon monoxide to dioxide or the decomposition of nitrous oxide to nitrogen and oxygen, iodine vapour catalyzing the decomposition of ether or acetaldehyde vapours, etc. The reaction rates in homogeneous catalysed reactions are invariably found to be proportional to the concentration of catalyst. Although the catalyst is received back entirely at the end of the reaction, yet it does actively participate in the reaction process. In enhancing the speed of a reaction, the catalyst does combine with a reactant or an intermediate formatting a complex which subsequently breaks up to yield the products along with the catalyst itself. The reactant with which the catalyst combines is often mentioned as a substrate. The catalyst really provides an alternative path for the transformation in which the required activation energy is less. (Fig.1)

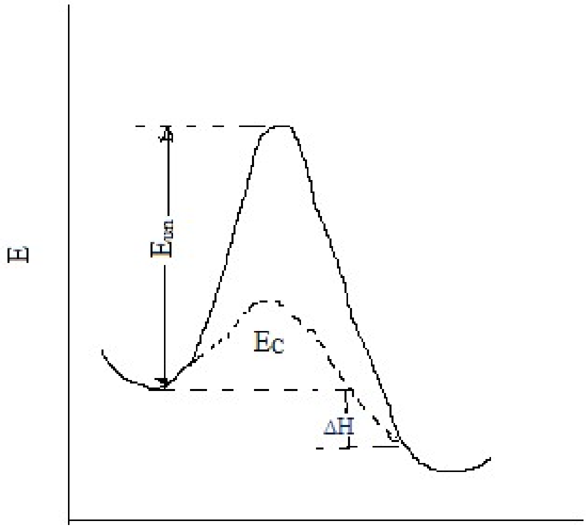


Fig 1: Activation energies of uncatalysed (E_m) and catalysed (E_c) reaction

Lesser activation energy permits larger amount of reaction in a given time. The rate, of course, depends upon the catalyst-concentration. For example, the uncatalysed decomposition of ethyl ether is found to a unimolecular reaction with activation energy of 53000 cal. When it is catalysed with I_2- vapour, the reaction is biomolecular one with the lesser activation energy of 24300 cal. The rate is given by

$$\frac{dx}{dt} = kC_{eth}C_{I_2}$$

Let us take a simple homogeneous catalysed reaction;

$$\text{(i) } S+C \underset{k_2}{\overset{k_1}{\rightleftharpoons}} X \qquad \text{(ii) } X \xrightarrow{k_3} P+C$$

Where S is substrate, P products , C catalyst and X, the intermediate compound.

The rate of formation of the product, $dC_p/dt=k_3C_x$

For the intermediate X, if we invoke the steady –state postulate,

$$dC_x/dt=k_1C_sC_c - k_2C_x - k_3C_x=0$$

i.e, $C_x= k_1C_sC_c / k_2+k_3$

The reaction rate,

$$dC_p/dt=k_3\ k_1C_sC_c / k_2+k_3 =k_c\ C_sC_c$$

It clearly shows that the rate is depend on the catalyst –concentration (C_c). For a given concentration of the catalyst,

$$dC_p/dt = k'\ C_s$$

where $k' = k_cC_c$, i.e., k' is proportional to C_c. The constant k_c is known as the catalytic coefficient for the catalyst.

1.3 Acid-Base Catalysis

(i) Since early days of study it was known that inversion of cane sugar solution is catalysed by acids. Ostwald showed that different acids have different catalytic activity, hydrochloric acid has a much greater activity than that of acetic acid. When Arrhenius theory of electrolytic dissociation was established, it was evident that the real catalysts are the H^+ ions in the reactions mentioned above. The rates of reaction were found to be proportional to the concentration of H^+ ions in the system during the inversion of sucrose.

$$C_{12}H_{22}O_{11} \xrightarrow{H^{+}} C_6H_{12}O_6 + C_6H_{12}O_6$$

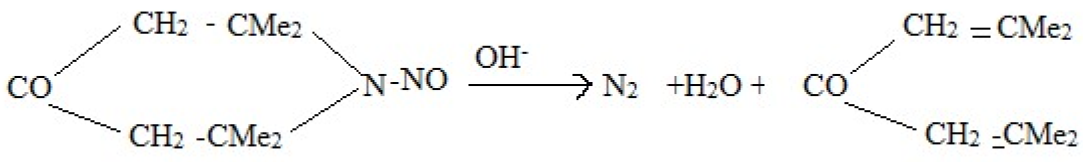
$$dx/dt = k_H.C_{H+}.C_{sugar}$$

where k_H is the catalytic coefficient for H^+ ions for the reaction. Another recation in which H^+ ions acts as catalyst is the inversion of menthone. Such reactions which are catalysed by H^+ ions only are said to be subject to specific hydrogen ion catalysis.

(ii) Similarly there are reaction which are catalysed by OH^- ions only and hence are said to belong to the group of specific hydroxylins ions catalysis. As examples we may cite the conversion of acetone into diacetone alcohol or the decomposition of nitroso-triacetoneamine.

$$CH_3COCH_3 + CH_3CO\,CH_3 \xrightarrow{OH^-} CH_3CO\,CH_2\text{-}C(CH_3)_2OH$$

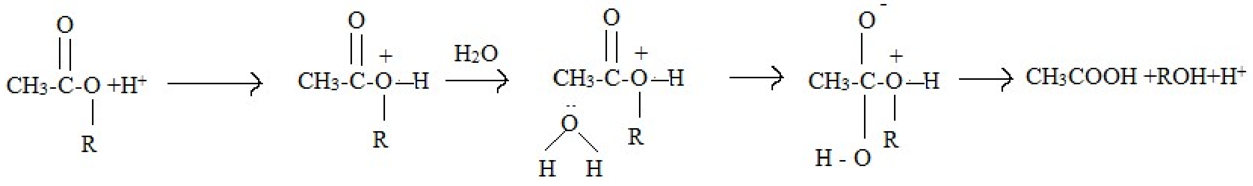
and



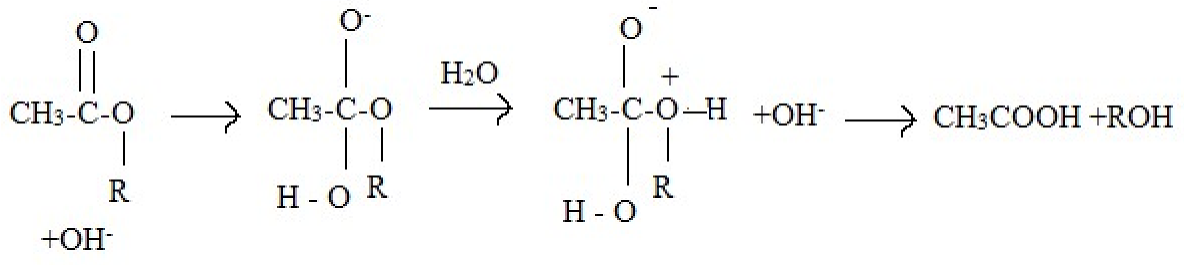
(Nitro triacetoneamine) (Phorone)

There are however some reactions in which both H^+ ions and OH^- ions acts as catalysts, probably along with water. The undissociated acids or base have negligible effect. The outstanding example of H^+ and OH^- ions catalysis is that the hydrolysis of ester. The mechanism of reactions may be expressed as follows:

(a) With H^+ -ions as catalyst



(b) With hydroxyl ion as catalyst



The rate if reaction is adequately expressed as

$$dx/dt = k_{H^+}C_{H^+}C_{ester} + k_{OH^-}C_{OH^-}C_{ester} + k_{H_2O}.C_{H_2O}$$

(iii) In the beginning of this century Taylor, Dawson and others made a significant observation. Some reactions which were known to be catalysed by H^+ ion seemed to be also influenced by undissociated acid molecules. For examples, the decomposition of diazoacetic ester was catalysed by picric acid. If sufficient picrate were added to the system to reduce the H^+ ion conc. to a negligible value, the rate of reaction was yet appreciably high. It was therefore concluded that the decomposition reaction is catalysed by H^+ ion and undissociated HA molecules. This idea then called ‘dual theory of catalysis’ was extended to include later all acids, as defined by Bronsted and Lowry, which would have catalysed effect. This is known as generalized acid catalysis. The reactions under this category would be catalysed by H^+, HA and cations of weak bases. Water, if present in the system, may act both as an acid or a base. An example of generalized acid catalysis is the iodination of acetone catalysed by monochloroacetic acid (HA) and its salt.

$$CH_3COCH_3 \longrightarrow CH_3C(OH){=}CH_2 \xrightarrow{I_2} CH_3COCH_2I + HI$$

The rate of reaction, $dx/dt = k_{H^+}C_{H^+}C_s + k_{H_2O}.C_{H_2O}C_s + k_{HA}C_{HA}C_s$

Where C_s is the concentration of the substrate.

By studying the reaction rate with known but different concentrations acid-salt (catalyst) mixture, it is possible to evaluate the k’s , the catalytic co-efficients.

(iv) Likewise, there are also reactions which subject to generalized base catalysis, in which OH^-, undissociated weak base, water, anions of weak acids acts as catalysts. The decomposition of nitramide in solution is catalysed not only by OH^- ion but also by Ac^-, H_2O etc. The catalyst process are:

$$\text{(i)}\ NH_2NO_2 + OH^- \longrightarrow H_2O + NHNO_2^- \quad ; \quad NHNO_2^- \longrightarrow N_2O + OH^-$$

$$\text{(ii)}\ NH_2NO_2 + Ac^- \longrightarrow AcH + NHNO_2^-$$

$$NHNO_2^- \longrightarrow N_2O + OH^-$$

$$OH^- + AcH \longrightarrow Ac^- + H_2O$$

The overall reaction rate would be,

$$dx/dt = k_{OH-}C_{OH-}C_s + k_{Ac-}C_{Ac-}\,C_s + k_{H2O.}C_{H2O}C_s$$

(v) Finally, there are some reactions such as mutarotation of glucose or the enolisation of acetone, which are subject to generalized acid- base catalysis. All acids and all bases including H^+, OH^-, HA, BOH, and anions of weak acids and cations of weak bases have catalytic effect on these reactions. Schematically, the mutarotation may be expressed as:

$$GH \xrightarrow{(H^+)} [HGH]^+ \xrightarrow{(-H^+)} HG$$

The reaction rate will be,

$$dx/dt = k_{OH-}C_{OH-}C_s + k_{Ac-}C_{Ac-}C_s + k_{H2O.}C_{H2O}C_s + k_{H+}C_{H+}C_s + k_{HA}C_{HA}C_s$$

The catalytic coefficients determined experimentally for this recation at 291^0K are: $k_{OH-} = 6x10^3$, $k_{H+} = 1.4x10^{-1}$, $k_{Ac-} = 2.7x10^{-2}$, $k_{AHc} = 2x10^{-3}$, $k_{H2O} = 6x10^{-3}$

That both acids and bases are active in catalyzing the process its convincingly demonstrated from the study of mutarotation of tetramethyl glucose. In absence of water, if the reactant is taken in base pyridine the rate is very slow. Similarly if it is taken in acid meta-cresol, there is hardly any mutarotation. But if the tetramethyl glucose is taken in a mixture of m-cresol and pyridine, the reaction is largely catalysed. The reaction thus requires the presence of both an acid and a base – a case of generalized acid –base catalysis.