Mechanism of a Reaction

Some examples

Def: A sequence of intermediate steps or elementary processes proposed to account for the overall stoichiometry of a reaction is called mechanism of the reaction.

Reaction 1

$2NO_2 + F_2 \longrightarrow 2NO_2F$ — order.

Rate $= k[NO_2][F_2]$ $\therefore n = 1+1 = 2$

mechanism

$NO_2 + F_2 \longrightarrow NO_2F + F$ — slow

$NO_2 + F \longrightarrow NO_2F$ — Fast

$2NO_2 + F_2 \longrightarrow 2NO_2F$

Reactive intermediate: F

Reaction 2

$NO_2(g) + CO(g) \longrightarrow NO(g) + CO_2(g)$

Rate $= k[NO_2]^2$ $n = 2$ = order

Step 1 $NO_2 + NO_2 \longrightarrow NO + NO_3$ — slow

$NO_3 + CO \longrightarrow CO_2 + NO_2$ — fast

$NO_2 + CO \longrightarrow CO_2 + NO$

$\therefore$ Reactive intermediate = NO_3

Reaction 3

$$2N_2O \longrightarrow 2N_2 + O_2$$

Step 1. $N_2O \longrightarrow N_2 + O$ slow

$N_2O + O \longrightarrow N_2 + O_2$ fast.

$2N_2O \longrightarrow 2N_2 + O_2$

Rate $= k[N_2O]$

Reactive intermediate = 'O'

Catalyst :

A catalyst is a substance which alters the rate of a chemical reaction without being used up in the reaction and can be recovered chemically. unchanged at the end of the reaction

Positive Catalyst	Negative Catalyst
Increases rate of reaction formed	Decreases the rate of the forward reaction

Examples +ve Catalyst

1. Decomp of $KClO_3$

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

2. Decomp of H_2O_2 / Pt. colloidal pt.

$$2H_2O_2 \xrightarrow{Pt} 2H_2O + O_2$$

3. oxidation of $HCl \rightarrow Cl_2$

$$4HCl + O_2 \xrightarrow{CuCl_2} 2H_2O + 2Cl_2$$

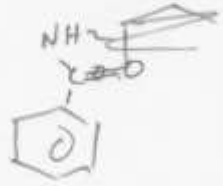
4. Hydrogenation of oils and fats

Veg. oil $+ H_2 \xrightarrow{Ni}$ Margarine.

(Finely divided Nickel)

Negative catalyst

1. Oxidation of Na_2SO_3 by air is retarded by alcohol.
2. Decomposition of H_2O_2 is reduced by ~~aceto Nitrile~~ acetanilide CH_3CONH_2



3. Oxidation of Chloroform by air is prevented by alcohol.

$$2CHCl_3 + O_2 \xrightarrow{C_2H_5OH} 2COCl_2 + 2HCl.$$

Homogenous catalysis :-

When reactants and catalyst are in the same phase the catalysis is termed homogenous catalysis

examples: (1) (Gas phase Reaction)

Oxidation of $SO_2 \rightarrow SO_3$ in the presence NO

$$2SO_{2(g)} + O_2 \xrightarrow{NO} 2SO_3$$

Lead chamber process

(Q1 NO, NO_2)

(1) $NO + \frac{1}{2}O_2 \rightarrow NO_2 + \cancel{\Theta}$

or $2NO + O_2 \rightarrow 2NO_2$

$SO_2 + NO_2 \rightarrow SO_3 + NO$

$NO + \frac{1}{2}O_2 \rightarrow NO_2$

$SO_2 + \frac{1}{2}O_2 \rightarrow SO_3$

- Catalyst is present along with the reactant.
- Reactive intermediate is always a product being used up in subsequent steps.

Homogenous catalysis

example ②

Hydrolysis of esters: in presence of mineral acids. $H_2SO_4(l)$

$$RCOOR'_{(l)} + H_2O_{(l)} \xrightarrow{H_2SO_4(l)} RCOOH + R'OH.$$

example 3

Hydrolysis of Cane sugar:

$$C_{12}H_{22}O_{11(l)} + H_2O_{(l)} \xrightarrow{H_2SO_4(l)} C_6H_{12}O_6 + C_6H_{12}O_6$$

(solution)

Glucose Fructose

Heterogenous Catalysis

When reactants and catalyst are in different phases they are called H.C.

(1) Haber Process

$$N_{2(g)} + 3H_{2(g)} \xrightleftharpoons{Fe(s)} 2NH_3$$

(2) Contact process (H_2SO_4)

$$2SO_{2(g)} + O_{2(g)} \xrightarrow[\text{or } N_2O_{5(g)}]{Pt(s)} 2SO_{3(g)}$$

(3) Ostwalds process
oxidation of NH_3 by O_2

$$4NH_{3(g)} + 5O_{2(g)} \xrightarrow{Pt} 4NO_{(g)} + 6H_2O_{(g)}$$

Theories of Catalysis

1. Intermediate Compound formation Theory.
2. Adsorption Theory.

① I.C.F.T

$$A + B \xrightarrow{X} *AB \longrightarrow \text{High Activation Energy.}$$

$$A + X \longrightarrow AX \leftarrow \text{Intermediate compound unstable.}$$

$$AX + B \longrightarrow AB + X$$

$$A + B \longrightarrow AB.$$

Repeat explanation (cont 8)

(Ex 1)

$$2SO_2 + O_2 \xrightarrow{NO} 2SO_3$$

Mechanism

$$2NO + O_2 \longrightarrow 2NO_2$$

(Int. mediat. Comp.)

$$2NO_2 + 2SO_2 \longrightarrow 2SO_3 + 2NO$$

$$2SO_2 + O_2 \longrightarrow 2SO_3$$

(Ex 2)

Fromation of Ethers

$$C_2H_5OH + C_2H_5OH \xrightarrow{H_2SO_4} C_2H_5\text{-}O\text{-}C_2H_5 + H_2O$$

Mechanism

① ~~$C_2H_5OHSO_4$~~

$$C_2H_5OH + H_2SO_4 \longrightarrow C_2H_5HSO_4 + H_2O$$

$$C_2H_5HSO_4 + C_2H_5OH \longrightarrow C_2H_5\text{-}O\text{-}C_2H_5 + H_2SO_4$$

$$2C_2H_5OH \longrightarrow C_2H_5\text{-}O\text{-}C_2H_5$$

Cat 9

1. Adsorption Theory

Free valence / Active sites.

- Due to adsorption increases conc. of reactants on the cat surface.
- Leads to chemisorption thereby causing weaking of its bonds and enter into bond formation with catalyst. - This decomposes to yield products.

4 steps)

(a) Adsorption of reactant molecules
(b) Formation of activated complex
(c) De composition of activated complex
(d) Desorption of products.

Slide- ed diagrams needed

$CH_2 = CH_2 + H_2 \longrightarrow CH_3 - CH_3$

(Cat 5)

Auto catalysis

The process in which one of the products formed acts as a catalyst.

example: Oxidation of Oxalic acid by acidified $KMnO_4$

$$5\ H_2C_2O_4 + 2KMnO_4 + 3H_2SO_4 \rightarrow 2MnSO_4 + K_2SO_4 + 10CO_2 + 8H_2O$$

Ionic

$$5\ C_2O_4^{2-} + 2MnO_4^- + 16H^+ \rightarrow 10\ CO_2 + 2Mn^{2+} + 8\ H_2O$$

Mn^{2+} formed acts as a catalyst.

So the reaction is slow at RT. Heat to 70°C add a few drops of $KMnO_4$ — then the reaction speeds up.

example

Hydrolysis of Ethyl acetate — Acid produced catalyses the reaction.

$$CH_3COOC_2H_5 + H_2O \rightarrow \underset{\downarrow}{CH_3COOH} + C_2H_5OH$$

H^+ = catalyst.

Induced Catalysis

When a chemical reaction influences the rate of some other reaction which does not occur under ordinary conditions, the phenomenon is called induced catalysis.

Reduction of Mercuric chloride by oxalic acid does not take place. But $KMnO_4$ can be reduced by oxalic acid. So the second reaction is found to enhance the first reaction.