SMT. NARSAMMA ARTS, COMMERCE AND SCIENCE COLLEGE

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Unit lll : Organic Compounds

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Part A

Organic compounds

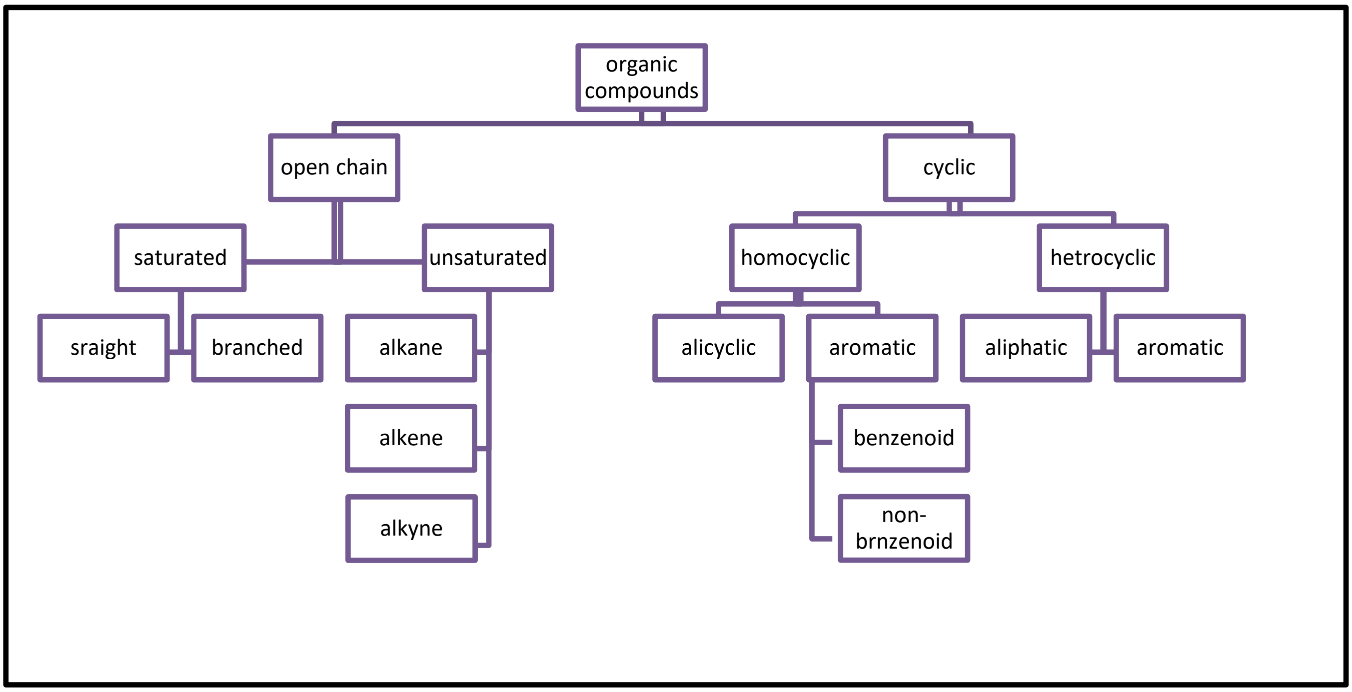
Organic chemistry started as the chemistry of life, when that was thought to be different from the chemistry in the laboratory. Then it became the chemistry of carbon compounds, Now it is both. It is the chemistry of the compounds of carbon along with other elements such as are found in living things and elsewhere.

Hydrocarbons

Hydrocarbons are organic compounds consisting entirely of hydrogen and carbon.

Classification

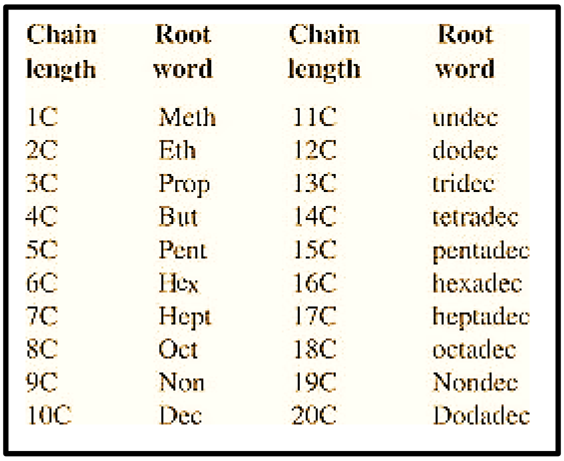
The organic compounds are mainly divided into two categories: open-chain compounds, also known as acyclic compounds and closed chain compounds, also known as cyclic compounds



Nomenclature

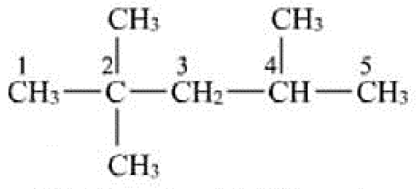
Organic chemistry deals with millions of compounds. In order to clearly identify them, a systematic method of naming has been developed and is known as the IUPAC (International Union of Pure and Applied Chemistry) system of nomenclature

1. First of all, the longest carbon chain in the molecule is identified. and it is considered as the parent or root chain.



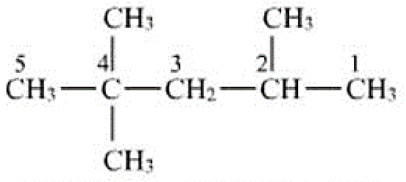
Chain length	Root word	Chain length	Root word
1C	Meth	11C	undec
2C	Eth	12C	dodec
3C	Prop	13C	tridec
4C	But	14C	tetradec
5C	Pent	15C	pentadec
6C	Hex	16C	hexadec
7C	Hept	17C	heptadec
8C	Oct	18C	octadec
9C	Non	19C	Nondec
10C	Dec	20C	Dodadec

2. The carbon atoms of the parent chain are numbered to identify the parent alkane and to locate the positions of the carbon atoms at which branching takes place due to the substitution of alkyl group in place of hydrogen atoms. The numbering is done in such a way that the branched carbon atoms get the lowest possible numbers.



$\overset{1}{CH_3}-\overset{2}{C}(CH_3)_2-\overset{3}{CH_2}-\overset{4}{CH}(CH_3)-\overset{5}{CH_3}$

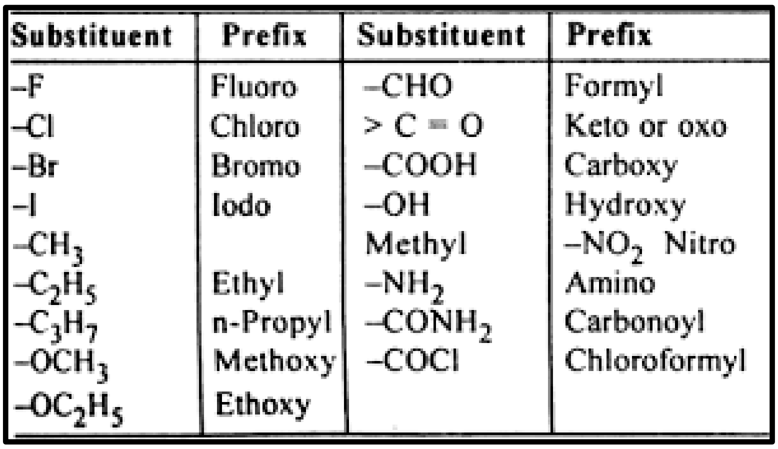
Set of locauts → 2, 2, 4 (correct)



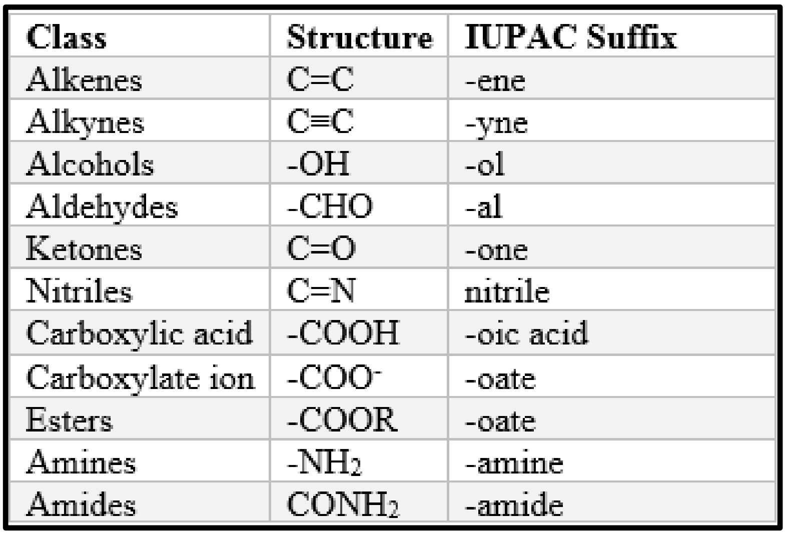
$\overset{5}{CH_3}-\overset{4}{C}(CH_3)_2-\overset{3}{CH_2}-\overset{2}{CH}(CH_3)-\overset{1}{CH_3}$

Set of locauts → 2, 4, 4 (Incorrect)

3. The names of alkyl groups attached as a branch are then prefixed to the name of the parent alkane and position of the substituents is indicated by the appropriate numbers.

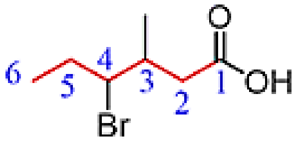


Substituent	Prefix	Substituent	Prefix
$-F$	Fluoro	$-CHO$	Formyl
$-Cl$	Chloro	$> C = O$	Keto or oxo
$-Br$	Bromo	$-COOH$	Carboxy
$-I$	Iodo	$-OH$	Hydroxy
$-CH_3$		Methyl	$-NO_2$ Nitro
$-C_2H_5$	Ethyl	$-NH_2$	Amino
$-C_3H_7$	n-Propyl	$-CONH_2$	Carbonoyl
$-OCH_3$	Methoxy	$-COCl$	Chloroformyl
$-OC_2H_5$	Ethoxy		



Class	Structure	IUPAC Suffix
Alkenes	C=C	-ene
Alkynes	C≡C	-yne
Alcohols	-OH	-ol
Aldehydes	-CHO	-al
Ketones	C=O	-one
Nitriles	C=N	nitrile
Carboxylic acid	-COOH	-oic acid
Carboxylate ion	$-COO^-$	-oate
Esters	-COOR	-oate
Amines	$-NH_2$	-amine
Amides	$CONH_2$	-amide

4. If two or more identical substituent groups are present then the numbers are separated by commas.
5. If the two substituents are found in equivalent positions, the lower number is given to the one coming first in the alphabetical listing
6. The longest chain of carbon atoms containing the functional group is numbered in such a way that the functional group is attached at the carbon atom possessing lowest possible number in the chain
7. The order of decreasing priority for some functional groups is: -COOH, –SO3H, -COOR (R=alkyl group), COCl, -CONH2, -CN,-HC=O, >C=O, -OH, -NH2, >C=C<.

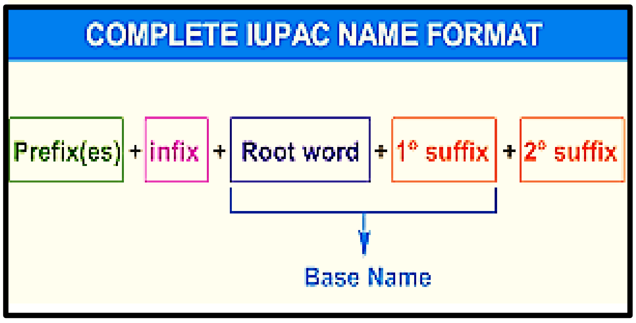


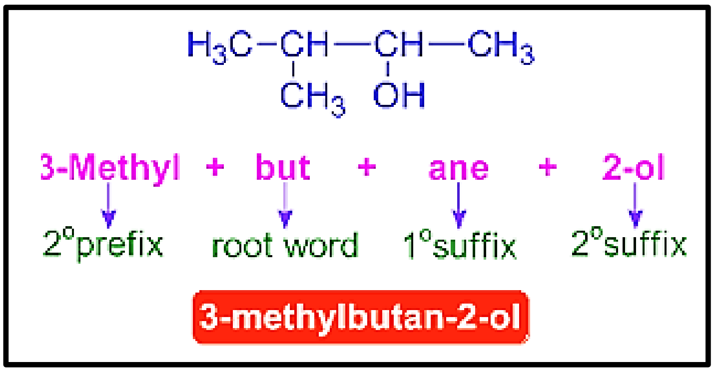
4-bromo-3-methylhexanoic acid

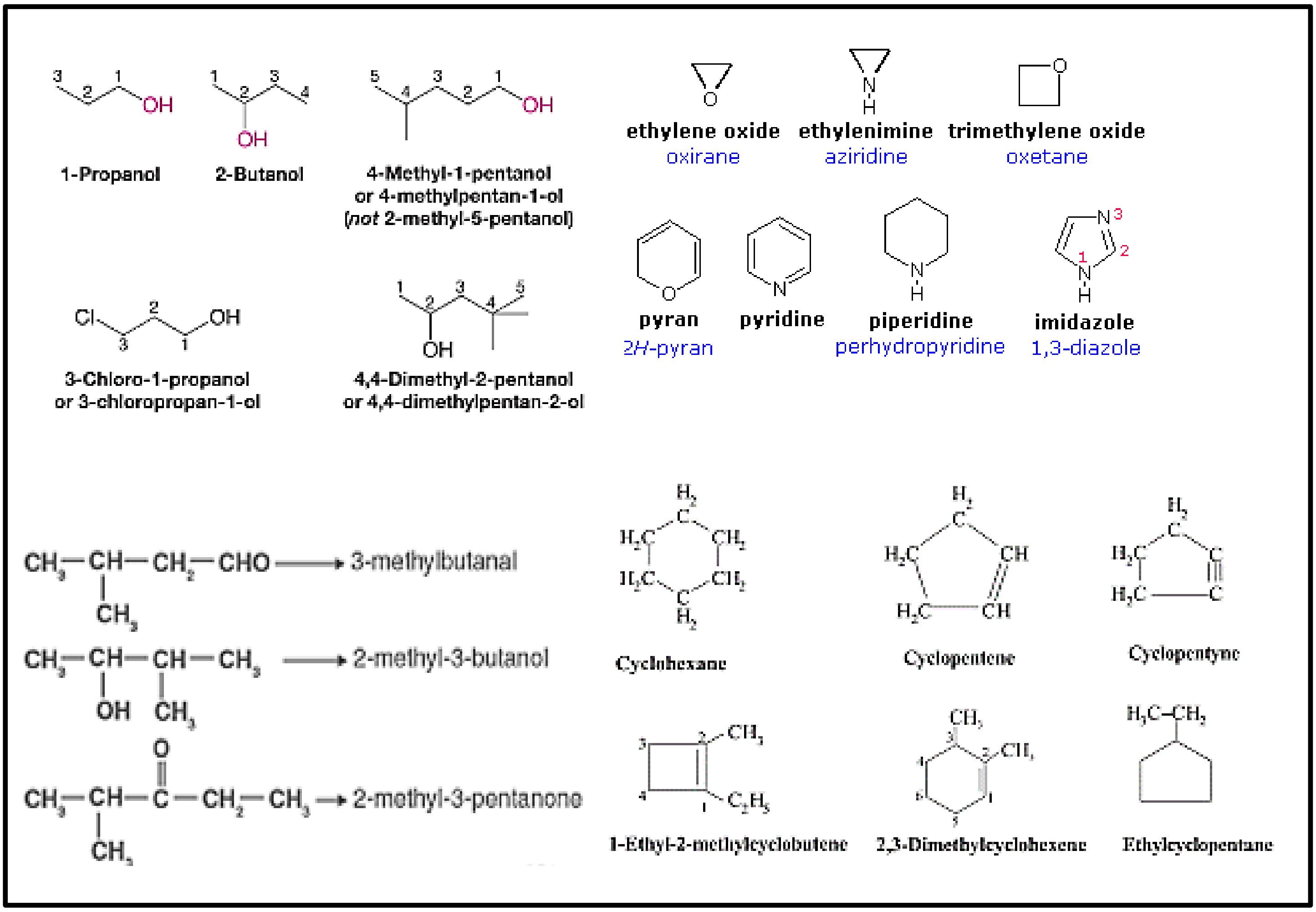
8. A saturated monocyclic compound is named by prefixing ‘cyclo’ to the corresponding straight chain alkane.

9. For IUPAC nomenclature of substituted benzene compounds, the substituent is placed as prefix to the word benzene

10. The position of substituents is defined by numbering the carbon atoms of the ring such that the substituents are located at the lowest numbers possible.







Hybridization

The process of mixing and recasting of atomic orbitals of the same atom having nearly the same energy to form a new set of equivalent hybrid orbitals having the same energies, shape and different orientations is called hybridization.

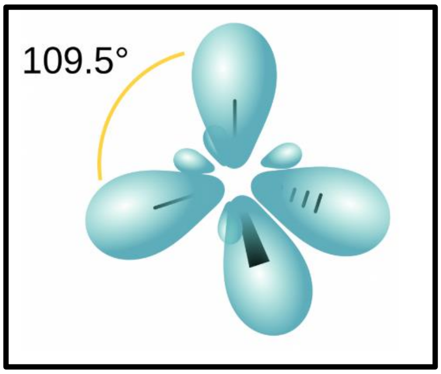
Types of hybridization

Different types of hybridization depend upon the number of type of atomic orbitals involved in mixing with corresponding geometry.

sp3 Hybridization

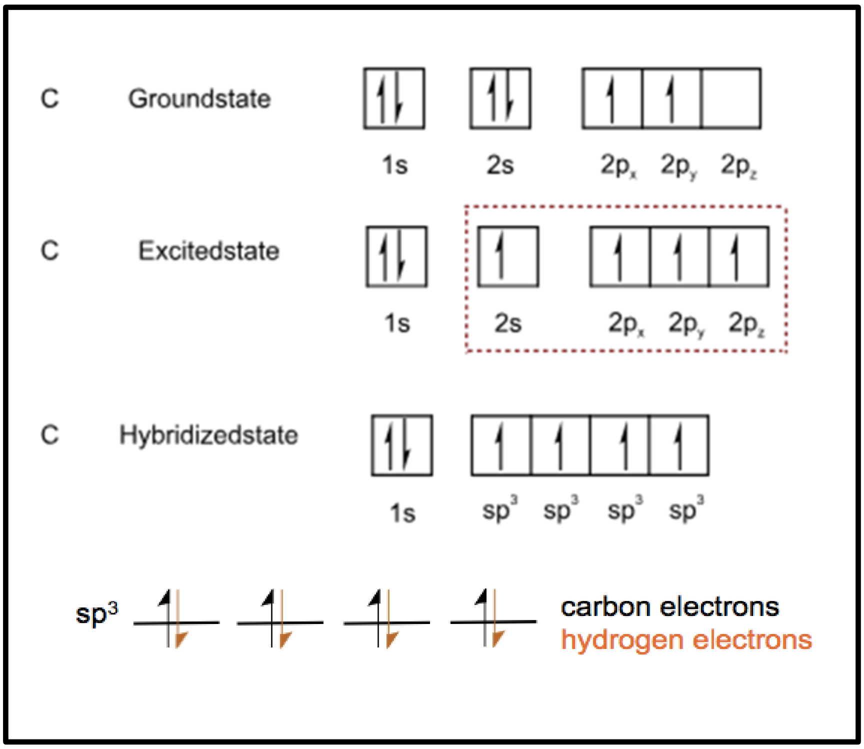
The process of mixing and recasting of one s-orbital and three p-orbitals of the valence shell of an atom of nearly the same energy to form three new hybrid orbitals of same energy is called as sp3 hybridization.

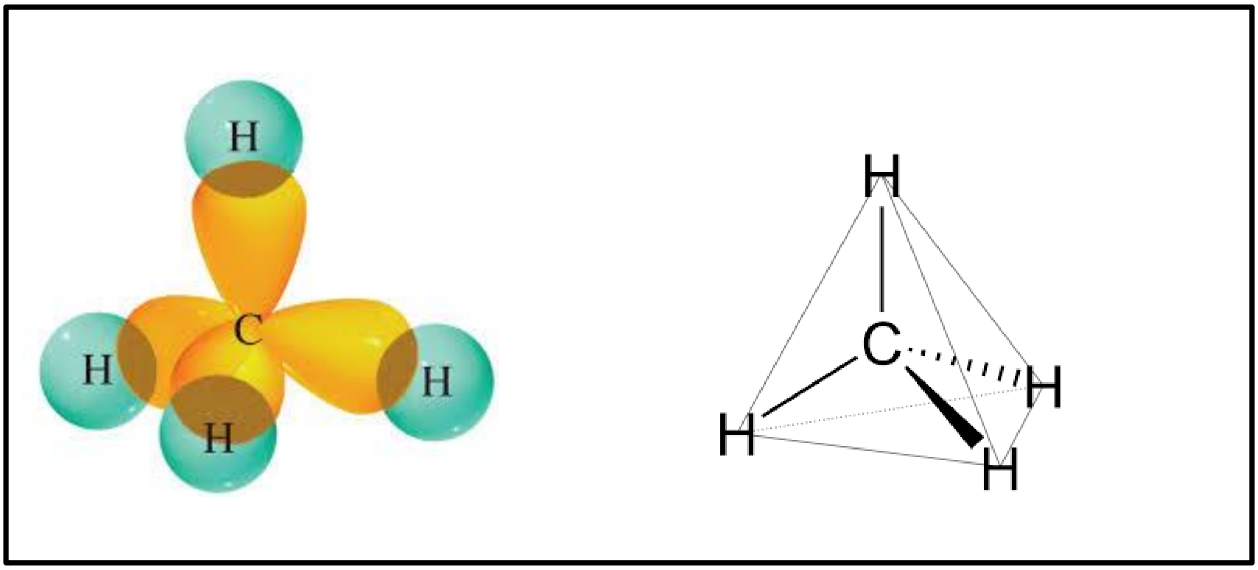
In sp^3 hybridization, each orbital consist of 25% s character and 75% p character.



Example: Methane

In methane (CH_4) central carbon atom undergo sp3 hybridization and bonded to four hydrogen atoms. C-H bonds are formed by linear overlap of sp3 hybrid orbital of carbon and s-orbital of hydrogen. Bond length of C-H bond is 1.112 A and bond energy is 406 KJ.

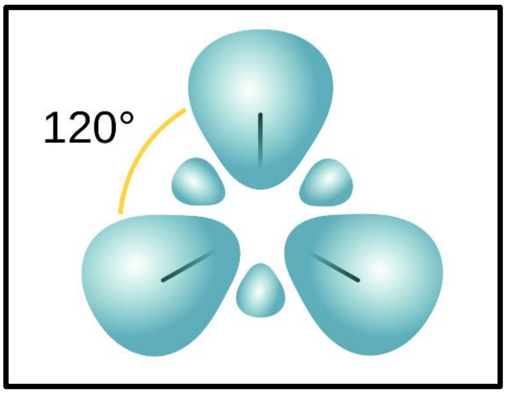




sp2 Hybridization

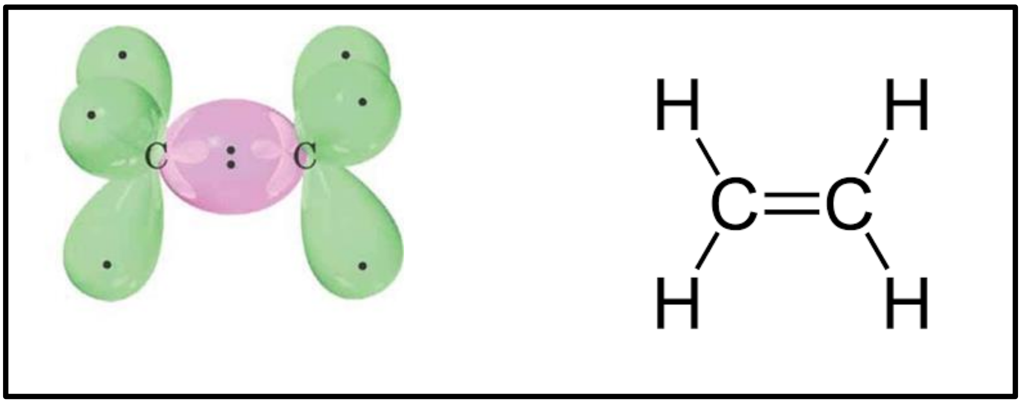
The process of mixing and recasting of one s-orbital and two p-orbitals of the valence shell of an atom of nearly the same energy to form four new hybrid orbitals of same energy is called as sp2 hybridization.

In sp² hybridization, each orbital consist of 33.33% s character and 66.66% p character.



Example: <u>Ethene</u>

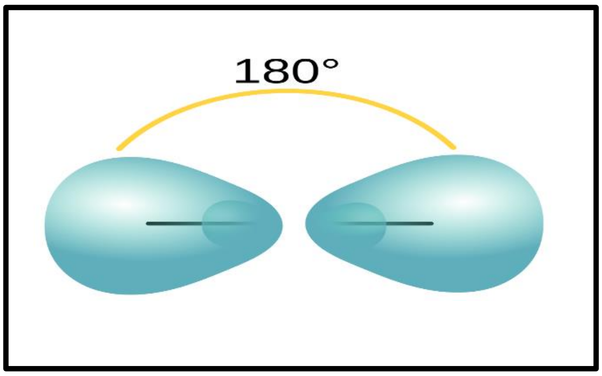
In ethylene (C_2H_4) each carbon atom undergo sp2 hybridization and bonded to four hydrogen atoms. C-H bonds are formed by linear overlap of sp2 hybrid orbital of carbon and s-orbital of hydrogen. Bond length of C-H bond is 1.103 A and bond energy is 435 KJ. In ethylene there is formation of C=C as well by lateral overlapping of p-orbitals. Bond length of C=C is 1.34 A and bond energy is 607 KJ.



sp Hybridization

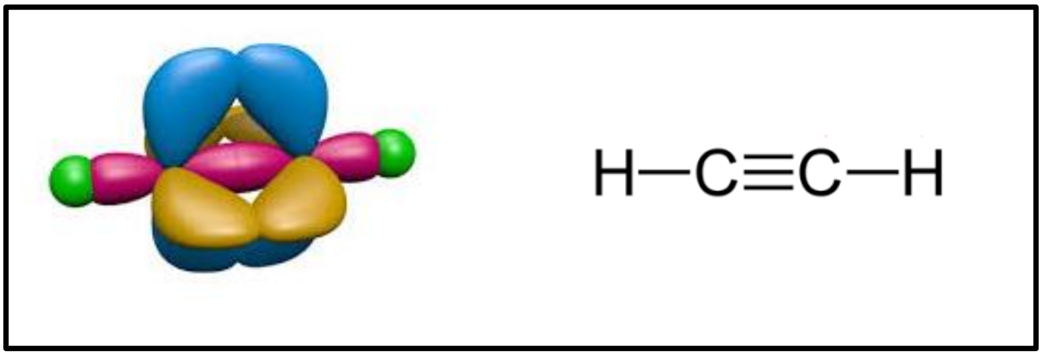
The process of mixing and recasting of one s-orbital and one p-orbitals of the valence shell of an atom of nearly the same energy to form two new hybrid orbitals of same energy is called as sp hybridization.

In sp hybridization, each orbital consist of 50% s character and 50% p character.



Example: Acetylene

In acetylene (C2H2) each carbon atom undergo sp hybridization and bonded to two hydrogen atoms. C-H bonds are formed by linear overlap of sp hybrid orbital of carbon and s-orbital of hydrogen. Bond length of C-H bond is 1.08 A and bond energy is 502 KJ. In acetylene there is formation of $C\equiv C$ as well by lateral overlapping of p-orbitals. Bond length $C\equiv C$ of is 1.20 A and bond energy is 802 KJ.



Bond length

The average distance between the centre of a nuclei of two bonded atoms in a molecule is called as bond length. bond length depends upon the hybridization and resonance in the molecule.

Single bond > double bond > triple bond

Sigma bond > pi bond

sp3 > sp2 > sp

Bond Energy OR Bond strength

Bond energy or bond strength is defined as the amount of energy required to break a bond in a molecule. Each bond has characteristic value of bond energy.

$$\boxed{\textbf{Bond energy} \propto \frac{\textbf{1}}{\textbf{Bond length}}}$$

c≡c > c=c > c-c

Dipole moment

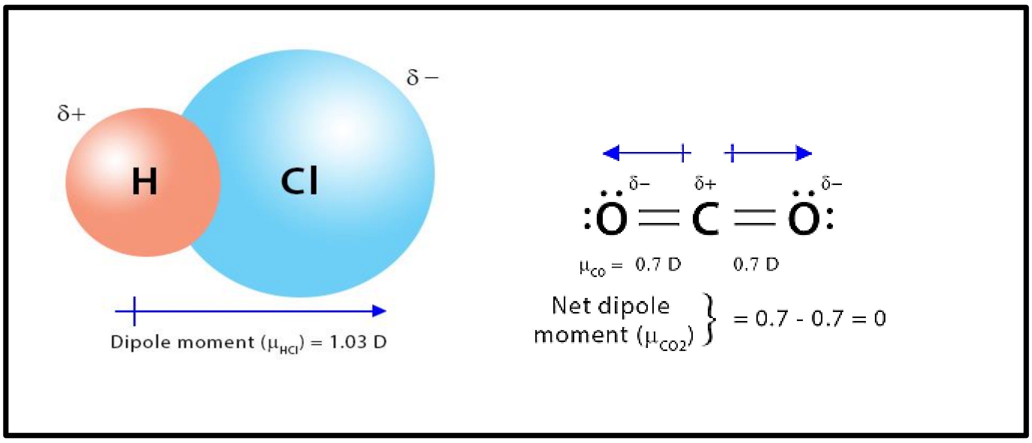
Dipole moment is defined as, The product of magnitude of charges on any atoms and the distance between them. Degree of polarizability of a molecule is usually expressed in terms of dipole moment.

Mathematically it is given by: $\boxed{\mu = q \cdot r}$

where, μ = dipole moment

q = charges on any atoms

r = distance between atoms



Applications

1) dipole moment is use to measure net molecular polarity.
2) It is use to measure bond angle in molecule.
3) It is use to measure size, shape of molecule.

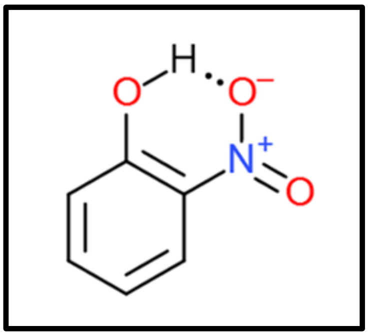
Hydrogen bonding

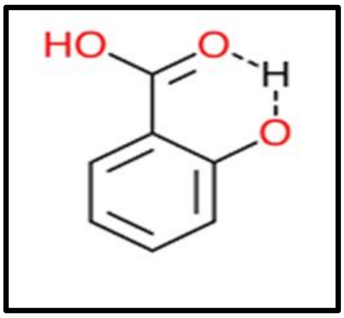
The electrostatic attractive force which binds hydrogen atom of one molecule with the electronegative atom of another molecule or same molecule is called as hydrogen bond phenomenon is known as hydrogen bonding. (Electronegative atoms such as: F, O, N)

There are two types of hydrogen bonding: intramolecular and intermolecular hydrogen bonding.

Intramolecular hydrogen bonding

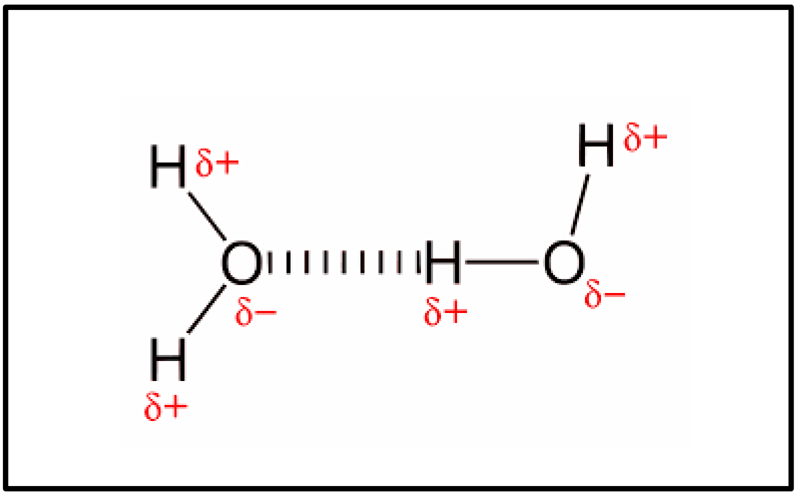
Intramolecular H-Bonding occurs when hydrogen and highly electronegative atom present in same molecule. The hydrogen bonding between the ortho substituted groups restricts the possibility of intermolecular hydrogen bonding. In meta and para position H-Bonding does not takes place because the groups are far away from each other.





Intermolecular hydrogen bonding

Intermolecular H-Bonding occurs between two neighboring molecules. It is weak attractive force between molecules, which have hydrogen atom in one molecule and electronegative atom in another molecule.



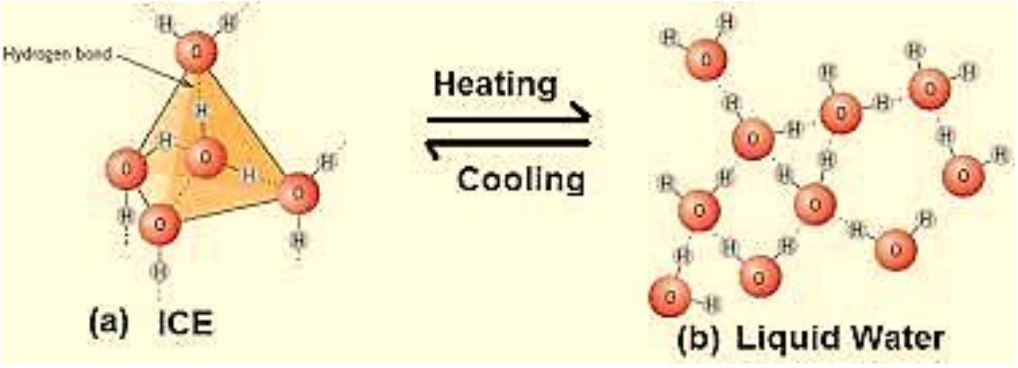
Effects of H-Bonding on physical properties:

1. Solubility: lower alcohols are soluble in water because of the H-Bonding which can takes place between water and alcohol molecule.
2. Volatility: as the compounds involving H-Bonding between different molecules have a higher boiling point, they are less volatile.
3. Viscosity and surface tension: the substances which contain H-Bonding exist as associated molecules. So, their flow becomes comparatively difficult. They have higher viscosity and surface tension.

Why ice floats?

In case of solid ice, H-Bonding gives rise to a cage like structure of water molecules. The molecules are not as closely packed as they are in liquid state. When ice melts, this cage like structure collapses, and the molecules come closer to each other.

Thus, for the same mass of water, the volume decreases and density increases. Therefore, ice has lower density than water. And that's why ice floats.



Part B

Inductive effect

the inductive effect depends upon the intrinsic tendency of a substituent to release or withdraw electrons. The electronegativity of atoms acting either through the molecular chain or space. The effect weakens steadily with increasing distance from substituent (i.e. distance dependent effect).

The inductive effect is a permanent state of polarization. The electron density in a bond between two atoms is not uniform. The electron density is denser toward the more electronegative atoms. One atom acquires a slightly negative charge and other atom get slightly positive charge which means the bond is polarized.

There are two categories of inductive effects:

-I effect:

The -I effect is seen around a more electronegative atom or group, and electron density is higher there than elsewhere in the molecule. Electron-withdrawing groups include halogen (F,Cl,Br,I) , nitro (NO2), cyno (CN), carboxy (COOH), ester (COOR), etc.

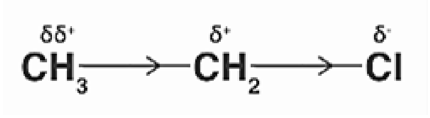
+I effect:

The +I effect is observed among the less electronegative atoms of the molecule by electron-donating groups. The alkyl groups are usually considered electron-donating groups (CH3, C2H5) etc.

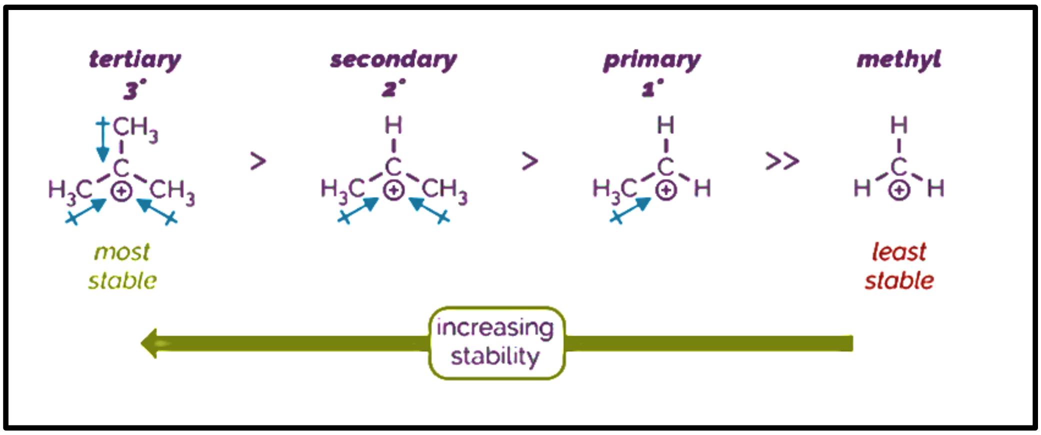
The inductive effect is works through several sigma bonds.

Electron-donating inductive effects (+*I*) stabilizes the positive charge.

Electron-withdrawing inductive effects (-*I*) stabilizes the negative charge.



$\overset{\delta\delta^+}{CH_3} \longrightarrow \overset{\delta^+}{CH_2} \longrightarrow \overset{\delta^-}{Cl}$



Applications:

1. To determine stability of free radicals, cations and anions.

Stability of free radical and carbocation is directly proportional to +I effect (3>2>1) whereas,

Stability of carbanion is directly proportional to -I effect (1>2>3).

2. To determine the strength of acids and bases.

Strength of acid is directly proportional to -I effect.

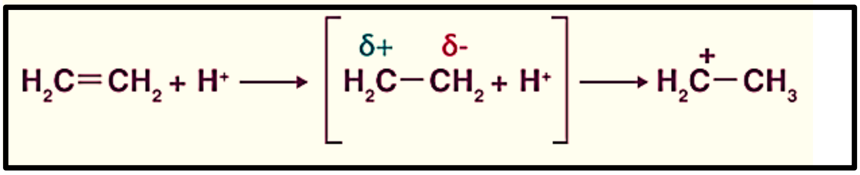
Electromeric effect

The temporary complete transfer of p-bonded electron pair from one atom to another by double or triple bond in the presence of a suitable attacking reagent (such as electrophile or nucleophile) is called as electromeric effect.

Due to electron transfer, one atom loses an electron get positive charge(+) while other atom gain electron get negative charge(−). This electron transfer shown by curved arrow(↷).

+E effect:

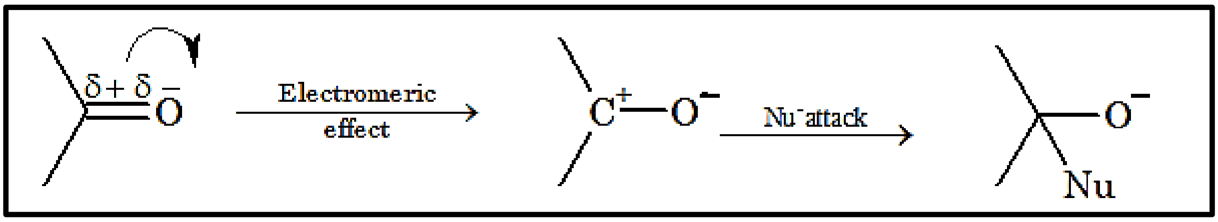
When the electron transfer of pi electron occurs towards the atom where attacking reagent is electrophile.



$$H_2C{=}CH_2 + H^+ \longrightarrow \left[\overset{\delta+}{H_2C}-\overset{\delta-}{CH_2} + H^+ \right] \longrightarrow H_2\overset{+}{C}-CH_3$$

-E effect:

When the electron transfer of pi electron occurs towards the atom where attacking reagent is nucleophile.



Applications:

1. It is used in electrophilic addition reactions of alkenes and alkynes.
2. It is used in nucleophilic sddition reaction of carbonyl compounds.

Resonance and mesomerism

The resonance effect involves delocalization of electrons typically pi electrons, due to overlap between certain orbitals And conjugation of electrons (i.e. alternate single and double bonds). Unlike inductive effect, the resonance effect do not depend upon distance.

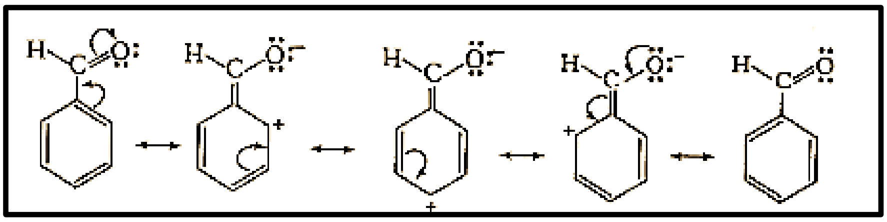
When the delocalization and conjugation of electrons involves functional group then it is known as mesomeric effect.

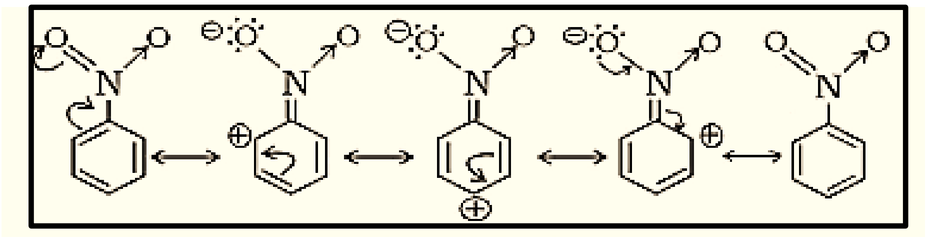
+M/+R effect:

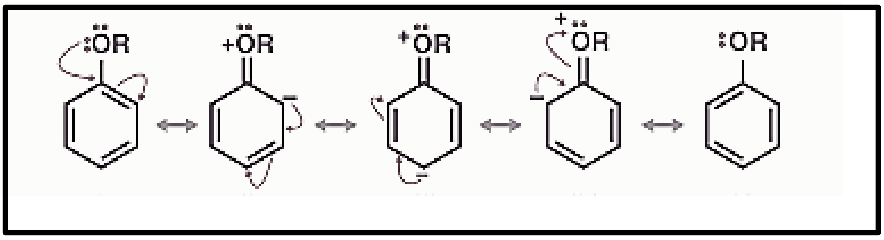
+ M/+R effect is the tendency of atoms or group of atoms to donate electron via resonance.

-M/-R effect:

- M/-R effect is the tendency of atoms or group of atoms to withdraw electron via resonance.





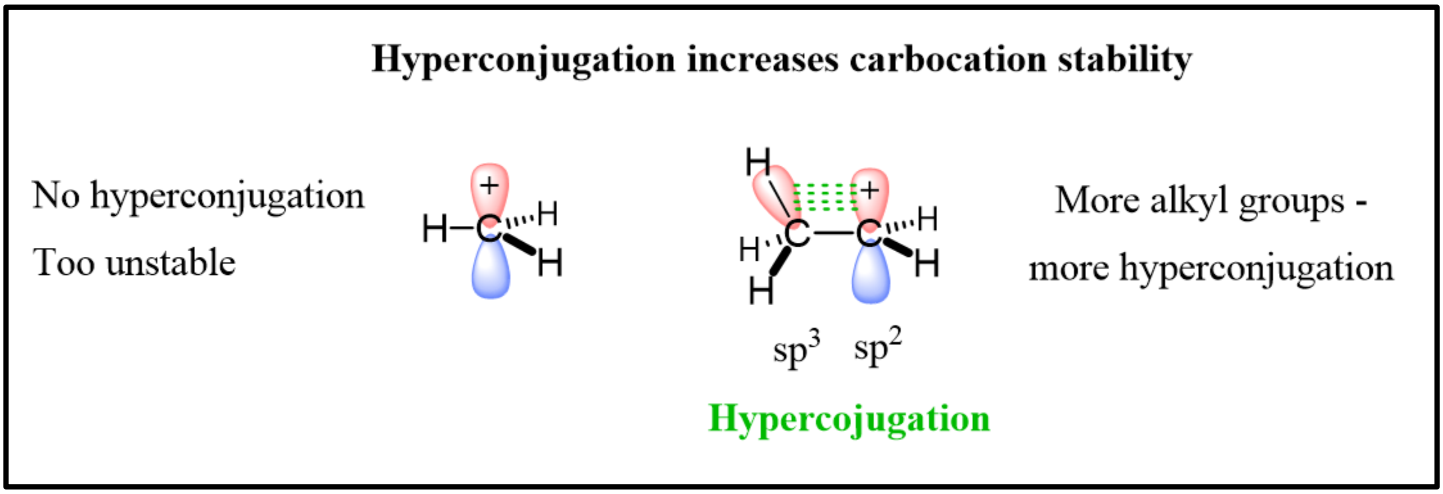


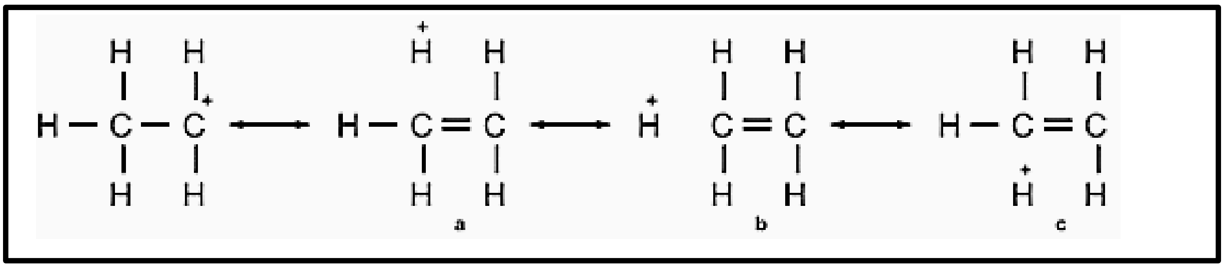
Applications:

1. It is useful to explain stability of molecules and ions.
2. To explain unexpected bond lengths in molecules.
3. Explains Acidity of phenol and basicity of amine.
4. Useful in mechanism of reactions.

Hyperconjugation

Delocalization of electrons through overlap between sigma bond orbital and pi bond orbital called as hyperconjugation. Hyperconjugation is also known as no bond resonance or baker Nathan effect. Hyperconjugation depends upon alpha(α)-hydrogen present in molecule.





Applications:

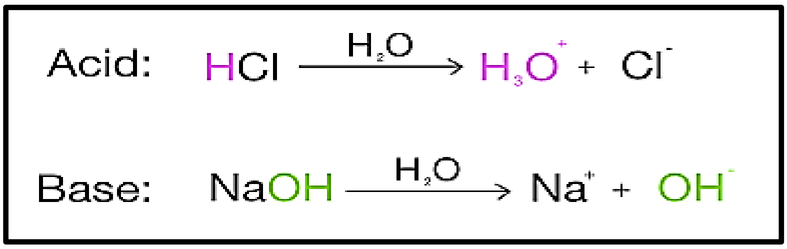
1. It is use to explain relative stability of alkene.
2. It is use to explain stability of intermediate such as carbocation and free radicals.

Acid Base Theories:

1) Arrhenius theory

Arrhenius acids yield hydrogen ions in aqueous solution.

Arrhenius bases yield hydroxide ions in aqueous solution.



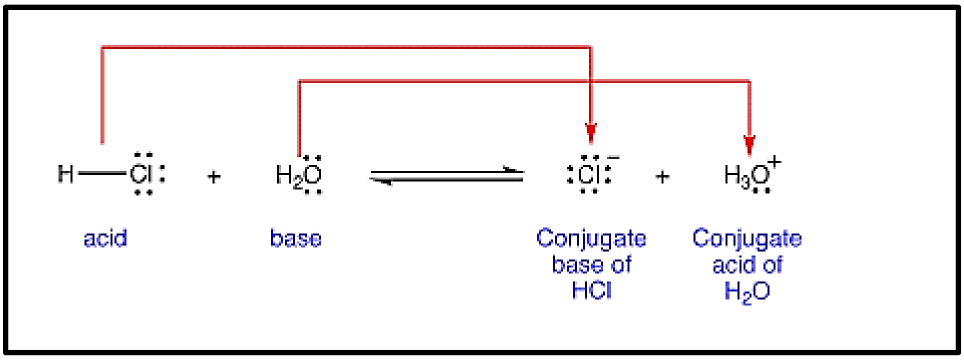
Acid: $HCl \xrightarrow{H_2O} H_3O^+ + Cl^-$

Base: $NaOH \xrightarrow{H_2O} Na^+ + OH^-$

2) Lowry Bronsted theory

Brønsted and Lowry defined an acid as a species with a tendency to lose a hydrogen ion and a base as a species with a tendency to gain a hydrogen ion

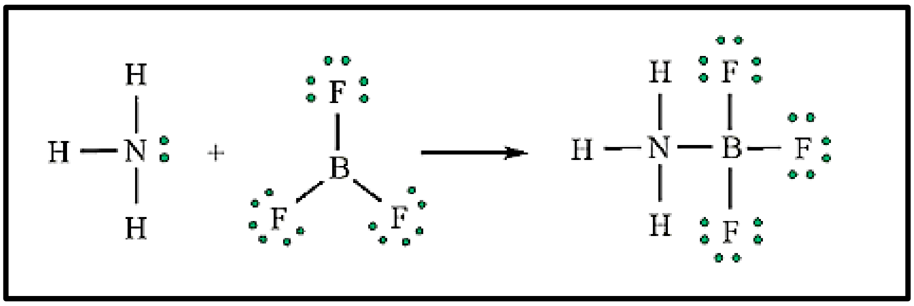
The Brønsted–Lowry strategy is to compare conjugate acids and bases, species differing only in the presence or absence of a proton, and describe reactions as occurring between a stronger acid and a stronger base to form a weaker acid and a weaker base.

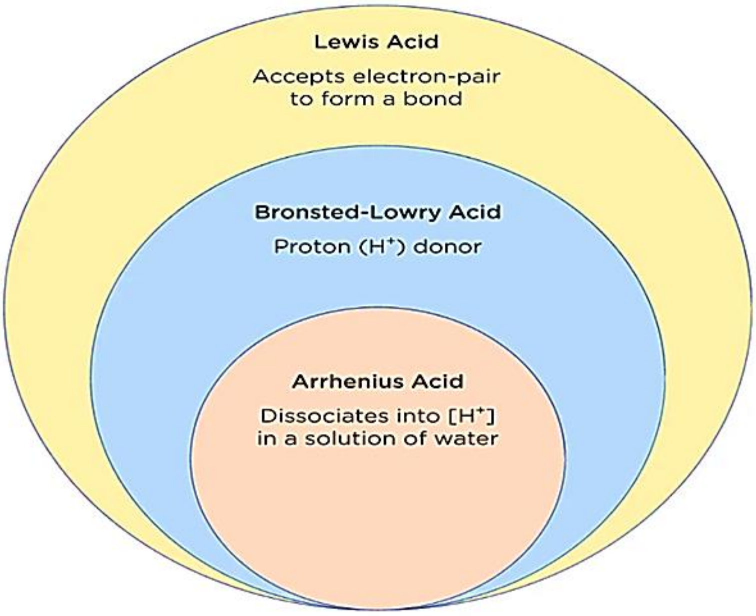


3) Lewis theory

According to the lewis definition, a base is a substance that can give electron pair and form covalent bond and an acid is a substance that can take up an electron pair to form covalent bond.

Thus an acid is electron-pair acceptor and a base is electron-pair donor.





Litmus test for acid and base:

Acid:

Blue litmus turns red.

Base:

Red litmus turns blue.

Ionization constant or dissociation constant

It is defined as the tendency of particular substance reversibly dissociate into ions in solution.

1. It is specific type of equilibrium constant.

2. A large value of Ka means the acid is a strong acid and a small value of Ka means the acid is a weak acid.

3. It is quantitative measure of strength of acid in solution.

4. Acidity expressed in terms of Ka

$$HA \rightleftharpoons H^{\oplus} + A^{\ominus}$$

$$\boxed{K_a = \frac{[H^+][A^-]}{[HA]}}$$

Acidity and pKa:

Chemists usually express the acidity constant, Ka, as its negative logarithm pKa.

The larger the value of the pKa, the weaker is the acid.

$$\boxed{\begin{array}{l} pKa = -\log_{10}(Ka) \\ pH = pKa + \log\left(\frac{[A]}{[HA]}\right) \end{array}}$$

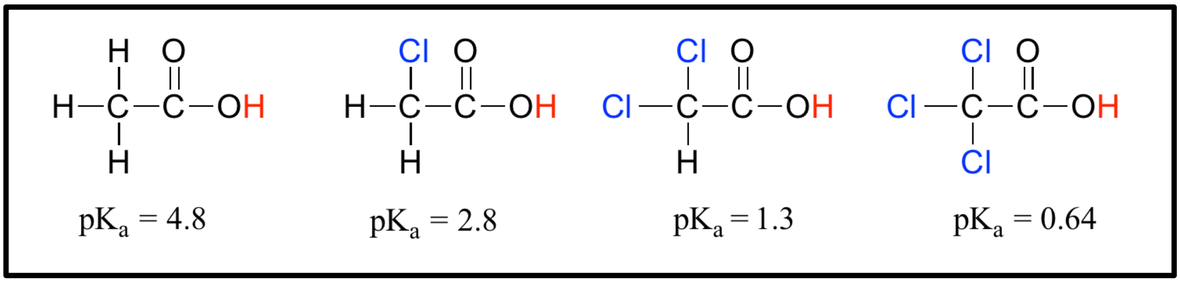
Acid	**pKa**
H2O (water)	15.7
C6H5OH (phenol)	9.9
C6H5COOH (benzoic acid)	4.1
CH3COOH (acetic acid)	4.75

Factors affecting pka value

1) Inductive effects:

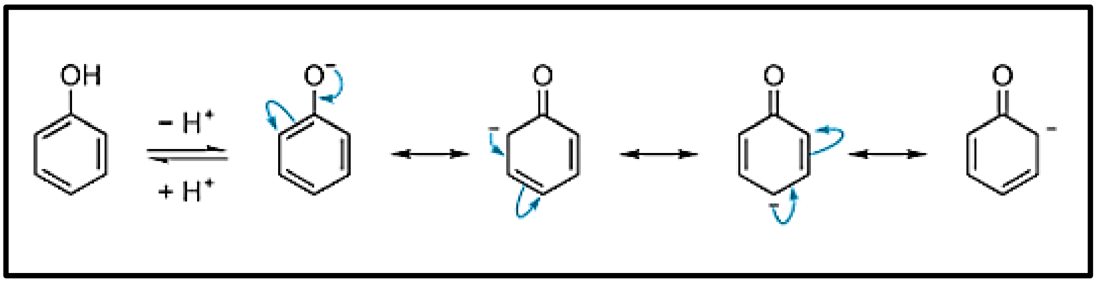
Inductive effect involve the donation or withdrawal electrons from an atom by a group connected to it through bonds. Electron donating groups increase the electron density while electron withdrawing groups decrease it. Atoms or groups that withdraw electron density away from a center increase its acidity while those which donate electrons to the center decrease its acidity.

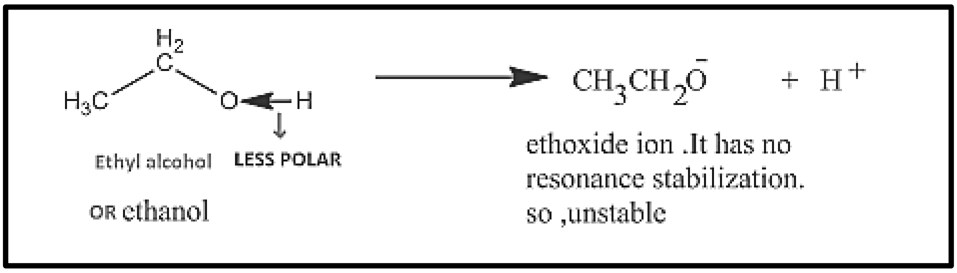
When a bond to hydrogen is more polarized away from the H (more like–δE–Hδ+–δE–Hδ+) it is easier to cleave off the hydrogen ion from that E-H bond. This may be seen from how the pK_a values of acetic acid and its mono-, di-, and tri-chlorinated derivatives decreases with the extent of chlorination of the methyl group.



2) Resonance effects:

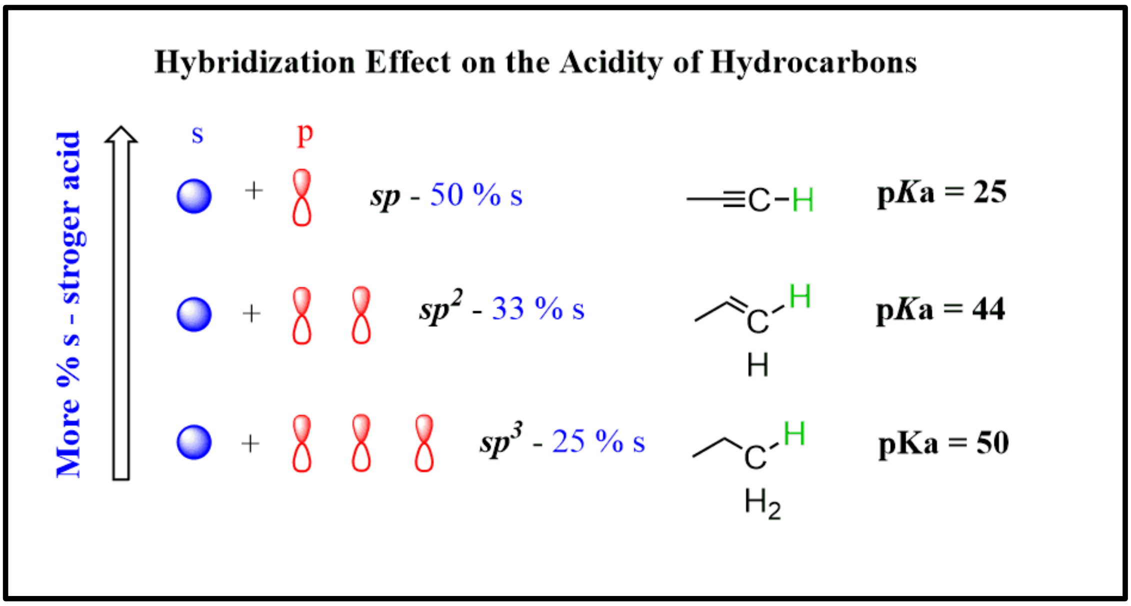
Resonance effect involve the donation or withdrawal of electrons from an atom by a group via delocalization and conjugation. When the conjugated bases of two species are compared, the species which conjugate base is more stabilize via resonance is more acidic.





3)Hybridization effect

Hybridization effect higher the percentage of s character of hybrid orbital bond is more closer to nucleus and more stable conjugate base.



Reference:

Introduction to organic compound- Clayden-Warren

Nomenclature- NCERT

Acid base theories- Graham Solomons

Electronic effects- Morrison Boyd

Other- AUCTA

Images- google

Expected questions

Fill in the blanks

1. organic compounds contains carbon & hydrogen called as **hydrocarbon**

2. organic compounds are classified into **two types** on basis of skeleton chain

3. the functional group of alcohol is **-OH**

4. mixing and recasting of one s and two p orbitals of nearly the same energy to produce three hybrid orbitals of the same energy is called as **sp2 hybridization**

5. inductive effect is defined as the permanent polarization created in covalent bond due to the displacement of **sigma electron** towards more electronegative atom

6. dipole moment is the product of the magnitude of the charge and the distance between the centres of positive and **negative charge**

7. as per lewis theory an acid may be defined as any substance that is capable of accepting an **electron pair**

MCQ

1.choose the correct statement regarding benzenoid and non benzenoid compound

a) both are cyclic structures

b) benzenoid and non benzenoid are aromatic compounds with conjugated pi system

c) both exhibits an extra stability

d) **all of above**

2.which pf the following terms denotes the number of carbon atom present in principal chain of the molecule

a)suffix b)prefix c)**root word** d)all of above

3.the primary suffix and generic name of saturated c-c hydrocarbon is

a)-**ane** b)-ene c)-yne d)all of above

4.geometry of methane molecule

a)trigonal planer b)octahedral c)TBP d)**tetrahedral**

5.which of the following shows positive inductive effect

a)-**CH3** b)-NR2 c)-NO2 d)-CN

6.which of the following group shows negative inductive effect

a)-CH3 b)-O- c)-C2H5 d)-**CN**

7.resonance effect is useful to explain

a)stability of molecules and ions

b)unexpected bond length in molecules and ions

c)acidity of phenols and basicity of amines and mechanism of reactions

d)**all of above**

8.which of the factors effect on the acidity and basicity of organic compounds

a)resonance b)inductive c)hybridization d)**all of these**

Long questions

1. Discuss classification of organic compounds on basis of carbon skeleton.
2. Discuss the sp3 hybridization with example.
3. Discuss the sp2 hybridization with example.
4. Discuss the sp hybridization with example.
5. Discuss the concept of hydrogen bonding and its types.
6. Explain inductive effect with applications.
7. Explain mesomeric effect with applications.
8. Explain hyperconjugation effect with applications.
9. Discuss the theories of organic acid and base.

Thankyou enjoy the process of learning……….