7.13 ACID-BASE CATALYSIS

Generally, homogeneous catalysis in solution is brought about by acids and bases. On the basis of studies done by Arrhenius and Ostwald in the hydrolysis of esters a nitrites, it was established that in acid-base catalysis, it is the hydrogen ion or hydromion which acts as catalyst.

Examples of acid-base catalysis

(i) Hydrolysis of an ester:

$$CH_3COOC_2H_5 + H_2O \xrightarrow{H^+ \text{ or } \atop OH^-} CH_3COOH + C_2H_5OH$$

(ii) Inversion of cane sugar:

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{H^+} C_6H_{12}O_6 + C_6H_{12}O_6$$

(iii) Conversion of acetone into diacetone alcohol

$$CH_3COCH_3 + CH_3COCH_3 \xrightarrow{OH^-} CH_3COCH_2 \cdot C(CH_3)_2OH$$

(iv) Decomposition of nitramide:

$$NH_2 \cdot NO_2 \xrightarrow{OH^-} N_2O + H_2O$$

The recent work has shown that all substances which have the tendency to le to gain protons can show catalytic activity, i.e., all Bronsted acids and bases acid-base catalysts.

Mechanism of acid-base catalysis

(i) In acid catalysis, the proton given by Bronsted acid forms an intermomplex with the reactant which then reacts to give back the proton (H⁺). For example, the hydrolysis of ester occurs in the following manner:

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(ii) The mechanism of keto-enol tautomerism of acetone is:

$$CH_{3} \longrightarrow C \longrightarrow CH_{3} \longrightarrow CH_{3} \longrightarrow CH_{3} \longrightarrow CH_{3} \longrightarrow CH_{2} + H^{+}$$

$$Keto form \qquad Intermediate \qquad Enol form \qquad complex$$

(b) In base catalysed hydrolysis, the OH⁻ ion or any Bronsted base accepts a proton from the reactant to form an intermediate complex which then reacts or decomposes to regenerate the OH⁻ or Bronsted base. In presence of OH⁻ ions, the decomposition of nitroamine can be shown as:

$$NH_2NO_2 + OH^- \longrightarrow NHNO_2^- + H_2O$$

$$\downarrow$$

$$N_2O + OH^-$$

or in presence of CH₃COO ions, on the court with the court of the court o

$$NH_2NO_2 + CH_3COO^- \longrightarrow NHNO_2^- + CH_3COOH$$
 \downarrow
 $N_2O + OH^-$

Over the OO HD when the state of the CH₃COOH
$$\longrightarrow$$
 CH₃COO⁻ + H₂O when the state of the st

7.14 ENZYME CATALYSIS

Enzymes are complex nitrogenous organic compounds which are produced by living plants and animals. Enzymes are actually high molecular mass protein molecules. Enzymes form colloidal solutions in water and are very effective catalysts. They catalyse numerous reactions, especially those connected with natural processes. Numerous reactions occur in the bodies of animals and plants to maintain the life process. These reactions are catalysed by enzymes. The enzymes are thus termed as bio-chemical catalysts and the phenomenon is known as bio-chemical catalysis.

Many enzymes have been obtained in pure crystalline state from living cells. However, the first enzyme was synthesised in the laboratory in 1969. The following are some of the examples of enzyme catalysis:

(i) Inversion of cane sugar: The invertase enzyme converts cane sugar into glucose and fructose.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{Invertase} C_6H_{12}O_6 + C_6H_{12}O_6$$
Cane sugar
Glucose
Fructose

(ii) Conversion of glucose into ethyl alcohol: The zymase enzyme converts glucose into ethyl alcohol and carbon dioxide.

$$C_6H_{12}O_6 \xrightarrow{\text{Zymase}} 2C_2H_5OH + 2CO_2$$
Glucose Ethyl alcohol

(iii) Conversion of starch into maltose: The diastase enzyme converts starch into maltose.

$$2(C_6H_{10}O_5)_n + nH_2O \xrightarrow{\text{Diastase}} nC_{12}H_{22}O_{11}$$
Starch

Maltose

(iv) Conversion of maltose into glucose: The maltase enzyme converts maltose into glucose.

$$C_{12}H_{22}O_{11} + H_2O \xrightarrow{\text{Maltase}} 2C_6H_{12}O_6$$

Maltose

Glucose

(v) Decomposition of urea into ammonia and carbon dioxide: The enzyme urease catalyses this decomposition.

$$NH_2CONH_2 + H_2O \xrightarrow{Urease} 2NH_3 + CO_2$$

(vi) In stomach, the pepsin enzyme converts proteins into peptides while in intestine, the pancreas trypsin converts proteins into amino acids by hydrolysis.

(vii) Conversion of ethyl alcohol into acetic acid: The Mycoderma aceti enzyme converts dilute solutions of alcohol into acetic acid and water.

$$C_2H_5OH + O_2 \xrightarrow{Mycoderma\ aceti} CH_3COOH + H_2O$$

(viii) Conversion of milk into curd: It is an enzymatic reaction brought about by lactic bacilli enzyme present in curds.

Table 7.1 gives the summary of some important enzymatic reactions:

Table 7.1 Some enzymatic reactions

CHARACTERISTICS OF ENZYME CATALYSIS

Enzyme catalysis is intermediate between homogeneous and heterogeneous catalysis. In general, it is similar to inorganic heterogeneous catalysis and sometimes it is called microheterogeneous catalysis. However, it is unique in its efficiency and high degree of specificity. The following characteristics are exhibited by enzyme catalysts:

- (i) Most efficient catalysts: The enzyme-catalysed reactions are very fast in comparison to the reactions catalysed by inorganic substances. This is due to the fact that activation energy of the reaction in presence of an enzyme is low. One molecule of an enzyme may transform one million molecules of the reactant per minute.
- (ii) High specific nature: Each enzyme is specific for a given reaction, *i.e.*, one catalyst cannot catalyse more than one reaction. For example, the enzyme urease catalyses the hydrolysis of urea only. It does not catalyse any other amide, not even methyl urea.
- (iii) Temperature dependence: The rate of an enzyme reaction depends on the temperature. The enzyme activity rises rapidly with temperature and becomes maximum at a definite temperature, called the **optimum temperature**. Beyond the optimum temperature, the enzyme activity decreases and ultimately becomes zero. The enzyme activity is destroyed at about 70°C. The optimum temperature of enzyme reactions occurring in the human body is 37°C. At higher temperatures (fever), the enzyme activity becomes less. The favourable temperature range for enzymatic activity is 25–37°C.
- (iv) pH dependence: The rate of an enzyme-catalysed reaction varies with pH of the system. The enzyme activity is maximum at a particular pH called optimum pH. The optimum pH of enzyme reactions occurring in human body is 7.4. The favourable pH range for enzymatic reactions is 5–7.
- (v) No effect on equilibrium state: Like ordinary catalysts, enzymes cannot disturb the final state of equilibrium of a reversible reaction.
- (vi) Colloidal nature: Enzymes form colloidal solutions in water. Their efficiency is retarded in presence of large quantities of electrolytes. Enzymes are destroyed by ultraviolet rays.
- (vii) Activators or co-enzymes: The enzymatic activity is increased in the presence of certain substances, known as co-enzymes. It has been observed that when a small non-protein (vitamin) is present along with an enzyme, the catalytic activity is enhanced considerably.

Activators are generally metal ions such as Na⁺, Mn²⁺, Co²⁺, Cu²⁺, etc. These metal ions, when weakly bonded to enzyme molecules, increase their catalytic activity. Amylase in presence of sodium chloride *i.e.*, Na⁺ ions are catalytically very active.

(viii) Inhibitors and poisons: Like ordinary catalysts, enzymes are also inhibited or poisoned by the presence of certain substances. The inhibitors or poisons interact

with the active functional groups on the enzyme surface and often reduce or completely destroy the catalytic activity of the enzymes.

The use of many drugs is related to their action as enzyme inhibitors in the body.

Mechanism of enzyme catalysis: There are a number of cavities present on the Mechanism of characteristic shape surface of colloidal particles of enzymes. These cavities are of characteristic shape surface of colloidal particles of single such as -NH₂, -COOH, -SH, -OH, etc. These are and possess active groups such as -NH₂, -COOH, -SH, -OH, etc. These are and possess active groups on the surface of enzyme particles. The molecules of the actually the active centres on the surface of enzyme particles. The molecules of the actually the active collides of the reactant (substrate), which have complementary shape, fit into these cavities just like a key fits into a lock. On account of the presence of active groups, an activated complex is formed which then decomposes to yield the products.

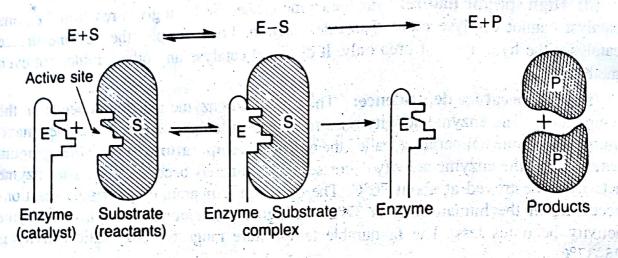


Fig. 7.12

Michaelis and Menten suggested the following mechanism for enzyme catalysis:

Step 1: Binding of enzyme to substrate to form an activated complex,

Step 2: Product formation in the activated complex,

Step 3: Decomposition of EP into products and enzyme again,

$$EP \longrightarrow P + E$$

This mechanism accounts for the high specificity of enzymatic reactions.

7.15 CATALYSTS IN INDUSTRY

walf solutions in water. Prefit

Some of the important technical catalytic processes are listed in Table 7.2 as to give an idea about the utility of catalysts in industries.

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