SG GOVT. DEGREE COLLEGE : PILER.

(Re- Accredited by NAAC with 'B' Grade)

DEPT. OF CHEMISTRY.

MINIMUM STUDY MATERIAL

Chemistry paper - II

I B.Sc SEM – II

2021 - 22

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This is the Minimum study material in chemistry, which is in accordance with the latest syllabus prescribed for B.Sc, 2nd semester of 1st year students by APSCHE, AP. We hope this material will be useful for students. I am very much thank full to ***Dr.M. Sudhakara Reddy***, Principal, SG Govt. Degree College, Piler; ***Sri C. Venkatarathnam***, Lecturer in-charge, Dept. of Chemistry, SG Govt. Degree College, Piler; ***Dr.S.Hari Prasad***, Lecturer in Statistics, Govt. Degree College, Kodur; ***Dr. K. Sivakumar*** , Associate Professor, Dept. of Chemistry, SV Arts College (TTD's), Tirupathi; ***Dr.P.Bhanuprkash***, Lecturer in Chemistry, PVKN Govt. College (A), Chittoor for their valuable suggestions and advice in the preparation of study material.

Further, we will always welcome for any constructive and thought provoking suggestions for the improvement of this study material.

Thank you
RAM BABU K

SEMESTER – II
Syllabus under CBCS (w. e. f. 2020-21)
Course I (Organic & General Chemistry)

ORGANIC CHEMISTRY

UNIT–I

Recapitulation of Basics of Organic Chemistry

Carbon-Carbon sigma bonds (Alkanes and Cycloalkanes)

Alkanes

General methods of preparation of alkanes – Wurtz reaction , Wurtz Fittig reaction, Corey House synthesis. Physical and chemical properties of alkanes. Isomerism and its effect on properties. Free radical substitutions - Halogenation, concept of relative reactivity v/s selectivity. Conformational analysis of alkanes (Conformations, relative stability and energy diagrams of Ethane, Propane and butane).

Cycloalkanes

General molecular formulae of cycloalkanes and relative stability, Baeyer strain theory, Cyclohexane conformations with energy diagram, Conformations of monosubstituted cyclohexane.

UNIT–II

Carbon-Carbon pi Bonds (Alkenes and Alkynes)

Alkenes

General methods of preparation, physical and chemical properties.Mechanism of E1, E2, E1cb reactions, Saytzeff and Hoffmann eliminations. Electrophilic Additions, mechanism of Markownikoff/Antimarkownikoff addition with suitable examples, syn and anti-addition; addition of H2, X2, HX.

oxy mercuration - demercuration, hydroboration- oxidation, ozonolysis, hydroxylation, Diels Alderreaction,1,2- and1,4-additionreactionsinconjugateddienes.

Alkynes

Reactions of alkynes; acidity, electrophilic and nucleophilic additions, hydration to form carbonyl compounds, Alkylation of terminal alkynes.

UNIT-III

Benzene and its reactivity

Concept of aromaticity, Huckel's rule - application to Benzenoid (Benzene, Naphthalene) and Non - Benzenoid compounds (cyclopropenylcation, cyclopentadienyl anion and tropyliumcation) Reactions - General mechanism of electrophilic aromatic substitution, mechanism of nitration, Friedel- Craft's alkylation and acylation. Orientation of aromatic substitution - ortho, para and meta directing groups. Ring activating and deactivating groups with examples (Electronic interpretation of various groups like NO2 and Phenolic). Orientation of (i) Amino, methoxy and methyl groups (ii) Carboxy, nitro, nitrile, carbonyl and sulphonic acid groups (iii) Halogens (Explanation by taking minimum of one example from each type)

GENERAL CHEMISTRY

UNIT-IV

1. **Surface chemistry**
   Colloids- Coagulation of colloids- Hardy-Schulze rule. Stability of colloids, Protection of Colloids, Gold number. Adsorption-Physical and chemical adsorption, Langmuir adsorption isotherm, applications of adsorption.
2. **Chemical Bonding**
   Valence bond theory, hybridization, VB theory as applied toClF_3, $Ni(CO)_4$. Molecular orbital theory -LCAO method, construction of M.O. diagrams for homo-nuclear and hetero-nuclear diatomic molecules (N_2, O_2, CO and NO).
3. HSAB
   Pearson’s concept, HSAB principle & its importance, bonding in Hard-Hard and Soft-Soft combinations.

UNIT-V

Stereochemistry of carbon compounds

Molecular representations- Wedge, Fischer, Newman and Saw-Horse formulae. Optical isomerism: Optical activity- wave nature of light, plane polarised light, optical rotation and specific rotation. Chiral molecules- definition and criteria(Symmetry elements)- Definition of enantiomers and diastereomers – Explanation of optical isomerism with examples- Glyceraldehyde, Lactic acid, Alanine, Tartaric acid, 2,3-dibromopentane. D,L, R,S and E,Z- configuration with examples. Definition of Racemic mixture – Resolution of racemic mixtures (any 3 techniques).

MODEL PAPER
FIRST YEAR B.Sc., DEGREE EXAMINATION
SEMESTER-II
CHEMISTRY COURSE -II: ORGANIC & GENERAL CHEMISTRY
Time: 3 hours Max Marks: 75

PART- A
5 X 5 = 25 Marks

Note : Answer any **FIVE** of the following questions. Each carries **FIVE** marks

1. Write different conformations of n-butane. Explain their relative stability.
2. Explain 1,2 & 1,4- addition reactions of conjugated dienes.
3. Explain the orientation effect of halogens on mono substituted benzene.
4. Explain the mechanism of E1CB elimination reaction.
5. Explain the structure of ClF_3 by Valency Bond theory.
6. What are Hard & soft acids & bases? Explain with examples.
7. Draw the Wedge, Fischer, Newmann & saw-Horse representations for Tartaric acid.
8. Define Enantiomers and Diastereomers and give two examples for each.

PART- B
10 X 5 = 50 Marks

Note : Answer **ALL** the questions. Each carries **TEN** marks

9. (a). (i) Write the preparation of alkanes by Wurtz and Corey-House reaction.
(ii) Explain Halogenation of alkanes. Explain the reactivity and selectivity in free-radical substitutions.

(or)

(b). (i) Explain Baeyer Strain Theory
(ii) Draw the conformations of Cyclohexane and explain their stability by drawing energy profile diagram.

10. (a). (i) Write any two methods of preparation of alkenes.
(ii) Explain the mechanism of Markownikiff and Anti-Markownikoff addition of HBr to alkene.

(OR)

(b). (i) Explain the acidity of 1-alkynes
(ii) How will you prepare acetaldehyde and acetone from alkynes?
(iii)Write alkylation reaction of terminal alkyne.

11. (a) Define Huckel rule of aromatic compounds. What are benzenoid and non-benzenoid aromatic compounds? Give examples.

(OR)

(b) Explain the mechanisms of Nitration and Friedel-Craft's alkylation of Benzene.

12. (a) (i) Define Hardy-Schulze rule & Gold number.
(ii) Differentiate Physisorption & Chemisorption. Explain Langmuir adsorption isotherm.

(OR)

(b) Construct the Molecular Orbital diagram for O_2 and NO and explain their bond order and magnetic property.

13 (a) Define racemic mixture. Explain any two techniques for resolution of racemic mixture.

(OR)

(b) (i) Define Optical activity and Specific rotation.
(ii) Draw the R & S isomers of Alanine, Glyceraldehyde.
(iii) Write the E & Z isomers of 2-butene.

UNIT - I

ALKANES

Alkanes are the simplest class of organic compounds containing Carbon – Hydrogen (C – H) and Carbon – Carbon (C – C) single covalent bonds. They do not have functional group. General formula of alkanes is CnH_{2n+2}.. n is number of carbon atoms in the molecules. When n = 1 the compound is the Methane (CH_4). When n = 2 the compound is Ethane (C_2H_6). They are relatively unreactive under ordinary conditions, but they can be forced to undergo reactions by drastic treatment. That is why they were named as "*paraffins*" (*Latin 'parum' = little, 'affins' = activity*).

PREPARATION METHODS

1.Wurtz's Reaction

This method was discovered by the French chemist WURTZ in 1855 and very convenient for preparing paraffins of higher molecular mass.

"Two moles of alkyl halides react with sodium metal in presence of dry ether solution in order to form a higher alkane" (Double number Carbons containing compound).

1. Wurtz's reaction is an organic chemical coupling reaction.
2. Alkyl bromides and iodides are preferred in this reaction.
3. It is suitable method for symmetrical alkanes having an even number of carbon atoms.
4. Tertiary alkyl halides are not used in this method.

$$R-X \;+\; 2Na \;+\; X-R \xrightarrow{dry\ ether} R-R \;+\; 2NaX$$

Ex:

$$CH_3\boxed{Br \;+\; 2Na \;+\; Br}CH_3 \xrightarrow{dry\ ether} CH_3-CH_3 \;+\; 2NaBr$$

Methylbromide Methylbromide Ethane

Two different alkyl halides are coupled to yield a mixture of three alkanes, it is known as "Crossed wurtz's" reaction.

Ex:

$$CH_3Br \;+\; 2Na \;+\; BrCH_2CH_3 \xrightarrow{Dry\ ether} CH_3CH_3 + CH_3CH_2CH_2CH_3 + CH_3CH_2CH_3$$

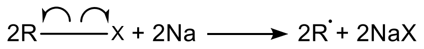
Methyl Bromide Ethyl Bromide Ethane Butane Propane

Mechanism

Free radical mechanism :

Free radical reaction mechanism involving free radicals as intermediate product, which can be broken down into the two steps.

STEP: 1 Formation of alkyl radical

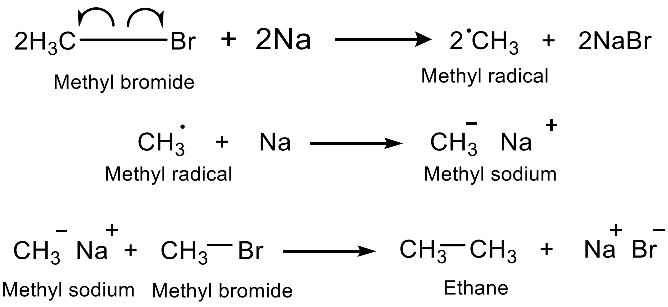


STEP: 2 Formation of alkane through sodiumalkyl

$$R^{\cdot} \;+\; Na \longrightarrow R^{-}Na^{+}$$

$$R^{-}Na^{+} + R-X \longrightarrow R-R \;+\; Na^{+}X^{-}$$

Ex:



Limitations

1. Commonly, only symmetric alkanes having an even number of carbon atoms can be synthesized
2. Methane cannot be synthesized by this reaction.
3. The Wurtz coupling method generally fails when tertiary alkyl halides are used.
4. Halogen compounds having other reactive functional groups like –OH, -COOH groups cannot be used.

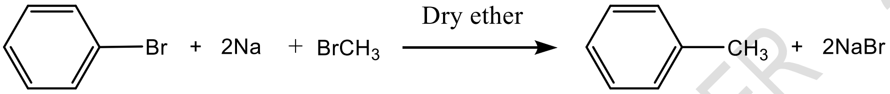
2. Wurtz - Fitting Reaction

One mole of ***Alkyl halide*** *and One mole of* ***Aryl halide*** *react with sodium metal in presence of dry ether solution in order to form A*lkylated aromatic hydrocarbon.

1. The Wurtz-Fitting reaction is the modification of Wurtz reaction.
2. It is the combination of Wurtz reaction and Fitting Reaction.

$$\underset{\text{Alkylhalide}}{R-X} \quad + \quad 2Na \; + \underset{\text{Arylhalide}}{XAr} \xrightarrow{dry\ et\square er} \underset{\text{Alkylareene}}{Ar-R} \; + \quad 2NaX$$

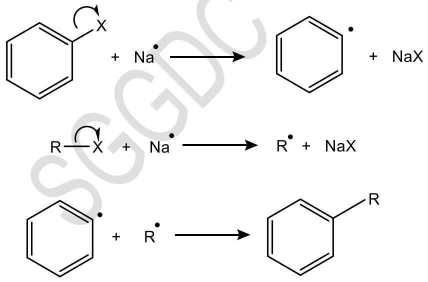
Ex:



Bromo benzane — Methyl bromide — Methyl benzene (or) toluene

Mechanism :

The reaction mechanism follows Radical mechanism



3.Corey - House Reaction

The ‘coupling reaction of alkyl halide with organic metallic compound’ is called as Corey-House Reaction. An alkyl halide and a lithium dialkylcuprate are reacted to give a higher hydrocarbon, and the reaction is proceeded by three steps

1.It is a better method than Wurtz’s reaction
2.It is particularly suitable for the preparation of unsymmetrical alkanes.
3.Lithiumdialkylcuprate is known as Gilman’s reagent.

Ex:

$$\underset{\text{Ethyl Iodide}}{CH_3CH_2I} \quad + \quad 2Li \xrightarrow{Dry\ ether} \underset{\text{Ethyl lithium}}{CH_3CH_2Li} \; + \quad LiI$$

$$2CH_3CH_2Li \quad + \quad CuI \; \rightarrow \underset{\text{Diethyllithiumcuprate}}{Li(CH_3CH_2)_2Cu} \; + \quad LiI$$

$$\underset{\text{Diethyllithiumcuprate}}{Li(CH_3CH_2)_2Cu} \quad + \underset{\text{Methyliodide}}{CH_3I} \xrightarrow{Dry\ ether} \underset{\text{Propane}}{CH_3CH_2CH_3} \quad + \quad CH_3CH_2Cu \; + \; LiI$$

HALOGENATION REACTION OF ALKANES

It involves the substitution of Hydrogen atoms of alkanes by halogen atoms. Alkanes react with halogens in presence of sunlight or U.V. light or at higher temperature $(200 - 300℃)$ one or more hydrogen atoms are replaced by the respective halogen atom.

1. Rate of halogenation depends upon the reactivity of Halogen and the reactivity of hydrogen in alkanes attached to primary, secondary and tertiary carbons.
2. The reactions with fluorine take place with explosive speed and the reaction with chlorine and bromine take place with ordinary rate.
3. The reaction with Iodine is reversible, that is why this reaction is carried out is the presence of oxidizing agents.
4. Relative reactivity of halogen on alkanes decreases with decrease in the electro negativity of halogen. The order of reactivity
$$F_2 \gg Cl_2 > Br_2 > I_2$$
5. The replacement of hydrogen atom by halogen is follows the following order
$$3°H > 2°H > 1°H > Methyl\ Hydrogen\ (CH_3)$$
6. Smaller amount of halogen gives only alkyl halide. If excess of halogen used, then poly halogenation takes place.

$$\underset{\text{Alkane}}{\text{R-H}} + \underset{\text{Halogen}}{X_2} \xrightarrow[250\text{ - }400^oC]{\text{sunlight}} \underset{\text{Alkylhalide}}{\text{R-X}} + HX$$

Ex: Chlorination of Methane.

$$\underset{\text{Methane}}{CH_3\text{-}H} + \underset{\text{Chloride}}{Cl_2} \xrightarrow[250\text{ - }400^oC]{\text{Sunlight}} \underset{\text{Methyl Chloride}}{CH_3-Cl} + HCl$$

7. Halogenation of higher alkane gives a mixture of isomeric alkyl halides.

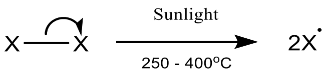
$$CH_3CH_2CH_3 + Cl_2 \longrightarrow \underset{\text{Smaller}}{CH_3CH_2CH_3Cl} + \underset{\text{Excess}}{CH_3CHClCH_3}$$

Mechanism

Halogenation is a free radical substitution in presence of sun light, UV light, peroxides, higher temperature. It takes place in the following steps.

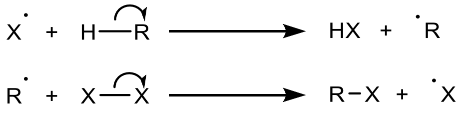
Step 1: *Chain Initiation*:

Halogen molecule split it into halogen free radical in presence of sunlight by homolysis. It is an endothermic process.



Step 2 : *Chain Propagation*:

Alkane reacts with halogen free radical to give alkane radical. Alkane radical than reacts with halogen molecule to give alkyl halide and new halogen radical. These two reactions are repeated until all the hydrogen atoms substituted. Therefore, it is called a chain propagation reaction.



Step 3 : *Chain Termination*:

Finally, any two free radicals combine to give stable molecule and the reaction stops.

$$X^{\cdot} + X^{\cdot} \longrightarrow X-X$$
$$R^{\cdot} + R^{\cdot} \longrightarrow R-R$$
$$R^{\cdot} + X^{\cdot} \longrightarrow R-X$$

Ex: *Chlorination of Methane* :

Methane reacts with chlorine in presence of U.V. light or at high temperature (300℃) to give methyl chloride or chloro methane and hydrogen chloride. This reaction does not stop at this stage, the remaining hydrogen atoms in the methyl chloride are successively replaced by chlorine atoms. The resulting mixture may be separated by fractional distillation. It has great Industrial importance.

$$CH_4 + Cl_2 \xrightarrow{Sunlight} \underset{\text{Methyl chloride}}{CH_3Cl} \quad + \quad HCl$$

$$CH_3Cl + Cl_2 \xrightarrow{Sulight} \underset{\substack{\text{Methyline}\\\text{chloride}}}{CH_2Cl_2} \quad + \quad HCl$$

$$CH_2Cl_2 + Cl_2 \xrightarrow{Sunlight} \underset{\text{Chloroform}}{CHCl_3} \quad + HCl$$

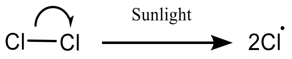
$$CHCl_3 + Cl_2 \xrightarrow{Sunlight} \underset{\substack{\text{Carbon}\\\text{tetrachloride}}}{CCl_4} \quad + \quad HCl$$

In actual practice all the above four $(CH_3Cl, CH_2C_2, CHCl_3, CCl_4)$ substitution products are formed. The extent to which end product is formed depends upon the amount of Chlorine used. Smaller amount of Chlorine gives only Chloromethane. If excess of Chlorine used, then poly Chlorination takes place.

Mechanism:

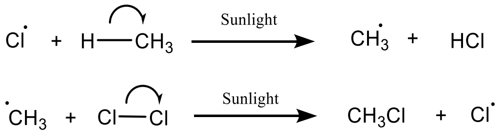
Chlorination of Methane is a free radical substitution reaction. It involves the following steps.

Step 1 : *Chain Initiation* :



$$Cl-Cl \xrightarrow{Sunlight} 2Cl^{\bullet}$$

Step 2 : *Chain Propagation* :



$$Cl^{\bullet} + H-CH_3 \xrightarrow{Sunlight} {}^{\bullet}CH_3 + HCl$$

$${}^{\bullet}CH_3 + Cl-Cl \xrightarrow{Sunlight} CH_3Cl + Cl^{\bullet}$$

Step 3 : *Chain Termination* :

$$Cl^{\bullet} + Cl^{\bullet} \longrightarrow Cl_2$$

$$Cl^{\bullet} + {}^{\bullet}CH_3 \longrightarrow CH_3Cl$$

$${}^{\bullet}CH_3 + {}^{\bullet}CH_3 \longrightarrow CH_3CH_3$$

REACTIVITY AND SELECTIVITY OF HALOGENATION

The reaction of alkane with fluorine takes place with explosive speed and the reactions with chlorine and bromine take place with ordinary rate. The reaction with iodine is reversible, that's why this reaction is carried out in the presence of oxidizing agents.

$$F_2 >> Cl_2 > Br_2 > I_2$$

Rate of halogenation reaction of alkane depends upon the reactivity of halogen and reactivity of different hydrogens in alkane attached to primary, secondary and tertiary carbons.

3° 'H' are more reactive than 2° and 1° 'H'; 2° 'H' are more reactive than 1° 'H'.

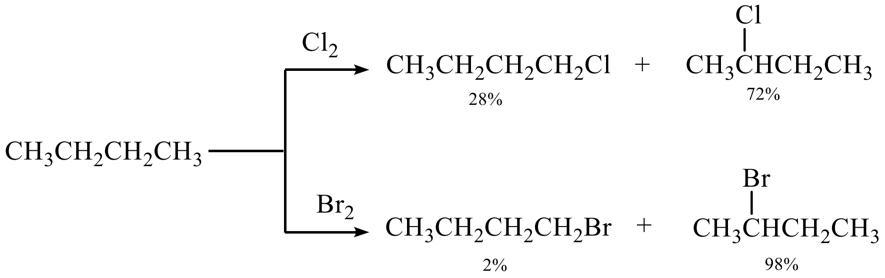
$$3°H \;>\; 2°H \;>\; 1°H$$

Halogenation reaction of alkanes reactivity and selectivity can be explained based on reactivity – selectivity principle. This principle states that

"If the attacking species is more reactive it will be less selective and relative yields can be predicted on the basis of probability factor. A less reactive species will be more selective forming one of the isomeric products exclusively".

Ex : Let us compare the yields of isomer products in the chlorination and Bromination of propane

In chlorination of butane 1 – chlorobutane and 2 – chlorobutane are formed in 28% and 72% yield respectively. But in the bromination of butane 2 – bromobutane is formed almost exclusively.



$$CH_3CH_2CH_2CH_3 \xrightarrow{Cl_2} \underset{28\%}{CH_3CH_2CH_2CH_2Cl} + \underset{72\%}{CH_3\overset{Cl}{C}HCH_2CH_3}$$

$$CH_3CH_2CH_2CH_3 \xrightarrow{Br_2} \underset{2\%}{CH_3CH_2CH_2CH_2Br} + \underset{98\%}{CH_3\overset{Br}{C}HCH_2CH_3}$$

from the above, it is clear that bromine is although less reactive and it is more selective.

CONFORMATIONAL ANALYSIS OF ALKANES

Conformational isomerism

Two or more stereoisomers which are inter convertible by C-C bond rotation at room temperature are called as “Conformational isomers” and the phenomenon is called “Conformational isomerism”.

Conformation**:**

Different 3-dimensional shapes that can be taken by a molecule by rotating about single bond.

1. CONFORMATIONS OF ETHANE

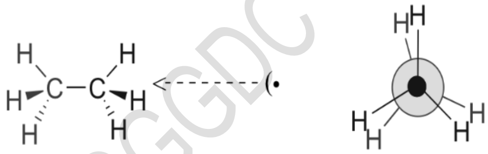
Ethane is a two carbons alkane. Molecular formula is C_2H_6 . Structure is CH_3-CH_3 . The central bond in the molecule of ethane is a single bond between two carbon atoms, each of which gets further linked to three hydrogen atoms. If one of the carbon atoms of ethane rotates around the central bond whereas the other is kept still, a large number of arrangements of the hydrogens of one carbon with respect to the hydrogens of the other carbon can be obtained.

Among the infinite number of possible conformations of ethane, three conformations represent the extremes. These are known

1. Eclipsed conformation
2. Staggered conformation
3. Skew (or) Gousche conformation.

1. Eclipsed Conformation

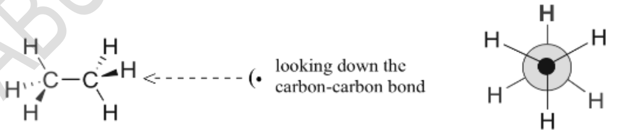
An extreme conformation would be one in which the rear methyl group gets completely eclipsed by the front methyl group.



'eclipsed' conformation

2. Staggered Conformation

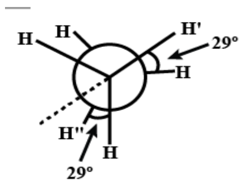
Another extreme conformation would be one in which the rear methyl group is rotated upside down and thus all the six hydrogen atoms are visible and would be as far apart from each other as possible.



'staggered' conformation
(Newman projection)

3. Skew Conformation

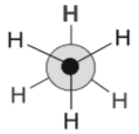
The infinite number of possible intermediate conformations between the two extreme conformations are known as skew conformations.



It is important to remark that all the above conformations of ethane would not be equally stable. Among the infinite number of conformations the staggered conformation most stable and the eclipsed conformation least stable. Stabilities of the skew conformations are in between these two extreme limits.

The relative stabilities of the various conformations of ethane

Staggered > **Skew** > **Eclipsed**



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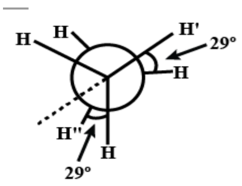

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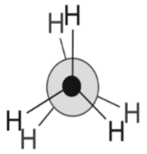
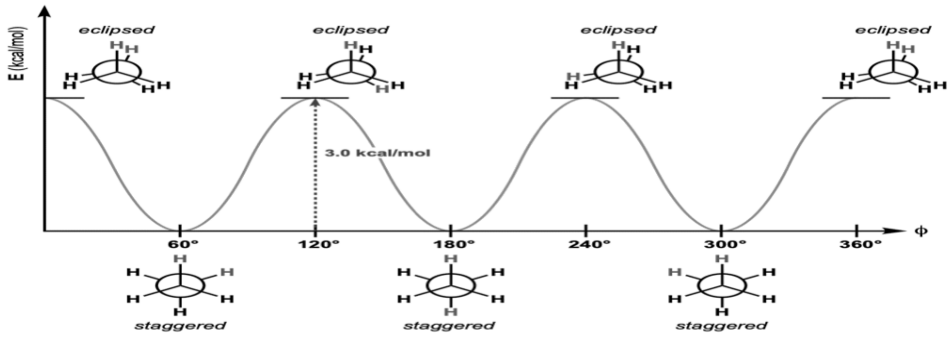


It is possible to explain this stability order in terms of repulsive interactions between bonding pairs of electrons. In the staggered conformation, the electron clouds of six carbon-hydrogen bonds attached to the central carbon-carbon sigma bond would be as far apart as possible. As a result, there is minimum repulsive interactions between these electron clouds. Therefore, this conformation is quite stable. On the other hand, in the skew and eclipsed conformations, the electron clouds become closer. This gives rise to repulsive interaction which become maximum in the eclipsed conformation where there is minimum separation of the electrons of the six C-H bonds.

The repulsive interaction between the electron clouds which affects the stability of a conformation is termed as torsional strain. Among all the conformation of ethane, staggered conformation is having the least torsional strain and hence most stable while eclipsed conformation is having the maximum torsional strain and hence least stable.

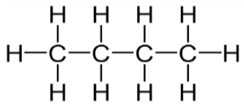
As a result, the potential energies of the skew and eclipsed conformations would increase and hence their stabilities decrease. It is to be noted that the staggered conformation is having the minimum and the eclipsed conformation is having the maximum potential energy. Further it is evident that the energy difference between the staggered and eclipsed conformations of ethane is 3 kcal or 12 kJ, which constitutes the conversion of staggered to eclipsed conformation. However, this energy barrier of 3 kcal or 12 kJ has been too small for either form to remain stable, i.e., the two forms are interred convertible since even at ordinary temperature and it is not possible to separate the different conformations of ethane. It is to be remembered that ethane is mostly in staggered form.



Energy profile diagram of Ethane

2. CONFORMATIONS OF n-BUTANE

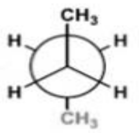
Butane is a four carbons alkane. Molecular formula is C_4H_{10}. Its structure is $CH_3CH_2CH_2CH_3$.



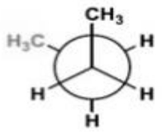
Thus, it is having three C-C single bonds around which rotation can occur. If rotation around the central C-C bond(C_2-C_3) is considered more than one staggered and eclipsed conformations would be observed.

a. Staggered conformations

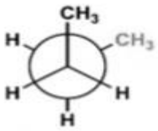
Staggered conformations have lower torsional energies and hence are more stable than eclipsed conformations. In case of n – butane three staggered conformations are possible.



I
anti - staggered



II
staggered



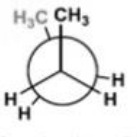
III
staggered

In anti or trans conformation I, the methyl groups are as far apart as possible, it is most stable. In II and III, the two methyl groups are crowded. Due to crowding of the methyl groups, the repulsion forces operate and raise the energy of the conformations which thus become less stable. Both anti and staggered forms are free of torsional strain. The anti-form I and the staggered from II or III are termed as conformational diastereomers.

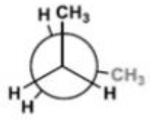
From the energy study of these three conformations, it is found that the anti-conformation, I is slightly more stable than the staggered conformations II or III only by 0.9 kcal/mole. It is important to note that the conformational isomers are readily interconvertible and hence cannot be separated.

b. Eclipsed conformations

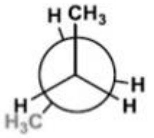
Like that of three staggered conformations, there are three eclipsed conformations of n – butane.



IV
fully eclipsed

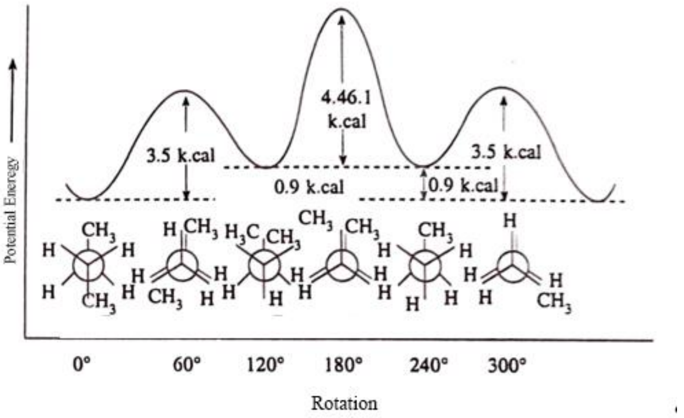


V
Partially eclipsed



IV
Partially eclipsed

In the fully eclipsed form IV, a methyl group is eclipsed by another methyl group, while in eclipsed forms, V and VI each of the methyl group is eclipsed by hydrogen. Of these two types of eclipsed conformations, the one having larger methyl groups eclipsing, i.e., IV, will naturally feel more repulsive force than the V and VI where a methyl group is eclipsed with a hydrogen atom. Thus out of these three conformations, IV is less stable while V and VI are more stable.



Energy profile diagram of Butane

Important conclusions:

(i). The fully staggered form(anti form) I is more stable than the fully eclipsed form IV by about 5.3 kcal/mole (22 kJ/mole).

(ii). The anti-form I is more stable than the staggered form II or III by about 0.9 kcal/mole (3.8 kJ/mole).

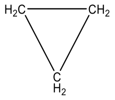
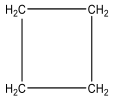
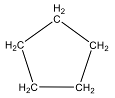
Thus, the relative stabilities of the six conformations of n – butane can be represented as below.

Anti staggered I	>	Staggered II	>	Staggered III	>	Partially Eclipsed V	>	Partially Eclipsed VI	>	Fully Eclipsed IV

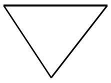
Thus, at any time, n–butane consists of an equilibrium mixture of all possible conformations.

CYCLOALKANES

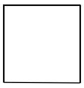
Alicyclic hydrocarbons are cyclic carbon compounds which are chemically similar to open chain hydrocarbons. These are also called as cycloalkanes or cycloparaffins. Cycloalkanes are believed to be formed by the removal of one hydrogen each from the first and last carbon atoms of an alkane. The general empirical formula of cycloalkanes homologous series is C_nH_{2n}. 'n' = 3,4,5……etc is an integer. Cyclopropane (C_3H_6) is the first member of this series.

No. of carbons	Root word	Formula	Name
3C	Prop		Cyclopropane
4C	But		Cyclobutane
5C	Pent		Cyclopentane

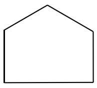
Cycloalkanes are represented by various geometrical forms for convenience. Each corner represents a CH_2 unless there is a substituent. A 'triangle' symbol is used for 'cyclopropane', 'square' for 'cyclobutane' , 'pentagon' and 'hexagons' are used for 'cyclopentane' and 'cyclohexane' respectively.



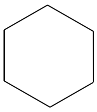
Cyclopropane



Cyclobutane



Cyclopentane



Cyclohexane

CYCLOALKANES – RELATIVE STABILITIES

BAEYER'S STRAIN THEORY

Based on the property's cycloalkanes, the lower cycloparaffins (cyclopropane and cyclobutane) are less stable and the rings are easily opened by the various reagents. Moreover, these reactions also indicate that the stability of the ring increases as the ring becomes larger upto six-membered

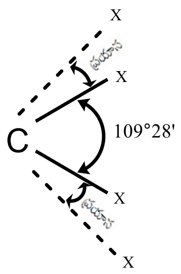
Cyclopropane < Cyclobutane < Cyclopentane < Cyclohexane

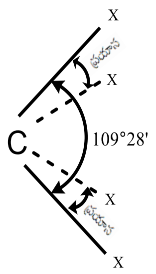
The opening of the ring (or instability) in case of three and four-membered compounds explained by 'Adolf Von Baeyer' (1885) in the form of theory commonly known as '**Baeyer' strain theory'.** He based his theory on Le Bel and vant Hoff's hypothesis.

Baeyer Strain Theory

The Baeyer strain theory is based on the following assumptions

1. Since carbon atom is tetrahedra in nature with all the four valencies directed towards four corners of regular tetrahedron, the angle between any two bonds should be $109°28'$. Thus any deviation from this value would result in an internal strain in molecule.
2. Deviation of bond angle is two types.
   a. Negative Deviation, and
   b. Positive Deviation.

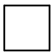
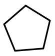
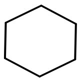




Negative deviation $> 109°28$ *Positive deviation* $< 109°28'$

3. All carbon atoms of cycloalkane ring are planar indicating that cyclopropane ring is an equilateral triangle. Cyclobutane ring is a square and other cycloalkane rings are regular polygons.
4. When these molecules assume the above planar structures, there is a deviation from the normal tetrahedral angle production a lot of strain in the molecule, this strain commonly known as angle strain, it is depends upon the extent of deviation of the bond angle from the normal tetrahedral angle value $(109°28')$.
5. Greater the deviation of the bond angle of the ring from $109°28'$, greater is the strain and consequently more unstable (more reactive) is the ring.
6. Baeyer showed that the deviation (d) in cycloalkanes from the normal tetrahedral angle can be calculated as below

$$d = \frac{1}{2}(\,Tetrahedral\ bond\ angle - Bond\ angle\ in\ cyclo\ alkane)$$

Cycloalkane	No. of Carbons	Structure	Bond angle	Bond strain
Cyclopropane	3		60°	$\frac{109°28' - 60°}{2} = +24°44'$
Cyclobutane	4		90°	$\frac{109°28' - 90°}{2} = +9°44'$
Cyclopentane	5		108°	$\frac{109°28' - 108°}{2} = +0°44'$
Cyclohexane	6		120°	$\frac{109°28' - 120°}{2} = -5°16'$

From the above data it is clear that the positive and negative value of valence angle deviation (d) indicate whether the bond angle (α) is lower or greater than the normal tetrahedra bond angle $(109°28')$ i.e., whether the strain is inward or outward.

Form the above data it is clear that the value of valence deviation is minimum in case of cyclopentane and not too large with cyclohexane, which led Baeyer to conclude that these rings are having minimum strain and hence more stable, less reactive than the cyclopropane and cyclobutane have greater amount of valence deviation is greater strain and hence are less stable, more reactive.

Limitation of Baeyer Strain Theory

1. Baeyer's strain theory explains relative stability of the various cyclic compounds up to six – membered rings or better to say up to five – membered rings, but it failed beyond this.
2. It could not explain why the higher cycloalkanes undergo substitution rather than addition reactions.

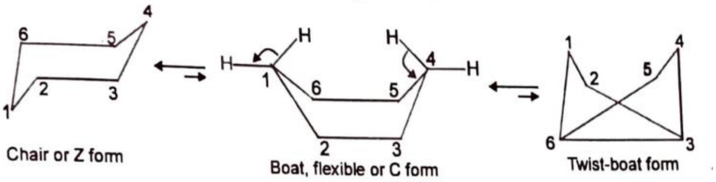
CONFORMATION OF CYCLOHEXANE

To explain the stability of cycloalkanes, Valence deviation is the criterion for determining the stability of cyclic alkanes, Sache and Mohr (1890) paid attention to this fact and proposed that

1. Rings with six or more carbon atoms are not planar but they are puckered.
2. These rings are called strain less rings because the carbon atoms lie in different planes and normal valency angle is retained.
3. The strain less conformations maintain normal tetrahedral bond angle of $109°28'$.

Ex: **Conformations of cyclohexane**

The two extreme strain less, multi planar or puckered conformations of cyclohexane are the more stable **chair** and the less stable **boat**. The twist-boat conformer is less stable than the chair by about 5.5 kcal/mole but is more stable than the boat; it is formed from the boat conformer by moving one hydrogen to the left and the other to the right



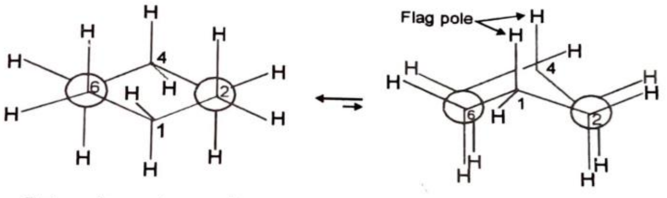
The chair and boat conformational isomers of cyclohexane are rapidly inter convertible at ordinary temperature and have not yet been isolated individually because the energy of inter conversion of these forms is only 5 kcal/mole. However, the chair form is considerably more stable than the boat form and is the conformation normally assumed by cyclohexane and its derivatives. At room temperature the ratio of chair to boat conformation at equilibrium is about 1000:1.

Relative stability of chair and boat forms

The relative instability of the boat form to the chair form is due to the following two facts.

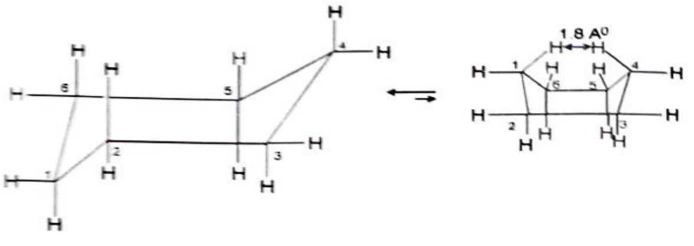
1. In the chair conformation of cyclohexane the hydrogens are staggered, i.e., they are present far away from each other and hence no steric repulsion, with the result the conformation has lower energy. Whereas in the boat form the hydrogens on four of the carbon atoms, namely $C_2 - C_3$ and $C_5 - C_6$ are eclipsed, which bring them substantially close together and hence a definite interference and repulsion (steric) develops between the hydrogens. Due to this steric repulsion between the hydrogen atoms in the boat form with a considerable torsional strain, hence it is less stable than the chair .

2. An additional strain in the boat conformation arises from the crowding of the so called 'flagpole hydrogens' on C_1 and C_4. The two hydrogens, one on C_1 and other on C_4 pointing towards each other are very close (1.83Å). This gives to strain in it, with the result the boat conformer becomes much less stable by 6.9 kcal/mole than the chair conformer.



Chair conformer (*most stable*)
Note all hydrogen atoms are staggered (far away from each other).

Boat conformer (*least stable*)
Note the hydrogen of C₂—C₃ and C₅—C₆ are eclipsed (crowded).

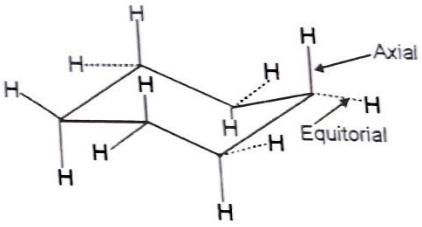


Chair form

Boat form

Since the ratio of boat to chair conformation is very small (1:1000). The bonds in the chair conformation of cyclohexane and its derivatives may be divided into two types. Six of these bonds (shown by full lines) are parallel to the axis of the ring, i.e., they point either up or down form the molecule, and called axial (a) bonds, whereas the other six bonds (shown by dotted lines) lie along the equator of the molecule, i.e., they point sideways from the molecule, and are called equatorial (e) bonds.

The various atoms for substituents attached to the axial and equatorial bonds are known as axial and equatorial, respectively atoms or substituents.



UNIT - II

ALKENES

Hydrocarbons with C-C multiple bonds are called as unsaturated compounds. The unsaturated compounds are further classified into alkenes and alkynes based on the type of multiple bonds. Alkenes are C-C double bond and alkynes are C-C triple bond compounds.

PREPARATION METHODS

1. **By the dehydration of alcohols**

The dehydration of alcohols with conc. H_2SO_4 at 100° C or Phosphoric acid at 200°C or by passing Alcohol vapours over Alumina, Al_2O_3 or P_2O_5 or anhydrous $ZnCl_2$ at 350 — 400°C gives alkenes.

$$R-CH_2-CH_2-OH \xrightarrow[Al_2O_3 \text{ or } P_2O_5,\ 350 - 400\ °C]{\text{Conc. } H_2SO_4,\ 100\ °C \text{ or}} R-CH{=}CH_2 + H_2O$$

The ease of dehydration follows the following order.

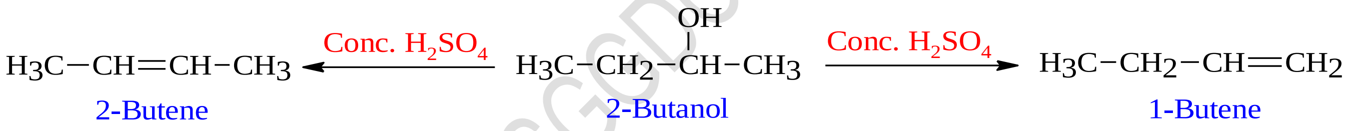
tert-alcohol > ***sec-alcohol*** > ***pri-alcohol***

The above order of dehydration is due to the following stability of carbocation formed during dehydration.

3° > **2°** > **1°** *(Relative order of stability of carbocations)*

Dehydration of unsymmetrical secondary or tertiary alcohols leads to the formation of two different akenes, dehydration can be predicated by Saytzeff's rule.

Ex : Dehydration of Butanol-1.



$$\underset{\text{2-Butene}}{H_3C-CH{=}CH-CH_3} \xleftarrow{\text{Conc. } H_2SO_4} \underset{\text{2-Butanol}}{H_3C-CH_2-\overset{\overset{\large OH}{|}}{C}H-CH_3} \xrightarrow{\text{Conc. } H_2SO_4} \underset{\text{1-Butene}}{H_3C-CH_2-CH{=}CH_2}$$

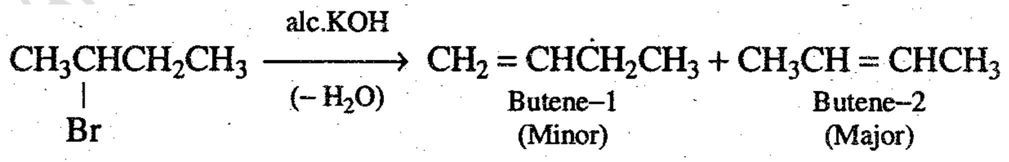
2. **By the dehydrohalogenation of alkyl halides:**

The dehydrohalogenation of alkyl halides with alc. KOH gives alkenes.

Ex:

$$CH_3CH_2.CH_2Br \xrightarrow{\text{alc. KOH}} CH_3CH = CH_2 + HBr \qquad \textbf{(Elim. reaction)}$$

If dehydrohalogenation of alkyl halides can give two products, the major product can be predicted according to Saytzeff rule.



$$\underset{\underset{\large Br}{|}}{CH_3CHCH_2CH_3} \xrightarrow[(-H_2O)]{\text{alc.KOH}} \underset{\substack{\text{Butene–1}\\ \text{(Minor)}}}{CH_2 = CHCH_2CH_3} + \underset{\substack{\text{Butene–2}\\ \text{(Major)}}}{CH_3CH = CHCH_3}$$

The ease of dehydrohalogenation (— HX) of alkylhalides follows the order

$\mathbf{3^0\ RX} > \mathbf{2^0\ RX} > \mathbf{1^0\ RX}$

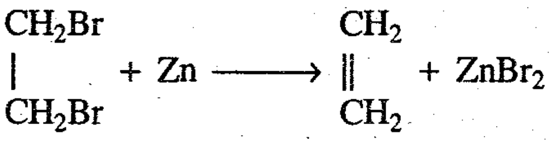
Further among the different halides, the order is

RI > **RBr** > **RCl**

3. By the dehalogenation of vicinal dihalides:

The dehalogenation of vicinal dihalides with zinc dust in alcohol gives alkenes.

Ex: 1, 2–Dibromoethane on dehalogenation with zinc dust gives ethylene.



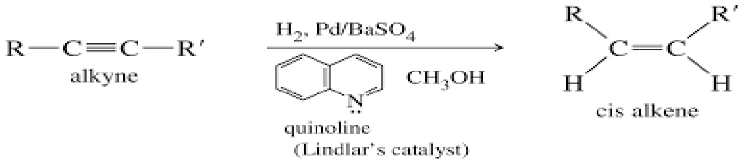
$$\begin{matrix} CH_2Br \\ | \\ CH_2Br \end{matrix} + Zn \longrightarrow \begin{matrix} CH_2 \\ \| \\ CH_2 \end{matrix} + ZnBr_2$$

4. From Alkynes.

By partial reduction, alkynes can be converted into Alkenes.

a. Formation of cis-Alkene.

An alkyne is hydrogenated with hydrogen in presence of Lindlar's Catalyst gives alkene. The addition of hydrogen converts alkyne to cis-alkene.



b. Formation of trans-alkene :

An alkyne is treated with Na / liquid NH_3 (Birch Reduction) gives trans alkene.

PROPERTIES OF ALKENES

PHYSICAL PROPERTIES.

a. The physical properties of alkenes are similar to those of the corresponding alkanes.

b. **Physical state:** The first three members ($C_2 – C_3$) are gases, the next 14 ($C_4 – C_{18}$) are liquids, and those containing more than 18 carbons are solids.

c. **Densities:** However, their densities gradually increase with increase in molecular weights.

d. **Boiling and Melting points:** Melting points and boiling points increase with increase in molecular weights. Branched chain alkenes have lower boiling point than corresponding straight chain alkenes. Cis alkenes have higher boiling point than trans alkenes.

e. **Solubility :** Alkenes are insoluble in water but are soluble in organic solvents like benzene, alcohols, ethers and carbon tetrachloride.

CHEMICAL PROPERTIES.

Functional group of alkenes is the carbon-carbon double bond. Thus, alkene chemistry is the chemistry of carbon-carbon double bond. Alkenes are more reactive than alkanes. Higher reactivity of alkenes relative to alkanes can be explained as follows

1. The double bond consists of one σ -and one π -bond.
2. The π -bond is formed by the sideways overlap of p-orbitals, which is less extensive. Therefore π – bond (bond energy = 263.5 kJ) is a weaker bond than a σ -bond (bond energy = 347.1KJ).
3. The electrons of the π -bond are more diffused in space. These are pushed outwards due to the repulsions between them than the electrons of the σ -bond.
4. The more diffused π -electrons are more exposed to any reactant. Carbon-carbon double bond can be easily attacked by the reagents that require electrons, i.e., electrophiles. Thus, π -bond of the carbon-carbon double bond acts as the source of electrons. It tends to convert itself to two strong σ -bonds when attacked by electrophiles. Hence, reactions of alkenes are mainly electrophilic addition reactions.

Alkenes are unsaturated hydrocarbons consisting of a sigma bond and a π – bond. The typical reactions of alkenes involve the breaking of the weak π – bond to form two sigma bonds. Such reactions are called addition reactions.

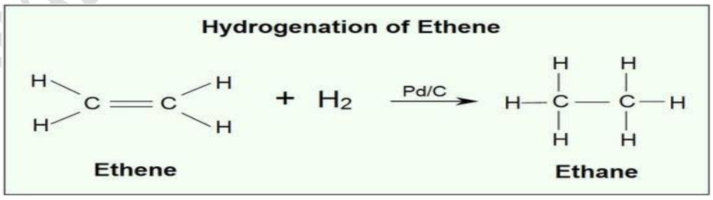
These addition reactions are usually electrophillic in nature as the π – electrons of carbon-carbon double bond are available to any species seeking electrons.

Important reactions

1. Addition of dihydrogen (H_2)
2. Addition of halogens (X_2)
3. Addition of halogen acid (HX)
4. Addition of sulphuric acid (H_2SO_4)
5. Addition of water (H_2O)
6. Oxidation
7. Ozonolysis (O_3)
8. Polymerization

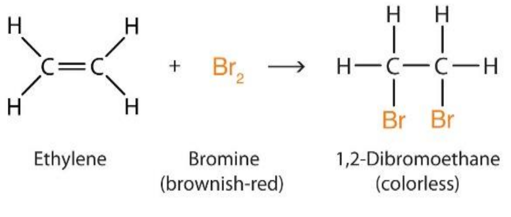
1. Addition of dihydrogen to alkene (H_2):

Alkenes react with dihydrogen in the presence of catalysts like finely divided nickel, palladium or platinum to form alkanes and these are cis –addition reactions.



1. Addition of Halogen (X_2):

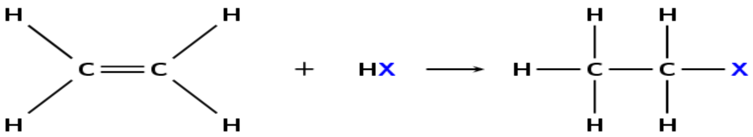
Alkenes react with halogens such as chlorine and bromine to form vicinal di-haloalkanes. The alkenes and the halogens are mixed together in an inert solvent like carbon tetrachloride.



During the addition reaction between ethene and bromine, the reddish brown colour of bromine gets decolorized due to the formation of di bromoethane. Hence, this reaction is used as a test for unsaturation.

2. **Addition of Halogen acid (HX)**

Alkenes react with halogen acids to form haloalkanes. Alkenes towards hydrogen iodide are more reactive than hydrogen bromide which in turn more reactive than hydrogen chloride.

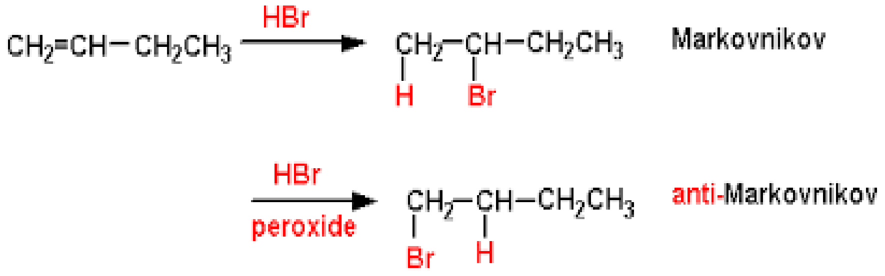


In the case of unsymmetrical alkene, two products are formed.

Ex:

1-butene reacts with hydrogen bromide to form 2-Bromobutane and 1-Bromobutane among which 2-Bromobutane is the major product in accordance with Markownikov"s rule.

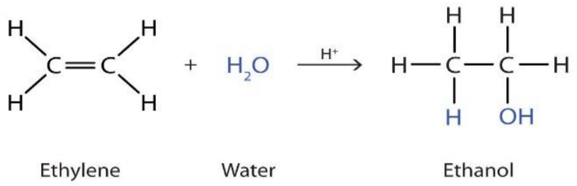
1-butene reacts with hydrogen bromide in presence of peroxide to form 2-Bromobutane and 1-Bromobutane among which 1-Bromobutane is the major product in accordance with anti-Markownikov"s rule, and is known as peroxide effect or Kharash effect

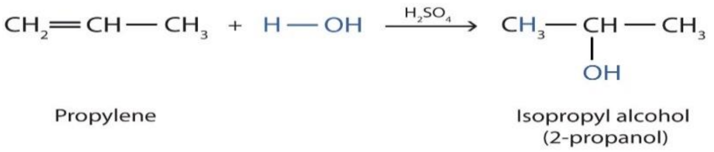


3. **Addition of water** (Hydration of alkenes)

Water molecule adds to an alkene molecule across the double bond in the presence of dilute acids and a catalyst.

Ex : Ethane gives ethanol when a mixture of Ethene and steam is passed over phosphoric acid and silica





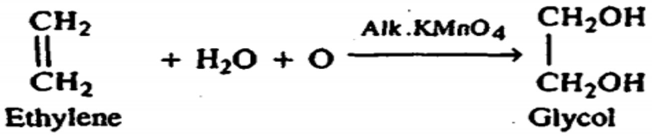
4. Oxidation reaction

Alkenes can be readily oxidized, but the nature of the products depends upon the oxidizing agent used.

Ex :

A. Alkenes on reacting with cold, dilute, alc.solution of potassium permanganate which is also called Bayer's reagent produce vicinal glycols, that is 1, 2-Diols.

Ex: Ethene on reaction with Bayer's reagent forms ethane 1, 2-diol (or) ethylene glycol.

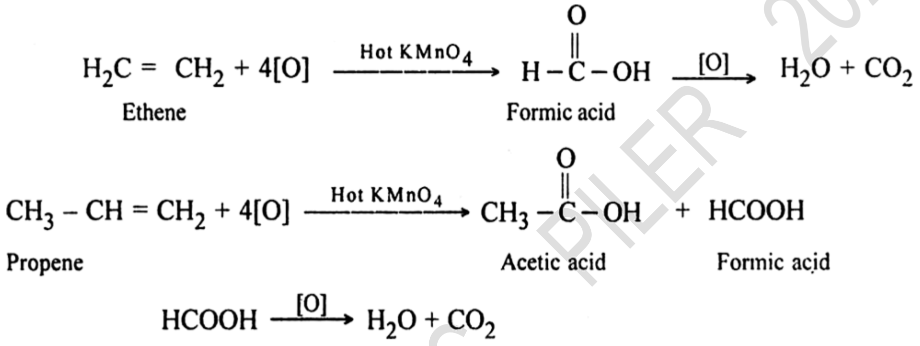


$$CH_2{=}CH_2 + H_2O + O \xrightarrow{Alk.KMnO_4} CH_2OH{-}CH_2OH$$

B. With acidified $KMnO_4$ (Or) $K_2Cr_2O_7$

Acidified Potassium permanganate (or) Potassium dichromate oxidises the dihydroxy compound so produced in reaction to ketone and /or carboxylic acid.

Ex:



$$H_2C = CH_2 + 4[O] \xrightarrow{Hot\ KMnO_4} H-\overset{\overset{O}{\|}}{C}-OH \xrightarrow{[O]} H_2O + CO_2$$

$$CH_3 - CH = CH_2 + 4[O] \xrightarrow{Hot\ KMnO_4} CH_3-\overset{\overset{O}{\|}}{C}-OH + HCOOH$$

$$HCOOH \xrightarrow{[O]} H_2O + CO_2$$

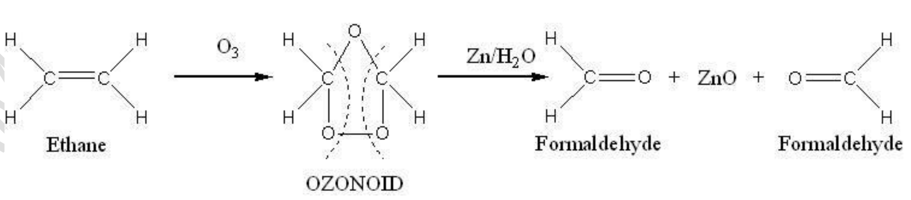
C. Ozonolysis

Alkenes react with ozone to form ozonide, which on further hydrolysis in the presence of zinc form either Aldehydes (or) Ketones (or) both, is known as 'Ozonolysis'.

The nature of the products (aldehydes and ketones) formed due to ozonolysis depends upon the location of the double bond in the parent alkene. Therefore, this reaction provides a very convenient way of locating the position of the double bond in any molecule.

Ex: When Ozone molecule is added across the double bond in Ethene to give Etheneozonide. This on hydrolysis form Formaldehyde (or) Methanal.

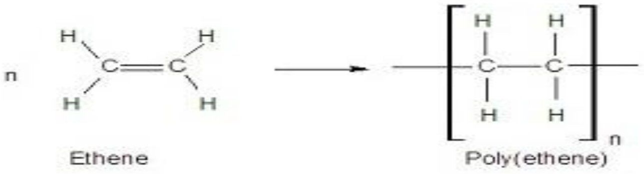
REDUCTIVE OZONOLYSIS



5. Polymerization

Alkenes undergo addition polymerization reaction when heated under pressure, in the presence of suitable catalysts. In this, a large number of molecules of the same species join together to form a giant molecule, called a polymer. The simple compounds which form the polymers are called monomers.

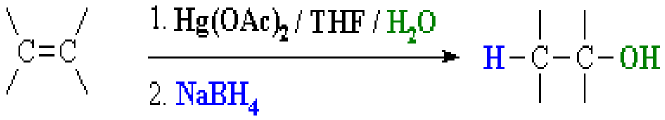
Ex : Ethene is heated to 100^0C under 1000 atm pressure in presence of oxygen, we get Polyethene



7. Oxymercuration–demercuration reaction.

The oxymercuration reaction is an electrophilic addition organic reaction that transforms an alkene into a neutral alcohol.

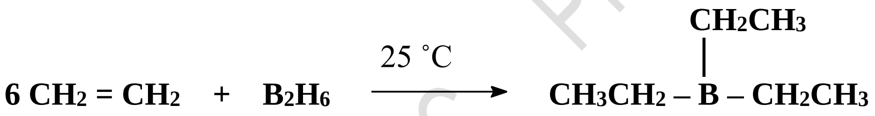
1. In oxymercuration, the alkene reacts with mercuric acetate (AcO–Hg–OAc) in aqueous solution to yield the addition of an acetoxymercury (HgOAc) group and a hydroxy (OH) group across the double bond.
2. The reaction follows Markovnikov's rule and it is an anti addition (the two groups will be trans to each other).
3. Oxymercuration followed by reductive demercuration, so it is called an oxymercuration–reduction reaction (or) oxymercuration–demercuration reaction.



8. Hydroboration–oxidation reaction

Diborane (B_2H_6) adds readily at 0 - 25°C to the double bond of olefins to form trialkylborane. The reaction is known as hydroboration.

Ex:

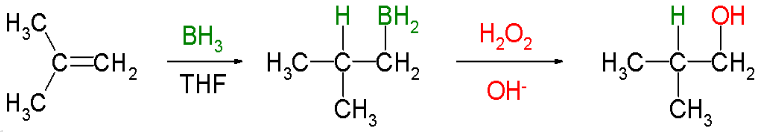


$$6\,CH_2=CH_2 + B_2H_6 \xrightarrow{25\,^\circ C} CH_3CH_2-\overset{\displaystyle CH_2CH_3}{\overset{|}{B}}-CH_2CH_3$$

Triethyl borane

1. Hydroboration–oxidation reaction is a two-step hydration reaction.
2. It is used for the synthesis of primary alcohols and alkanes.
3. The process results in the syn addition.
4. Hydroboration–oxidation is an anti-Markovnikov reaction.

Ex: Synthesis of Alcohol



Ex: Synthesis of alkane

$$2\,(CH_3CH_2CH_2CH_2)_3B \xrightarrow{H_2O\,/\,H^+} 6\,CH_3CH_2CH_2CH_2CH_3 + H_3BO_3$$

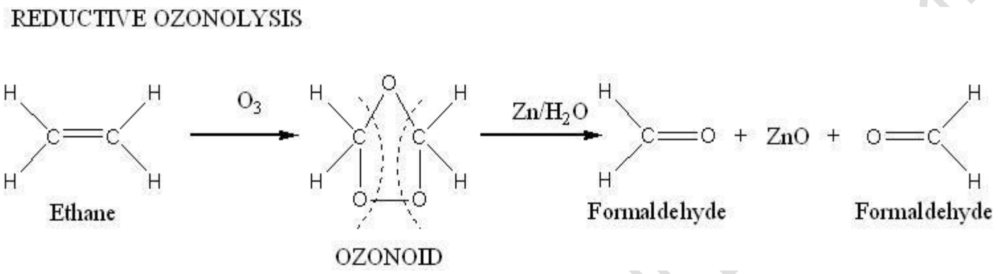
OZONOLYSIS

Unsaturated hydrocarbons (Alkene or Alkyne) react with ozone to form ozonide, which on hydrolysis in the presence of zinc dust form either Aldehydes (or) Ketones (or) both, is known as ‘Ozonolysis'.

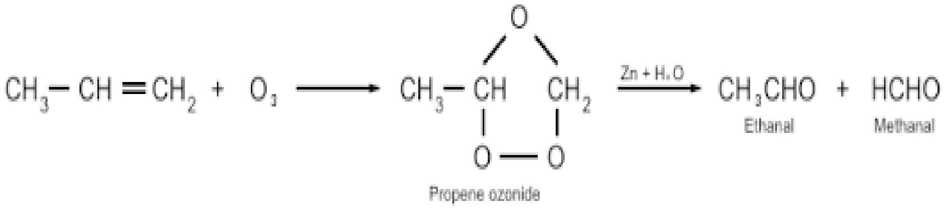
1. The nature of the product (aldehyde or ketone) formed by the ozonolysis depends upon the location of the double bond in the parent alkene.
2. This reaction provides a very convenient way of locating the position of the double bond in any molecule and estimation of amount of unsaturation.

Ex:

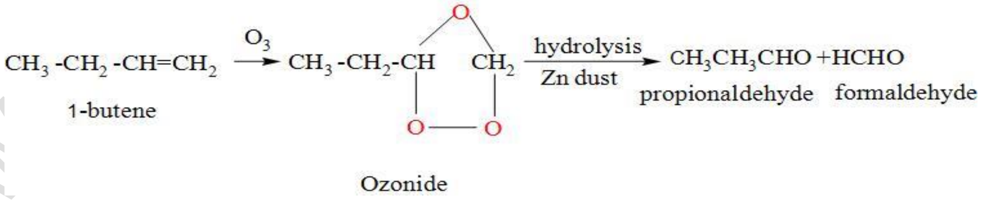
1. Ethene gives Etheneozonide with ozone. This on hydrolysis in presence of zinc dust gives two moles of formaldehyde.



2. Propene gives propeneozonide with ozone. This on hydrolysis in presence of zinc dust gives formaldehyde and acetaldehyde.



3. 1-butene gives buteneozonide with ozone. This on hydrolysis in presence of zinc dust gives formaldehyde and propionaldehyde.



MARKOWNIKOFF’S RULE.

Alkene react with hydrogen halide to form alkyl halide.

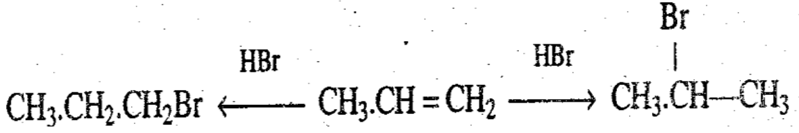
Ex :

$$\underset{\text{Alkene}}{CH_2=CH_2} + HX \dashrightarrow \underset{\text{Alkyl halide}}{CH_3CH_2X}$$

In case of symmetrical olefin only one alkyl halide is formed while in case of unsymmetrical alkene two different alkyl halides are possible.

In the addition of hydrogen halide to an unsymmetrical Alkene is governed by Markownikoff rule.

“The electrophilic(H^+) part of the reagent (HX) is added to that Carbon atom of the double bond which bears the more number of hydrogen atoms.”



$$CH_3.CH_2.CH_2Br \xleftarrow{HBr} CH_3.CH=CH_2 \xrightarrow{HBr} CH_3.\overset{\overset{Br}{|}}{C}H-CH_3$$

MECHANISM

STEP : 1

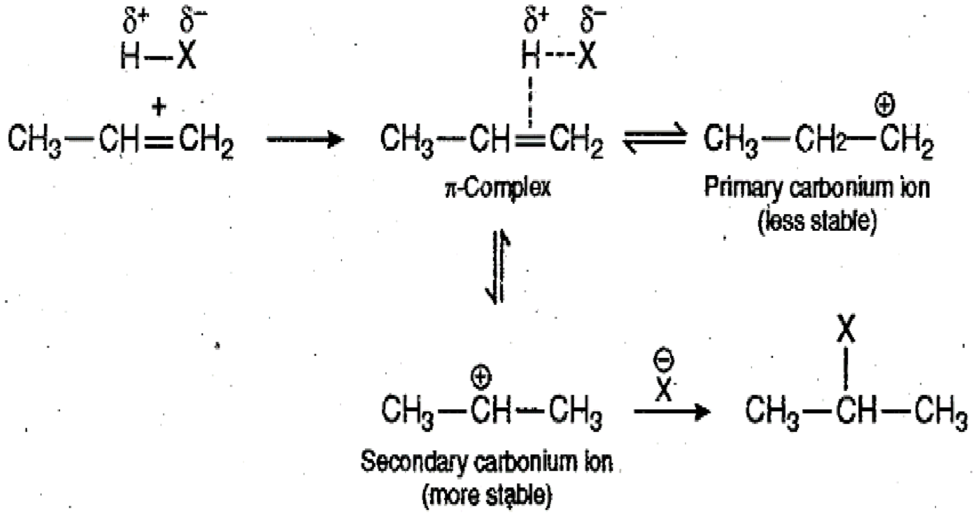
As the hydrogen bromide molecule approaches the π-electron could of the olefin, its permanent polarization, which is due to greater electronegativity of bromine than that of hydrogen is increased. With the result the hydrogen($H^{\delta+}$) atom of the hydrogen bromide reaches closer to the π-electron source than the bromine atom and thus forms a π-complex. The π-complex is then converted into carbocation.

If the olefin is unsymmetrical, two carbocations may be formed, but out of which the more stable carbocation is predominates. Stability order of carbocations.

Tertiary > Secondary > Primary

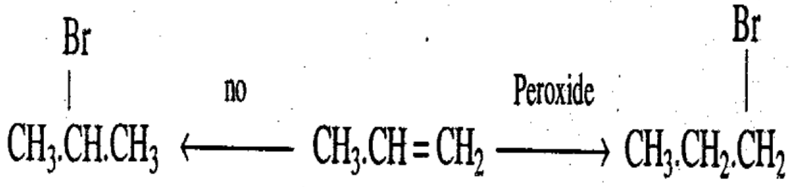
STEP : 2

The second step consists in the rapid combination of the carbocation with the bromide anion.



ANTI-MARKOWNIKOFF'S RULE (OR) PEROXIDE EFFECT

In the addition of hydrogen bromide to unsymmetrical alkene in the presence of air, peroxide (or) light yields mainly n-alkyl bromide. This phenomenon is known as the peroxide effect (or) Kharasch effect. (It does not apply to additions involving HF, HCl, HI)



$$CH_3.\overset{\overset{Br}{|}}{CH}.CH_3 \xleftarrow{no} CH_3.CH=CH_2 \xrightarrow{Peroxide} CH_3.CH_2.\overset{\overset{Br}{|}}{CH_2}$$

MECHANISM :
Mechanism of the reaction proceeds through free-radical mechanism.

1.Chain- Initiation :
Peroxides are relatively unstable compounds and undergo thermal (or) photochemical dissociation to produce a free alkoxy radical (RO), which then attacks HBr to form a bromine radical.

2. Chain-propagation :
The bromine radical attacks the olefin to form the most stable bromoalkyl free-radical.

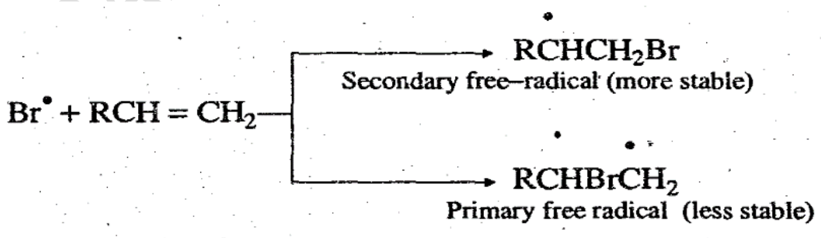
Tertiary > Secondary > Primary

The latter then reacts with HBr to form *anti-Markownikoff's product* and another bromine radical which can further propagate the reaction.

3. Chain termination :
Chain termination occurs by combination of bromine radicals with themselves (or) with alkyl radicals, (or) by coupling or disproportionation of alkyl radicals

$RO\text{—}OR \longrightarrow 2R\dot{O}$ (R oftenly is C_6H_5CO—)

$\dot{R}O + HBr \longrightarrow ROH + Br^{\bullet}$



$$R\dot{C}HCH_2Br + HBr \longrightarrow RCH_2CH_2Br + \dot{B}r$$

DIENES

Dienes are unsaturated hydrocarbons containing two Carbon-Carbon double bonds in their molecules.

1. Dienes also called Alkadienes
2. These can be represented by the general formula, C_nH_{2n}-2.
3. These are isomeric with Alkynes.

TYPES OF DIENES

Depending upon the position of double bonds, three types of dienes are known.

1. Isolated dienes
2. Cumulated dienes
3. Conjugated dienes

1. Isolated dienes

The dienes in which double bonds are separated by more than one single bond are called isolated dienes (or) non-conjugated dienes.

Ex:

CH_2=CH-CH_2–CH=CH_2
1,4-pentadiene

CH_2=CH-CH_2-CH_2-CH=CH_2
1,5-hexadiene

2. Cumulated dienes

The dienes in which two double bonds are present between successive carbon atoms are called cumulated dienes (or) allenes.

Ex:

CH_2=C=CH_2
Allene

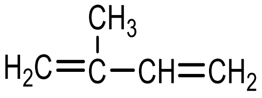
CH_3–CH=C=CH_2
Methylallene

3. Conjugated dienes

The dienes in which two double bonds are separated by one single bond are called conjugated dienes.

Ex:

CH_2=CH–CH=CH_2
1,3 – butadiene



$$H_2C=\overset{\overset{\displaystyle CH_3}{|}}{C}-CH=CH_2$$

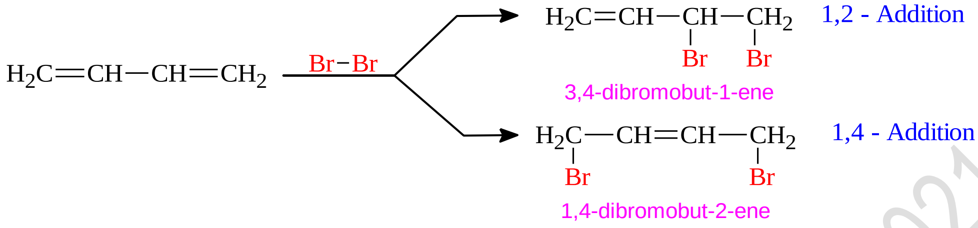
Isoprene

Reactions of Dienes

1. Addition of halogens (X_2):

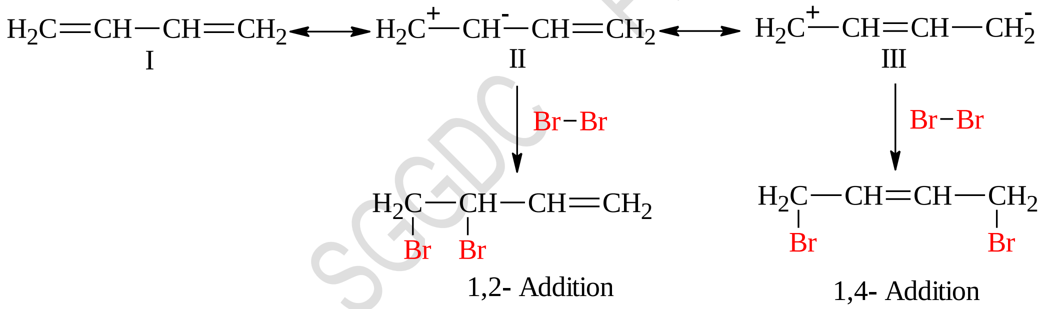
When treated with halogens 1,3-Butadiene forms a mixture of two products namely 3,4-dihalobutene-1 (1,2-addition or expected addition) and 1,4-dihalobutene-2 (1,4-addition or the unexpected addition).

Ex: 1,3-Butadiene and Bromine.



Mechanism

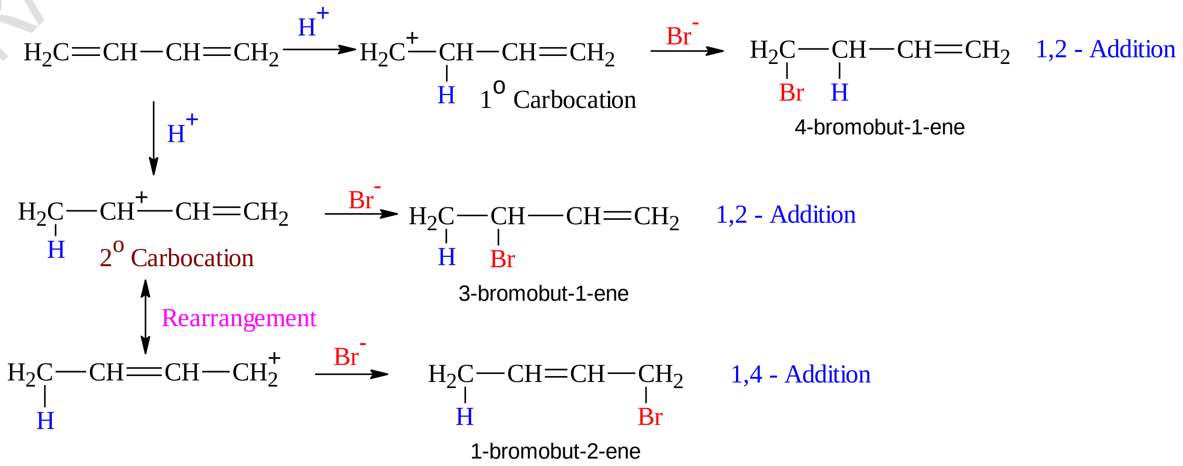
The formation of two products is explained on the basis of the fact that the molecule of a 1,3-butadiene, is a resonating hybrid of the following possible structures. With the result the reagent bromine may add either on structure II to form 1, 2-addition product or on structure III to form 1, 4-addition product.



2. Addition of halogen acid (HX) :

The electrophilic addition of halogen acids (HX) leads to the formation of two products. The relative amounts of the 1 and 3-Haloalkenes produced depend upon the temperature and solvent used during reaction. At low temperature 1,2-addition product is the major product and at high temperature 1,4-addition product is the major product.

Ex: 1,3-Butadiene and Hydrogenbromide.

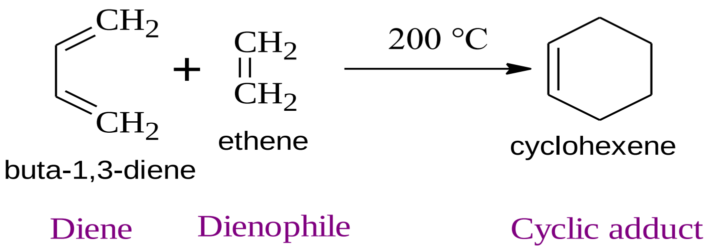


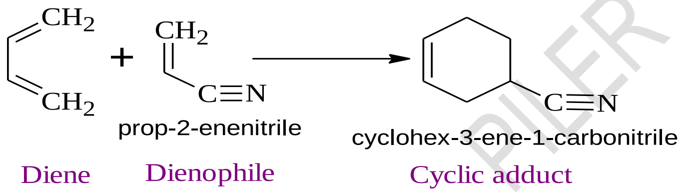
DIELS – ALDER REACTION

The cyclo addition reaction of Conjugated Dienne and Dienophile is known as Diels-Alder reaction.

1. Dienophile is an unsaturated molecule (usually substituted with an electron attracting group)
2. The formed cyclic product is cyclic olefin. (*usually called as adduct*)
3. It is the prototypical example of a concerted mechanism of a pericyclic reaction.
4. It is believed to occur via a single cyclic transition state with out any intermediate.

Ex:





Applications of Diels-Alder reaction

This reaction is used in the synthesis of

1. Natural products like rubber and plastic.
2. Synthetic steroids
3. In the field of pharmaceuticals and biomedical engineering.

UNIT - III

AROMATICITY

The property of an unsaturated compound exhibiting unexpected stability and behaving as saturated compound is called Aromaticity.

Aromaticity – Characteristics

Ex :

a. Unusual stability
b. Substitution rather than addition
c. Resistant to oxidation

Aromaticity – Requirements :

Aromatic compounds must be fulfil the following requirements.

1. The compound must be cyclic and planar structure with delocalised π bonds.
2. The compound stabilised with conjugation and resonance.
3. Compounds must be obeys the Huckel's rule.

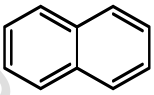
Huckel's rule : *The planar rings with 2,6,10,14….delocalised π electrons (4n+2 π electrons) should be aromatic in nature.*

In 4n+2, value of 'n' = 0,1,2,3,4,….

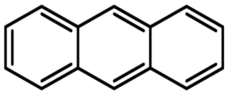
'n' value	4n+2 π electrons	Example
0	2	Cyclopropenyl cation
1	6	Benzene, Cyclopenta dienyl anion, Cyclo hepta trienyl cation (Tropelium cation)
2	10	Naphthalene
3	14	Anthracene, Phenanthrene.

Ex:

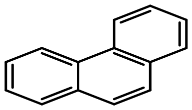
Benzene



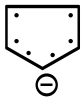
Naphthalene



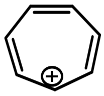
Anthracene



Phenanthrene



Cyclopentadienyl anion



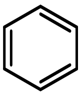
Cycloheptatrienyl cation
(Tropylium cation)

Aromaticity – Benzenoid compounds

Aromatic compounds having benzene ring in skeleton are called Benzenoid compounds.

Ex :

1. **Benzene :**
   a. Molecular formula of the benzene : C_6H_6
   b. It is planar cyclic compound with conjugation and resonance.
   c. It has 6 delocalised π electrons in cyclic system. (Satisfies Huckel's rule).



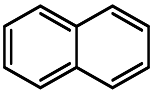
4n+2 where n=1

$4 \times 1 + 2 = 6$

No. of π electrons = 6

$\therefore$ So, Benzene is aromatic in nature.

2. **Naphthalene**
   a. Molecular formula of the Naphthalene : $C_{10}H_8$
   b. It is planar cyclic compound with conjugation and resonance.
   c. It has 10 delocalised π electrons in cyclic system. (Satisfies Huckel's rule).



4n+2 where n = 2

$4 \times 2 + 2 = 10$

No. of π electrons = 10

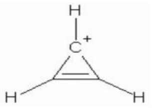
$\therefore$ So, Naphthalene is aromatic in nature.

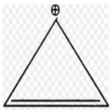
Aromaticity – Non Benzenoid compounds :

Aromatic compounds without having benzene ring in skeleton are called Non-Benzenoid compounds.

Ex:

1. **Cyclopropenyl cation**
   a. Molecular formula of the Cyclopropenyl cation : ${}^{+}C_3H_3$
   b. It is planar cyclic compound with conjugation and resonance.
   c. It has 2 delocalised π electrons in cyclic system. (Satisfies Huckel's rule).





4n+2 where n = 0

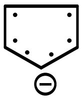
$4 \times 0 + 2 = 2$

No. of π electrons = 2

$\therefore$ So, Cyclopropenyl cation is aromatic in nature.

2. Cyclopentadienyl anion

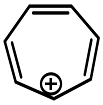
a. Molecular formula of the Cyclopentadienyl anion : $^{-}C_5H_5$
b. It is planar ring compound with conjugation and resonance.
c. It has 6 delocalised π electrons in cyclic system. (Satisfies Huckel's rule).



4n+2 where n = 1
4 x 1 + 2 = 6
No. of π electrons = 6
∴ So, Cyclopentadienyl anion is aromatic in nature.

3. Tropylium cation (Cycloheptatrienyl cation)

a. Molecular formula of the Tropylium cation: $^{+}C_7H_7$
b. It is planar ring compound with conjugation and resonance.
c. It has 6 delocalised π electrons in cyclic system. (Satisfies Huckel's rule).



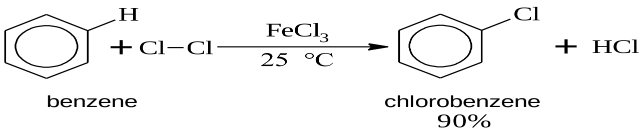
4n+2 where n = 1
4 x 1 + 2 = 6
No. of π electrons = 6
∴ So, Tropylium cation is aromatic in nature.

ELECTROPHILIC SUBSTITUTION

The replacement of an atom or group attached to the carbon atom of the benzene ring by another atom or group is known as substitution reaction.

1. In benzene substitution reactions involving the attack of electrophiles (electrophilic substitution reaction).
2. It believed to proceed by bimolecular (SE^2) mechanism.

   Ex :



General mechanism of electrophilic substitution reaction.

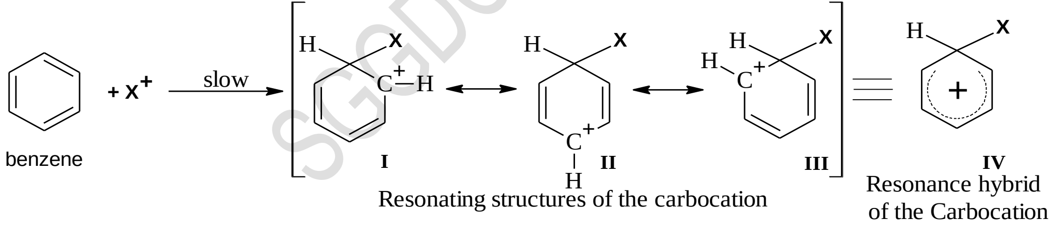
Aromatic electrophilic substitution reactions are believed to proceed by bimolecular (SE^2) mechanism. Which involves three steps.

Step : 1 Generation of electrophile from reagent.

$$X\text{-}Y + Cat \longrightarrow X^+ + Cat\text{-}Y^-$$

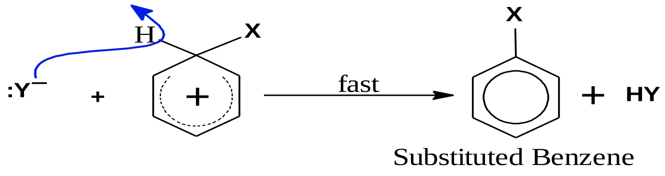
Step : 2 Formation of the intermediate carbonium ion

The electrophile then attaches to the negative center, resulting in the formation of an intermediate known as arenium cation (carbocation), I. The formation of intermediate carbocation ion is a slow step, it constitutes rate determining step of the complete reaction.



Step : 3 Formation of the product

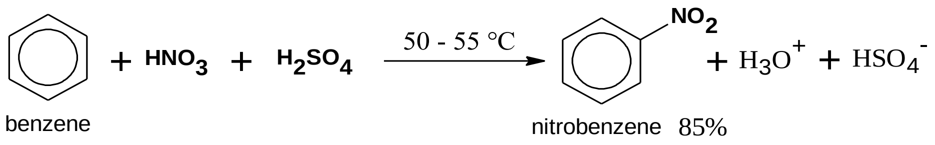
The reaction is completed by the abstraction of a proton from the carbon atom bearing electrophile by an anionic species ($:Y^-$) present in the reaction mixture to form the substituted product.



Ex:

1. **Nitration of Benzene:**

Benzene reacts with nitrating mixture (Mixture of Con.HNO_3 + Con.H_2SO_4) at less than 60^0C gives nitrobenzene. The reaction is much faster at 50 – 55 ˚C .



Mechanism:

Nitration reaction of benzene proceed by bimolecular (SE_2) mechanism. Which involves three steps

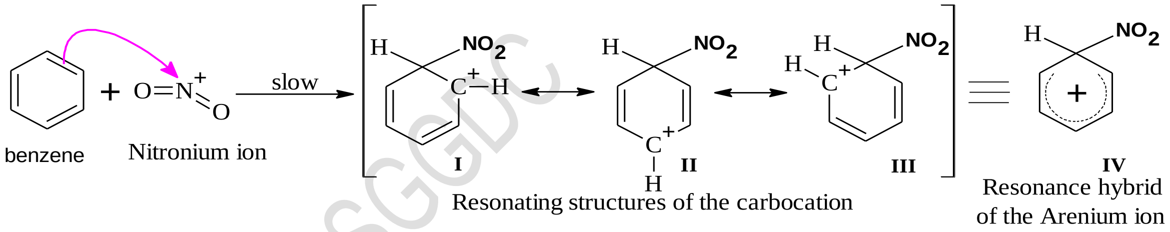
Step : 1 Generation of electrophile

Nitric acid accepts a proton from the sulfuric acid followed by dissociation into nitronium ion and water.

$$HNO_3 + 2H_2SO_4 \longrightarrow NO_2^+ + 2HSO_4^- + H_3O^+$$

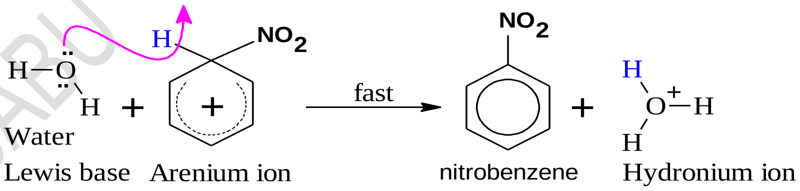
Step : 2 Attacking of electrophile

The nitronium ion is the electrophile in nitration; it reacts with benzene to form resonance stabilized arenium ion.



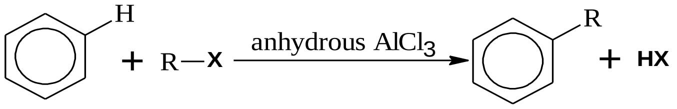
Step : 3 Formation of the product:

The arenium ion loses a proton to form nitrobenzene.



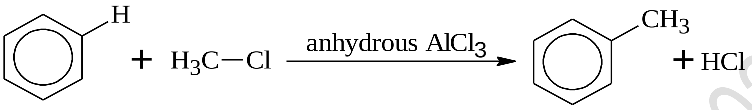
2. Friedel – Craft's alkylation:

Benzene reacts with alkyl halide (RX) in the presence of Lewis acid (anhydrous $AlCl_3$) to give alkyl benzene is known as Friedel – Craft's alkylation reaction .



Ex :

Benzene reacts with methyl chloride in the presence of anhydrous $AlCl_3$ to give toluene (Methyl benzene).



Mechanism:

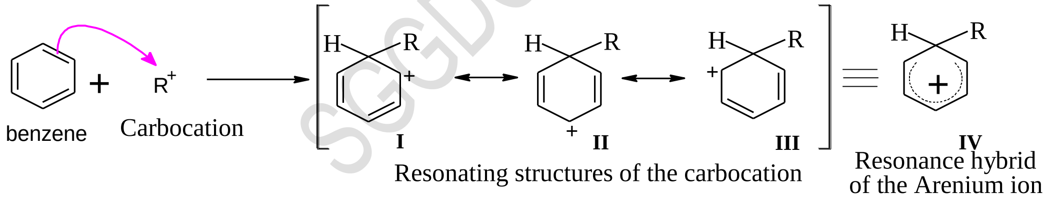
Friedel-Craft's alkylation of benzene proceed by bimolecular (SE^2) mechanism. Which involves three steps

Step : 1 Generation of electrophile:

$$RCl + AlCl_3 \longrightarrow {}^{+}R + AlCl_4^{-}$$

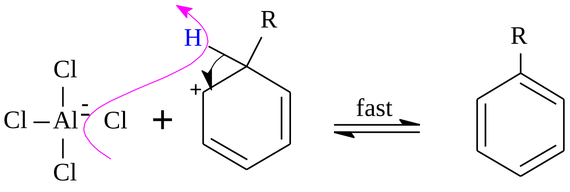
Step : 2 Attacking of electrophile:

Alkyl carbocation is the electrophile; it reacts with benzene to form a resonance stabilized arenium ion.



Step : 3 Formation of the product:

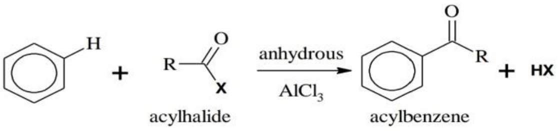
The arenium ion then loses a proton to $AlCl_4^{-}$ to form the methyl benzene.



1. This reaction can yield products having rearranged carbon skeletons when 1^0 and 2^0 alkyl halides are used as starting material.

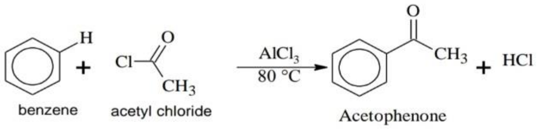
3. Friedel – Craft's acylation:

Benzene reacts with acyl halide (RCOX) in the presence of Lewis acid (anhydrous $AlCl_3$) to give acyl benzene is known as Friedel – Craft's acylation reaction



Ex :

Benzene reacts with acetyl chloride or acetic anhydride in the presence of anhydrous $AlCl_3$ to give acetophenone.



Mechanism:

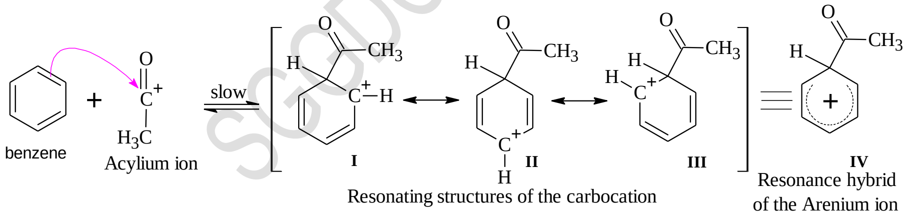
Friedel-Craft's acylation of benzene proceed by bimolecular (SE_2) mechanism. Which involves three steps

Step : 1 Generation of electrophile:

$$CH_3COCl + AlCl_3 \longrightarrow {}^{+}COCH_3 + AlCl_4^-$$

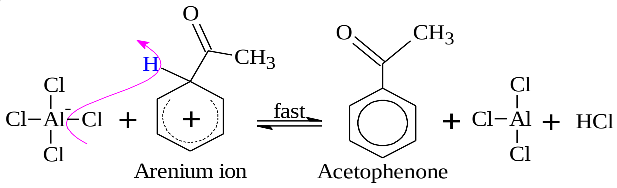
Step : 2 Attacking of electrophile:

Acylium ion is the electrophile; it reacts with benzene to form a resonance stabilized arenium ion.



Step : 3 Formation of the product:

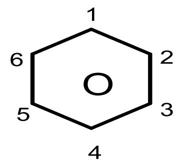
The arenium ion then loses a proton to $AlCl_4^-$ to form the acetophenone.

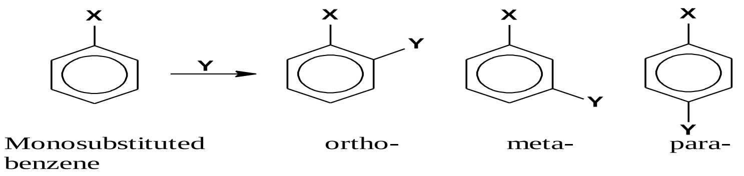


BENZENE - ORIENTATION OF AROMATIC SUBSTITUTION

Benzene molecular formula is C_6H_6. It is an aromatic compound and it undergoes electrophilic substitution reactions. In benzene all the six hydrogen atoms are identical. So the first substituent may occupy any of the six positions on the ring.

In mono substituted benzene 2,6 positions are called ortho (o) positions, 3,5 positions are called meta(m) positions and 4th position is called para (p) position. When a second substituent (say Y) is introduced into a monosubstituted derivative, three isomeric disubstituted products are possible.





The nature of the group already present (X) on the benzene nucleus that directs the new incoming group (Y) either to ortho and para positions (both) or only to meta- position. *This directing effect of the group already present on the benzene nucleus is known as directive influence of the group* or *orientation effect.*

"Any group that increases the electron density will facilitate further substitution, i.e, makes the benzene ring to be more reactive than benzene".

The electronic density in the benzene nucleus is governed by

a. Inductive effect (I)
b. Electromeric effect (E)
c. Mesomeric effect (M)
d. Hyperconjugation

On the basis of the effect all the known groups in organic chemistry have been classified into two types.

1. Electron releasing groups (or) o,p-directing groups
2. Electron attracting (or) Withdrawing (or) m-directing groups.

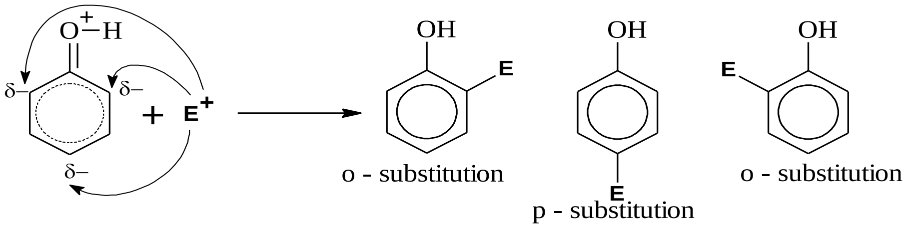
1. Electron releasing groups (or) o,p-directing groups

a. *These groups direct the incoming group mainly to the ortho and para positions.*
b. *The presence of these groups, except halogens, enhances further electrophilic substitution in the benzene nucleus (i.e.,* they activate the nucleus)
c. *They are known as* ***activating groups***.

—NH$_2$, —NHR, —NR$_2$, —OH, —OR, —SH, —SR, —CH$_3$, —CH$_2$R, —CHR$_2$, —CR$_3$, —NHCOCH$_3$, —Cl, —Br, —I, —CH$_2$OH, —CH$_2$C1, -CH$_2$NH$_2$, —CH$_2$CN, —CH$_2$COOH, —CH = CH$_2$, —CH = CH.COOH, —C$_6$H$_5$.

o, p - directing groups increase the electron density at *o*- and *p*- positions of the benzene nucleus by donating the electrons. The o,p- positions becomes the point of relatively high electron density and thus the new group (electrophile, E) will go to the o,p- positions.

Ex :

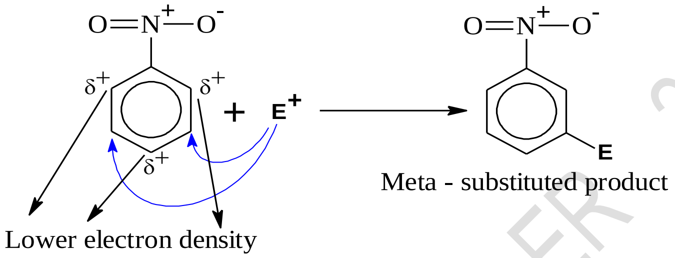


2. **Electron attracting (or) Withdrawing (or) m-directing groups.**
   a. *These groups direct the new entering group mainly to the meta- position.*
   b. *The presence of these groups hinders further electrophilic substitution (i.e.,* they deactivate the benzene ring)
   c. *They are known as **deactivating groups**.*

Ex **:**

$—NO_2^+$, $—CN$, $—NC$, $—SO_2OH$, $—SO_2C1$, $—CHO$, $—COR$, $—COOH$, $—COCl$, $—COOR$, $—CCl_3$, $—NH_3^+$, $—^+NH_2R$, $—^+NHR_2$, $—^+NR_3$.

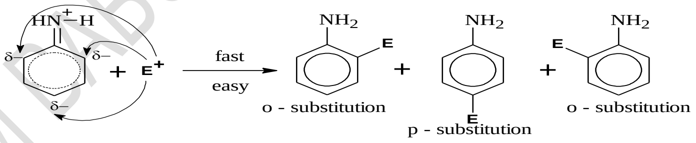
m- directing groups withdraw electrons from the *o*- and *p*- positions of the benzene nucleus. The *m*- position becomes the point of relatively high electron density and thus the new group (electrophile, E) will go to the *m*- position.

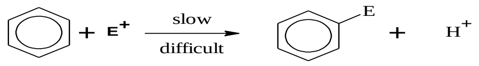


ORIENTATION OF DIFFERENT GROUPS

Ex: **1. Amino ($-NH_2$) group**

Due to the presence of lone pair of electrons on the nitrogen of aniline the amino, $—NH_2$ group exhibits + E and + M effects which overcome the – I effect of nitrogen. Since the conjugative or tautomeric (T) effect is more the amino group increases electron density at the o- and p- positions of benzene. Hence it is o-, p-directing and ring activating. Hence it follows that aniline is more prone for electrophilic substitution.

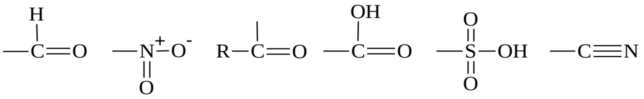




On the other hand, the electron density over the six carbons in benzene is uniformly distributed; no electron rich positions in it. Hence it is less vulnerable for electrophilic substitution than aniline or any benzene derivative of o-, p-director.

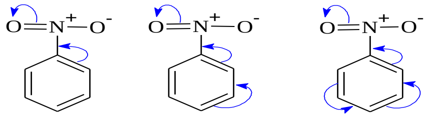
Ex: 2. <u>Nitro (-NO_2) group</u>

All the m-directing groups either possess a positive charge, e.g, —$^{+}NR_3$ or the key atom of the substituent has a more electronegative atom linked by a multiple bond, viz.

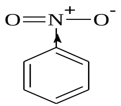


The benzene nucleus containing these groups will undergo all the three effects in such a manner that the *displacement of the electrons takes place away from the nucleus and towards the group (— effect).*

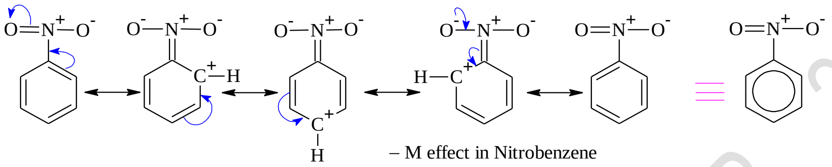
Ex : Nitro group in benzene undergoes —I, —E and —M effects



– E effect in Nitrobenzene

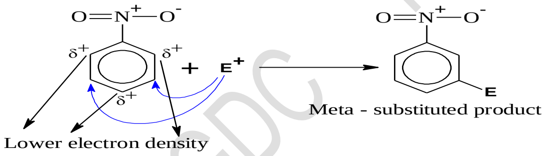


– I effect in Nitrobenzene



– M effect in Nitrobenzene

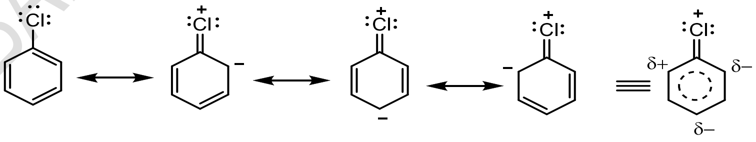
Thus all the three effects reinforce each other in case of m- directing groups and hence withdraw electrons from the *o-* and *p-* positions of the benzene nucleus. The overall result is that the *m-* position becomes the point of relatively high electron density and thus the new group (electrophile, E) will go to the *m-* position.

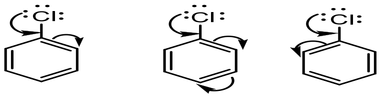


Moreover, *since the m- position is almost unaffected and the o- and p- positions have decreased electron density, the group is said to deactivate the benzene nucleus, i.e.,* it hinders further substitution and hence known as **deactivating group**.

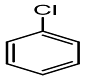
Ex : 3. <u>Halogen group (-X)</u>

Halogen group deactivates ring due to strong inductive effect (-I). Here tautomeric effect is greater than inductive effect. Hence it is O,P-directing and it is difficult to carry substitution in halo benzene than benzene because in benzene -I effect is absent.



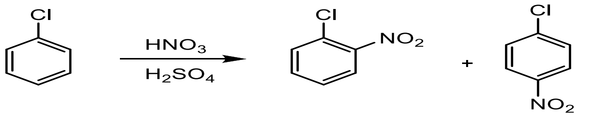


Electromenic effect (+E)



Inductive effect (-I)

Ex: Chlorobenzene on nitration with conc. HNO_3 and cone. H_2SO_4 gives o-nitro chlorobenzene and p-nitrochlorobenzene.



UNIT - IV
CHEMICAL BONDING

SALIENT FEATURES OF VALENCE BOND THEORY

1. A covalent bond is formed by the overlapping of atomic orbitals containing unpaired electrons with opposite spins.
2. Each of bonded atoms retains its own atomic orbital, the electron pair in the overlapping orbital, is shared by both the atoms.
3. The bond strength depends upon the extent of overlapping. Greater the overlapping greater will be the strength.

   p-p > s-p > s-s
4. The overlapping orbitals are directional expect 'S' and the resultant bond also directional. This gives the definite geometry to the covalent molecule.
5. If the overlapping takes places along the inter nuclear axis then a strong bond (σ bond) is formed. The side was (later) overlapping leads to weak bond (π bond).
6. The number of bonds formed by an atom is equal to the no.of unpaired electrons in the valence shell.
7. In some cases more no. of bonds are formed by the excitation of electrons.

Draw backs of Valence bond theory

1. This theory is limited to valence electron of the bonded atoms.
2. The atomic orbitals are moving round the nucleus of the participated atom.
3. It does not explain the excited states.
4. It does not explain the magnetic property of the molecules.
5. It does not explain the bond order and fractional bond order of the molecule.

STRUCTURE OF CHLORINETRIFLUORIDE (ClF_3)

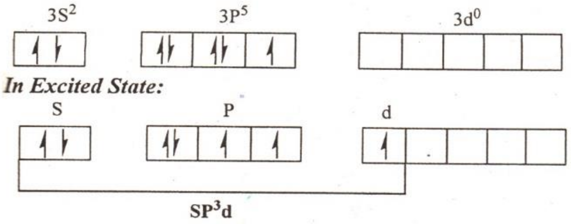
1. In ClF_3 molecule chlorine is the central atom.

   Its atomic number : 17

   Ground state outer electronic configuration : $3S^2, 3p^5, 3d^0$

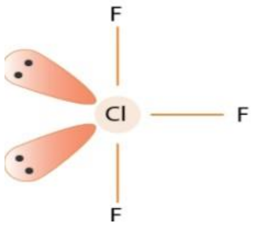
   In its first excited state, undergo 'sp^{3}d' hybridization to give five identical hybrid orbitals out

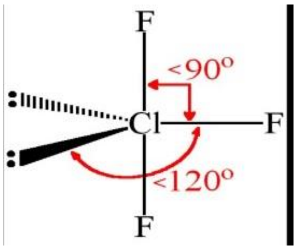
   of which two contains pairs and the remaining three posses unpaired electron.



2. Fluorine atomic number : 9

   Ground state outer electronic configuration : 2S^2 2P^5
3. In ClF_3 formation single electron 'sp3d' hybrid orbital overlapped with single electron 'p' orbital of fluorine atom form σ bond (sp^{3}d-p).
4. Shape of the molecule should be trigonal bipyramidal (TBP). But due to the 'lp-lp', 'lp-bp' and 'bp-bp' repulsion, shape of the molecule become 'T- shaped'.

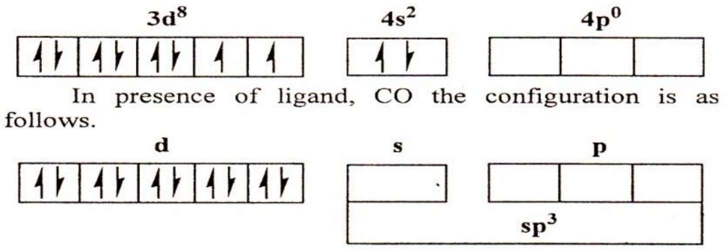




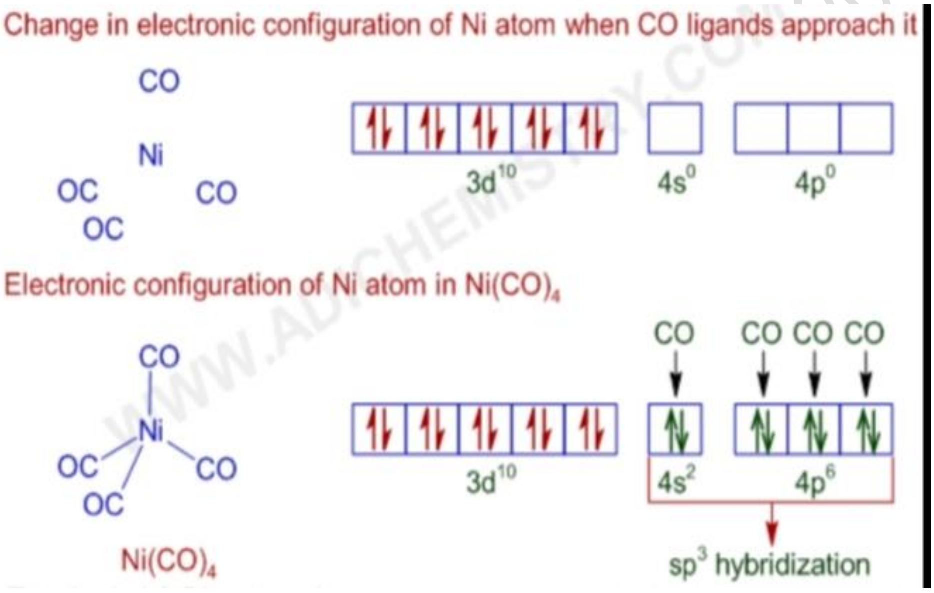
STRUCTURE OF NICKEL TETRA CARBONYL (Ni $(CO)_4$)

1. In Ni $(CO)_4$ molecule Nickel is the central atom.
   Its atomic number : 28
   Ground state outer electronic configuration : $3d^8 4s^2 4p^0$

After rearrangement of electrons in presence of 'CO' ligands, Nickel undergo 'sp^3' hybridization to give four empty identical hybrid orbitals.



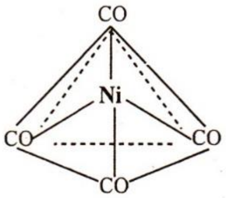
In presence of ligand, CO the configuration is as follows.


Change in electronic configuration of Ni atom when CO ligands approach it

Electronic configuration of Ni atom in $Ni(CO)_4$

In Ni $(CO)_4$ molecule formation empty 'sp^3' hybrid orbitals nickel accept electrons from four 'CO' molecules to give $Ni(CO)_4$

2. Shape of the molecule is tetrahedral.



MOLECULAR ORBITAL THEORY (MOT)

Molecular Orbital Theory was proposed by HUND'S , MULLIKAN, JONE'S and ….. in 1932. It explains the formation of covalent bond in molecules, ions.

Salient features

1. The atomic orbitals (AO) of atoms combine to form molecular orbitals (MO). The number of molecular orbitals formed is equal to the number of atomic orbitals combined. After formation of molecular orbitals, atomic orbitals loses their identity.
3. Atomic orbitals are mono centric, molecular orbitals are poly centric.

4. According to LCAO approach
   Molecular orbital are formed by the linear combination of atomic orbitals.
5. Two types of molecular orbitals are formed. They are
   i. Bonding molecular orbital (BMO)
   ii. Anti-bonding molecular orbital (ABMO)
6. Bonding molecular orbital (BMO)
   a. Bonding molecular orbitals are formed by the additive combination of wave functions of atomic orbitals whose wave functions are ψ_A and ψ_B.
   $$\psi_{BMO} = \psi_A + \psi_B$$
   b. These are formed when the lobes of combining atomic orbitals with same sign

   c. The energy of bonding molecular orbital will be lower than those of combining atomic orbitals.
   d. These are represented with σ, π, …. Etc
   e. The electron density of BMO is greater than the sum of the electron density of isolated atomic orbitals.
   f. These are more stable due to less repulsions between the nucleuses, by combination of these strong bond is formed.

7. Anti-Bonding molecular orbital (ABMO)
   a. Anti-Bonding molecular orbitals are formed by the subtractive combination of wave functions of atomic orbitals whose wave functions are ψ_A and ψ_B.
   $$\psi_{ABMO} = \psi_A - \psi_B$$
   b. These are formed when the lobes of combining atomic orbitals with opposite sign

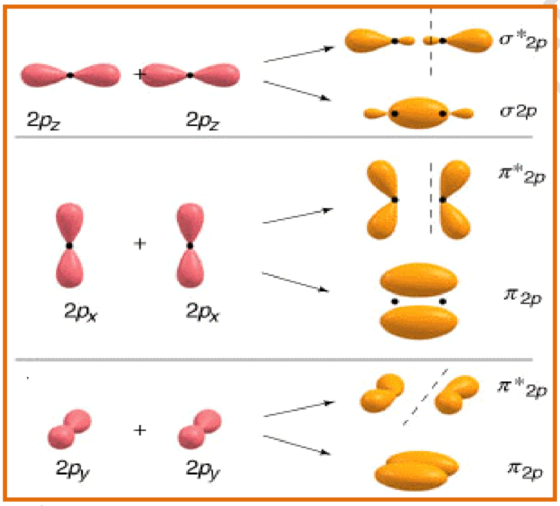
   c. The energy of anti-bonding molecular orbital will be higher than those of combining atomic orbitals.
   d. These are represented with σ*, π*,…. Etc
   e. The electron density of ABMO is smaller than the sum of the electron density of isolated atomic orbitals.
   f. These are less stable due to more repulsions between the nucleuses, by combination of these weak bond is formed.

8. The filling of electrons in molecular orbitals follows Aufbau's principle, Hund's rule and Pauli's exclusion principle.
   The electrons in completely filled molecular orbitals are not participated in bonding, these are called Non-bonding electrons.
   The electrons in incompletely filled molecular orbitals are participated in bonding, these are called bonding electrons.

9. Molecular orbitals are denoted with 'λ' quantum number . It is similar with Principal quantum number 'n'. Values are ranges from 0, ±1, ±2, ±3,….etc

   Ex : $\lambda = 0$ molecular orbital is σ
   $\lambda = 1$ molecular orbital is π
   $\lambda = 2$ molecular orbital is

10. Atomic orbitals of similar energy only combine to form molecular orbitals. Shape of the molecular orbitals depend on the shape of the combining atomic orbitals.
    a. Combination of atomic orbitals are in symmetrical about the inter nuclear axis, σ molecular orbital is formed. ('s' and 'p_z' orbitals form σ molecular orbital)
    b. Combination of atomic orbitals are in unsymmetrical about the inter nuclear axis, π molecular orbital is formed. ('p_x' and 'p_y' orbitals form π molecular orbital)



11. The increasing order of energies of molecular orbitals are as follows.
    a. Up to 14 total number of electrons in diatomic molecules

    $\sigma 1s < \sigma^*1s < \sigma 2s < \sigma^*2s < \pi 2p_x = \pi 2p_y < \sigma 2p_z < \pi^*2p_x = \pi^*2p_y < \sigma^*2p_z$

    b. More than 14 total number of electrons in diatomic molecules

    $\sigma 1s < \sigma^*1s < \sigma 2s < \sigma^*2s < \sigma 2p_z < \pi 2p_x = \pi 2p_y < \pi^*2p_x = \pi^*2p_y < \sigma^*2p_z$

12. The relative energies of different orbitals

    Bonding molecular orbital < Atomic orbital < Anti-Bonding molecular orbital

13. Bond order

The number of covalent bonds between two atoms is called as bond order.
In a molecule it is calculated from the number of electrons in bonding and anti-bonding molecular orbitals.

$$\text{Bond order} = \frac{1}{2}(\text{Number of BMO electrons - Number of ABMO electrons})$$
$$= \frac{1}{2}(N_b - N_a)$$

a. Information conveyed by bond order

1. If bond order is zero or less than zero, it indicates that the molecule **does not exist**.
2. If bond order is fractional value like $\frac{1}{2}$, it indicates that the molecule exists with odd electrons, but it is unstable.
3. If bond order is 1, 2 and 3, it indicates that the molecule is stable and the two atoms are held together by a single, double and triple bond respectively.

b. Bond order is inversely proportional to bond length and directly proportional to bond energy.

Ex: Bond length : $N_2 < O_2 < F_2$
Bond energy : $N_2 > O_2 > F_2$

Bond order	Example	Bond length (pm)
3	N_2 (N≡N)	110
2	O_2 (O=O)	121
1	F_2 (F-F)	142

**** ****

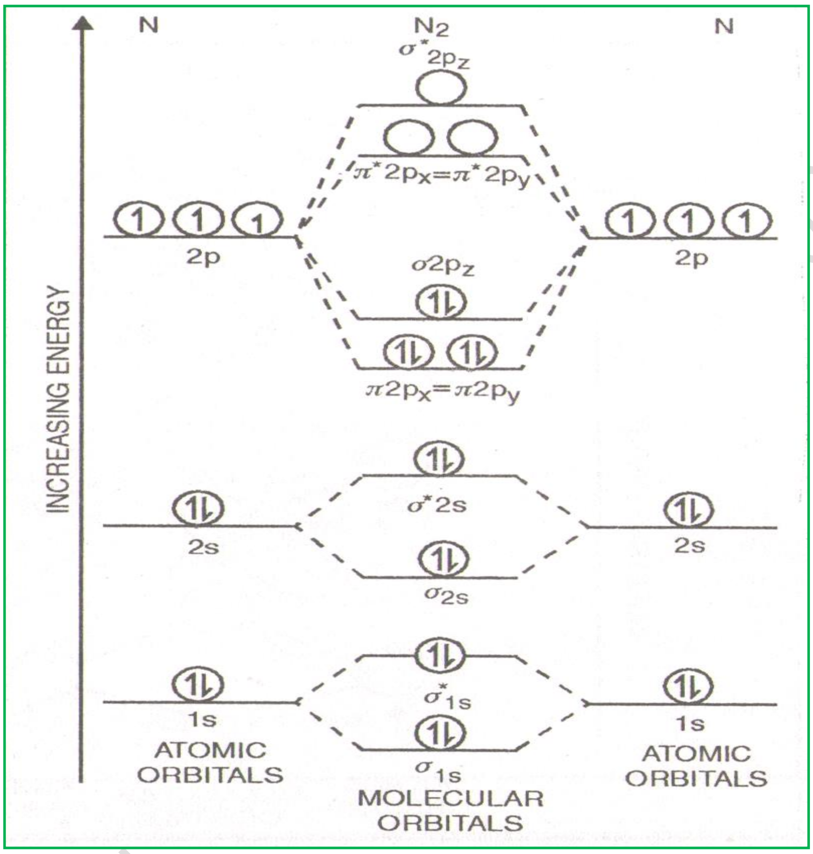
COMPARE VALENCE BOND THEORY (VBT) - MOLECULAR ORBITAL THEORY (MOT)

Valence bond theory (VB)	Molecular orbital theory (MOT)
Covalent bond is formed by the overlap of orbitals.	Covalent bond is formed by the combination of orbitals.
Based on approximation.	Based on approximation.
The orbitals that overlap have nearly same energies.	The orbitals that combine have nearly same energies.
An electron is moving in the field of one nucleus (Atomic orbitals are monocentric).	An electron is moving in the field of more than one nucleus (Molecular orbitals are polycentric).
Covalent bond has a directional character.	Covalent bond has a directional character.
In this method, the atomic orbitals retain their individuality.	In molecules the atomic orbitals lose their individuality.
Atomic orbitals with paired electrons do not involve in bond formation.	Molecular orbitals with paired electrons may involve in combination of orbitals.
This method supports the concept of resonance and hybridization.	This method cannot involve the concept of resonance and hybridization.
This method fails to explain the paramagnetic nature of oxygen.	This method explains the paramagnetic nature of oxygen.

MOLECULAR ORBITAL ENERGY LEVEL DIAGRAM OF NITROGEN (N_2)

1. Atomic number of Nitrogen : 7

   Electronic configuration : $1S^2\ 2S^2\ 2p^3$.
2. Number of participated electrons : 14 (7+7)
3. Number of participated atomic orbitals : 10 (5+5)
4. Number of formed molecular orbitals : 10 (5 BMO + 5 ABMO)



5. Electronic configuration of molecule : $\sigma 1S^2\ \ \sigma^*1S^2\ \ \ \sigma 2S^2\ \ \sigma^*2S^2\ \ \pi 2Px^2, \pi 2Py^2\ \ \sigma 2Pz^2$
6. Number of BMO electrons : 10

   Number of ABMO electrons : 04
7. BO = $\frac{1}{2}$(BMO electrons – ABMO electrons)

   $= \frac{1}{2}(10 - 04)$

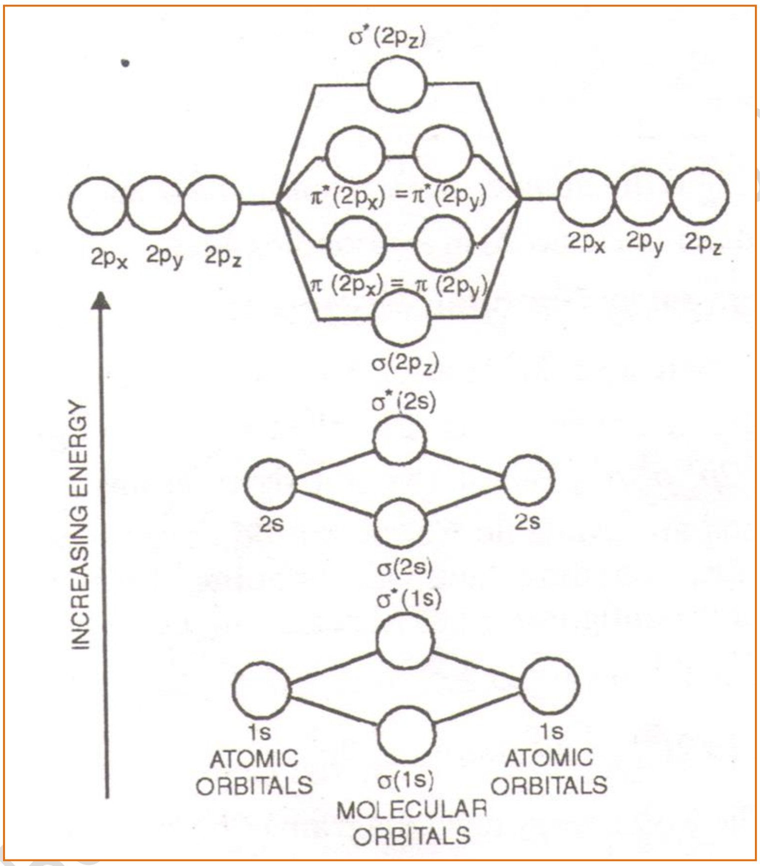
   $= 3$

   Thus nitrogen molecule contains a triple bond N≡N (one sigma and two Pi bonds).
8. Magnetic character : There is no unpaired electron in any orbital, hence N_2 molecule is **diamagnetic**.

MOLECULAR ORBITAL ENERGY LEVEL DIAGRAM OF OXYGEN (O_2)

1. Atomic number of Oxygen : 8

   Electronic configuration : $1S^2\ 2S^2\ 2p^4$.
2. Number of participated electrons : 16 (8+8)
3. Number of participated atomic orbitals : 10 (5+5)
4. Number of formed molecular orbitals : 10 (5 BMO + 5 ABMO)



5. Electronic configuration : $\sigma 1s^2\ \sigma{*}1s^2\ \ \sigma 2s^2\ \ \sigma{*}2s^2\ \ \sigma 2p_z^2\ \ \pi 2p_x^2\ \ \pi 2p_y^2\ \ \pi{*}2p_x^1\ \ \pi{*}2p_y^1$
6. Number of BMO electrons : 10

   Number of ABMO electrons : 06
7. $\text{BO} = \frac{1}{2}$ (BMO electrons – ABMO electrons)

   $= \frac{1}{2}$ (10 - 06)

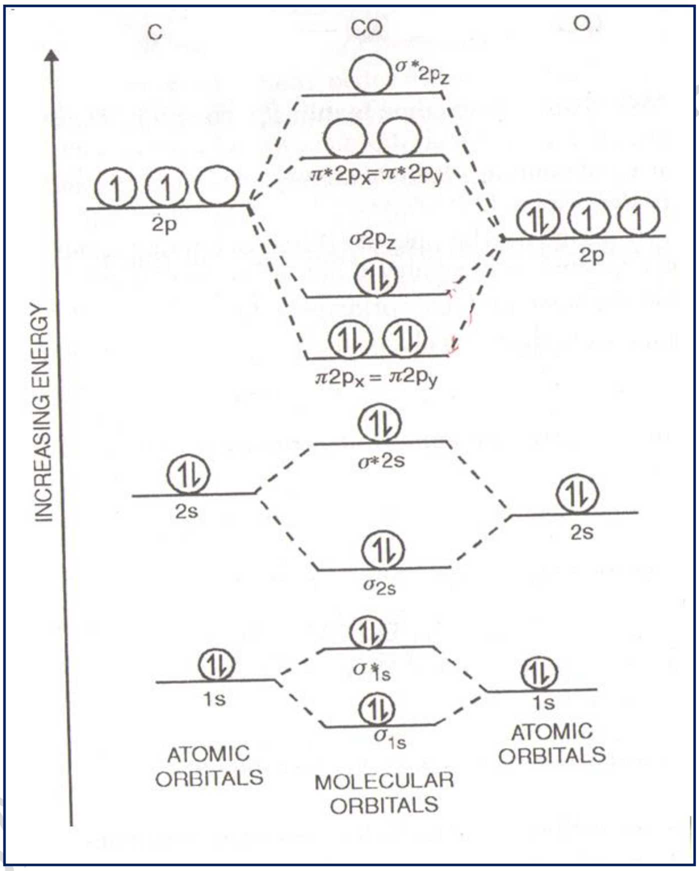
   = 2

Thus Oxygen molecule contains a double bond O=O (one sigma and one pi bond).

8. Magnetic character : There are two unpaired electrons, one each in $\pi{*}2p_y$ and $\pi{*}2p_z$ orbitals, hence O_2 molecule is **paramagnetic**.

MOED OF CARBONMONOXIDE (CO)

1. Atomic number of carbon : 6
   Electronic configuration : $1S^2\ 2S^2\ 2p^2$.
   Atomic number of oxygen : 8
   Electronic configuration : $1S^2\ 2S^2\ 2p^4$.
2. Number of participated electrons : 14 (6+8)
3. Number of participated atomic orbitals : 10 (5+5)
4. Number of formed molecular orbitals : 10 (5 BMO + 5 ABMO)



5. Electronic configuration of molecule : $\sigma 1S^2\ \ \sigma^*1S^2\ \ \ \sigma 2S^2\ \ \sigma^*2S^2\ \ \pi 2Px^2, \pi 2Py^2\ \ \sigma 2Pz^2$
6. Number of BMO electrons : 10

   Number of ABMO electrons : 04
7. BO = $\frac{1}{2}$ (BMO electrons – ABMO electrons)

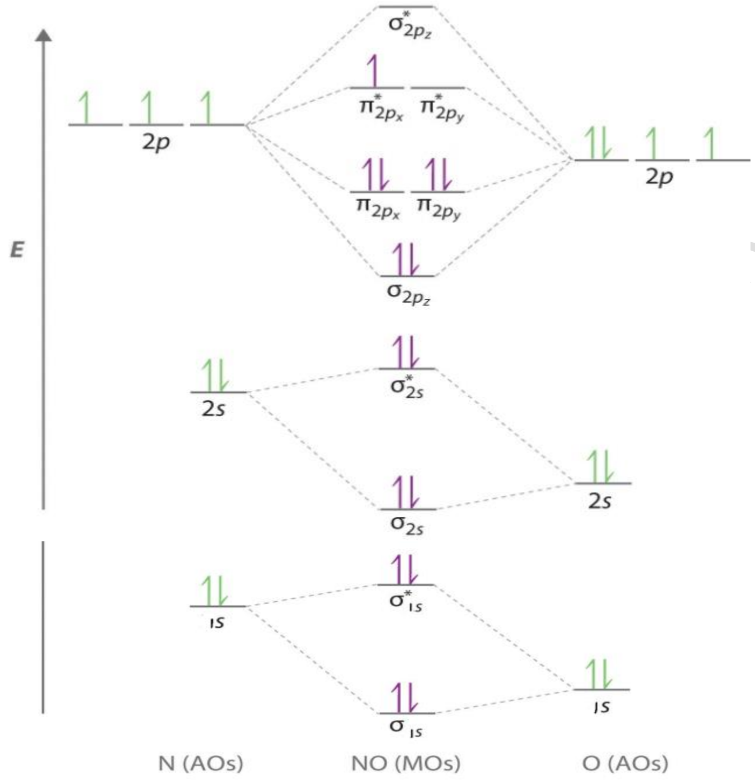
   = $\frac{1}{2}$ (10 - 04)
   = 3

   Thus CO molecule contains a triple bond C≡O (one sigma and two Pi bonds).
8. Magnetic character : There is no unpaired electron in any orbital, hence CO molecule is diamagnetic.

MOED OF NITRIC OXIDE (NO)

1. Atomic number of Nitrogen : 7
   Electronic configuration : $1S^2\ 2S^2\ 2p^3$.
   Atomic number of oxygen : 8
   Electronic configuration : $1S^2\ 2S^2\ 2p^4$.

2. Number of participated electrons : 15 (7+8)
3. Number of participated atomic orbitals : 10 (5+5)
4. Number of formed molecular orbitals : 10 (5 BMO + 5 ABMO)



5. Electronic configuration of molecule : $\boldsymbol{\sigma 1s^2\ \sigma^* 1s^2\ \sigma 2s^2\ \sigma^* 2s^2\ \sigma 2p_z^2\ \pi 2p_x^2\ \pi 2p_y^2\ \pi^* 2p_x^1\ \pi^* 2p_y^0}$
6. Number of BMO electrons : 10

   Number of ABMO electrons : 05
7. BO = $\frac{1}{2}$ (BMO electrons – ABMO electrons)

   $= \frac{1}{2}$ (10 - 05)

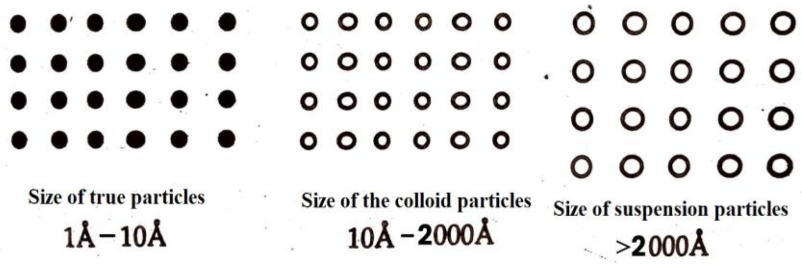
   = 2.5
8. Magnetic character : There is one unpaired electron in $\pi^* 2p_y$ orbital, hence NO molecule is **paramagnetic**.

COLLOIDS (OR) SOLS

The colloidal solutions or colloidal dispersions are intermediate between true solutions and suspensions. In other words, the diameter of the dispersed particles in a colloidal dispersion is more than that of the solute particles in a true solution and smaller than that of a suspension.

When the diameter of the particles of a substance dispersed in a solvent ranges from about 10Å to 2000Å, the system is termed a colloidal solution, colloidal dispersion, or simple a colloid.

The material with particle size in the colloidal range is said to the colloidal state.



STABILITY OF COLLOIDS (OR) SOLS

Sols are thermodynamically unstable and the dispersed phase (colloidal particles) tend to separate out on long standing due to the Vander Waal's attractive forces. However, sols tend to exhibit some stability due to

1. Stronger repulsive forces between the similarly charged particles
2. Particle-solvent interactions:
   Due to strong particle-solvent (dispersion medium) interactions, the colloidal particles get strongly solvated.
3. The colloid particles should be either naturally charged or it should be charged by the addition of some other substance called stabilizer. The stabilizer has one of the following actions.
   a. It may produce charge on the neutral particles of the lyophobic sols.
   b. It may decrease the surface tension between the two immiscible liquids and bring them into colloidal state (emulsion).
   c. It may convert an immiscible liquid into emulsion by referential wetting.

COAGULATION (OR) FLOCCULATION (OR) PRECIPITATION

"The phenomenon of the precipitation of a colloidal solution by the addition of the excess of an electrolyte is called coagulation or flocculation."

The colloid particles are electrically charged, when as electrolyte is added to colloidal solution, the particles of the solution take up oppositely charged ions and thus, get neutralized. The neutral particles then comes closer and get accumulated to form bigger particles which settle down in the form of precipitate.

The coagulation of the lyophobic sols can be carried out by following methods.

1. By electrophoresis

In electrophoresis the colloidal particles move towards oppositely charged electrode. When these come in contact with the electrode for long these are discharged and precipitated.

2. By mixing two oppositely charged sols

When oppositely charged sols are mixed in almost equal proportions, their charges are neutralized. Both sols may be partially or completely precipitated as the mixing of ferric hydroxide $(+ve\ sol)$ and arsenious sulphide $(-ve\ sol)$ bring them in precipitated form. This type of coagulation is called mutual coagulation or material coagulation.

3. By boiling

When a sol is boiled, the adsorbed layer is disturbed due to increased collisions with the molecules of dispersion medium. This reduces the charge on the particles and ultimately, they settle down to form a precipitate.

4. By persistent dialysis

On prolonged dialysis, the traces of the electrolyte present in the sol are removed almost completely and the colloids become unstable.

5. By addition of electrolytes

The particles of the dispersed phase i.e., colloids bear some charge. When an electrolyte is added to sol, the colloidal particles take up ions carrying opposite charge from the electrolyte. As a result, their charge gets neutralized and this causes the uncharged, particles to come closer and to get coagulated or precipitated.

Ex:

$BaCl_2$ solution is added to As_2S_3 sol the Ba^{+2} ions are attracted by the negatively charged sol particles and their charge gets neutralized. This lead to coagulation.

HARDY - SCHULZE RULE

The coagulation capacity of different electrolytes is different. It depends upon the valency of the active ion are called flocculating ion, which is the ion carrying charge opposite to the charge on the colloidal particles. Hardy Schulze studied the rates of coagulation several colloidal solutions and gave generalization know as Hardy – Schulze rule,

According to Hardy – Schulze rule,

"The power of coagulation of a colloidal particle depends upon the valency of the ion bearing a charge opposite to that of the colloidal particle."

"*Greater the valency of the active ion or flocculating ion, greater will be its coagulating power".*

Ex:

1. The ions carrying the charge opposite to that of sol particles are effective in causing coagulation of the sol.
2. Coagulating power of an electrolyte is directly proportional to the valency of the active ions

Ex :

1. Coagulate negative sol of As_2S_3, the coagulation power of different cations has been found to decrease in the order as,

$$Al^{+3} > Mg^{+2} > Na^{+1}$$

2. Similarly, to coagulate a positive sol such as $Fe(OH)_3$, the coagulating power of different anions has been found to decrease in the order

$$[Fe(CN)_6]^{-4} > PO_4^{-3} > SO_4^{-2} > Cl$$

For the precipitation of negatively charged sol a 'divalent' ion nearly 70 times as efficient as the monovalent cation while trivalent cat ion is nearly 500 times as effective.

COAGULATION (OR) FLOCCULATION VALUE

"The minimum concentration of an electrolyte which is required to cause the coagulation of a sol is known as flocculation value."

(or)

"The number of millimoles of an electrolyte required to bring about the coagulation of one litre of a colloidal solution is called its flocculation value."

The smaller the coagulation value the higher the precipitating power of an ion.

$$Cogaulation\ value\ of\ floculation\ value\ \propto \frac{1}{Coagulation\ power}$$

Flocculation values of some electrolytes

Ex: $Fe(OH)_3 Sol$ $(+ve)$		Ex: $As_2S_3\ Sol$ $(-ve)$	
Electrolyte	Concentration (millimoles/litre)	Electrolyte	Concentration (millimloles/litre)
$NaCl, (Cl^-)$	9.3	$NaCl, (Na^+$	51
$KCl, (Cl^-)$	9.0	$KCl, (K^+)$	50
$K_2SO_4, (SO_4^{2-})$	0.20	$BaCl_2, (Ba^2$	0.69
$K_3Fe(CN)_6, [Fe(CN]$	0.096	$AlCl_3(Al^{3+}]$	0.093

It may be noted how rapidly the precipitation power increases with the increase of valence. The ratio for the mono -, di -, and trivalent anion or cation are approximately 1:40:90 for $Fe(OH)_3$ sol and 1:70:500 for the As_2S_3 sol.

PROTECTION OF COLLOIDS - GOLD NUMBER

Lyophilic sols are more stable than lyophobic sols. Lyophobic sols can be easily coagulated by the addition of small quantity of an electrolyte. When a lyophilic sol is added to any lyophobic sol, it becomes less sensitive towards electrolytes. Thus, lyophilic colloids can prevent the coagulation of any lyophobic sol.

"*The property of lyophilic sols to prevent the precipitation of a lyophobic sols is called protection."*

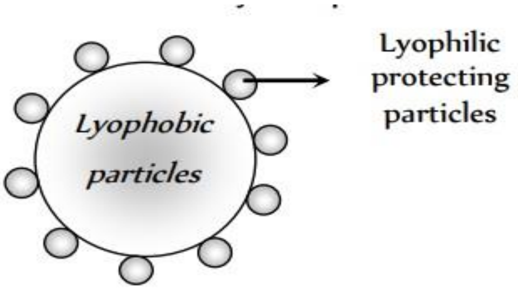
or

"The phenomenon of preventing the coagulation of a lyophobic sol by the addition of some lyophilic colloid is called sol protection or protection of colloids."

The lyophilic sol used to protect a lyophobic sol from precipitation is referred to as a protective colloid.

Mechanism of sol protection

The actual mechanism of sol protection is very complex. However it may be due to the adsorption of the protective colloid on the lyophobic sol particles, followed by its solvation.



Protection of colloids

Gold number

Zsigmondy introduced a term called ‘gold number’ to describe the protective power of different colloids.

It is defined as

“The number of milligrams of the lyophilic sol (protective colloid) which prevents the coagulation of 10 ml of red gold sol on the rapid addition of 1 ml of 10 per cent sodium chloride solution.”

The onset of precipitation of the gold sol is indicated by a color change from red to blue when the particle size just increases.

The gold numbers of hydrophilic colloids are given in the table. The smaller the gold number of a hydrophilic colloid, the greater is tis protective power. Gelatin has a small gold number and is an effective protective colloid. Starch has a very high value, which shows that it is an ineffective protective colloid.

$$Protectivepower \propto \frac{1}{Gold\ number}$$

Gold number of some hydrophilic substances

Hydrophilic substance	**Gold number**
Gelatin	0.005 – 0.01
Sodium caseinate	0.01
Hemoglobin	0.03 – 0.07
Gum Arabic	0.15 – 0.25
Sodium aleate	0.4 – 1.0
Gum tragacanth	2
Potato starch	25

SURFACE CHEMISTRY

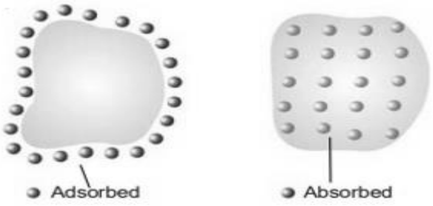
The branch of physical chemistry, which deals the nature of surfaces and also with the chemical and physical processes which takes place on the surfaces, is called surface chemistry. In surface chemistry, we study the phenomenon of adsorption, catalysis and colloidal properties.

Adsorption

The phenomenon of attracting and retaining the molecules of a substance on the surface of a liquid or solid resulting in to higher concentration of the molecules on the surface is called adsorption. Adsorption of solid or on solution surfaces is an important surface effect which is useful to understand many physical

Absorption

It is the phenomenon in which a substance is uniformly distributed throughout the bulk, i.e., it is the penetration of the substance through the surface into the bulk of the solid.
Ex: Water vapours are absorbed by anhydrous $CaCl_2$



Adsorption versus absorption

DIFFERENCE BETWEEN ADSORPTION AND ABSORPTION

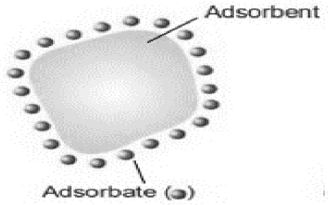
Adsorption	Absorption
It is a surface phenomenon.	It concerns with the whole mass of the absorbent.
In it, the substance is only retained on the surface and does not go into the bulk or interior of the solid or liquid.	It implies that a substance is uniformly distributed, through the body of the solid or liquid.
In it the concentration of the adsorbed molecules is always greater at the free phase.	In it the concentration is low.
It is rapid in the beginning and slows down near the equilibrium.	It occurs at the uniform rate.
Ex: 1. Water vapours adsorbed by silica gel. 2.NH_3 is adsorbed by charcoal.	Ex: 1.Water vapours absorbed by anhydrous $CaCl_2$ 2. NH_3 is absorbed in water forming NH_4OH

Adsorbate

The substance which gets adsorbed on any surface is called adsorbate.
Ex: If a gas gets adsorbed on to the surface of a solid, then the gas is termed as the adsorbate.

Adsorbent

The substance on the surface which adsorption takes place is called adsorbent.
Ex: If a gas gets adsorbed on to the surface of a solid, then the solid is termed as the adsorbent.



Adsorbate and adsorbent illustration

PHYSICAL ADSORPTION AND CHEMICAL ADSORPTION

Depending upon the nature of force existing between adsorbate molecule and adsorbent adsorption is types

a. **Physical adsorption:** If the forces of attraction existing between adsorbate and adsorbent are Vander Waal's forces, the adsorption is called physical adsorption. This type of adsorption is also known as physisorption or Vander Waal's adsorption. It can be easily reversed by heating or decreasing the pressure.

b. **Chemical adsorption:** If the forces of attraction existing between adsorbate particles and adsorbent are almost of the same strength as chemical bonds, the adsorption is called chemical adsorption. This type of adsorption is also called as chemisorption or Langmuir adsorption. This type of adsorption cannot be easily reversed.

COMPARISON BETWEEN PHYSICAL ADSORPTION AND CHEMICAL ADSORPTION

Physical adsorption (Physisorption (or) Vander Waal's adsorption)	**Chemical adsorption** (Chemisorption (or) Langmuir adsorption)
Force of attraction are Vander Waal's forces.	Forces of attraction are chemical bond forces.
Low heat of adsorption usually in range of 20-40 kJ/mol	High heat of adsorption in the range of 50-400 kJ/mol
It is usually takes place at low temperature and decreases with increasing temperature.	It takes place at high temperature
It is reversible	It is irreversible
It forms multimolecular layers.	It forms monomolecular layers.
It does not require any activation energy.	It requires high activation energy.
High pressure is favorable. Decrease of pressure causes desorption	High pressure is favorable. Decrease of pressure does not cause desorption.
It is not very specific.	It is highly specific.

ADSORPTION ISOTHERMS - LANGMUIR ADSORPTION ISOTHERM

A mathematical equation, which describes the relationship between pressure (p) of the gaseous adsorbate and the extent of adsorption at any fixed temperature, is called adsorption isotherms.

The extent of adsorption is expressed as mass of the adsorbate adsorbed on one unit mass of the adsorbent. Thus, if 'x' grams of an adsorbate is adsorbed on 'm' grams of the adsorbent, then

$$Extent\ of\ adsorption = \frac{x}{m}$$

Various adsorption isotherms are commonly employed in describing the adsorption data. The isotherms observed by Freundlich and Langmuir are important.

Langmuir adsorption isotherm

Irving Langmuir in 1916 derived a simple adsorption isotherm, on theoretical considerations based on kinetic theory of gases. This is named as Langmuir adsorption isotherm. It has been found that it is in agreement with experimental observations over a wide range of pressures then the Freundlich isotherm. However, we may consider Freundlich adsorption isotherm as a special case of Langmuir adsorption isotherm.

Salient Features of Langmuir Adsorption Theory.

1. The surface of a solid is homogeneous and it possesses same adsorption sites.
2. Adsorption takes place on the surface of the solid only till the whole of the surface is completely covered with a unimolecular layer of the adsorbed gas.

3. Adsorption is reversible, an equilibrium state is established between two opposing processes, namely Condensation of the gas molecules on the solid surface and Evaporation (desorption) of the gas molecules from the surface back into the gaseous phase.

4. The rate of condensation depends upon the uncovered surface of the adsorbent available for condensation. Naturally, at start when whole of the surface is uncovered the rate of condensation is very high and as the surface is covered more and more, the rate of condensation progressively decreases. On the contrary, the rate of evaporation depends upon the covered surface and hence increases as more and more of the surface is covered ultimately an equilibrium will be set up at a stage when the rate of condensation becomes equal to the rate of evaporation (adsorption equilibrium).
5. The rate of condensation also depends upon the pressure of the gas since according the kinetic theory of gases, the number of molecules striking per unit area is proportional to the pressure.

   Mathematically, $\frac{x}{m} = \frac{ap}{1+bp}$

   where 'a' and 'b' are constants and their value depends upon the nature of gas (adsorbate), nature of the solid adsorbent and the temperature. Their values can be determined from the experimental data

Consider a gas occupies an area 'θ' on the unit surface of adsorbent, then the area of adsorbent left for further adsorption is '(1-θ)'. Let the pressure if gas be 'p' mm.

The rate of condensation is proportional to the vacant area left on the surface and the pressure of the gas

$$\text{Rate of condensation} \;\alpha\; (1-\theta)\,P = K_1 (1-\theta)\,P \quad --- \quad (1)$$

The rate of evaporation depends on the area of the adsorbent that is occupied

$$\text{Rate of evaporation} \;\alpha\; \theta$$
$$= K_2\theta \qquad ---(2)$$

At equilibrium, Rate of condensation = Rate of evaporation

$$K_1 (1-\theta)\,P = K_2\theta$$
$$K_1 (P - P\theta) = K_2\theta$$
$$K_1 P - K_1 P\theta = K_2\theta$$
$$K_1 P = K_1 P\theta + K_2\theta$$
$$K_1 P = \theta\,(K_1 P + K_2)$$
$$\therefore\ \theta = \frac{K_1\,P}{K_1 P + K_2} \qquad -------(3)$$

Divide numerator & denominator of (3) by K_2

$$\Longrightarrow\ \theta = \frac{\frac{K_1}{K_2}\,P}{\frac{K_1}{K_2}\,P + \frac{K_2}{K_2}} \ \Longrightarrow\ \theta = \frac{\frac{K_1}{K_2}\,P}{\frac{K_1}{K_2}\,P + 1}$$

Since $\frac{K_1}{K_2}$ = b (another constant)

$$\Longrightarrow\ \theta = \frac{b\,P}{b\,P+1} \quad ---- \quad (4)$$

The mass of gas adsorbed depends on ‘θ’

$$\therefore \frac{x}{m} \ \alpha \ \theta$$

(or)

$$\frac{x}{m} = K_3 \, \theta$$

$$\frac{x}{m} = \frac{K_3 \, bP}{1+bP}$$

x = Mass of the gas (adsorbate)
m = Mass of the solid (adsorbent)

K_3 b = ‘a’ another constant

$$\frac{x}{m} = \frac{aP}{1+bP} \qquad \text{---- (5)}$$

This is called Langmuir isotherm

Divide (5) by ‘P’ on both sides

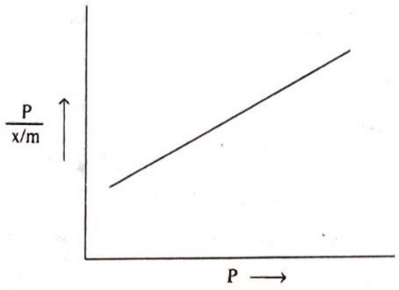
$$\frac{\frac{x}{m}}{P} = \frac{a}{1+bP}$$

⇒ Reverse it,

$$\frac{P}{\frac{x}{m}} = \frac{1+bP}{a}$$

$$\Rightarrow \frac{\mathbf{P}}{\frac{\mathbf{x}}{\mathbf{m}}} = \frac{\mathbf{1}}{\mathbf{a}} + \frac{\mathbf{b}}{\mathbf{a}}\,\mathbf{P} \qquad \text{---- (6)}$$

This is an equation for a straight line and a graph for ‘P/(x/m)’ Vs ‘P’ is straight line.



Merits of the Langmuir’s theory.

1. The mechanism of adsorption presented by Langmuir’s explains chemical adsorption.
2. Langmuir’s theory is more satisfactory than the Freundlich’s equation while explaining physical adsorption of gases on different adsorbents whenever saturation is approached.
3. No deviations are observed at moderately high pressures.
4. The values of ‘a’ and ‘b’ can be calculated from the slope and intercept of the plot.
5. It can be used to determine the surface are of an adsorbent.

Limitation of Langmuir’s theory

1. Langmuir’s theory of unimolecular adsorption is valid only at low pressures and high temperatures.
2. When the pressure is increased or temperature is lowered, additional layers are formed. This has led to the extension to modern concept of multilayer adsorption.

APPLICATION OF ADSORPTION

The phenomenon of adsorption finds a number of applications. Important applications are given as follows.

1. **In Gas masks:**

   This apparatus is used to adsorb poisonous gases (Cl_2, CO, Oxide of sulphur etc.) and thus purify the air for breathing.

2. **For desiccation or dehumidification:**

   These substances can be used to reduce/remove water vapours or moisture present in the air. Silica gel and alumina are used for dehumidification in electronic equipment.

3. **Removal of colouring matter from solution :**

   Ex :

   a. Animal charcoal removes colours of solutions by adsorbing coloured impurities.
   b. Animal charcoal is used as decolouriser in the manufacture of cane sugar.

4. **Heterogeneous catalysis :**

   Mostly heterogeneous catalytic reactions proceed through the adsorption of gaseous reactants on solid catalyst.

   Ex:

   a. Finely powdered nickel is used for the hydrogenation of oils.
   b. Finely divided Vanadiumpentaoxide (V_2O_5) is used in the Contact process for the manufacture of sulphuric acid.

5. **Separation of inert gases :**

   Due to the difference in degree of adsorption of gases by charcoal, a mixture of inert gases can be separated by adsorption on coconut charcoal at different low temperatures.

6. **Softening of hard water:**

   The hard water is made to pass through a column packed with zeolite (sodium aluminium silicate) Ca^{+2}, Mg^{+2} ions which are responsible for hardness, get adsorbed on zeolite, exchanging sodium ions.

   $$Na_2Al_2Si_2O_8 + CaCl_2 \rightarrow CaAl_2Si_2O_8 + 2NaCl$$

   The exhausted zeolite is regenerated with 10% of sodium chloride solution.

   $$CaAl_2Si_2O_8 + 2NaCl \rightarrow Na_2Al_2Si_2O_8 + CaCl_2$$

7. **De-ionisation of water.**

   a. Water can be de-ionised by removing all dissolved salts with the help of cation and anion exchanger resin. Cation-exchanger is an organic synthetic resin such as polystyrene, containing a macro anion ($R-SO_3^-$ etc.) which has adsorbed H^+ ions. A resin containing a basic group (R_3N^+ etc.) which has adsorbed OH^- ions acts as anion exchanger.

8. **In curing diseases :**

   A number of drugs are adsorbed on the germs and kill them or these are adsorbed on the tissues and kill them.

9. **Cleaning agents :**

   Soap and detergents get adsorbed on the interface and thus reduce the surface tension between dirt and cloth, subsequently the dirt is removed from the cloth.

10. **Froth floatation process :**

    A low grade sulphide ore is concentrated by separating it from silica and other earthy matter by this method.

11. **In adsorption indicators :**

    Surface of certain precipitates such as silver halide, have the property of adsorbing some dyes like eosin, fluorescein etc.

12. **Chromatographic analysis:**

    The phenomenon of adsorption has given an excellent technique of analysis known as chromatographic analysis.

13. **In dyeing :**

    Many dyes get adsorbed on the cloth either directly or by the use of mordants.

HSAB

Pearson's hard and soft acids and bases (HSAB)

Hard and Soft acids and bases (HSAB) theory is introduced by **Ralph Pearson** (1963) to explain the stability of metal complexes and the mechanisms of their reactions.

Classification:

According to this theory, the metals and ligands can be classified into Hard and Soft and Border line types.

The criterion of the hardness (or) softness is described to the hardness of the electron could associated with a particular species.

'*A firmly held electron – cloud having low polarizability makes the species "Hard", while an easily polarizable electron cloud makes the species "Soft". The third category with intermediate characters will be a "Border line".*

I a. Hard acids

Hard acids are metal cations which are.

c. Smaller in size ($< 90\ pm$)
d. High positive charge
e. Strongly solvated (not easily polarizable)
f. The ions (or) molecules having less number of valence electrons.
g. Empty orbitals in the valence shell.
h. Low electronegativity ($0.7 - 1.6$)
i. With high energy LUMO's

Ex : H^+, Li^+, Na^+, K^+ Rb^+, Cs^+, Be^{2+}, Mg^{2+}, Ca^{2+}, Sr^{2+}, Ba^{2+}, Mn^{2+}, $(CH_3)_2Sn^{2+}$, VO^{2+}, UO^{2+},

b. Soft acids

Soft acids are metal cations which are

a. Larger in size ($> 90\ pm$)
b. Low positive charge
c. Weakly solvated (easily polarizable)
d. The ions (or) molecules having larger number of valence electrons
e. Completely filled orbitals in the valence shell.
f. Intermediate electronegativities (1.9 – 2.5)
g. With low energy of LUMO's

Ex: Cu^+, Ag^+, Au^+, Hg^+, Tl^+, CH_3Hg^+, HO^+, RO^+, RS^+, RSe^+, RTe^+, Br^+, I^+,
Pt^{2+}, Pd^{2+}, Cd^{2+}, Hg^{2+}, Ti^{3+} , Te^{4+}, Pt^{4+}, BH_3,

c. Border line acids

Border line acids are metal cations which are intermediate characters between hard and soft acids.

Ex: NO^+, $C_6H_5^+$, R_3C^+ e^{2+}, Co^{2+}, Ni^{2+}, Cu^{2+} Zn^{2+}, Pb^{2+}, Sn^{2+}, Os^{2+}, Rh^{3+}, Sb^{3+}, Bi^{3+}, Rh^{3+}

II a. Hard base

Hard bases are those ligands in which donor atom have

a. Small in size (around 120 pm)
b. Higher electronegativity (3.0 – 4.0)
c. Low polarizability
d. Difficult to be oxidized
e. High energy HOMO’s

Ex : OH^-, RO^-, CH_3COO^-, F^-, Cl^-, ClO^-, NO_3^-, CO_3^{2-}, SO_4^{2-}, O^{2-}, PO_4^{3-}, NH_3, NH_2, N_2H_4, H_2O, R_2O, ROH

b. Soft base

Soft bases are those ligands in which donor atom have

a. Large in size $(> 170 pm)$
b. Intermediate electronegativity $(2.5 - 3.0)$
c. High polarizability
d. Easily undergo oxidization
e. Lower energy HOMO’s

Ex : H^-, R^-, I^-, SCN^-, CN^-, RS^-, $S_2O_3^{2-}$, CO, RNC, C_2H_4, C_6H_6, R_3P, R_3As, $(RO)_3P$, R_2S, RSH

c. Borderline base

Borderline base are those ligands in which donor atoms have intermediate characters between hard and soft bases.

Ex: Br^-, NO_2^-, N_3^-, SO_3^{2-}, N_2, C_2H_5N, $C_6H_5NH_2$

From the above concepts. It may be noted that

a. These is no sharp line which divides hard and soft acids and bases.

b. The complex is most stable when acid and base are either both soft and both hard.

c. The complex in least stable when acid and base one of them is very hard and the other very soft

HSAB (or) PEARSON'S PRINCIPLE

In order to predict the stability of a complex formed between hard and softacids and bases, Pearson suggested a rule called Pearson's HSAB principle (or) HSAB principle. According to this principle

"Hard acids prefer to form bond with Hard bases and Soft acids prefer to form bond with Soft bases"

$$Hard\ acid \quad + \quad Hard\ base \quad \rightarrow \quad Stable\ complex$$

$$Soft\ acid \quad + \quad Soft\ Base \quad \rightarrow \quad Stable\ complex$$

1. Hard acids and hard bases are not easily polarizable. So, the bonding between them is predominantly **ionic**.
2. Soft acids and soft bases are usually polarizable. So, the bonding between them is predominantly **covalent**.
3. The interaction between hard acid – soft base or soft acid – hard base are mostly polar covalent and tend to be more reactive or less stable.
4. The polar covalent compound readily form either more ionic or more covalent compounds if they are allowed to react.

Limitations of HSAB concept:

According to HSAB concept, hard and soft classification is useful but it has some limitations which are given as follows

1) The prime limitation of the HSAB concept is that it is widely general and has no any direct quantitative scale of acid and base strength.
2) The internal acid base strength is not explained.

   Ex: OH^- and F^- ions are both hard bases, where OH^- in nearly 10^{13} times stronger base than F^- ion.

   Correlation between hardnes and inherent acid base strength is yet to be developed.
3) Interpretation of different reactions by splitting the participants into acids base fragment is quite arbitrary to some extent.

   Ex: The reaction between ethanol and acetic acid may be interpreted for esterification in two ways.

   Break – I $CH_3CO^+OH^-$ $C_2H_5O^- H^+$

   Break – II $CH_3COO^- H^+$ $C_2H_5{}^+OH^-$

   In the above cases, break (I) explains the observed behavior but break(II) cannot be ignored and must be taken into consideration.

Hard – Hard and Soft – Soft combination : Bonding theories

Several theories have been given to explain the stability of compounds formed by Hard – Hard and Soft – Soft interactions. But, no theory is satisfactorily explains stability of compounds. Some of the theories are discussed below.

1. Ionic bond theory (Hard – Hard interactions) (Electrostatic (or) Ionic interactions)

It is the most accepted theory. According to this theory ionic bond is formed by the interactions of hard acids and hard bases. We know that hard acids have generally vacant orbitals. So, these can accept electrons form hard bases. As a result, positive and negative charge develops. The electrostatic forces of attraction between two oppositely charged ions is inversely proportional to the inter nuclear distance. The inter molecular distance will be less in case of smaller ions. Therefore, the electrostatic attractions between two ions will be greater consequently resultant bond will be ionic nature (Hard-Hard combination), it will be highly stable.

$$\text{Hard } acid + \text{Hard } base \rightarrow \text{Ionic } complex$$

Ex: The bond between Na^+ (Hard acid) and OH^- (Hard base) is predominantly ionic.

$$Na^+ + OH^- \rightarrow NaOH$$

2. Covalent bond theory (Soft – Soft interactions)

According to this theory covalent bond is formed by the interaction of soft acids and soft bases. This is because the soft acid and soft base have large size. It can be explained on the basis of polarization of species. Soft acids are generally transition metal ions, which have six (or) more d – electrons. The (n – 1)d sub shells are easily polarized.

Soft bases are generally, the donor atom with intermediate electronegativity (2.5–3). Hence these are easily polarizable. Therefore, the complexes formed by the soft acids and soft bases have covalent nature (Soft-Soft combination), it will be highly stable..

$$Soft\ acid + Soft\ base \rightarrow Covalent\ complex$$

Ex: The bond between $Ag+$ (soft acid) and I− (soft base) is predominately covalent.

$$Ag^+ + I^- \rightarrow AgI$$

3. $\pi - bond\ theory$

This theory was given by Mulliken (1955) and J. Chatt to explain Soft – Soft interactions on the basis of π – bond.

Soft acids are have low oxidation state and have a large number of d – electronswhich can form $\pi -$ bond by donating electrons to such ligands in which empty d– orbitals are available on the basic atoms like P, As, S etc.,

Some $\pi -$ boding ligands like heavier halogens, PH_3 etc., are soft bases. These ligands have d – orbitals, which enhance the $\pi - bonding$. So, the complex formed is very stable.

4. Pitzer's theory

According to this theory the forces between the interacting groups (Soft – Soft) are London, Van der Waals forces. These forces depend upon the protection of polarizability of interacting groups. London dispersion energies stabilize between two large polarizable atoms. These energies increase with an increase in the size and polarizability. Soft acids and soft bases have large value of polarizability. Hence Soft – Soft interactions are more stable as compared to Soft – Hard interactions.

From the above discussion it is clear that

"Hard – Hard interactions are Ionic and Soft – Soft interactions are covalent involving also π– bonds".

Applications of HSAB (or) Pearson's principle

HSAB principle is extremely useful in explaining several chemical aspects, some of which are discussed below

1) **Stability of compounds**

The HSAB explained the relative stability of the compounds. The compound formed form hard acid and hard base, soft acid and soft base will be more stable. The compound formed from a soft acid and hard base and vice-versa will be less stable.

Ex: *Soft acid* + *Soft base* → *Stable complex*

$Ag^+ + 2I^- \rightarrow AgI_2^-$

Hard acid + *Hard base* → *Stable complex*

$Co^{+3} + 6F^- \rightarrow [CoF_6]^{3-}$

Soft acid + Hard → Less stable *complex*

$Ag^+ + 2F^- \rightarrow AgF_2^-$

2) **Solubility of compounds:**

According to the HSAB, the hard solvents will prefer to dissolve hard solutes and soft solvents dissolve soft solutes.

Ex: $Hg(OH)_2$ dissolves in acidified aqueous solutions but HgS does not.

3) To predict the course of reactions

HSAB has been used to predict the course of many reactions.

Ex: In exothermic reactions

- Combination of hard and hard acid gives stable compound
- Combination of soft and hard gives less stable compound.Ex:

1) $H^+ + CH_3HgOH \rightarrow H_2O + CH_3Hg^+$
2) $H^+ + CH_3HgSH \rightarrow H_2S + CH_3Hg^+$

According this HSAB principle, the reaction (1) goes to right as the hard acid H^+ binds strongly to hard base OH^- to produce stable product H_2O.

On the other hand the reaction (2) is favored to left where soft base SH^- will tendto remain combined with soft acid CH_3Hg^+ instead of hard acid H^+.

4) **Catalytic power**

Catalytic power of metals may be accounted from the fact that "the soft metal atoms will easily adsorbs soft bases on their surface".

5) **Poisoning of metal catalyst:**

HSAB prominently is used to reduce the catalytic property of metals.

Ex: Soft metals like Pd and Pt act as catalyst in many reactions. Soft bases like P, As. CO, olefins poison the catalyst by adsorbing strongly on the surface of metal, thereby blocking the active sties and reduce the strength of catalyst. These catalysts are not affected by hard bases like N,F, etc…

6) Occurrence of minerals :

The existence of some metals in nature can be explained with the help of HSAB principle. If a metal ore present in the earth's crust, is the combination of hard, soft acid bases.

Ex : Hard acids like Ca^{+2}, Mg^{+2}, Al^{+3} ….. etc combine with hard bases like CO_3^{-2} , O^{-2} to form ores like $CaCO_3$, Al_2O_3 etc. but do not exist as sulphides because sulphide is a soft base.

$CaCO_3$	→	Ca^{+2}	CO_3^{-2}
Ore		Hard acid	Hard base
Al_2O_3	→	Al^{+3}	O^{-2}
Ore		Hard acid	Hard base
CuS	→	Cu^{+2}	S^{-2}
Ore		Soft acid	Soft base
Ag_2S	→	Ag^{+}	S^{-2}
Ore		Soft acid	Soft base

7) HSAB Principle is used to predict the rate of reaction between electrophile andnucleophile.

8) Hard soft acid base characters of species can be explain based on oxidationstates, usually an increase in hardness with increase in oxidation state.

Ex:

Variable oxidation states of transition elements, hardness increase by the increase of oxidation state

Ni^{0} − soft acid

Ni^{+2} −Border line acid

Ni^{+4} − Hard acid

9) Symbiosis :

According to Jorgenson's,

Soft ligand have a tendency to combine with a center already associated with soft ligand and hard ligand have a tendency to combine with a center already associated with hard ligand. This tendency has been termed as symbiosis.

Ex:

(i) The hard ligands, F^- -ion combines with BF_3 to form a stablecomplex, BF_4^-

$$_4 \quad BF_3 + F^- \rightarrow BF_4^-$$

(ii) The soft acid BH_3 will prefer combine with a soft base hydride (H^-) ion.

$$\underset{\text{Diborane}}{B_2H_6} + 2H^- \rightarrow 2\,BH_4^-$$

It may be noted that compounds having mixed substituents like BF_3H^- and BH_3F^- are not preferred. So, such compounds when allowed to interact,spontaneously form BF_4^- and BH_4^-

$$BH_3F^- + BF_3H^- \rightarrow BF_4^- + BH_4^-$$

Similarly, the following reactions takes place spontaneously.

$$CH_3F + CHF_3 \rightarrow CH_4 + CF_4$$

****** ****** *******

UNIT - V

STEREO CHEMISTRY

The branch of chemistry which deals with three dimensional structure of molecule and their effect on physical and chemical properties is known as stereochemistry.

Molecular Representations

Projection Formulae

"Writing of three dimensional structures on two dimensional objects like paper or black board is called projection formulae".

There are 4 types of projection formulae. They are

1. Wedge formulae
2. Fischer projection formulae
3. Newman projection formulae
4. Saw-horse formulae

1. Wedge formula

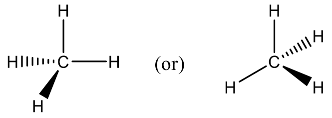
a. Normal lines (–) are used to indicate the bonds which are present in the plane of the object.

b. Solid wedge (▶) is used to represent the bonds which are above the plane for wards the observer.

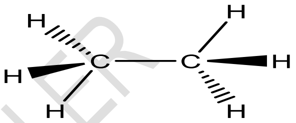
c. Broken wedge is used to indicate the bonds which are below the plane (away from the observer).

Ex:

CH_4 (Methane)



C_2H_6 (Ethane)



2. Fischer projection formula

a. A cross is used to represent the tetrahedral structures in Fischer projection formula.

b. The groups which are in horizontal position are infront of paper plane, the groups which are in vertical position are behind the paper plane and the carbon atom to which 4 groups are attached is in the plane of the paper.

Ex: CH_4 (Methane)

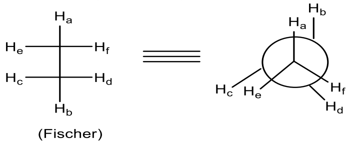
3. Newman projection formula

a. In Newman projection formula, the molecule is viewed from one end.

b. The carbon atom near the eye is represented by a point and three atoms (or) groups attached to the carbon by three equally spaced radii (120°).

c. The carbon atom away from the eye is designated by a circle and three atoms (or) groups attached to it by three equally spaced radii.

Ex: C_2H_6(Ethane)



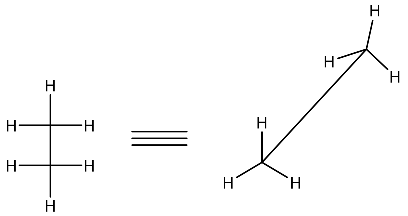
4. Saw-horse formula

a. The saw-horse formula is the formula obtained when the fischer projection is viewed slightly from above in about 45° angle.

b. The bond between two carbon atoms is drawn diagonally and is slightly elongated for clarity.

c. The lower left hand carbon is considered to be towards front and upper right hand carbon towards back.

Ex: C_2H_6(Ethane)



OPTICAL ISOMERISM

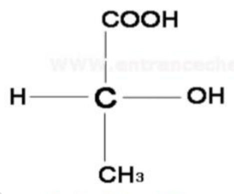
Compounds having the same molecular formula and same properties but differ in the rotation of plane polarised light are called optical isomers and the phenomenon is called optical isomerism.

1. Optical isomerism is exhibited by the compounds having atleast one asymmetric carbon atom.
2. The isomer which rotates the plane polarised light towards right or clockwise direction is called Dextro rotatory. It is represented by 'd' or '(+)'
3. The isomer which rotates the plane polarised light towards left or anti-clockwise direction is called Leavo rotatory. It is represented by 'l' or '(-)'
4. Compounds which rotates the plane polarised light in any direction are called optically active compounds.
   Compounds which do not rotates the plane polarised light in any direction are called optically inactive compounds.

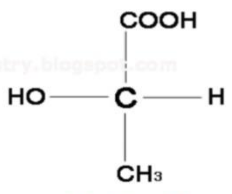
5. The optical isomers which are non-superimposable mirror images are called Enantiomers.
   The optical isomers which are non-superimposable and not mirror images are called Diastereomers.

Ex : **1. Optical isomerism of Lactic acid** :

1. Lactic acid molecular structure is $CH_3.CHOH.COOH$.
2. It contains one asymmetric carbon.
3. Three forms of lactic acid are known, Two are optically active and third is optically inactive.
   a. 'd' form rotates the PPL to the right, it can be obtained from ***meat extracts*** and is known as sarcolactic acid.
   b. 'l' form rotates the PPL to the left, it can be obtained during fermentation of sucrose.
   c. An equimolar mixture of 'd' and 'l' forms gives a racemic lactic acid, it is optically inactive due to the external compensation. It is obtained from Sour milk.



d- lactic acid

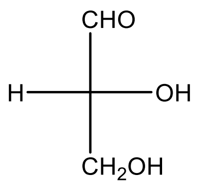


l- lactic acid

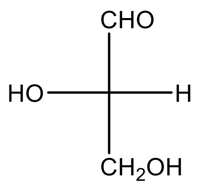
2. Optical isomerism of Glyceraldehyde :

1. Glyceraldehyde molecular structure is $CH_2OH.CHOH.CHO$.
2. It contains one asymmetric carbon.
3. Three forms of Glyceraldehyde are known, Two are optically active and third is optically inactive.
4. 'd' form rotates the PPL to the right, 'l' form rotates the PPL to the left.
5. An equimolar mixture of 'd' and 'l' forms gives a racemic Glyceraldehyde, it is optically inactive due to the external compensation.

D (+) - glyceraldehyde

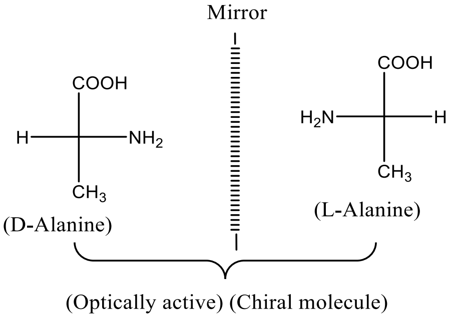


L(-)-Glyceraldehyde



3. Optical isomerism of Alanine :

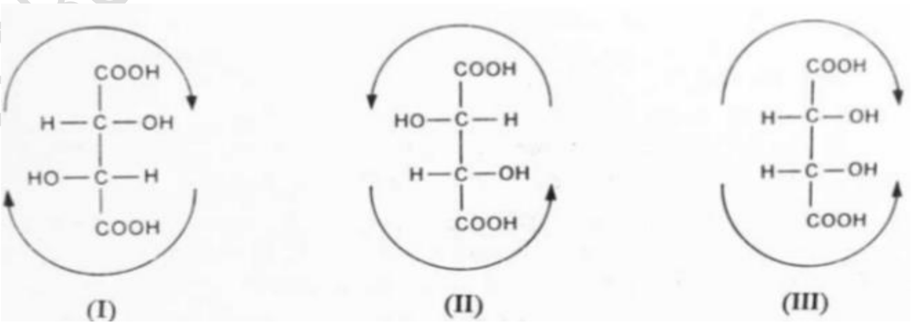
1. Alanine molecular structure is $CH_3.CH(NH_2).COOH$.
2. It contains one asymmetric carbon.
3. Three forms of Alanine are known, Two are optically active and third is optically inactive.
4. 'd' form rotates the PPL to the right, 'l' form rotates the PPL to the left.
5. An equi molar mixture of 'd' and 'l' forms gives a racemic Alanine, it is optically inactive due to the external compensation.



4. Optical isomerism of Tartaric acid :

1. Tartaric acid is dicarboxylic acid and it has two asymmetric carbons.
2. Four forms of Tartaric acid are known, Two are optically active and remaining two are optically inactive.

   a. 'd' form rotates the PPL to the right and it is obtained from natural sources like tamarind and grapes.
   b. 'l' form rotates the PPL to the left and it is prepared from racemic mixture.
   c. An equimolar mixture of 'd' and 'l' forms gives a racemic Tartaric acid, it is optically inactive due to the external compensation.
   d. Meso tartaric acid , it optically inactive due to the internal compensation.
   e. It can be prepared by synthetic methods.



d-Tartaric acid l-Tartaric acid Meso-Tartaric acid

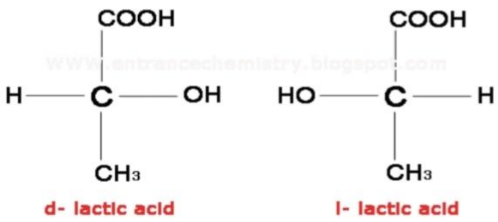
ENANTIOMERS

The optical isomers which are non-superimposable mirror images are called Enantiomers.

Characteristics

- Enantiomers have same physical properties.
- Their rates of reaction with other optically active reagents are different.
- Enantiomers differ in their biological properties.
- Enantiomers rotate the plane polarized light in opposite directions but to the same extent.
- These cannot be separated by physical methods, because these are with same physical properties.
- An equimolar mixture of two enantiomers is called a racemic mixture (± form, (dl) form). Such a mixture is optically inactive due to the external compensation.
- Number of Enantiomers = 2^n n = Number of chiral carbons

Ex : Lactic acid



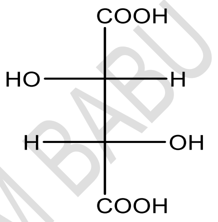
DIASTEREOMERS

The optical isomers which are non-superimposable and non-mirror images of each other are called Diastereomers.

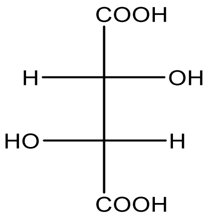
Characteristics

- They have different physical and chemical properties.
- They may have rotation in same or different direction to different extent.
- They differ in rates of reaction with a certain substances.
- They can be separated by physical methods like fractional crystallisation etc. because these are differ by physical properties.

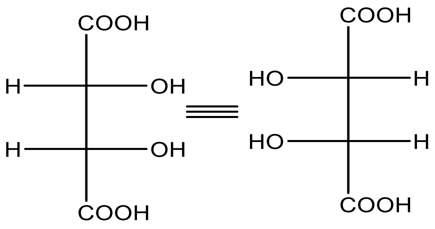
Ex: Tartaric acid



D-tartonic acid
I



L-tartaric acid
II



Meso-tartoric acid
III

$[\alpha]_\lambda^t = +12°$ $[\alpha]_\lambda^t = -12°$ $[\alpha]_\lambda^t = 0°$

I, III = Diastereomers

II, III = Diastereomers

I, II = Enantiomers

In the above example structure I and II are enantiomers, structure I and III, II and III are diastereomers

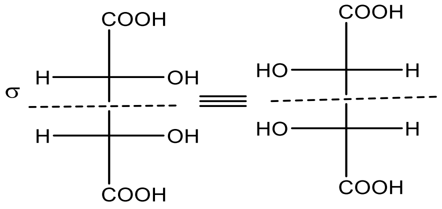
MESOCOMPOUNDS (MESOMERS)

The compounds which contain two or more chiral centres and are optically inactive due to the presence of plane of symmetry (σ) are called Mesomers.

a. The optically inactive is due to internal compensation.
b. The net rotation in meso compounds is zero.
c. Number of meso isomers = $2^{(n/2-1)}$

n = number of chiral carbons

Ex: Meso-tartaric acid



(Optically inactive due to σ)

$[\alpha]_{\lambda}^{t} = 0°$

CONFIGURATION

"The three dimensional arrangement of atoms or groups around a chiral carbon in a molecule called as its configuration".

There are two methods in use to express the configuration.

They are:

1. D,L – Configuration (Relative Configuration)
2. R,S – Configuration (Absolute Configuration)

D,L – CONFIGURATION

(Relative Configuration)

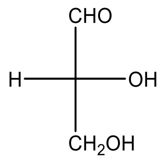
Relative Configuration :

Configuration of groups will be observed by taking a configuration standard reference is known as Relative Configuration.

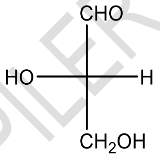
a. D,L configuration introduced by Fischer and Rosanov.

b. Glyceraldehyde has been chosen as arbitrary standard (reference) for the 'D' and 'L' notation. Glyceraldehyde having the –OH group on the right was arbitrary given the symbol 'D' and the –OH group on the left was arbitrary given the symbol 'L'.

D (+) - glyceraldehyde

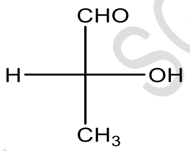


L(-)-Glyceraldehyde

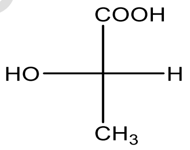


c. Any stereo isomer which can be like D-Glyceraldehyde will belongs to D-series and any stereo isomer which can be like L-Glyceraldehyde will belongs to L-series

Ex :



(D-Lactic acid)

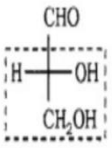


(L-Lactic acid)

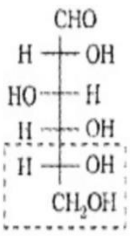
d. Generally it is used to describe the configuration of carbohydrates.

e. D,L-configuration is useful to know the configuration of last or bottom chiral carbon in molecules having more than one chiral centres.

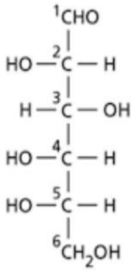
Ex :



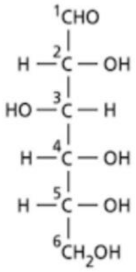
D- (+) - Glyceraldehyde



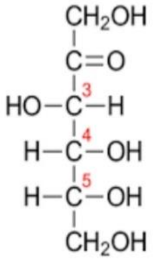
D-(+) - Glucose



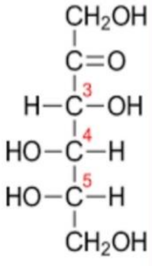
L-Glucose



D-Glucose



D-Fructose



L-Fructose

f. This method is not very useful to describe the configuration in molecules having two more asymmetric carbons.

R,S-Configuration

(Absolute Configuration) or (CIP Nomenclature)

Absolute configuration :

The precise arrangement of groups at a stereogenic center is known as Absolute configuration.

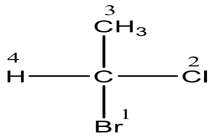
RS-Configuration or CIP nomenclature :

Cahn, Ingold and Prelog introduced a simple procedure to assign configuration for an optically active compounds, called as "RS-Configuration" or "CIP nomenclature". The procedure involves the following two steps.

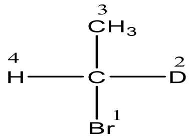
Step-1: Assign the Priorities to the Groups.

Priorities are assigned to four atoms or groups directly attached a chiral carbon. This involves a set of rules known as sequence rules.

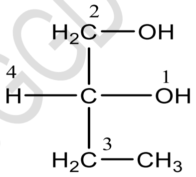
Rule-1: The atom with highest atomic number gets highest priority and atom with lowest atomic number gets least priority.



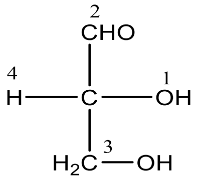
Rule-2: If the atoms are isotopes of same element, the atom of higher mass number gets highest priority.



Rule-3: If the first atom of two or more groups attached to chiral carbon is same, then relative priorities are given by comparing second or even third atoms of the respective groups.



Rule-4: If an atom is attached to a double bond, it is considered as two atoms and if an atom is attached to a triple bond, it is considered as three atoms.



Step-2: Assign the Configuration

The least priority group (4) should be written away from the eye in the molecule after assigning the priorities. The remaining three groups or atoms which are closer to the eye is now observed. The arrangement of groups from 1 → 2 → 3 is in clock wise, the compound is assigned "R-configuration". If it is anticlockwise, it is assigned "S-configuration". (R = Rectus = Right side, S = Sinister = Left side)

Case :1 When the atom or group of lowest priority is at the top, bring the lowest priority group to bottom by the rotate the molecule 1800.

Case : 2 When the atom or group of lowest priority is at the right hand side on horizontal line, in such case keep the top position fixed and change the position of other groups in anticlock wise direction, so that the group of a lowest priority comes to the bottom.

Case : 3 When the atom or group of lowest priority is at the left hand side on horizontal line, in such case keep the top position fixed and change the position of other groups in clock wise direction, so that the group of a lowest priority comes to the bottom.

Ex :

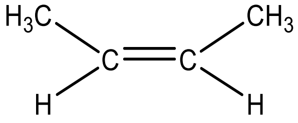
GEOMETRICAL ISOMERISM

"The two stereoisomers which differ in the spatial arrangement of atoms or groups around carbon-carbon double bond are called Geometrical isomers" and the phenomenon is known as Geometrical isomerism.

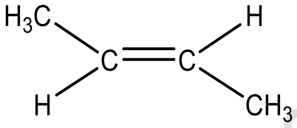
Conditions for Geometrical isomerism

1. The molecule must have a C=C bond.
2. There must be two different groups attached to each carbon atom of double bond.
3. The isomer in which similar groups are present on one side of the double bond is called "Cis-isomer" and the isomer with similar groups on opposite side of double bond is called "trans-isomer".

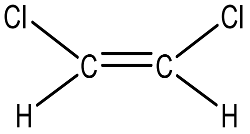
Ex:



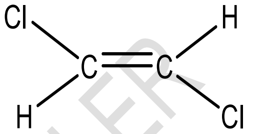
trans-1-butene



trans-2-butene



trans-1,2-dichloroethene



trans-1,2-dichloroethane

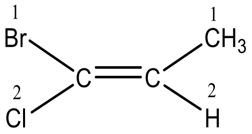
E,Z - NOMENCLATURE

Cis-trans nomenclature cannot be used when C=C has four different groups. In such cases E,Z-nomenclature is used. This system is based on a priority system developed by Cahn, Ingold and Prelog. The procedure involves the following two steps.

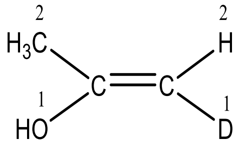
Step-1: Assign the Priorities to the Groups.

Assign priority to the two groups attached to each of the doubly bonded carbon by using "CIP sequence rules".

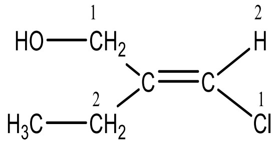
Rule-1: The atom or group with highest atomic number gets highest priority.



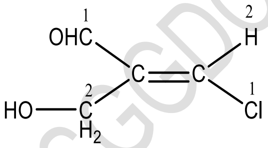
Rule-2: In case of isotopes, the isotope of highest mass number gets highest priority.



Rule-3: If two atoms directly attached to C=C are the same, then priorities are given by comparing second, third or fourth atoms of the respective groups.



Rule-4: A doubly or triply bonded atom is considered to be equivalent to two or three atoms.

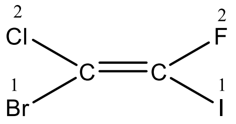


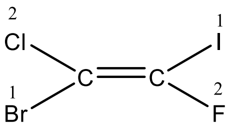
Step-2: Assign the Configuration

a. If the atoms or groups of highest priority are on the same side of double bond, the compound is assigned Z-configuration. (Z = Zusamen = Together)
b. If the atoms or groups of highest priority are on opposite sides of double bond, the compound is assigned E-configuration. (E = Entgegen = Opposite)

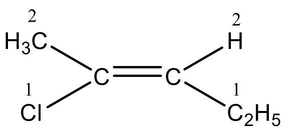
Ex: Z- Isomers E- Isomers

1)

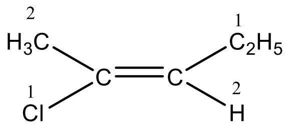




2)



(Z-isomer)



(Z-isomer)

RACEMIC MIXTURE

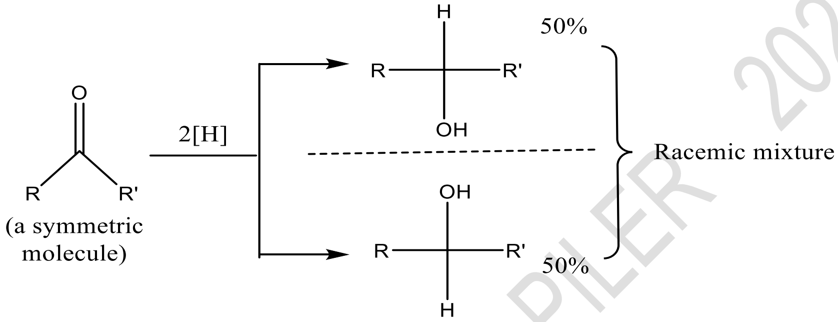
Mixing of enantiomers in equal quantities (1:1), results in zero optical rotation type of mixture is called "Racemic mixtures".

a. They are denoted by (dl) or (±).
b. The process of formation of racemic mixture is called "Racemisation".
c. It is optically inactive because the two enantiomers rotate the plane polarised light equally in opposite directions and cancel each other's rotation. This phenomenon is called external compensation
d. Racemic mixtures are formed by various ways.

Ex:

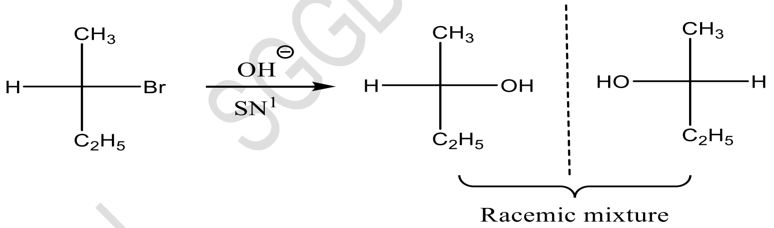
a. From synthesis of asymmetric (Chiral) molecules from symmetric molecules (a chiral)

Ex:



b. By racemisation process**:**

Conversion of pure enantiomers into racemic mixture is called racemisation.



RESOLUTION

Separation of dextro (+) and laevo (-) forms from a racemic mixture (±) is called "resolution".

The main difficulty in the process of resolution is that 'd' and 'l' forms have identical physical and chemical properties, so they cannot be separated by ordinary methods. However the following methods can be used for this purpose.

a. **Physical method :**

Crystals of 'd' and 'l' isomers in the mixture have different shapes. They are mirror images with each other. These can be separated with the help of magnifying lens. It involves lot of time.

Ex: *The racemic mixture of sodium ammonium tartarate has two distinct type of crystals which have object and mirror image relationship. Pasteur separated this mixture into two with the help of microscope with lot of patience.*

b. **Biochemical method**

In biochemical method, micro organisms (like mould, fungi, bacteria, yeast) are used to separate the racemic mixture. The micro organism consumes either (+) or (-) and leaves pure enantiomer. By this method one enantiomer is lost. Hence this method is not recommended for resolution.

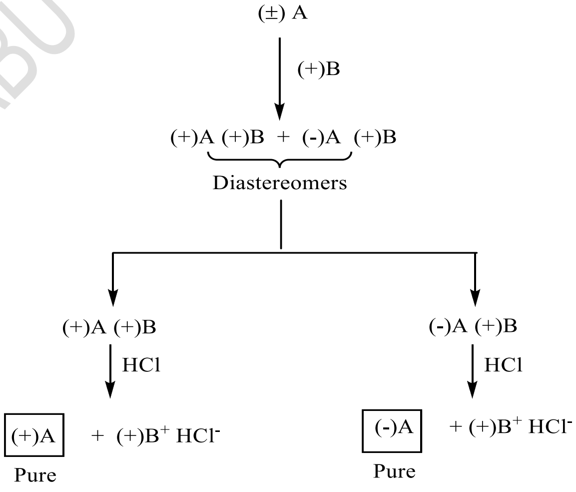
Ex: *The bacteria Penicillium glaucum, the green mold found on aging fruits and cheese, selectively consumes the (+) isomer of* (±) *ammonium tartarate in its metabolic process. Hence (-) siomer is left out in the solution in pure form.*

c. **Chemical method (**Diastereomeric Method**)**

It is the most useful method for separating enantiomers involves converting them into diastereomers, which are differ in all properties, hence are separable. The separated diastereomers converted back into the enantiomers.

Ex:

To separate the racemic mixture (±) of a carboxylic acid 'A'. A base '(+)B' is allowed to react with '(±)A'. It forms '(+) A (+B) salt' and '(-) A (+B) salt', which are diastereomers. Since the physical properties of diastereomers are different, they are separated easily. The separated salts are treated with strong acids like HCl to get pure enantiomers '(+)A' and '(-)A'. It is very convenient and important method.



Ex: Resolution of racemic Lactic acid.

Racemic Lactic acid solution treated with optically active base (-)brucine. They gives two salts in solution. They are '(-)brucine(+)lactate' and '(-)brucine(-)lactate'. At first we will get low soluble '(-)brucine(+)lactate' as crystals. The isolated salts neutralised with dil acids, to give pure (+) and (-) forms of lactic acid.