Semester – VI

DSE – 1B

Chapter 18 I

Bio-Organic Chemistry

November 2006 Saturday

ENZYMES

(1) Introduction and Historical perspective
(2) Chemical and Biological catalysis
(3) Biological Catalysis
(4) Classification and Nomenclature
(5) Extraction and Purification of enzymes
(6) Reversible and Irreversible inhibition.

#(1) Introduction and Historical perspective

Perhaps oldest known bio-chemical and bio-organic phenemenon is fermentation of Juices to alcoholic beverages. Also this was first chemical transformation which was catalysed by enzymes, contained within living yeast cell i.e It was discovered in 18th century that fermentation which lead to conversion of sugar into carbondioxide and alcohal.

Sugar $\xrightarrow{\text{Enzyme}}$ Glucose + Fructose

Glucose/fructose $\xrightarrow{\text{Enzyme}}$ $C_2H_5OH + CO_2 \uparrow$
alcohol.

In 19th century witnessed both the identification of ~~fermentation~~ as physiological act of yeast cell and introduction of Pasteur's view that life and fermentation are inseparable. But now, extraction of enzymes from bio-cell was known. ~~and this~~

In 1897 E. Buchner required quantity of ~~purification~~ purified protein for therapeutic purpose. he grounded yeast and sand, filtered the broken cell and added large amount of sugar to the filtrate as preservative. To his astonishment sugar was rapidly fermented by the cell free extract.

In 1905, Harder and Young made and important contribution, when they showed that Zymase displaced by Buchner required the addition of heat stable eco-factor or co-enzyme.

In 1930-1940 decade Warburg and his school were successfully in purifying and crystallizing a number of respiratory enzymes. In Warburg institute reversible dissociated the enzyme into a protein part i.e. <u>apoenzyme</u> and co-factor

(prosthetic group). The separated components were inactive.

Efforts to break enzymes into their components and reassembling them culminated in 1969 the first chemical synthesis of enzymes RIBONUCLEASE.

Along with studies on enzyme structure, investigations of techniques and describing the kinetics parameters of enzyme-catalysed reaction went on at equal pace. The total out come of these efforts, there were several theories and their mechanism of the catalytic activity of enzymes comes into light of Bio-organic Chemistry.

Investigation on mechanism of enzyme-action were mainly carried out in the beginning of 20th century and this led to two main aspects.

(A) A group of enzymologists regarded enzymes simply as catalytic protein, Such studies were preceded by development of elaborate apparatus & techniques for obtaining the enzymes in pure state.

Research in this field has provided molecular and kinetic data and has led to general acceptance of ENZYME - SUBSTRATE compound theory.

(B) On the other side, work was done by considering enzymes as cog in the complicated metabolic machinery of the cell.

Such investigation little cared for purity of enzymes, but they worked on bio-chemical aspect and can establish metabolic cycles & gave more fundamental understanding of cellular energetics.

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#(2) CHEMICAL & BIOLOGICAL CATALYSIS

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② CHEMICAL & BIOLOGICAL CATALYSIS

CHEMICAL CATALYSIS and its Characteristics :-

A catalysts are the substances which alter / change the rate of reaction, but is recovered chemically unchanged at the end of the reaction. This phenomeno is known as chemical catalysis.

e.g In oxidation of oxalic acid by

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Acidified $KMnO_4$ velocity increases as the reaction progresses. Here rate acceleration is due to the Mn^{+2} ions which is formed during the reaction. This typer of phenomen is known as Auto-Catalysis.

$$2MnO_4^- + 5\begin{matrix}COO^- \\ COO^-\end{matrix} + 16H^+ \longrightarrow 2Mn^{+2} + 10CO_2 + 8H_2O$$

(pink) (colourless)

A catalyst increases the reaction rate it is called positive catalyst and the phenomen is called positive catalyst / positive catalysis reaction

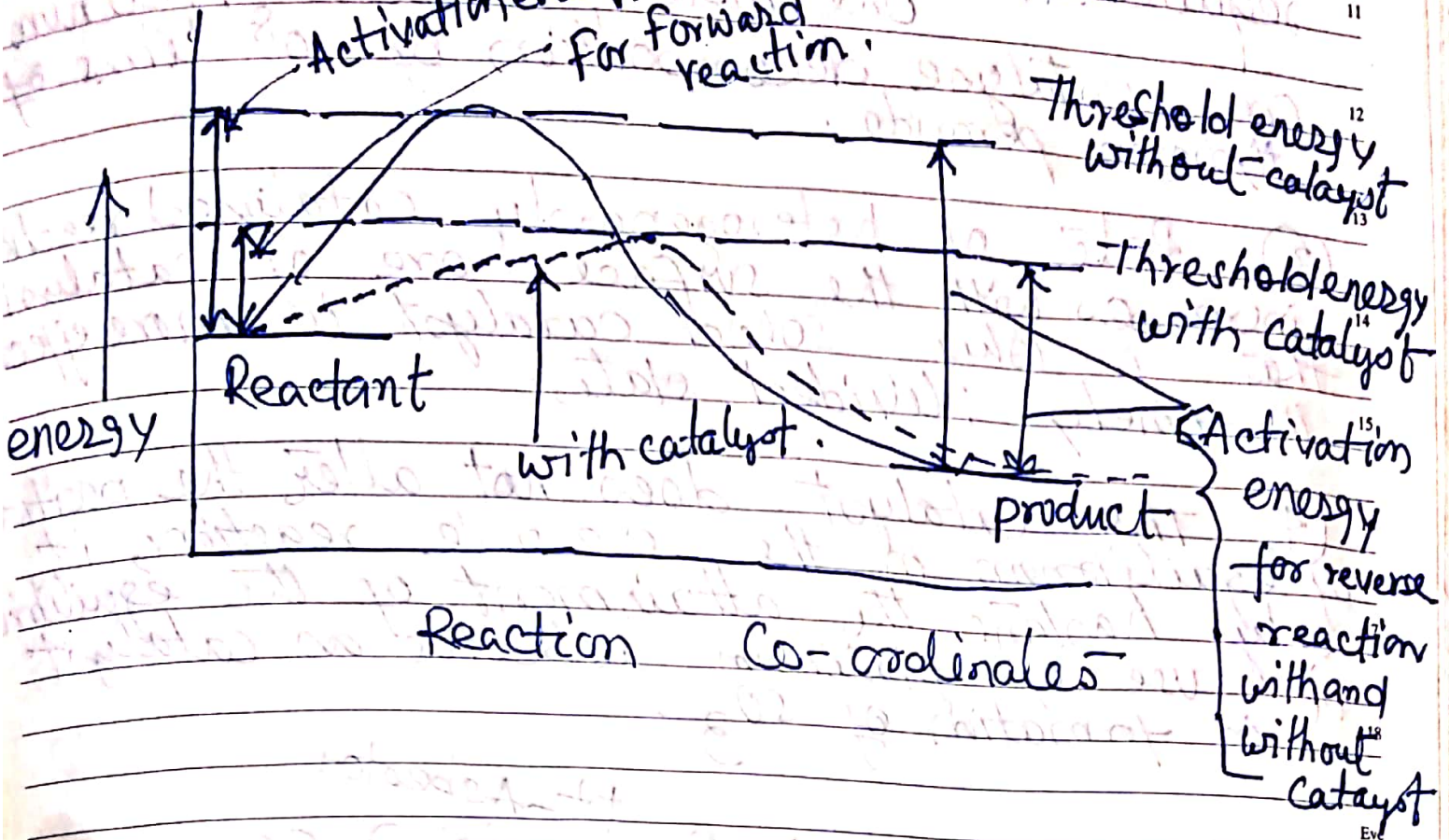
$$KClO_3 \xrightarrow[800^\circ C.]{\Delta} 2KCl + 3O_2\uparrow$$

Eve But in presence of MnO_2 (Catalyst)

$$KClO_3 \xrightarrow[600^\circ C]{\Delta} 2KCl + 3O_2\uparrow$$

Exact mechanism by which catalyst enhances rate of reaction, This can not be understanded, However it is believed

that catalytic rate acceleration is due to the fact that it provides new alternate low energy pathway for the reaction by lowering the energy of transition state. This can be explain by diagram given below.



Characteristics of catalyst.

Chemical catalysis is characterized by following aspects

① It remains unchanged in regard to amount and composition at the end of the reaction, However it

may undergo some physical change during the chemical reaction.

(2) Only a small amount of catalyst is required i.e one mole of colloidal Platinum can catalyse decomposition of 10^8 Litres of Hydrogen peroxide.

(3) Rate of heterogenously catalysed reactions increases with the surface area of catalyst that is why solid catalyst is more effective in finely divided state.

(4) The catalyst does not alter the position of equilibrium in the reversible reaction, it only hastens the attainment of the equilibrium i.e use of platinum asbestos as catalyst in formation of SO_3.

Eve

$$2SO_2 + O_2 \underset{}{\overset{Pt-Asbestos}{\rightleftharpoons}} 2SO_3$$

It causes change in the rate of reaction but does not alter the composition of reactant and product at equilibrium at given condition of temp and pressure

(5) Catalyst does not initiate the

reaction, it only alters reaction rate.

(6) Catalyst is specific in nature i.e for a particular reaction a particular type of catalyst is required.

$$KClO_3 \xrightarrow{(MnO_2)} 2KCl + 3,O_2 \uparrow$$

$$C_6H_{12}O_6 \xrightarrow[Zymase]{} 2CH_3-CH_2-OH + 2CO_2 \uparrow$$

Alcohal.

(7) Catalyst only change rate of reactions but they do not intiate that i.e $KClO_3$ is decomposed on heating to give KCl and O_2 gas in absence of or presence of catalyst, However MnO_2 will enhance rate of decomposition.

Similarly H_2 & N_2 always combine to form NH_3, but in presence of catalyst accelarates rate of formation. But there are some exception. Carbon monoxide

and H_2 gives different products in presence of different catalyst

(i) $CO + H_2 \xrightarrow{(Cu\text{-catalyst})} HCHO$ methanal

(ii) $CO + 2H_2 \xrightarrow{(ZnO + Cr_2O_3)} CH_3OH$ methanol

(iii) $CO + 3H_2 \xrightarrow{(Ni\text{-catalyst})} CH_4 + H_2O$ methane.

(8) Catalyst work most effectively at certain specific temperature, This temp is known as optimum temp. below or above this temperature catalyst does not work.

(9) Last point is, certain substances are MAR effectiveness of catalyst, they are known as catalytic poisons.