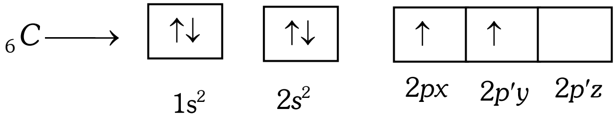
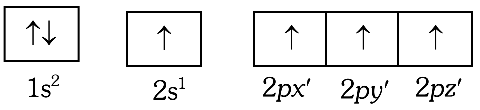
The chemical properties of an element depend on the electronic configuration of the outershell. Carbon has four electrons in its outershell.

According to the ground state electronic configuration of carbon, carbon is divalent. Tetravalency of carbon can be explained by promoting one $2s$ - electron to a $2pz$ orbital. Some energy must be supplied to the system in order to effect this promotion. This promotion requires energy about 96 kcal/mol, but this energy is more than regained by the concurrent farmation of chemical bonds.

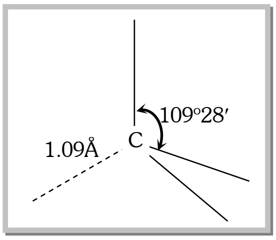


Carbon in ground state



Carbon in excited state

The four valencies of carbon atom are similar and they are symmetrically arranged around the carbon atom. According to Le Bel and Van't Hoff the four valencies of carbon do not lie in one plane. They are directed towards the corners of a regular tetrahedron with carbon atom at the centre and the angle between any two valencies is $109^o28'$.



Bonding in organic compounds.

The organic compounds are carbon compounds consisting of one or more carbon atoms. Carbon must form only covalent bonds, *i.e.*, it should share its valency electrons with other atoms.

According to the modern concept, a covalent bond is formed between two atoms if there is an overlapping of an atomic orbital of one atom with an atomic orbital of another atom. The overlapping is possible by two ways,

(1) **End to end overlapping :** This type of overlapping is possible between $s-s, s-p_x$ and p_x-p_x atomic orbitals. The molecular bond formed is termed as sigma (σ) bond.

(2) **Sidewise or parallel or lateral overlapping :** Such overlapping is possible between $p-p$ atomic orbitals. The molecular bond formed is termed as $pi(\pi)$ bond.

σ-Bond	π-Bond
Formed by End to End overlap of AO's.	**Formed by lateral overlap of p-orbitals.**
Has cylindrical charge symmetry about bond axis.	**Has maximum charge density in the cross-sectional plane of the orbitals.**
Has free rotation	**No free rotation, i.e., frozen rotation**
Low energy	**Higher energy**
Only one σ bond can exist between two atoms,	**One or two π bonds can exist between two atoms.**
Sigma bonds are directional. Thus the geometry of the molecule depends on the σ bonds.	**π bonds are not directional. Geometry of the molecule not depends on π bond.**
Area of overlapping is higher hence bond is stronger.	**Area of overlapping is small hence bond is weaker.**
σ bond can have independent existance.	**π bond always exist along with a σ bond and π bond is formed after the formation of σ bond.**

Hybridisation in Organic Compounds.

(1) The process of mixing atomic orbitals to form a set of new equivalent orbitals is termed as ***hybridisation***. There are *three types* of hybridisation encountered in carbon atom. These are,

(i) sp^3 ***hybridisation*** (involved in saturated organic compounds containing only single covalent bonds),

(ii) sp^2 ***hybridisation*** (involved in organic compounds having carbon linked by double bonds) and

(iii) *sp* ***hybridisation*** (involved in organic compounds having carbon linked by a triple bonds).

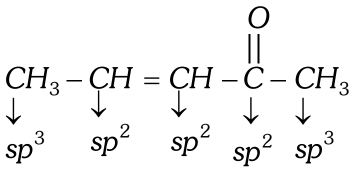
Type of hybridisation	Number of orbitals used	Number of unused p-orbitals	Bond	Bond angle	Geometry	% s-character
sp^3	1s and 3p	Nil	Four -σ	109.5°	Tetrahedral	25 or 1/4
sp^2	1s and 2p	One	Three -σ One -π	120°	Trigonal	33.33 or 1/3
sp	1s and 1p	Two	Two -σ Two -π	180°	Linear	50 or 1/2

(2) Determination of hybridisation at different carbon atoms : It can be done by two methods,

(i) ***First method*** **:** In this method hybridisation can be know by the number of $\pi-$ bonds present on that particular atom.

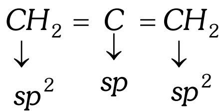
Number of π– bond/s	0	1	2
Type of hybridisation	sp^3	sp^2	sp

Examples **:** (i)



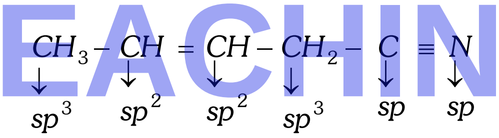
$$\underset{\downarrow\atop sp^3}{CH_3}-\underset{\downarrow\atop sp^2}{CH}=\underset{\downarrow\atop sp^2}{CH}-\underset{\downarrow\atop sp^2}{\overset{O\atop ||}{C}}-\underset{\downarrow\atop sp^3}{CH_3}$$

(ii)



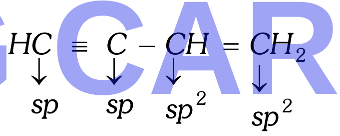
$$\underset{\downarrow\atop sp^2}{CH_2}=\underset{\downarrow\atop sp}{C}=\underset{\downarrow\atop sp^2}{CH_2}$$

(iii)



$$\underset{\downarrow\atop sp^3}{CH_3}-\underset{\downarrow\atop sp^2}{CH}=\underset{\downarrow\atop sp^2}{CH}-\underset{\downarrow\atop sp^3}{CH_2}-\underset{\downarrow\atop sp}{C}\equiv\underset{\downarrow\atop sp}{N}$$

(iv)



$$\underset{\downarrow\atop sp}{HC}\equiv\underset{\downarrow\atop sp}{C}-\underset{\downarrow\atop sp^2}{CH}=\underset{\downarrow\atop sp^2}{CH_2}$$

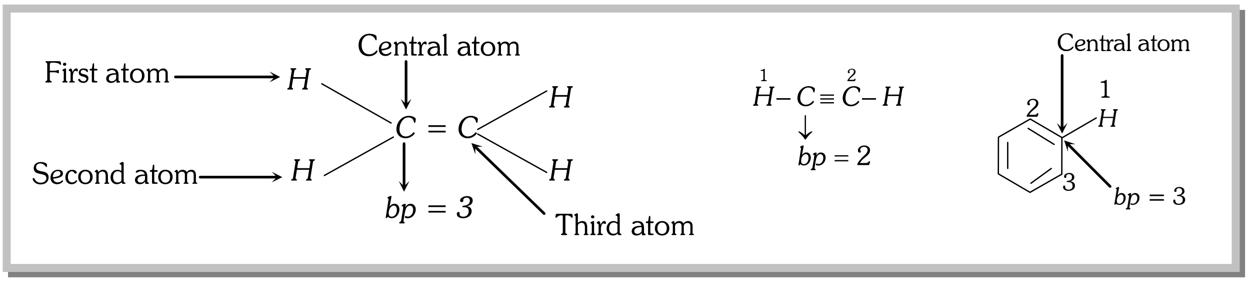
Note : ✹ In diamond carbon is sp^3 hybridised and in graphite carbon is sp^2 hybridised.

✹This method can not be used for those atoms of the molecule which have positive charge, negative charge or odd electron.

(ii) ***Second method*** **:** (Electron pair method)

ep = *bp* + *lp*; where *ep* = electron pair present in hybrid orbitals , *bp* = bond pair present in hybrid orbitals

Number of *bp* = Number of atoms attached to the central atom of the species



Number of *lp*'s can be determined as follows,

(a) If carbon has π - bond/s or positive charge or odd electron, than *lp* on carbon will be zero.

(b) If carbon has negative charge, then *lp* will be equal to one.

Number of electron pairs (*ep*) tells us the type of hybridisation as follows,

ep	**2**	**3**	**4**	**5**	**6**
Type of hybridisation	sp	sp^2	sp^3	sp^3d	sp^3d^2

Example :

(i) $CH_2=\overset{\oplus}{C}H \downarrow$ $\quad bp=2,\ lp=0,\ ep=2, sp$

(ii) $CH_2=\overset{\ominus}{C}H \downarrow$ $\quad bp=2,\ lp=1,\ ep=3, sp^2$

(iii) $CH_2=\overset{\bullet}{C}-CH_3$ with CH_3 below the C $\quad bp=3,\ lp=0,\ ep=3, sp^2$

(iv) $CH\equiv\overset{\ominus}{C} \downarrow$ $\quad bp=1,\ lp=1,\ ep=2, sp$

(v) $CH_3-\overset{\ominus}{C}H-CH_3 \downarrow$ $\quad bp=3,\ lp=1,\ ep=4, sp^3$

(3) Applications of hybridisation

(i) ***Size of the hybrid orbitals*** : Since s - orbitals are closer to nucleus than p - orbitals, it is reasonable to expect that *greater the s character of an orbital the smaller it is*. Thus the decreasing order of the size of the three hybrid orbitals is opposite to that of the decreasing order of s orbital character in the three hybrid orbitals.

$sp^3 > sp^2 > sp$

(ii) ***Electronegativity of different orbitals***

(a) Electronegativity of s-orbital is maximum.

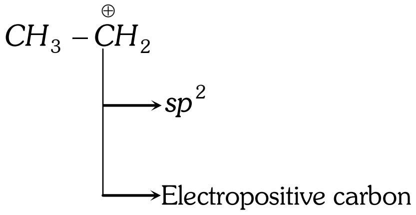
(b) Electronegativity of hybrid orbital $\propto$ % s-character in hybrid orbitals

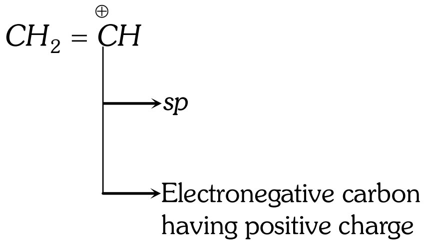
Orbital	sp	sp^2	sp^3
% s - character	50	33.33	25

$\xrightarrow{\hspace{8cm}}$

s-character in decreasing order and electronegativity in decreasing order

Thus sp-hybrid carbon is always electronegative in character and sp^3- hybrid carbon is electropositive in character. sp^2-hybrid carbon can behave as electropositive (in carbocation) as well as electronegative (in carbanion) in character.





(c) Electronegativity of different hybrid and unhybrid orbitals in decreasing order is as follows

$$\xrightarrow{s > sp > sp^2 > sp^3 > p}$$

% s - character in decreasing order and electronegativity in decreasing order.

(iii) ***Bond length variation in hydrocarbons***

$$\% \text{ } s \text{ orbital character} \propto \frac{1}{C-C \text{ bond length}} \propto \frac{1}{C-H \text{ bond length}}$$

Bond type (C – H)	***Bond length***	***Bond type (C – C)***	***Bond length***
$sp^3 - s$ **(alkanes)**	**1.112Å**	$sp^3 - sp^3$ **(alkanes)**	**1.54 Å**
$sp^2 - s$ **(alkenes)**	**1.103Å**	$sp^2 - sp^2$ **(alkenes)**	**1.34Å**
$sp - s$ **(alkynes)**	**1.08Å**	$sp - sp$ **(alkynes)**	**1.20Å**

Note : ✸ C–C bond length in benzene lies between single and double bond due to resonance. (1.40Å).

(iv) ***Bond strength in hydrocarbons*** : *The shorter the bond, the greater the compression between atomic nuclei and hence greater the strength of that bond is.* Thus the bond formed by sp hybridised carbon is strongest (i.e., it has maximum bond energy) while that formed by sp^3 hybridised carbon is the weakest (i.e., it has minimum bond energy). This is evident by the bond energies of the various types of $C-H$ and $C-C$ bonds.

Bond type (C – H)	*Bond energy* **(kcal/mole)**	***Bond type (C – C)***	***Bond energy* (kcal/mole)**
$sp^3 - s$ **(in alkanes)**	**104**	$sp^3 - sp^3$ **(in alkanes)**	**80 – 90**
$sp^2 - s$ **(in alkenes)**	**106**	$sp^2 - sp^2$ **(in alkenes)**	**122 – 164**
$sp - s$ **(in alkynes)**	**121**	$sp - sp$ **(in alkynes)**	**123 – 199**

(v) ***Acidity of hydrocarbons***

(a) Hydrogen present on electronegative carbon is acidic in character.

(b) Acidity of hydrogen is directly proportional to the electronegativity of atom on which hydrogen is present.

Thus

$$\xrightarrow{\quad H{-}O{-}H \qquad NH_3 \qquad CH{\equiv}CH \quad}$$

Electronegativity of atom in decreasing order
Acidity of compounds in deceasing order

(c) Acidity of hydrocarbon ∝ % *s-character*

	$CH\equiv CH$	$CH_2=CH_2$	CH_3-CH_3
% *s*-character	50	33.33	25
pKa	25	44	50

$\longrightarrow$ *s*- character in decreasing order and acidity in decreasing order

Note : ✸ Acidity $\propto Ka$ and Acidity $\propto \frac{1}{pKa}(pKa=-\log Ka)$

✸Order of acidic nature of alkynes is, $HC\equiv CH > HC\equiv C-CH_3$

✸The relative acidic character follows the order;

$H_2O > ROH > HC\equiv CH > NH_3 > CH_2\equiv CH_2 > CH_3-CH_3$

Obviously, the basic character of their conjugate bases follows the reverse order, i.e.,

$CH_3CH_2^{\ominus} > CH_2=CH^{\ominus} > NH_2^{\ominus} > HC\equiv C^{\ominus} > RO^{\ominus} > HO^{\ominus}$

Dipole moment of Organic Compounds.

(1) Due to differences in electronegativity polarity developes between two adjacent atoms in the molecule (*i.e.,* in a bond). The degree of polarity of a bond is called dipole moment. Dipole moment is represented by μ and its unit is Debye (D).

$$\mu = e \times l$$

Where, $e =$ magnitued of separated charge in e.s.u., $l =$ internuclear distance between two atoms *i.e.*, bond length in *cm*.

The dipole moment is denoted by arrow head pointing towards the positive to the negative end ($\mapsto$).

(2) Dipole moment of the compound does not depend only on the polarity of the bond but also depends on the shape of the molecule.Dipole moment of symmetrical compound is always zero, ($\mu = 0$). Symmetrical compounds are those compounds which fulfil following two conditions,

(i) Central atom is bonded with the same atoms or groups.*Examples* : $\underset{\text{Symmetrical molecules}}{H_2, BF_3, CS_2, CH_2 = CH_2, CH \equiv CH}$

(ii) Central atom should have no lone pair of electrons.

Examples : $\underset{\text{Symmetrical molecules}}{CCl_4, CH_4, BH_3, CO_2}$ $\quad \underset{\text{Unsymmetrical molecules}}{H_2\ddot{O},\ H_2\ddot{S}}$

Note : ✹ Compounds which have regular tetrahedral structure has no dipole moment.

(3) $\mu \propto$ electronegativity of central atom or surrounding atoms present on the central atom of the molecule.

$$\underset{\substack{\text{Electronegativity in decreasing order} \\ \mu \text{ is also in decreasing order}}}{CHF_3 \quad CHCl_3 \quad CHBr_3 \quad CHI_3 \longrightarrow}$$

$$\underset{\substack{\text{Electronegativity of central atom is in decreasing} \\ \text{order } \mu \text{ is also in decreasing order}}}{NH_3 \quad PH_3 \quad AsH_3 \quad SbH_3 \longrightarrow}$$

Note : ✹ Decreasing order of dipole moment in $CH_3Cl, CH_2Cl_2, CHCl_3$ and CCl_4 is

$$CH_3Cl > CH_2Cl_2 > CHCl_3 > CCl_4$$

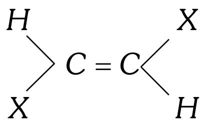
μ = 1.86 D 1.62 D 1.03 0

✹Alkynes has larger dipole moment because the electronegativity of $sp - C$ is more than that of $sp^2 - C$.

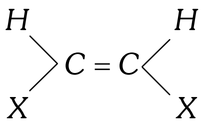
(4) μ cis $> \mu$ trans in geometrical isomers.

(5) Dipole moment of the trans derivative of the compound $(a)(b)C = C(a)(b)$ will only be zero if both a and b will be in the form of atoms.

Example :



$\mu = 0$



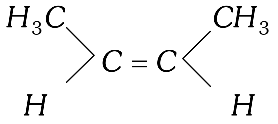
$\mu \neq 0$

($X = Cr, Br, I$ or F)

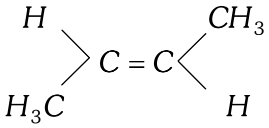
If both will not be atoms then μ trans may or may not be zero.

If group have non-linear moments, then the dipole moment of the trans isomer will not be zero. If group have linear moments, then the dipole moment of the trans isomer will be zero.

Example :



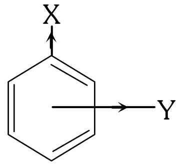
$\mu = 0.33D$



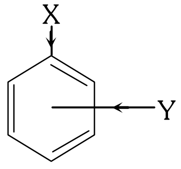
$\mu = 0D$

(6) Dipole moment of disubstituted benzene

(i) When both groups X and Y are electron donating or both groups are electron with drawing



or



Then, $\mu = \sqrt{\mu_1^2 + \mu_2^2 + 2\mu_1\mu_2 \cos\theta}$

Where, μ_1 = dipole moment of bond $C - X$, μ_2 = dipole moment of bond $C - Y$, θ = angle between X and Y.

If value of θ will be more, then $\cos\theta$ will be less. Hence, dipole moment will be as,

$$\xrightarrow[\mu \text{ in decreasing order}]{o\text{–derivative} \; > m\text{-derivative} \; > p\text{-derivative}}$$

(ii) When one group is electron with drawing and the other group is electron donating then,

$$\mu = \sqrt{\mu_1^2 + \mu_2^2 - 2\mu_1\mu_2 \cos\theta}$$

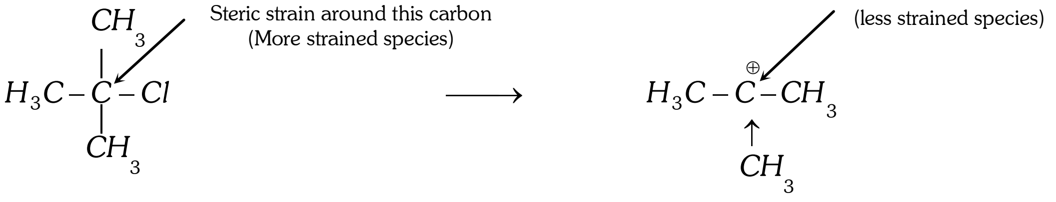
Hence, dipole moment is as follows,

$$\xrightarrow[\mu \text{ in decreasing order}]{o\text{–derivative} \; > m\text{-derivative} \; > p\text{-derivative}}$$

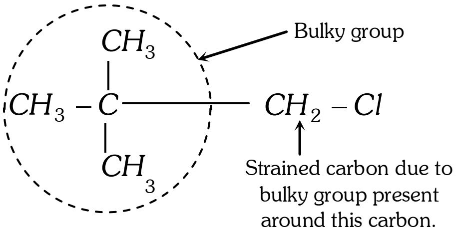
Steric effect.

On account of the presence of bulkier groups at the reaction centre, they cause mechanical interference and with the result that the attacking reagent finds it difficult to reach the reaction site and thus slows down the reaction. This phenomenon is called **steric hinderance or steric effect**.

(1) Tertiary alkyl halides having bulky groups form tertiary carbocation readily when hydrolysed because of the presence of the three bulky groups on the carbon having halogen.



(2) Primary alkyl halide having quaternary β-carbon does not form transition state because of the steric strain around α-carbon by the β-carbon. To release the strain it converts into carbocation.



(3) Steric strain inhibits the resonance. This phenomenon is known as **steric inhibitions of resonance**.

Intermolecular forces.

In an ionic compound, the structural units are ions. These ions are held together by very powerful electrostatic forces are known as inter ionic forces. On the other hand, in non-ionic (covalent) compounds, the structural units are molecules. These molecules are held together by very weak forces are known as **intermolecular forces or secondary forces**. Secondary forces are of the following types,

(1) Dipole – dipole forces. (2) Van der Waal's forces. (3) Hydrogen bond.

(1) Dipole – Dipole Forces : These forces exist between polar molecules which have permanent dipoles. The interactions of the **permanent dipole** in different molecules are called **dipole-dipole forces (DF).** Magnitude of DF depends on the dipole moment (μ) of the bond of the compound and intermolecular distance (d),

$DF \propto \mu \quad \propto \frac{1}{d^4}$ (i.e. these forces are effective only over short distance)

$$\text{Example} \xrightarrow[\text{d in increasing order, } \mu \text{ in decreasing order and DF also in decreasing order}]{CH_3-Cl,\ CH_3-Br,\ CH_3-I}$$

(2) Vander Waal's forces : These forces exist between non-polar molecules. The intermolecular electrostatic attractions between nuclei of one molecule and electrons of the other molecule are called **Vander Waal's forces (*VF*)**. Magnitude of *VF* depends on the number of electrons (e^-) and protons (p) in the molecule as well as on the intermolecular distance (d),

$VF \propto$ number of e^- and p; $\propto 1/d^7$; $\propto MW$; $\propto$ Surface area of the molecule and

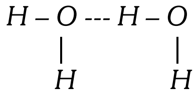
$\propto$ Symmetry of the molecule (symmetry of molecule decreases intermolecular distance (d)).

(3) Hydrogen bonding : An electrostatic attractive force between the covalently bonded hydrogen atom of one molecule and an electronegative atom (such as F, O, N) of the other molecule is known as **hydrogen bonding**.

Examples of H-bonding in between the two molecules of same or different compounds are

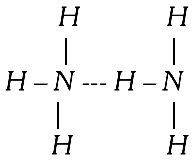
$H-F \cdots H-F$

Hydrogen fluoride (associated)



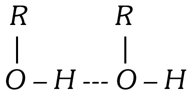
$$\underset{\displaystyle H}{\underset{|}{H-O}} \cdots \underset{\displaystyle H}{\underset{|}{H-O}}$$

Water (associated)



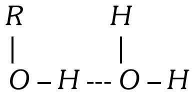
$$\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{H-N}} \cdots \underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{H-N}}$$

Ammonia (associated)



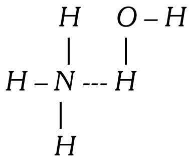
$$\overset{\overset{\displaystyle R}{|}}{O}-H \cdots \overset{\overset{\displaystyle R}{|}}{O}-H$$

Alcohol (associated)



$$\overset{\overset{\displaystyle R}{|}}{O}-H \cdots \overset{\overset{\displaystyle H}{|}}{O}-H$$

Alcohol and Water



$$\underset{\underset{\displaystyle H}{|}}{\overset{\overset{\displaystyle H}{|}}{H-N}} \cdots \overset{\overset{\displaystyle O-H}{|}}{H}$$

Ammonia and water

Nature and Importance of Hydrogen bonding

(i) Hydrogen bond is merely an electrostatic force rather than a chemical bond.

(ii) Hydrogen bond never involves more than two atoms.

(iii) Bond energy of hydrogen bond is in the range of 3 to 10 *kcal/mol* or 10 to 40 *kJ/mol*, i.e., about 1/10th the energy of a covalent bond.

(iv) With the increase of electronegativity of the atom to which hydrogen is covalently linked, the strength of the hydrogen bond increases.

(v) All the three atoms in $X-H\text{- - -}X$ lie in a straight line.

(vi) The bond length of hydrogen bond is of the order of 250 to 275 *pm*.

The relative order of these intermolecular forces is,

Hydrogen bonding > dipole-dipole forces > Vander waal's forces.

Mechanism of organic reactions.

When a chemical reaction takes place between two or more chemical species, new products are formed. This change is represented by a chemical equation. In a chemical equation, reactants are written on the left hand side while the products are written on the right hand side. The two are separated by an arrow (→). The reactants normally consists of two species,

(1) **Substrate :** The species, which is attacked by some other chemical species, is called a substrate.

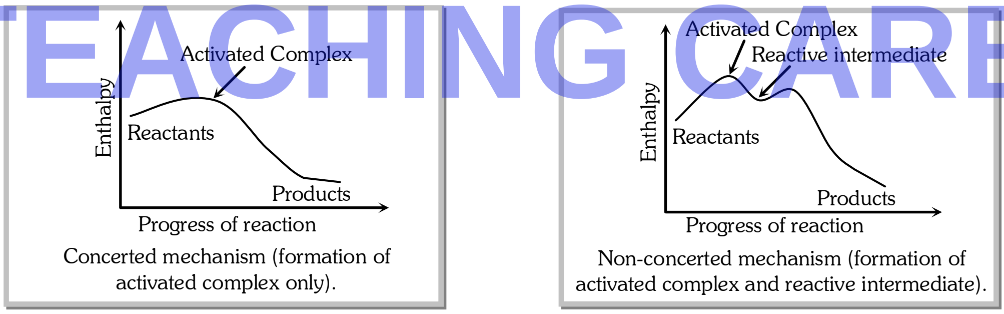
(2) **Reagent :** The species, which attacks the substrate in order to get the major product, is called a reagent. Thus, Substrate + Reagent → Products.

Normally, a substance and a chemical reagent form a highly energetic species, called **activated complex**, before it changes into the product. In certain cases, a relatively energetically more stable species than the activated complex may also be formed. It is called **reaction intermediate**. Thus, a chemical reaction, in general, may follow either of the following two paths,

Path I : Substrate + Reagent → Activated complex → Products

Path II : Substrate + Reagent → Activated complex → Intermediate → Products.

The detailed step by step description of a chemical reaction is called *mechanism of a reaction* which is only a hypothesis. If the reaction mechanism involves the breaking and making of bonds simultaneously without the formation of any intermediate, it is called **concerted mechanism**. On the other hand, if the reaction mechanism involve the formation of intermediates before the formation of products, it is called **non-concerted mechanism**.



Concerted mechanism (formation of activated complex only).

Non-concerted mechanism (formation of activated complex and reactive intermediate).

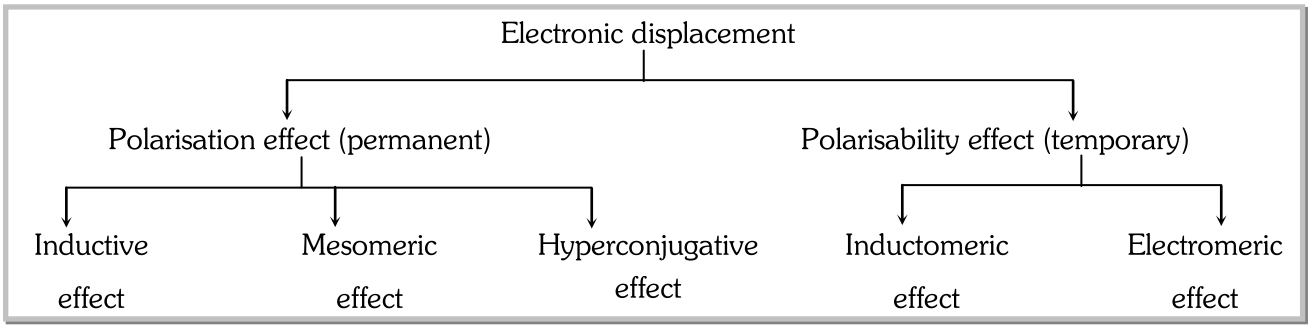
Enthalpy curves for concerted and Non-concerted mechanisms

To understand clearly the mechanism of various organic reactions, it is essential to have knowledge about the following concepts;

- Electronic displacements in covalent bonds,
- Cleavage (fission or breaking) of covalent bonds,
- Nature of attacking reagents.

Electronic displacement in covalent bonds.

It is observed that most of the attacking reagents always possess either a positive or a negative charge, therefore for a reaction to take place on the covalent bond the latter must possess oppositely charged centres. This is made possible by displacement (partial or complete) of the bonding electrons. The electronic displacement in turn may be due to certain effects, some of which are **permanent** and others are **temporary**. The former effects are permanently operating in the molecule and are known as **polarisation effects**, while the latter are brought into play by the attacking reagent and as soon as the attacking reagent is removed, the electronic displacement disappears; such effects are known as the **polarisability effects**.



Inductive effect or Transmission effect

(1) When an electron with drawing (X) or electron-releasing (Y) group is attached to a carbon chain, polarity is induced on the carbon atom and on the substituent attached to it. This permanent polarity is due to electron displacement due to difference in electronegativities. This is called *inductive effect or simply as I – effect.*

$$C-C-C-C \;\; Non\ polar$$

$$C^{\delta\delta\delta\delta^+}\longrightarrow C^{\delta\delta\delta^+}\longrightarrow C^{\delta\delta^+}\longrightarrow C^{\delta^+}\longrightarrow X^{\delta^-} \qquad C^{\delta\delta\delta\delta^-}\longleftarrow C^{\delta\delta\delta^-}\longleftarrow C^{\delta\delta^-}\longleftarrow C^{\delta^-}\longleftarrow Y^{\delta^+}$$

(2) Important features of Inductive effect

(i) It is a permanent effect in the molecule or ion.

(ii) It operates through σ bonds.

(iii) It is generally observed in saturated compounds.

(iv) The shared pair of electrons although permanently shifted towards more electronegative atom, yet remains in the same valence shell.

(v) As a result of electron shifting, the more electronegative end acquires partial negative charge and the other acquires partial positive charge.

(vi) The inductive effect is not confined to the polarization of one bond but is transmitted along a chain of carbon atoms through σ bonds. However, the effect is insignificant beyond second carbon in the chain.

(vii) Inductive effect brings changes in physical properties such as dipole moment, solubility, etc. It affects the rates of the reaction.

(viii) Carbon-hydrogen bond is taken as a standard of inductive effect. Zero effect is assumed for this bond. Atoms or groups which have a greater electron withdrawing capacity than hydrogen are said to have–I effect whereas atoms or groups which have a greater electron releasing power are said to have +I effect.

$$\underrightarrow{\overset{\oplus}{N}H_3 > NO_2 > CN > SO_3H > CHO > CO > COOH > COCl > COOR > CONH_2 > F > Cl > Br > I > OH > OR > NH_2 > C_6H_5 > H}$$

–I power of groups in decreasing order with respect to the reference H

$$\underrightarrow{\text{ter. alkyl} > \text{sec. alkyl} > \text{pri. alkyl} > CH_3 > H}$$

+ I power in decreasing order with respect to the reference H

+ I power ∝ number of carbon's in same type of alkyl groups

$$\underrightarrow{CH_3-CH_2-CH_2-CH_2- > CH_3-CH_2-CH_2- > CH_3-CH_2-}$$

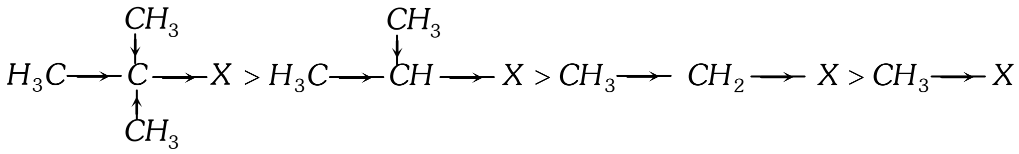
+ I power in decreasing order in same type of alkyl groups

(3) Application of Inductive effect

(i) ***Magnitude of positive or negative charge*** **:** Magnitude of +*ve* charge on cations and magnitude of –*ve* charge on anions can be compared by + I or – I groups present in it.

Magnitude of +*ve* charge $\propto \dfrac{1}{+I \text{ power of the group}}$	Magnitude of –*ve* charge $\propto \dfrac{1}{-I \text{ power of the group}}$
Magnitude of +*ve* charge ∝ –I power of the group	Magnitude of –*ve* charge ∝ + I power of the group

(ii) ***Reactivity of alkyl halide*** **:** + I effect of methyl group enhances – I effect of the halogen atom by repelling the electron towards tertiary carbon atom.



$$H_3C \rightarrow \underset{\overset{\uparrow}{CH_3}}{\overset{\overset{CH_3}{\downarrow}}{C}} \rightarrow X > H_3C \rightarrow \overset{\overset{CH_3}{\downarrow}}{CH} \rightarrow X > CH_3 \rightarrow CH_2 \rightarrow X > CH_3 \rightarrow X$$

Tertiary > Secondary > Primary > Methyl

(iii) ***Dipole moment*** **:** As the inductive effect increases, the dipole moment increases.

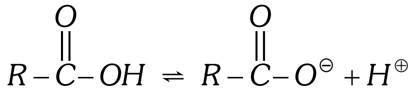
$CH_3 \rightarrow I$	$CH_3 \rightarrow Br$	$CH_3 \rightarrow Cl$
1.64 D	1.79 D	1.83 D

$\xrightarrow{\qquad\qquad\qquad\qquad}$

Inductive effect increases

(iv) ***Relative strength of the acids*** (Acidic nature of $-COOH$)

(a) An acid may be defined as a species that has the tendency to loose proton. Furthermore, the strength of an acid depends on the tendency to release proton when the acid is dissolved in water.



$$R-\overset{\overset{O}{\|}}{C}-OH \rightleftharpoons R-\overset{\overset{O}{\|}}{C}-O^{\ominus}+H^{\oplus}$$

(b) The relative strength of acids are measured in their ionisation constants (K_a or pK_a values).

$$\underset{\text{Acid}}{HA} \rightleftharpoons H^{\oplus}+A^{\ominus};\ K_a=\frac{[H^{\oplus}][A^{\ominus}]}{[HA]};\ pK_a=-\log K_a$$

Greater the value of K_a or lower the value of pK_a stronger will be the acid.

(c) Any group or atom showing +I effect decreases the acid strength as it increases the negative charge on the carboxylate ion which holds the hydrogen firmly. Alkyl groups have + I effect.

Thus, acidic nature is, $HCOOH > CH_3COOH > C_2H_5COOH > C_3H_7COOH > C_4H_9COOH$

$\xrightarrow{\qquad\qquad\qquad\qquad\qquad\qquad}$

(+ Inductive effect increases, so acid strength decreases)

Formic acid, having no alkyl group, is the most acidic among these acids.

(d) The group or atom having – I effect increases the strength as it decreases the negative charge on the carboxylate ion. Greater is the number of such atoms or groups (having – I effect), greater is the acid strength.

Thus, acidic nature is, $\underset{\substack{\text{Trichloro}\\\text{acetic acid}}}{CCl_3COOH} > \underset{\substack{\text{Dichloro}\\\text{acetic acid}}}{CHCl_2COOH} > \underset{\substack{\text{Monochloro}\\\text{acetic acid}}}{CH_2ClCOOH} > \underset{\text{Acetic acid}}{CH_3COOH}$

$\xleftarrow{\qquad\qquad\qquad\qquad\qquad\qquad}$

(– Inductive effect increases, so acid strength increases)

(e) Strength of aliphatic carboxylic acids and benzoic acid

$$\underset{+I\ \text{group}}{\underset{\uparrow}{R}} \rightarrow COOH \qquad \underset{-I\ \text{group}}{\underset{\uparrow}{C_6H_5}} \leftarrow COOH$$

Hence benzoic acid is stronger acid then aliphatic carboxylic acids but exception is formic acid. Thus,

$$\underrightarrow{HCOOH \qquad C_6H_5COOH \qquad RCOOH}$$

Acid strength in decreasing order

Note : ✹ Decreasing order of acids : $NO_2CH_2COOH > FCH_2COOH > ClCH_2COOH > BrCH_2COOH$.

$F_3C-COOH > Cl_3C-COOH > Br_3C-COOH > I_3C-COOH$.

(v) ***Acidity of alcohols*** **:** Acidity of alcohol depends on the stability of alkoxide ion (i.e., conjugate base of alcohol) which is obtained by the dissociation of alcohols.

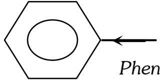
$$R-O-H \rightleftharpoons \underset{\text{Alkoxide ion}}{R-\overset{\ominus}{O}}+\overset{\oplus}{H}$$

Acid strength of alcohol $\propto$ stability of alkoxide ion

The decreasing order of acid strength of acid strength in alcohols is also due to +I effect of alkyl groups.

$$\underset{\text{Methyl alcohol}}{CH_3OH} > \underset{\text{Ethyl Alcohol}}{CH_3CH_2OH} > \underset{\text{Iso-propyl alcohol}}{(CH_3)_2CHOH} > \underset{\text{Tert-butyl alcohol}}{(CH_3)_3COH}$$

As compared to water, phenol is more acidic (–I effect) but methyl alcohol is less acidic (+I effect).



$$\underset{\text{Phenol}}{\leftarrow OH} > \underset{\text{Water}}{H-OH} > \underset{\text{Methyl alcohol}}{CH_3 \longrightarrow OH}$$

(vi) ***Relative strength of the bases*** (Basic nature of $-NH_2$)

(a) A base may be defined as a species which is capable of accepting a proton. Base strength is defined as the tendency to donate an electron pair for sharing.

(b) The relative strength of bases are measured in their ionisation constants (K_b or pK_b values).

$$\underset{\text{Base}}{BOH} \rightleftharpoons B^{\oplus}+OH^{\ominus}\ ;\ K_b=\frac{[B^{\oplus}][OH^{\ominus}]}{[BOH]}\ ;\ pK_b=-\log K_b$$

Greater the value of K_b or lower the value of pK_b stronger will be the base.

(c) The difference in base strength in various amines can be explained on the basis of inductive effect. The +I effect increases the electron density while –I effect decreases. The amines are stronger bases than NH_3 as the alkyl groups increase electron density on nitrogen due to + I effect while $ClNH_2$ is less basic due to –I effect. "So more is the tendency to donate electron pair for coordination with proton, the more is basic nature, i.e., more is the negative charge on nitrogen atom (due to +I effect of alkyl group), the more is basic nature".

Thus, the basic nature decreases in the order; $\underset{\text{Diethyl amine}}{(C_2H_5)_2NH} > \underset{\text{Ethyl amine}}{CH_3CH_2NH_2} > \underset{\text{Methyl amine}}{CH_3NH_2} > \underset{\text{Ammonia}}{NH_3} > \underset{\text{Chloro amine}}{ClNH_2}$

The order of basicity is as given below;

Alkyl groups (R–)	**Relative base strength**
CH_3	$R_2NH > RNH_2 > R_3N > NH_3$
C_2H_5	$R_2NH > RNH_2 > NH_3 > R_3N$
$(CH_3)_2CH$	$RNH_2 > NH_3 > R_2NH > R_3N$
$(CH_3)_3C$	$NH_3 > RNH_2 > R_2NH > R_3N$

Note : ✹ The relative basic character of amines is not in total accordance with inductive effect $(t > s > p)$ but it is in the following order: Secondary > Primary > Tertiary. The reason is believed to be steric factor.

✹In gas phase or in non aqueous solvents such as chlorobenzene etc, the solvation effect, i.e., the stabilization of the conjugate acid due to H-bonding are absent and hence in these media the basicity of amines depends only on the +I effect of the alkyle group thus the basicity of amines follows the order : $3^o > 2^o > 1^o > NH_3$.

(d) As compared to ammonia, methylamine is more basic (+I effect) but aniline is less basic and diphenylamine is still more weaker (– I effect).

$$CH_3NH_2 > NH_3 > C_6H_5NH_2 > (C_6H_5)_2NH$$

(vii) ***Basicity of alcohols*** : The decreasing order of base strength in alcohols is due to +I effect of alkyl groups.

$$\underset{(3^o)}{(CH_3)_3COH} > \underset{(2^o)}{(CH_3)_2CHOH} > \underset{(1^o)}{CH_3CH_2OH} > \underset{methyl\,/\,alcohol}{CH_3OH}$$

In Lucas test of making distinction between three types $(1^o, 2^o$ and $3^o)$ of monohydric alcohols,

$$\left[\underset{(Base)}{R-OH} + \underset{(Acid)}{HCl(conc.)} \xrightarrow{anhyd.\,ZnCl_2} \underset{(White\ ppt.)}{R-Cl} + H_2O\right]$$

The basic character of alcohols is in the order, benzyl $> 3^o > 2^o > 1^o$ and hence, the strongest base (3^o) will be reacting fastest with conc. HCl in presence of anhydrous $ZnCl_2$ (Lucas reagent) and gives white turbidity immediately.

(viii) ***Stability of carbonium ion*** :+I effect tends to decrease the $(+ve)$ charge and –I effect tends to increases the $+ve$ charge on carbocation.

$$(CH_3)_3C^{\oplus} > (CH_3)_2CH^{\oplus} > CH_3CH_2^{\oplus} > CH_3^{\oplus}$$

(ix) **Stability of carbanion :** Stability of carbanion increases with increasing – I effect.

$$CH_3^{\ominus} > CH_3CH_2^{\ominus} > (CH_3)_2CH^{\ominus} > (CH_3)_3C^{\ominus}$$

Resonance effect or mesomeric effect

(1) The effect in which π electrons are transferred from a multiple bond to an atom, or from a multiple bond to a single covalent bond or lone pair (s) of electrons from an atom to the adjcent single covalent bond is called *mesomeric effect* or simply as *M-effect*. In case the compound in question is having conjugated system of double bonds, the mesomeric effect is transmitted through whole of the conjugated system and thus the effect may better be known as **conjugative effect**.

(2) Important features of mesomeric effect

(i) It is a permanent effect present in the molecule in the ground state.

(ii) It is operative in unsaturated compounds especially having conjugated systems.

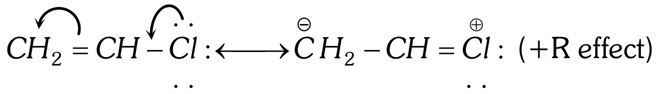
(iii) It involves electrons of π-bonds or lone pair of electrons. This effect operates through conjugative mechanism.

(iv) In this effect the electron pair is completely transferred and thus full positive and negative charges are developes.

(v) It affects the physical properties such as dipole moment, solubility etc. Rate of reaction fo the substance is also affected.

(vi) Groups which have the capacity to increase the electron density of the rest of the molecule are said to have $+M$ effect. Such groups possess lone pairs of electrons. Groups which decrease the electron density of the rest of the molecule by withdrawing electron pairs are said to have $-M$ effect, e.g.,

(a) The groups which donate electrons to the double bond or to a conjugated system are said to have $+M$ *effect or* $+R$ *effect.*

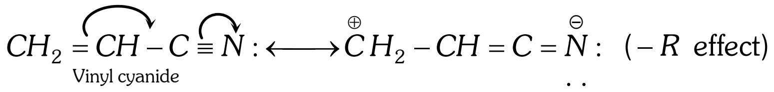


$$\underset{\text{Vinyl chloride}}{CH_2=CH-\ddot{\underset{\cdot\cdot}{Cl}}:}\longleftrightarrow \overset{\ominus}{C}H_2-CH=\overset{\oplus}{\underset{\cdot\cdot}{Cl}}:\ (+\text{R effect})$$

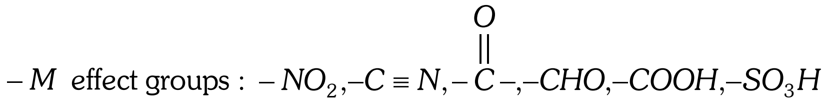
In vinyl chloride $C-Cl$ bond has double bond character due to resonance.

$+M$ *effect groups* : $-Cl,-Br,-I,-\ddot{N}H_2,-NR_2,-OH,-OR,-SH,-OCH_3,-\ddot{\underset{\cdot\cdot}{S}}R$

(b) The groups which withdraw electrons form the double bond or from a conjugated system towards itself due to resonance are said to have $-M$ effect or $-R$ effect.

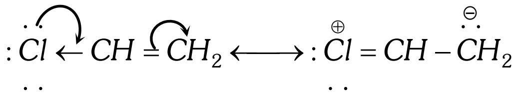


$$\underset{\text{Vinyl cyanide}}{CH_2=CH-C\equiv N:}\longleftrightarrow \overset{\oplus}{C}H_2-CH=C=\overset{\ominus}{\underset{\cdot\cdot}{N}}:\ (-R\text{ effect})$$



$$-M\text{ effect groups}:\ -NO_2,-C\equiv N,-\overset{\overset{O}{\|}}{C}-,-CHO,-COOH,-SO_3H$$

(vii) The inductive and mesomeric effects, when present together, may act in the same direction or oppose each other. The mesomeric effect is more powerful than the former. For example, in vinyl chloride due to – I effect the chlorine atom should develop a negative charge but on account of mesomeric effect it has positive charge.



$$:\ddot{\underset{\cdot\cdot}{Cl}}\leftarrow CH=CH_2\longleftrightarrow :\overset{\oplus}{\underset{\cdot\cdot}{Cl}}=CH-\overset{\ominus}{\ddot{C}}H_2$$

(3) Application of mesomeric effect : It explains,

(i) Low reactivity of aryl and vinyl halides,

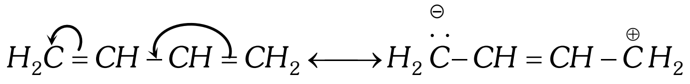
(ii) The acidic nature of carboxylic acids,

(iii) Basic character comparison of ethylamine and aniline,

(iv) The stability of some free radicals, carbocations and carbanions.

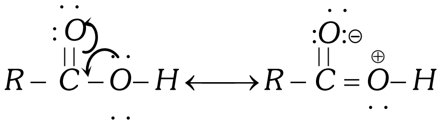
(4) **Difference between Resonance and Mesomerism :** Although both resonance and mesomerism represent the same phenomenon, they differ in the following respect : Resonance involves all types of electron displacements while mesomerism is noticeable only in those cases where a multiple bond is in conjugation with a multiple bond or electron pair.

Example : (i)



$$H_2C=CH-CH=CH_2 \longleftrightarrow H_2\overset{\ominus}{\ddot{C}}-CH=CH-\overset{\oplus}{C}H_2$$

(ii)



$$R-\overset{\overset{..}{:O}}{\overset{||}{C}}-\underset{..}{\dot{O}}-H \longleftrightarrow R-\overset{:\overset{..}{O}:^{\ominus}}{\overset{|}{C}}=\underset{..}{\overset{\oplus}{O}}-H$$

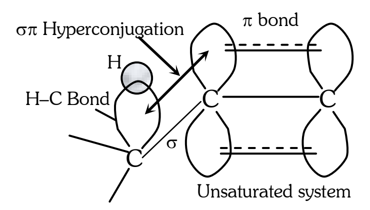
Both (i) and (ii) are the examples of mesomerism and resonance effect. Let us consider the following example $H \longrightarrow \underset{..}{\overset{..}{Cl}}: \longleftrightarrow \overset{\oplus}{H}\overset{\ominus}{Cl}$. Such an electron displacement is the example of resonance only (not the mesomerism).

Hyperconjugative effect

(1) When a $H-C$ bond is attached to an unsaturated system such as double bond or a benzene ring, the sigma (σ) electrons of the $H-C$ bond interact or enter into conjugation with the unsaturated system. *The interactions between the electrons of π systems (multiple bonds) and the adjacent σ bonds (single $H-C$ bonds) of the substituent groups in organic compounds is called hyperconjugation*. The concept of hyperconjugation was developed by Baker and Nathan and is also known as *Baker and Nathan effect*.

In fact hyperconjugation effect is similar to resonance effect. Since there is no bond between the α-carbon atom and one of the hydrogen atoms, the hyperconjugation is also called *no-bond resonance*.

(2) **Orbital concept of hyperconjugation** : The orbital concept of hyperconjugation may be explained with the help of propene. In this, the electron pair of $C-H$ bond (σ-bond) is involved in conjugation with the π-electron pair of the double bond. Therefore, hyperconjugation involves delocalisation of σ-electrons of $H-C$ bond through overlapping of p-orbitals of double bond as shown in figure.



Orbital representation of σ-π hyperconjugation

(3) **Structural requirement for hyperconjugation**

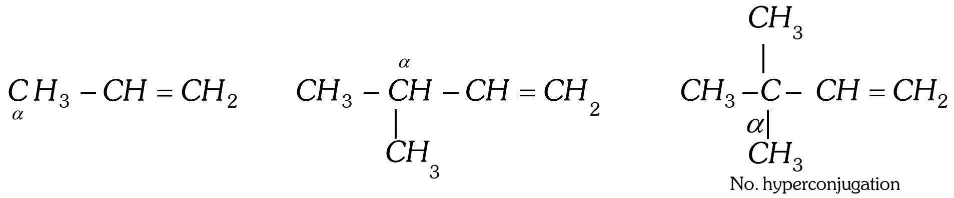
(i) Compound should have at least one sp^2-hybrid carbon of either alkene alkyl carbocation or alkyl free radical.

(ii) α-carbon with respect to sp^2 hybrid carbon should have at least one hydrogen.

If both these conditions are fulfilled then hyperconjugation will take place in the molecule.

(iii) Hyperconjugation is of three types

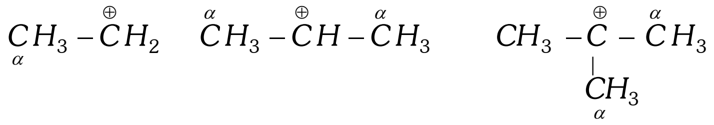
(a) σ *(C – H),* π *conjugation* : This type of conjugation occurs in alkenes.



$$\underset{\alpha}{C}H_3-CH=CH_2 \qquad CH_3-\underset{\underset{CH_3}{|}}{\overset{\alpha}{CH}}-CH=CH_2 \qquad CH_3-\underset{\underset{CH_3}{\alpha|}}{\overset{\overset{CH_3}{|}}{C}}-CH=CH_2$$

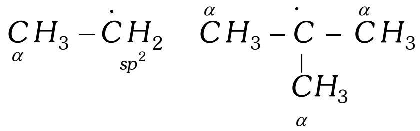
No. hyperconjugation

(b) σ (*C* – *H*), *positive charge conjugation* : This type of conjugation occurs in alkyl carbocations.



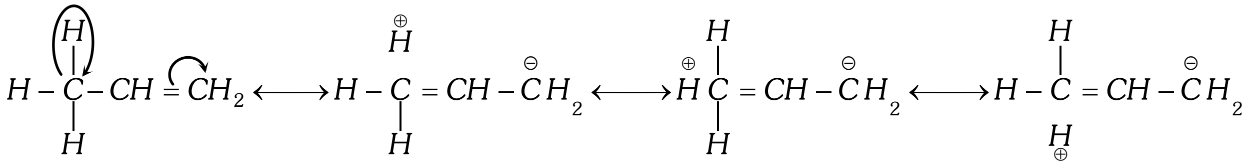
$$\underset{\alpha}{C}H_3-\overset{\oplus}{C}H_2 \qquad \overset{\alpha}{C}H_3-\overset{\oplus}{C}H-\overset{\alpha}{C}H_3 \qquad CH_3-\underset{\underset{\alpha}{CH_3}}{\overset{\oplus}{C}}-\overset{\alpha}{C}H_3$$

(c) σ (*C* – *H*), *odd electron conjugation* : This type of conjugation occurs in alkyl free radicals.



$$\underset{\alpha}{C}H_3-\underset{sp^2}{\overset{\cdot}{C}}H_2 \qquad \overset{\alpha}{C}H_3-\underset{\underset{\alpha}{CH_3}}{\overset{\cdot}{C}}-\overset{\alpha}{C}H_3$$

(iv) Resonating structures due to hyperconjugation may be written involving "*no bond*" between the alpha carbon and hydrogen atoms.



$$H-\underset{H}{\overset{H}{C}}-CH=CH_2 \longleftrightarrow H-\underset{H}{\overset{\overset{\oplus}{H}}{C}}=CH-\overset{\ominus}{C}H_2 \longleftrightarrow \overset{\oplus}{H}\,\underset{H}{\overset{H}{C}}=CH-\overset{\ominus}{C}H_2 \longleftrightarrow H-\underset{\underset{\oplus}{H}}{\overset{H}{C}}=CH-\overset{\ominus}{C}H_2$$

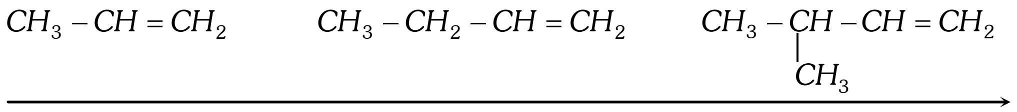
(v) Number of resonating structures due to the hyperconjugation = Number of α -hydrogens + 1.

Structure	***Number of α-hydrogens***	***Number of resonating structures***
$CH_3-CH=CH_2$	**3**	**4**
$CH_3-CH_2-CH=CH_2$	**2**	**3**
$CH_3-CH=CH-CH_3$	**6**	**7**
$CH_3-\overset{\oplus}{C}H_2$	**3**	**4**
$CH_3-\overset{\oplus}{C}-CH_3$	**6**	**7**
$CH_3-\underset{CH_3}{\overset{\oplus}{C}}-CH_3$	**9**	**10**

(4) Applications of hyperconjugation

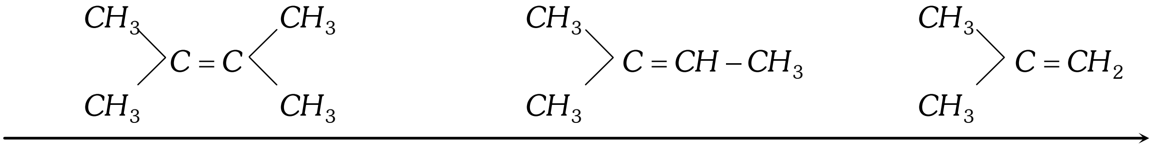
(i) ***Stability of alkenes*** **:** Hyperconjugation explains the stability of certain alkenes over other alkenes.

Stability of alkenes ∝ Number of alpha hydrogens ∝ Number of resonating structures



$$CH_3-CH=CH_2 \qquad CH_3-CH_2-CH=CH_2 \qquad CH_3-\underset{CH_3}{CH}-CH=CH_2$$

Stability in decreasing order



Number of alpha hydrogens in decreasing order

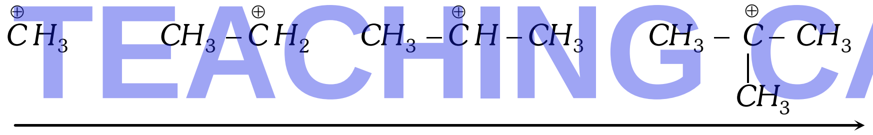
stability of alkenes in decreasing order

(ii) ***Carbon-carbon double bond length in alkenes*** **:** As we know that the more is the number of resonating structures, the more will be single bond character in carbon-carbon double bond.

Thus, bond length between carbon double bond ∝ number of resonating structures. Examples,

Structure	***Number of α-hydrogens***	***Number of resonating structures***	***Carbon-carbon double bond length in Å***
$CH_2=CH_2$	**Zero**	**Zero**	**1.34 Å**
$CH_3-CH=CH_2$	**3**	**4**	**1.39 Å**
$CH_3-CH_2-CH=CH_2$	**2**	**3**	**1.37 Å**
$CH_3-\underset{CH_3}{\underset{\vert}{CH}}-CH=CH_2$	**1**	**2**	**1.35 Å**
$CH_3-\underset{CH_3}{\underset{\vert}{\overset{CH_3}{\overset{\vert}{C}}}}-CH=CH_2$	**Zero**	**Zero**	**1.34 Å**

(ii) ***Stability of alkyl carbocations*** **:** Stability of alkyl carbocations ∝ number of resonating structures ∝ number of resonating structures ∝ number of alpha hydrogens.



$$\overset{\oplus}{C}H_3 \qquad CH_3-\overset{\oplus}{C}H_2 \qquad CH_3-\overset{\oplus}{C}H-CH_3 \qquad CH_3-\underset{CH_3}{\underset{\vert}{\overset{\oplus}{C}}}-CH_3$$

Number of α-hydrogens in increasing order

Stability in increasing order

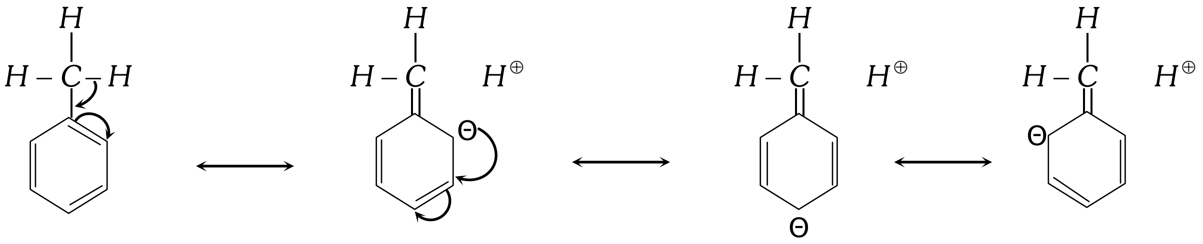
(iv) ***Stability of alkyl free radicals*** : Stability of alkyl free radicals can be explained by hyperconjugation. Stability depends on the number of resonating structures.

Structure	$\dot{C}H_3$	$CH_3-\dot{C}H_2$	$CH_3-\dot{C}H-CH_3$	$CH_3-\underset{CH_3}{\underset{\vert}{\dot{C}}}-CH_3$
No. of resonating structures	0	4	7	10

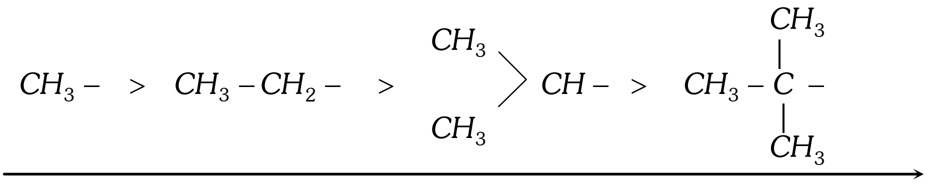
Number of resonating structures in increasing order

Stability is in increasing order

(v) ***Electron releasing (or donating) power of R in alkyl benzene*** **:** CH_3-(or alkyl group) is $+R$ group, ortho-para directing group and activating group for electrophilic aromatic substitution reaction because of the hyperconjugation.



The electron donating power of alkyl group will depends on the number of resonating structures, this depends on the number of hydrogens present on α-carbon. The electron releasing power of some groups are as follows,



$$CH_3- \; > \; CH_3-CH_2- \; > \; (CH_3)_2CH- \; > \; CH_3-\overset{CH_3}{\underset{CH_3}{C}}-$$

Increasing inductive effect
Electron donating power in decreasing order due to the hyperconjugation.

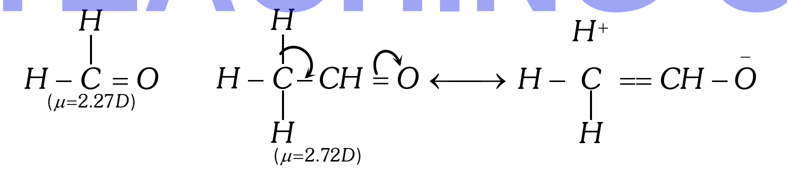
(vi) ***Heat of hydrogenation*** **:** It is the heat *evolved/mol* in the addition of hydrogen to form a saturated hydrocarbon.

$\rangle C=C\langle + H_2 \longrightarrow \rangle CH-CH\langle + E(kcal)$ where E is the heat of hydrogenation.

Lesser the heat of hydrogenation, lesser is the internal energy and more is stability of the system. Hyperconjugation decreases the heat of hydrogenation. For ethylene it is 32.8 *kcal/mol* and for propylene, 30.1 *kcal/mol* respectively.

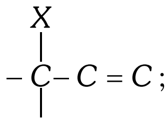
(vii) ***Dipole moment*** **:** Since hyperconjugation causes the development of charges, it also affects the dipole moment in the molecule.

The increase in dipole moment, when hydrogen of formaldehyde $(\mu = 2.27D)$ is replaced by methyl group, *i.e.*, acetaldehyde $(\mu = 2.72D)$ can be referred to hyperconjugation, which leads to development of charges.



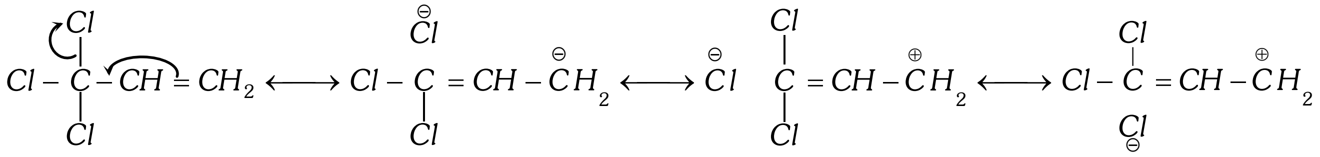
(viii) ***Orienting influence of alkyl group in*** o, p***-positions and of*** $-CCl_3$ ***group in*** m***-position*** **:** Ortho-para directing property of methyl group in toluene is partly due to $+I$ effect and partly due to hyperconjugation.

(5) **Reverse Hyperconjugation :** The phenomenon of hyperconjugation is also observed in the system given below,

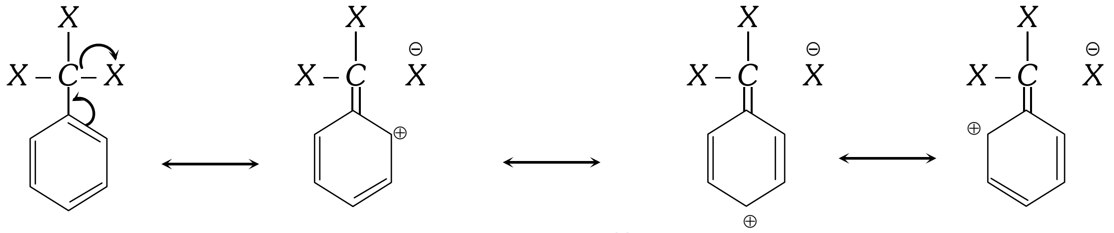


$-\overset{X}{\underset{|}{C}}-C=C$; where $X =$ halogen

In such system the effect operates in the reverse direction. Hence the hyperconjugation in such system is known as reverse hyperconjugation.



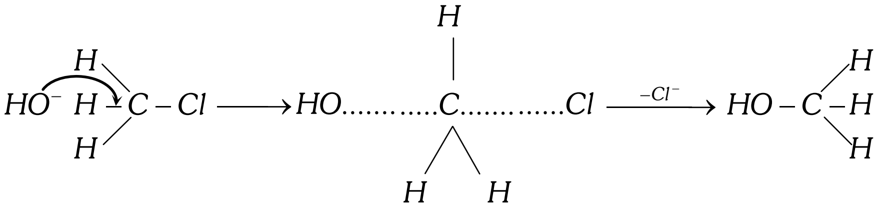
The *meta* directing influence and dectivating effect of CX_3 group for electrophilic aromatic substitution reaction can be explained by this effect.



Inductomeric effect

Inductomeric effect is the temporary effect which enhance the inductive effect and it accounts only in the presence of an attacking reagent.

Example,



In methyl chloride the –I effect of Cl group is further increased temporarily by approach of hydroxyl ion.

Electromeric effect

(1) The phenomenon of movement of electrons from one atom to another in multibonded atoms at the demand of attacking reagent is called electromeric effect. It is denoted as E-effect and represented by a curved arrow ($\curvearrowright$) showing the shifting of electron pair.

$$A\overset{\frown}{=}B \xrightarrow[\text{Reagent}]{E} \overset{\oplus}{A}-\overset{\ominus}{B}:$$

(2) Important features of electromeric effect

(i) It is a temporary effect

(ii) It is brought into play instantaneously at the demand of the attacking reagent. However as soon as the attacking reagent is removed, original electronic condition is restored.

$$>C^{\delta^+}=O^{\delta^-} \xrightarrow[\text{reagent}]{\text{attacking}} >\overset{\oplus}{C}-\overset{\ominus}{O} \xrightarrow[\text{reagent removed}]{\text{attacking}} >C^{\delta^+}=O^{\delta^-}$$

(iii) The electromeric effect is of common occurrence during addition of polar reagents on $C=C$, $C=O$ and $C\equiv N$ bonds etc.

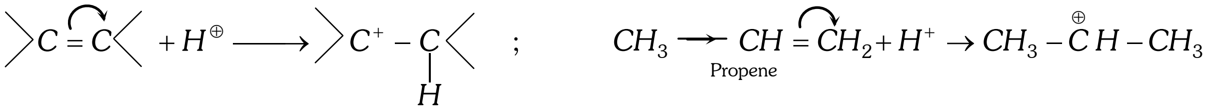
(iv) The effect involves the complete transference of π electrons.

(v) In this effect the displaced electrons leave their orbitals and take a new position.

(vi) In this there is complete charge separation and ions are formed.

(vii) There are two types of electromeric effects, i.e., $+E$ *effect or* $-E$ *effect.*

(a) When the transfer of electrons take place towards the attacking reagent, the effect is called $+E$ effect. The addition of acids to alkenes.

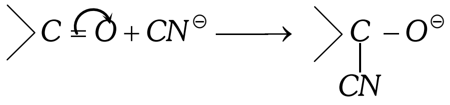


$$>C\overset{\frown}{=}C< + H^{\oplus} \longrightarrow >C^{+}-\underset{\displaystyle H}{\underset{|}{C}}< \quad ; \qquad \underset{\text{Propene}}{CH_3 \rightarrow CH\overset{\frown}{=}CH_2} + H^{+} \rightarrow CH_3-\overset{\oplus}{C}H-CH_3$$

Since, $-CH_3$ group is electron repelling, the electrons are transferred in the direction shown.

The attacking reagent is attached to that atom on which electrons have been transferred.

(b) When the transfer of electrons takes place away from the attacking reagent, the effect is called $-E$ effect. Example, The addition of cyanide ion to carbonyl compounds.

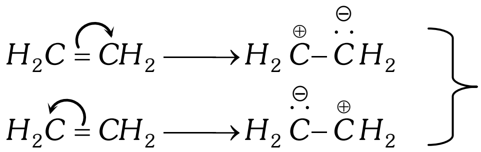


$$>C=O+CN^{\ominus}\longrightarrow\ >\underset{\underset{\displaystyle CN}{|}}{C}-O^{\ominus}$$

The attacking reagent does not attached to that atom on which electrons have been transferred.

(3) Direction of the shift of electron pair : The direction of the shift of electron pair can be decided on the basis of following points.

(i) When the groups linked to a multiple bond are similar, the shift can occur to either direction. For example, in ethylene the shift can occur to any one of the carbon atoms.

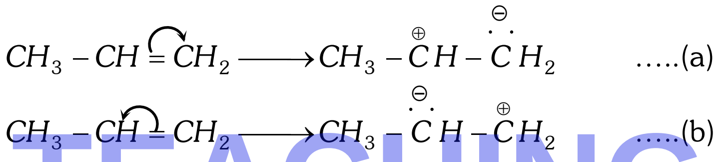


$$H_2C=CH_2\longrightarrow H_2\overset{\oplus}{C}-\overset{\ominus}{\ddot{C}}H_2$$

$$H_2C=CH_2\longrightarrow H_2\overset{\ominus}{\ddot{C}}-\overset{\oplus}{C}H_2$$

Both are similar

(ii) When the dissimilar groups are linked on the two ends of the double bond, the shift is decided by the direction of inductive effect. For example, in propylene the shift can be shown in the following ways,

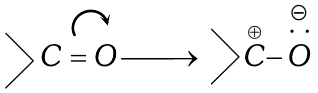


$$CH_3-CH=CH_2\longrightarrow CH_3-\overset{\oplus}{C}H-\overset{\ominus}{\ddot{C}}H_2 \quad .....(a)$$

$$CH_3-CH=CH_2\longrightarrow CH_3-\overset{\ominus}{\ddot{C}}H-\overset{\oplus}{C}H_2 \quad .....(b)$$

Due to electron repelling nature of methyl group, the electronic shift occurs according to Eq. (a) way and not by Eq. (b) way.

In the case of carbonyl group, the shift is always towards oxygen, *i.e.*, more electronegative atom.



$$>C=O\longrightarrow\ >\overset{\oplus}{C}-\overset{\ominus}{\ddot{O}}$$

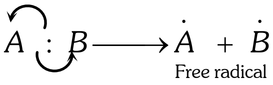
Note: ✹ In cases where inductive effect and electromeric effect simultaneously operate, usually electrometric effect predominates.

Cleavage (fission or breaking) of covalent bonds.

Breaking of covalent bond of the compound is known as **bond fission**. A bond can be broken by two ways,

(1) Homolytic bond fission or Homolysis

(i) In homolysis, the covalent bond is broken in such a way that each resulting species gets its own electron. This leads to the formation of odd electron species known as **free radical**.



$$A:B\longrightarrow \dot{A}+\dot{B}$$

Free radical

(ii) The factor which favours homolysis is zero or a small difference in electronegativity between A and B.

(iii) Homolysis takes place in gaseous phase or in the presence of non polar solvents (CCl_4, CS_2), peroxide, UV light, heat $(\geq 500^{\circ}C)$, electricity and free radical.

(iv) Mechanism of the reaction in which homolysis takes place is known as homolytic mechanism or free radical mechanism.

(2) Heterolytic bond fission or heterolysis

(i) In heterolysis, the covalent bond is broken in such a way that one species (i.e., less electronegative) is deprived of its own electron, while the other species gains both the electrons.

$$\overset{\curvearrowleft}{A : B} \longrightarrow \underset{\text{carbanion}}{\overset{\ominus}{A}:} + \underset{\text{carbocation}}{\overset{\oplus}{B}}$$

Thus formation of opposite charged species takes place. In case of organic compounds, if positive charge is present on the carbon then cation is termed as **carbocation**. If negative charge is present on the carbon then anion is termed as **carbonion**.

(ii) The factor which favours heterolysis is a greater difference of electronegativity between A and B.

(iii) Mechanism of the reaction in which heterolysis takes place is known as heterolytic mechanism or ionic mechanism.

(iv) The energy required for heterolysis is always greater than that for homolysis due to electrostatic force of attraction between ions.

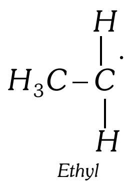
Reaction Intermediates.

Short lived fragments called reaction intermediates result from homolytic and heterolytic bond fission. The important reaction intermediates are free radicals, carbocations, carbonions, carbenes, benzyne and nitrenes.

Free radicals

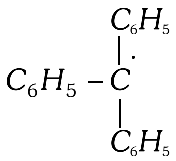
A free radical may be defined as an atom or group of atoms having an odd or unpired electron. These result on account of homolytic fission of a covalent bond and are denoted by putting a dot (.) against the symbol of atom or group of atoms.

$\underset{\text{Chlorine free radical}}{\dot{Cl}}$; $\underset{\text{Hydrogen free radical}}{\dot{H}}$; $\underset{\text{Methyl free radical}}{H_3\dot{C}}$;



$H_3C-\dot{C}H_2$ (with H above and below C)

Ethyl free radical



$(C_6H_5)_3\dot{C}$

Triphenyl methyl radical

The first stable organic free radical was triphenyl methyl radical and it was prepared by **Gomberg**.

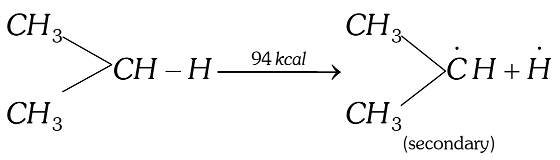
(1) Characteristics of free radical.

(i) The formation of free radical is initiated by heat, light or catalysts.

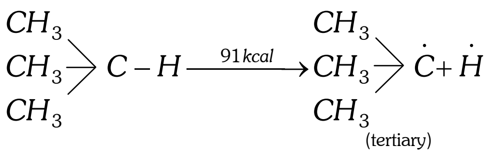
(a) $Cl : Cl \xrightarrow[\text{sunlight}]{\text{Energy}} \dot{Cl} + \dot{Cl}$

(b) $H_3C : H \xrightarrow{102\,kcal} H_3\dot{C} + \dot{H}$

(c) $H_3C-CH_2-H \xrightarrow{97\,kcal} \underset{\text{(primary)}}{H_3C-\dot{C}H_2} + \dot{H}$

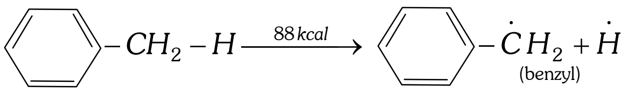
(d) 

$$(CH_3)_2CH-H \xrightarrow{94\,kcal} \underset{\text{(secondary)}}{(CH_3)_2\dot{C}H} + \dot{H}$$

(e) 

$$(CH_3)_3C-H \xrightarrow{91\,kcal} \underset{\text{(tertiary)}}{(CH_3)_3\dot{C}} + \dot{H}$$

(f) $CH_2=CH-CH_2-H \xrightarrow{86\,kcal} \underset{\text{(allyl)}}{CH_2=CH-\dot{C}H_2} + \dot{H}$

(g) 

(h) $CH_3-NH_2 \xrightarrow{heat\,/\,light} \dot{C}H_3+\dot{N}H_2$

(ii) Free radicals are generally electrically neutral.

(iii) There are seven electrons in the out most orbit of carbon of carbon free radicals.

(iv) Owing to the presence of an odd electron; a carbon radical is paramagnetic in nature. Due to this reason free radicals are highly reactive.

(v) Free radicals are neutral electrophiles.

(vi) Chemical reactions which takes place with the formation of free radical as an intermediate are known as free radical reactions. These reactions takes place in three steps,

(a) Initiation (b) Propagation and (c) Termination

Each of these steps, in turn, may involve two or more steps.

(a) *Initiation step* **:** In this step, homolytic bond fission takes place in the presence of initiator, *i.e.*, peroxide, $h\upsilon$, heat etc. The process is always endothermic.

$$Cl-Cl \xrightarrow[\Delta]{h\upsilon\ or} \dot{C}l+\dot{C}l \quad \Delta H=+ve$$

(b) *Propagation step* **:** Propagation step is always two or more than two step process and **all propagation steps should be exothermic, otherwise free radical reactions would not take place**.

***Propagation step I* :** In this step, formation of free radical as reaction intermediate takes place. For example,

$$CH_3-H+\dot{C}l \longrightarrow \dot{C}H_3+HCl \qquad \Delta H= \text{negative}$$

***Propagation step II* :** Reaction intermediate reacts with reagent to give the product.

$$\dot{C}H_3+Cl-Cl \longrightarrow CH_3-Cl+\dot{C}l \qquad \Delta H= \text{negative}$$

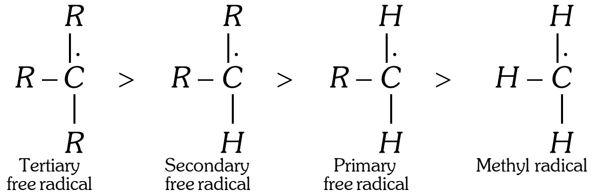
(c) *Termination step* **:** In this step, free radical formed in the last propagation step (generally propagation step II) is destroyed by the addition of free radical or by the addition of some impurities like $CHCl_3$ or CCl_4.

$$\dot{C}l+\dot{C}l \longrightarrow Cl_2$$

Reaction velocity of free radical reaction is very-very high.

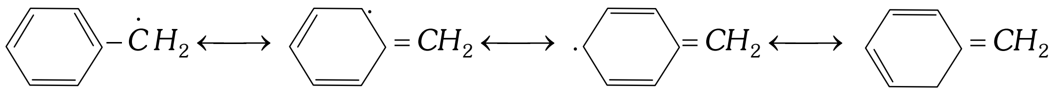
Note:✹Certain compounds, known as inhibitor, retar velocity of free radical reactions. Common inhibitors are O_2, I_2, *p*-benzoquinone and diphenylamine.

(2) Relative stabilities of free radicals : The tertiary alkyl free radicals are most stable and methyl free radial is least stable, *i.e.*, the free radical formed easily has greater stability.



$$R_3\dot{C} > R_2\dot{C}H > R\dot{C}H_2 > \dot{C}H_3$$

Benzyl and allyl free radicals are resonance stabilized hence are more stable than alkyl free radicals.



Benzyl free radical

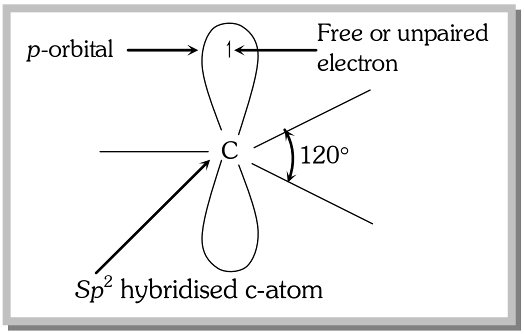
$$CH_2 = CH - \dot{C}H_2 \longleftrightarrow \dot{C}H_2 - CH = CH_2 \text{ (Allyl)}$$

Relative stability of free radicals are : Benzyl > allyl > 3^o > $2^o > 1^o$ > methyl, vinyl

The stability of various free radicals can be compared from their bond dissociation energies (the energy required for the homolytic cleavage of the covalent bond in the molecule to form two radicals). In general, the smaller the amount of energy required for bond breaking, the more stable is the radical.

(3) Structure of alkyl free radicals : The carbon atom of alkyl free radicals which is bonded to only three atoms or groups of atoms is sp^2 hybridized. Thus, free radicals have a planar structure with odd electron situated in the unused p-orbital at right angles to the plane of hybrid orbitals.

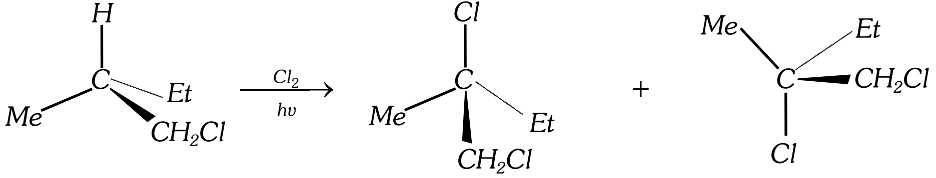
However, in the substituted alkyl radicals the 's' character of these orbitals has been found to increase, thus, tending to the pyramidal shape.



$\dot{C}H_3 < \dot{C}H_2F < \dot{C}HF_2 < \dot{C}F_3$.

So, CF_3 is essentially pyramidal in shape.

(4) Stereochemistry of free radicals : To learn about the stereochemistry of free radical reaction. We choose the reaction, chlorination of 1-chloro-2-methyl butane. The reaction products are,



If we review the insight of the reaction, it is clear that the reaction involves racemization at the reaction centre. The free radical should have the sp^2 hybridisation. Obviously a Cl_2 molecule could attack either the upper or lower lobe of the p-orbital with equal chances, leading to racemic mixture.

$$\text{Intermediate} \xrightarrow{Cl_2} \underset{(50\%)}{d-\text{form}} + \underset{(50\%)}{l-\text{form}}$$

(5) Reactions involving free radicals,

(i) Chlorination of alkanes

(ii) Pyrolysis of alkanes

(iii) Wurtz reaction

(iv) Anti-markownikoff rule

(v) Kolbe electrolytic synthesis

(vi) Polymerisation initiated by free radical.

Carbonium ions (carbocations)

Carbocation is defined as a group of atoms which contain positively charged carbon having only six electrons. It is obtained by heterolytic fission of a covalent bond involving carbon atom. It is denoted by putting a positive charge (+) against the symbol of group of atoms.

$$\underbrace{\underset{\text{Methyl carbonium ion}}{CH_3^{\oplus}} \qquad \underset{\text{Ethyl carbonium ion}}{C_2H_5^{\oplus}}}_{\text{Primary}} \qquad \underbrace{\underset{\text{Isopropyl carbonium ion}}{(CH_3)_2CH^{\oplus}}}_{\text{Secondary}} \qquad \underbrace{\underset{\text{Tert. Butyl carbonium ion}}{(CH_3)_3C^{\oplus}}}_{\text{Tertiary}}$$

(1) Characteristics of carbocations

(i) The formation of carbocations can be done,

(a) By heterolysis of halogen compounds : $(CH_3)_3-C-Cl \longrightarrow (CH_3)_3\overset{\oplus}{C}+\overset{\ominus}{Cl}$

(b) *By protonation of alkenes or alcohols* : $CH_2=CH_2 \overset{H^{\oplus}}{\rightleftharpoons} \overset{\oplus}{C}H_2-CH_3$

$$R-O-H \overset{H^{\oplus}}{\rightleftharpoons} R-\overset{\oplus}{O}H_2 \overset{-H_2O}{\rightleftharpoons} R^{+}+H_2O$$

(c) *By decomposition of Diazo compounds* **:** $C_6H_5-N_2-Cl \xrightarrow{-Cl} C_6H_5\overset{\oplus}{N}_2 \xrightarrow{-N_2} \overset{\oplus}{C}_6H_5+N_2$

(ii) Carbocations are not electrically neutral.

(iii) There are six electrons in the out most orbit of carbon of carbocation i.e., 2 electrons less than octet.

(iv) A carbocation is diamagnetic in nature due to all paired electrons.

(v) Carbocations are charged electrophiles i.e., they react with nucleophilic reagents. The order of reactivity of carbocations is, Primary (1°) > Secondary (2°) > Tertiary (3°)

(2) Types of carbocations : Carbocations can be classified into the following types,

(i) Alkyl carbocations

(a) When positive charge is present on the alkyl carbon, carbocation is known as alkyl carbocation.

(b) *Alkyl carbocation is of four types*

$$\underset{\text{Methyl carbocation}}{\overset{\oplus}{C}H_3} \qquad \underset{\text{Primary alkyl carbocations}}{R-\overset{\oplus}{C}H_2} \qquad \underset{\text{Secondary alkyl carbocations}}{R-\overset{\oplus}{C}H-R} \qquad \underset{\text{Tertiary alkyl carbocations}}{R_3\overset{\oplus}{C}}$$

(c) *Stability of alkyl carbocations can be explained by*

Inductive effect and Hyperconjugation.

(d) *According to these two effects the stability order is as follows* :

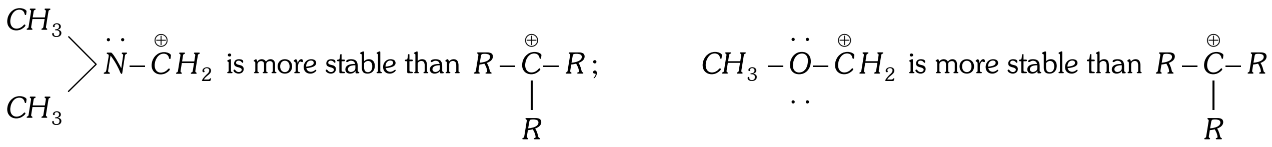
$$R-\underset{\substack{| \\ R}}{\overset{\oplus}{C}}-R \qquad R-\overset{\oplus}{C}H-R \qquad R-\overset{\oplus}{C}H_2 \qquad \overset{\oplus}{C}H_3$$

$$\xrightarrow{\hspace{20em}}$$

Stability in decreasing order

(e) If α-atom with respect to carbocationic carbon has one or more than one lone pair of electrons then lone pair of electrons strongly stabilises a carbocation due to the delocalisation.

Alkoxy and amino groups are important substituents for such type of carbocations.



$(CH_3)_2\ddot{N}-\overset{\oplus}{C}H_2$ is more stable than $R-\overset{\oplus}{C}(R)-R$; $CH_3-\ddot{\underset{..}{O}}-\overset{\oplus}{C}H_2$ is more stable than $R-\overset{\oplus}{C}(R)-R$

(ii) **Vinyl carbocation** : When positive charge is present on vinylic carbon then carbocation is known as vinyl carbocation, $CH_2=\overset{\oplus}{C}H$

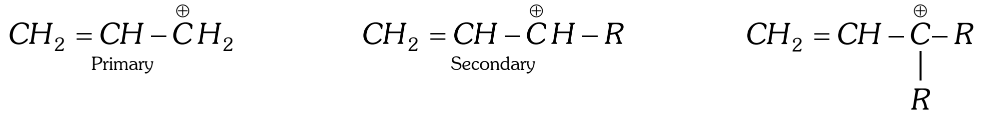
This carbocation is the least stable because positive charge is present on the electronegative carbon.

(iii) **Allyl carbocation :** $(CH_2=CH-\overset{\oplus}{C}H_2)$

(a) When positive charge is present on the allylic carbon of the allyl group, the carbocation is known as allyl carbocation.

(b) Allyl carbocations are more stable than the alkyl carbocations due to the resonance. Allyl carbocations are stabilised by delocalisation (or resonance).

(c) Allyl carbocations are of the following types,



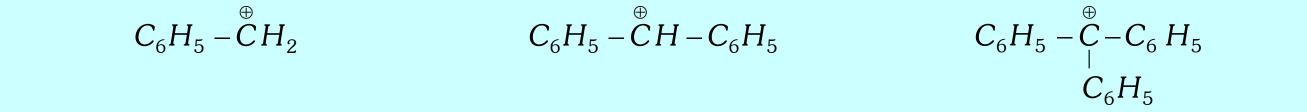
$CH_2=CH-\overset{\oplus}{C}H_2$ Primary $CH_2=CH-\overset{\oplus}{C}H-R$ Secondary $CH_2=CH-\overset{\oplus}{C}(R)-R$ Tertiary

(d) Stability of primary, secondary and tertiary allyl carbocations can be compared by, Inductive effect and Hyperconjugation. Thus, tertiary is more stable than secondary which is more stable than primary allyl carbocation.

(iv) **Phenyl methyl carbocations**

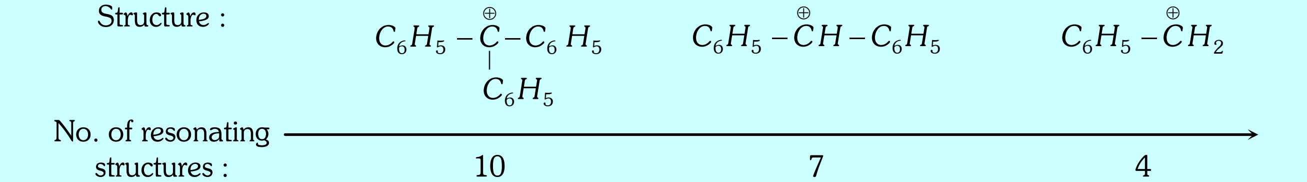
(a) When positive charge is present on benzyl carbon, carbocation is known as phenyl methyl carbocation.

(b) Phenyl methyl carbocations are of three types,



$C_6H_5-\overset{\oplus}{C}H_2$	$C_6H_5-\overset{\oplus}{C}H-C_6H_5$	$C_6H_5-\overset{\oplus}{C}(C_6H_5)-C_6H_5$
Benzyl carbocation or Phenyl methyl carbocation (1°-carbocation)	Diphenyl methyl carbocation (2°-carbocation)	Triphenyl methyl carbocation (3°-carbocation)

(c) Stability of phenyl methyl carbocations can be explained by resonance.



Structure :	$C_6H_5-\overset{\oplus}{C}(C_6H_5)-C_6H_5$	$C_6H_5-\overset{\oplus}{C}H-C_6H_5$	$C_6H_5-\overset{\oplus}{C}H_2$
No. of resonating structures : $\longrightarrow$	10	7	4

(i) Number of resonating structures in decreasing order

(ii) Stability in decreasing order.

(d) Phenyl methyl carbocations are more stable than allyl carbocations due to the number of resonating structures.

(v) **Aromatic carbocations**

(a) Cations in which positive charge is present on carbon of aromatic system is known as aromatic carbocation.

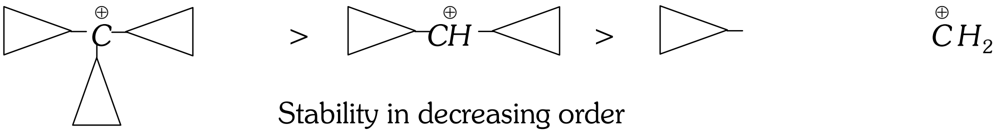
(b) Aromatic carbocations are so stable that even their solid states are known. For example tropolium carbocation as tropolium bromide is a yellow solid. It fact tropolium carbocation is about 10^{11} times more stable than triphenyl methyl carbocation .

(c) Cations obeying Huckel (4n+2) rule are stable because they are aromatic and there is complete delocalisation of positive charge.

(vi) **Cyclopropyl methyl carbocations**

(a) These carbocations are very stable carbocations. They are more stable than benzyl carbocations.

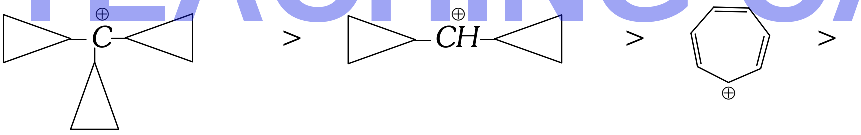
(b) Stability of cyclopropy methyl carbocations increases with every cyclopropyl group. Thus additional cyclopropyl group has commulative additive effect on the stability. Thus,



Stability in decreasing order

(c) The special stability is a result of conjugation between the bent orbitals of the cyclopropyl ring and the vacant- p -orbital of the cationic carbon.

(3) **Relative :** Stability of different types of carbocations in decreasing order

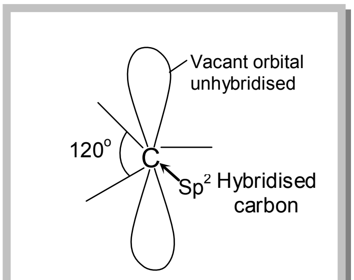


$$(C_6H_5)_3\overset{\oplus}{C} > (C_6H_5)_2\overset{\oplus}{C}H > C_6H_5-\overset{\oplus}{C}H_2 \ge CH_2=CH-\overset{\oplus}{C}H_2 \ge$$

$$R-\underset{\displaystyle R}{\underset{|}{\overset{\oplus}{C}}}-R > R-\overset{\oplus}{C}H-R > R-\overset{\oplus}{C}H_2 > \overset{\oplus}{C}H_3 > CH_2=\overset{\oplus}{C}H$$

Note : ✹ More stable is a carbocation, the more easily it is formed.

(4) **Structure of carbocation :** The carbon atom in carbocation is sp^2 hybridised. The three sp^2 hybrid orbitals form three σ bonds with hydrogen or other carbon atoms of alkyl groups. The unhybridised p -orbital of carbon remains vacant. Since it involves sp^2 hybridisation, its structure is planar with a bond angle of 120° .



Planar structure of carbocation

(5) **Reactions involving carbocations**

(i) Electrophilic addition reactions (ii) SN^1 reactions (iii) Electrophilic substitution reactions

(iv) Molecular rearrangement reactions, e.g., Pinacole-Pinacolone rearrangement.

(6) **Rearrangement in carbocations**

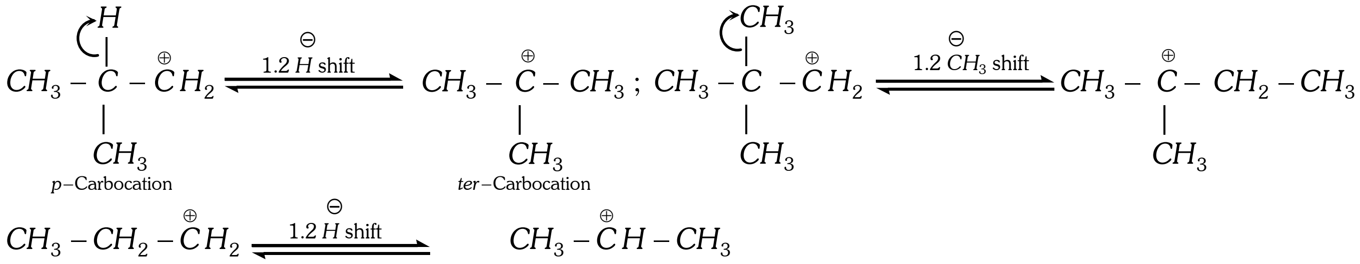
(i) Rearrangement takes place in primary and secondary carbocations.

p-carbocation $\xrightleftharpoons{\text{Rearrangement}}$ ter-carbocation or sec. carbocation

Driving force for rearrangement is the stability factor (Less stable species wants to convert into more stable species).

(ii) For rearrangement, carbocation should have at least three carbons. (α, β and γ).

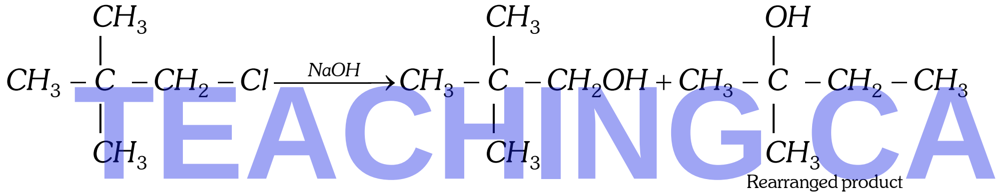
(iii) If β-carbon has hydrogen as well as alkyl group then rearrangement is due to the migration of hydrogen in the form of hydride ion from β to α-carbon. If β-carbon has only hydrogens then hydrogen migrates. If β-carbon has only alkyl groups then alkyl group migrates from β to α-carbon.



$$\underset{p-\text{Carbocation}}{CH_3-\overset{H}{\underset{CH_3}{C}}-\overset{\oplus}{C}H_2} \xrightleftharpoons{\overset{\ominus}{\text{1.2 } H \text{ shift}}} \underset{ter-\text{Carbocation}}{CH_3-\overset{\oplus}{\underset{CH_3}{C}}-CH_3}\ ;\ CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{\oplus}{C}H_2 \xrightleftharpoons{\overset{\ominus}{\text{1.2 } CH_3 \text{ shift}}} CH_3-\overset{\oplus}{\underset{CH_3}{C}}-CH_2-CH_3$$

$$CH_3-CH_2-\overset{\oplus}{C}H_2 \xrightleftharpoons{\overset{\ominus}{\text{1.2 } H \text{ shift}}} CH_3-\overset{\oplus}{C}H-CH_3$$

Note : ✹ If the number of products of the reaction is more than the expected products then product formation takes place by formation of carbocation and there is rearrangement in carbocation.



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2-Cl \xrightarrow{NaOH} CH_3-\overset{CH_3}{\underset{CH_3}{C}}-CH_2OH + \underset{\text{Rearranged product}}{CH_3-\overset{OH}{\underset{CH_3}{C}}-CH_2-CH_3}$$

Carbanions

A carbanion may be defined as a species containing a carbon atom carrying a negative charge. These are generated by the heterolytic fission of covalent bond involving carbon atom in which the atom linked to carbon goes without the bonding electrons.

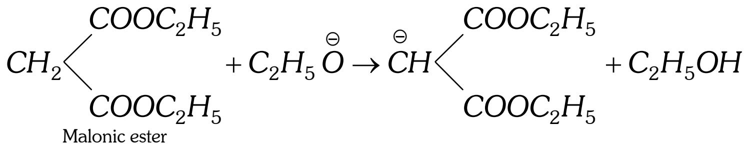
It is denoted by putting a negative charge (–) against the symbol of group of atoms.

$$\underbrace{\underset{\text{Methyl carbanion}}{CH_3^{\ominus}} \qquad \underset{\text{Ethyl carbanion}}{C_2H_5^{\ominus}}}_{\text{Primary}} \qquad \underbrace{\underset{\text{Isopropyl carbanion}}{(CH_3)_2CH^{\ominus}}}_{\text{Secondary}} \qquad \underbrace{\underset{\text{Tert. butyl carbanion}}{(CH_3)_3C^{\ominus}}}_{\text{Tertiary}}$$

(1) Characteristics of carbanions,

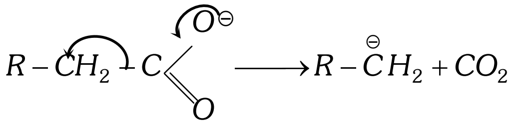
(i) The formation of carbanions can be done,

(a) By attack of base on hydrogen atom : Organic compounds which possess a labile or acidic hydrogen have the tendency to produce carbanions as in the case of reactive methylene compounds which lose proton in presence of sodium ethoxide (C_2H_5ONa).



$$\underset{\text{Malonic ester}}{CH_2\left\langle \begin{matrix} COOC_2H_5 \\ COOC_2H_5 \end{matrix} \right.} + C_2H_5\overset{\ominus}{O} \rightarrow \overset{\ominus}{C}H\left\langle \begin{matrix} COOC_2H_5 \\ COOC_2H_5 \end{matrix} \right. + C_2H_5OH$$

(b) By decarboxylation of carboxylate ion :



(c) By the formation of organometallic compound ; $CH_3-Cl \xrightarrow{Mg/ether} CH_3MgCl \longrightarrow \overset{\ominus}{C}H_3 + Mg^{\oplus}Cl^{\ominus}$

(ii) Carbanions are not electrically neutral.

(iii) There are eight electrons in the outermost orbit of carbanionic carbon hence its octet is complete.

(iv) A carbanion is diamagnetic in nature due to all paired electrons.

(v) Carbanions are charged nucleophiles *i.e.*, they react with electrophilic reagents. The order of reactivity of carbanions is, Tertiary (3°) > Secondary (2°) >Primary (1°) (Decreasing order)

(2) **Stability of carbanions :** The stability of carbanion may be explained by

(i) ***Electronegativity of carbanionic carbon***

Stability $\propto$ Electronegativity of carbanionic carbon $\propto \%$ s-character of carbanionic carbon

$$CH_3-\underset{\underset{sp^3}{\uparrow}}{\overset{\ominus}{C}}H_2 \qquad CH_2=\underset{\underset{sp^2}{\uparrow}}{\overset{\ominus}{C}}H \qquad CH\equiv\underset{\underset{sp}{\uparrow}}{\overset{\ominus}{C}}$$

$\longrightarrow$

% s-character in increasing order.
Stability in inceasing oder.

(ii) ***Inductive effect*** **:** Stability of carbanions depends on the +I or – I group as follows :

(a) Stability $\propto \dfrac{1}{+I \text{ power of the group}}$

$$\overset{\ominus}{C}H_3 \qquad R\rightarrow\overset{\ominus}{C}H_2 \qquad R\rightarrow\overset{\ominus}{C}H_2\leftarrow R \qquad R\rightarrow\underset{\underset{R}{\uparrow}}{\overset{\ominus}{C}}\rightarrow R$$

$\longrightarrow$

+ I power in increasing order.
Stability in decreasing order.

(b) Stability of carbanions $\propto -I$ power of the group.

For example :

$$I\longrightarrow\overset{\ominus}{C}H_2 \qquad Br\longrightarrow\overset{\ominus}{C}H_2 \qquad Cl\longrightarrow\overset{\ominus}{C}H_2 \qquad F\longrightarrow\overset{\ominus}{C}H_2$$

$\longrightarrow$

$-I$ power of halo group is in increasing order
Stability is in increasing order

(iii) ***Delocalisation or Resonance*** **:** Allyl and benzyl carbanions are stabilised by delocalisation of negative charge.

$$\underset{2}{CH_2=CH-\overset{\ominus}{C}H_2} \qquad \underset{4}{C_6H_5-\overset{\ominus}{C}H_2} \qquad \underset{7}{(C_6H_5)_2\overset{\ominus}{C}H} \qquad \underset{10}{(C_6H_5)_3\overset{\ominus}{C}}$$

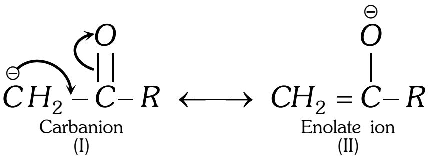
$\longrightarrow$

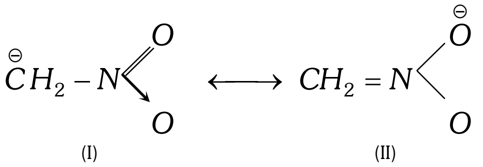
Number of resonating structures is in increasing order
Stability is in increasing order.

(iv) ***Stabilisation by sulphur and phosphorous*** **:** Attachment of carbanionic carbon of a sulphur and phosphorus atom causes an increase in carbanion stability.

The cause of stability is due to the delocalisation of negative charge of carbanion by vaccant d-orbital $p\pi - d\pi$ bonding) of phosphorus and sulphur.

(v) ***Stabilisation by >C=O, –NO₂ and CN groups present on carbanionic carbon*** :These groups stabilise carbanion by resonance effect.





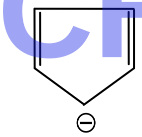
Contribution of structure (II) will be more than (I) because in (II) negative charge is present on electronegative oxygen.

(vi) **Stability of Aromatic carbanions**

(a) Anions in which negative charge is present on carbon of aromatic system is known as aromatic carbanions.

(b) Aromatic carbanions are most stable carbanions.

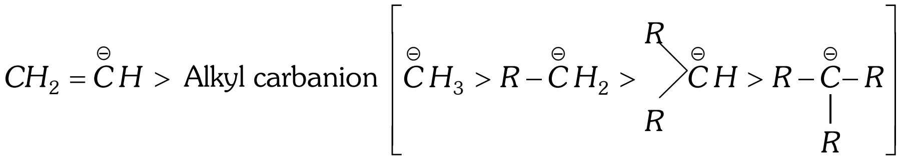
(c) Anions obeying Huckel rule are stable because they are aromatic and there is complete delocalisation of negative charge.



Cyclopentadienyl anion

(3) **Relative stability of different types of carbanions in decreasing order**

Aromatic carbanion > Benzyl carbanion > Allyl carbanion > $CH\equiv\overset{\ominus}{C}$ >

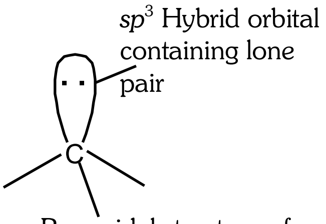


$$CH_2=\overset{\ominus}{C}H > \text{Alkyl carbanion}\left[\overset{\ominus}{C}H_3 > R-\overset{\ominus}{C}H_2 > R_2\overset{\ominus}{C}H > R-\overset{\ominus}{\underset{R}{\underset{|}{C}}}-R\right]$$

(4) **Structure of carbanion :** The negatively charged carbon atom in carbanion is sp^3 hybridised. Therefore, it has a pyramidal structure. Three of the four sp^3 hybridised orbitals form 3σ bonds with hydrogen or carbon atom of the alkyl group. The fourth sp^3 hybrid orbital contains the lone pair of electrons.

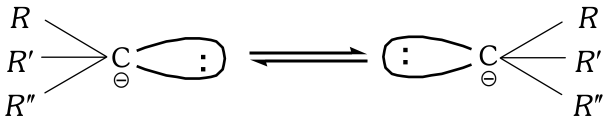
Note : ✸ Geometry of allyl and benzyl carbanion is almost planar and hybridisation is sp^2.

✸Methyl anion is isostructural (pyramidal) and isoelectronic (eight valency electrons) with ammonia.



Pyramidal structure of carbanion

✹The carbanions having three different bulky groups are not optically active. It is due to pyramidal structure of carbanion which is not rigid and shows a rapid equilibrium between following two enantiomeric pyramidal structures.



(5) **Reactions involving carbanions**

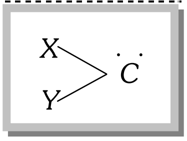
(i) Condensation reactions of carbonyl compounds, i.e., Aldol condensation, Perkin reaction, Reformatsky reaction etc.

(ii) Condensation reaction of ester; Claisen condensation.

(iii) Witting reaction.

Carbenes

A carbene may be defined as a species in which carbon atom has six electrons in the outer shell (electron deficient), out of which two constitute a lone pair and two are shared. So they are divalent carbon species containing two unpaired electrons and possess no charge.



The simplest carbene is $\ddot{C}H_2$ which known as methylene. Substituted carbenes are simply named as derivative of carbenes. For example, $\underset{\text{Phenyl carbene}}{C_6H_5-\ddot{C}H}$ $\underset{\text{Dialkyl carbene}}{R-\ddot{C}-R}$ $\underset{\text{Dichloro carbene}}{\ddot{C}Cl_2}$

(1) **Characteristics of carbnes**

(i) Carbenes can be formed,

(a) By the photochemical decomposition or pyrolysis of aliphatic diazo compounds or ketenes.

$$\underset{\text{Diazo methane}}{CH_2N_2} \xrightarrow[(UV)]{h\nu \text{ or heat}} \underset{\text{Carbene}}{:CH_2} + N_2\,; \qquad R-CHN_2 \xrightarrow{h\nu \text{ or heat}} \underset{\text{Alkyl carbene}}{RCH:} + N_2$$

$$RCO-CHN_2 \xrightarrow{h\nu \text{ or heat}} \underset{\text{Acyl carbene}}{RCO-CH:} + N_2\,;\ \underset{\text{Ketene}}{CH_2=C=O} \longrightarrow \underset{\text{Carbene}}{:CH_2} + CO$$

(b) By the action of a base on suitable polyhalogen compound.

$$\underset{\text{Chloroform}}{CHCl_3} + C_2H_5ONa \longrightarrow \underset{\text{Dichloro carbene}}{:CCl_2} + C_2H_5OH + NaCl$$

$$CHCl_3 + \underset{\text{Tert. butoxide ion}}{(CH_3)_3CO^{\ominus}} \rightleftharpoons (CH_3)_3C-OH + :CCl_3 \longrightarrow :CCl_2 + Cl^-$$

(ii) Carbenes are related to carbanions through the α-elimination reaction.

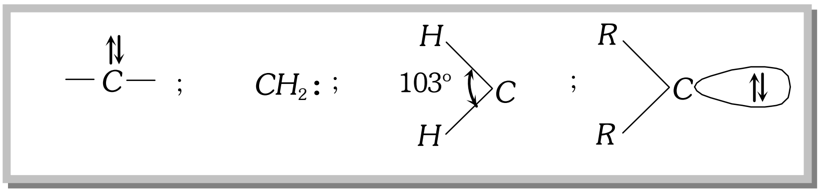
$$CHX_3 \xrightarrow{alc.KOH/\Delta} H^{\oplus} + \overset{\ominus}{C}X_3$$
$$\downarrow$$
$$\ddot{C}X_2 + X^{\ominus}$$

(iii) Carbenes are neutral, divalent, highly reactive carbon intermediates. They works as electrophiles.

(2) **Types and stability of carbenes**

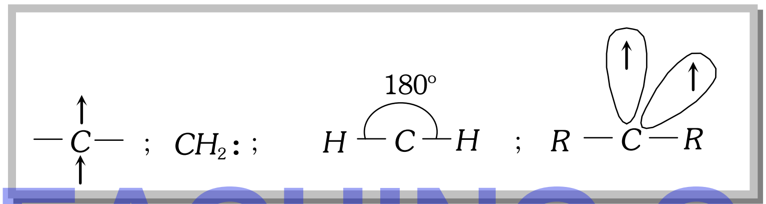
Carbenes are of two types

(i) ***Singlet*** : When both the electrons go into one orbital and have opposite spin (antiparallel), *i.e.*, the unshared electrons are paired in one orbital and has a bent strucutre.



The singlet state is actually found to have $H-C-H$ bond angle 103° (between 90^o to 120^o) and a $C-H$ bond length of 1.12Å. It is generally considered as the less stable.

(ii) ***Triplet*** : When the two electrons go into different orbitals and have same spin (parallel), i.e., the unshared electrons are not paired. Such carbene would have a permanent magnetic moment and would exist in three closely grouped energy state, if it were placed in a magnetic field. Such a state is called triplet state and is believed to be a linear molecule.

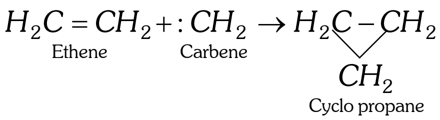


With $H-C-H$ bond angle 180^o and a $C-H$ bond length of 1.03Å, it might be considered as a free diradical and is more stable.

(3) Reactions involving carbenes

(i) ***Addition to alkenes*** **:** Formation of cyclo alkane derivatives, e.g.,

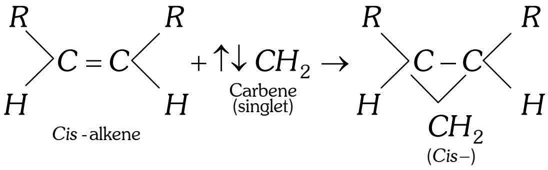
(a)



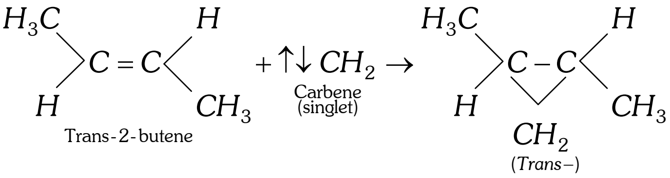
$H_2C=CH_2 + :CH_2 \rightarrow H_2C-CH_2$ (bridged by CH_2)

Ethene Carbene Cyclo propane

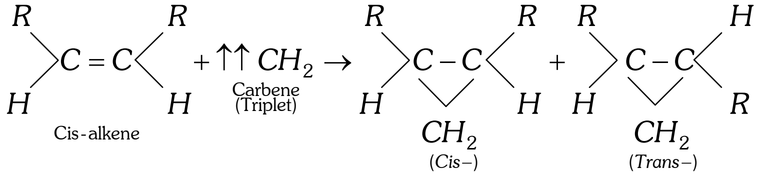
(b)



(c)



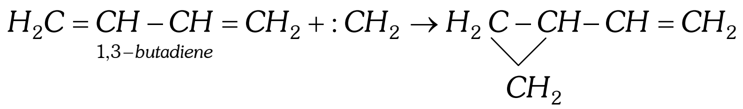
(d) Conversely, the triplet carbenes add on alkenes in a non-stereo specific manner to form both (cis- and trans-) products.



(e) In case of conjugated or cumulative dienes, the addition always occurs exclusively at 1,2-position.

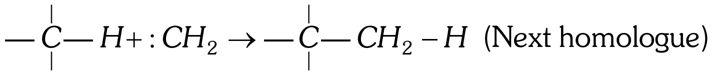
$H_2C=C=CH_2 + :CH_2 \rightarrow H_2C-C=CH_2$, CH_2 below

1,2–propadiene

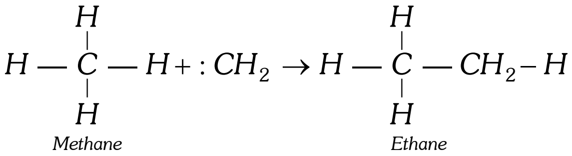


$$\underset{1,3-butadiene}{H_2C=CH-CH=CH_2}+:CH_2 \rightarrow H_2\underset{\diagdown\;\diagup}{C-CH}-CH=CH_2$$
$$CH_2$$

(ii) ***Insertion reactions*** **:** Carbenes are also used in its insertion between the $C-H$ bond, e.g.,

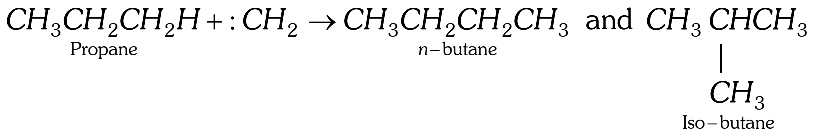


$$-\overset{|}{\underset{|}{C}}-H+:CH_2 \rightarrow -\overset{|}{\underset{|}{C}}-CH_2-H \text{ (Next homologue)}$$



$$\underset{Methane}{H-\overset{H}{\overset{|}{\underset{\underset{H}{|}}{C}}}-H}+:CH_2 \rightarrow \underset{Ethane}{H-\overset{H}{\overset{|}{\underset{\underset{H}{|}}{C}}}-CH_2-H}$$

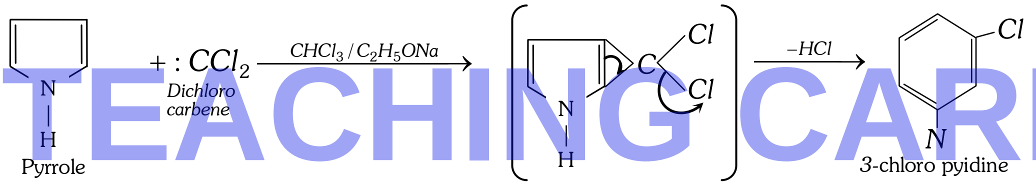
Further it can be inserted in all the possible positions (pri-, sec-, tert-).



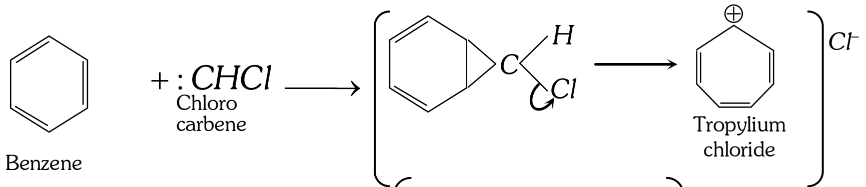
$$\underset{\text{Propane}}{CH_3CH_2CH_2H}+:CH_2 \rightarrow \underset{n-\text{butane}}{CH_3CH_2CH_2CH_3} \text{ and } \underset{\text{Iso}-\text{butane}}{CH_3\underset{\underset{CH_3}{|}}{CH}CH_3}$$

(iii) ***Ring expansion reactions*** **:** These involve the addition of a halogeno carbene across a double bond followed by rearrangement.

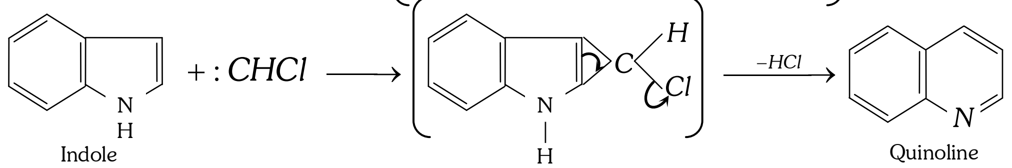
(a)



(b)



(c)

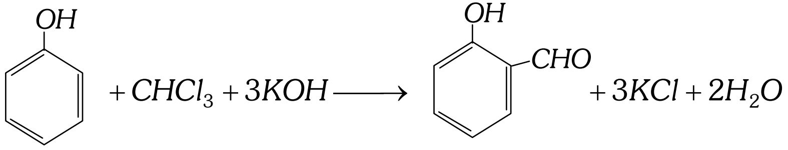


(iv) ***Carbylamine reaction*** **:** By heating a mixture of primary amine and chloroform with ethanolic potassium hydroxide to form isocyanide (carbylamine) is known as carbylamine reaction.

$$RNH_2+CHCl_3+3KOH \rightarrow RNC+3KCl+3H_2O$$

Mechanism : $CHCl_3 \xrightarrow[(-H_2O)]{OH^-} :\overset{\ominus}{C}Cl_3 \longrightarrow \underset{\text{Dichloro carbene}}{:CCl_2}+Cl^-$

(v) ***Reimer-Tiemann reaction*** **:** Phenol on heating with chloroform and aqueous alkali followed by acid hydrolysis to yield salicylaldehyde is known as Reimer-Tiemann reaction.



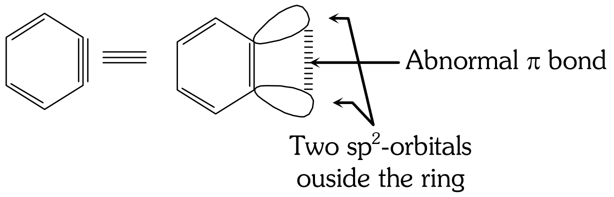
Comparision of Free radical, Carbocation, Carbanion and Carbene

Characteristic	Free radical	Carbocation	Carbanion	Carbene
Nature	**Neutral having odd electron**	**Positive charge on C**	**Negative charge on C**	**Neutral, divalent with 2 unshared electrons**
Hybridisation	**sp^2**	**sp^2**	**sp^3 (non-conjugated)** **sp^2 (Conjugated)**	**(i) sp^2 (singlet)** **(ii) sp (triplet)**
Structure	**Planar**	**Planar**	**Pyramidal/Planar**	**(i) Planar (singlet)** **(ii) Linear (triplet)**
Magnetism	**Paramagnetic**	**Diamagnetic**	**Diamagnetic**	**(i) Diamagnetic** **(ii) Paramagnetic**
Stability order	$Ph_3\dot{C} > Ph_2\dot{C}H > Ph\dot{C}H_2 >$ $CH_2=CH-\dot{C}H_2 > 3^o > 2^o >$ $1^o > \dot{C}H_3 > CH_2=\dot{C}H$	$Ph_3\overset{+}{C} > Ph_2\overset{+}{C}H >$ $Ph\overset{+}{C}H_2 > CH_2=CH-\overset{+}{C}H_2 >$ $3^o > 2^o > 1^o > CH_3$	$Ph_3\overset{\ominus}{C} > Ph_2\overset{\ominus}{C}H >$ $Ph\overset{\ominus}{C}H_2 >$ Allyl> $\overset{\ominus}{C}H_2 > 1^o > 2^o > 3^o$	**Triplet > singlet**

Benzyne

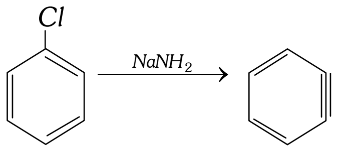
(1) 1, 2-Didehydrobenzene, C_6H_4 and its derivatives are called benzyne or arynes and the simplest member is benzyne.

(2) It is neutral reaction intermediate derived from benzene ring by removing two substituents, of *ortho* positions, one in the form of electrophile and other in the from of nucleophile leaving behind two electrons to be destributed between two orbitals.



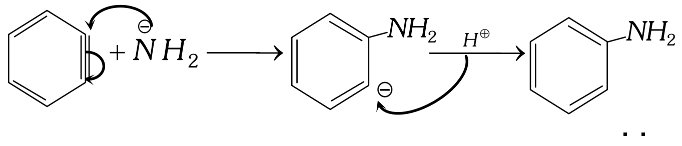
(3) Benzye intermediate is aromatic in character.

(4) When halobenzene is heated with sodamide formation of benzyne takes place.



(5) (i) It behaves as dienophile and gives Diels-Alder reaction with diene.

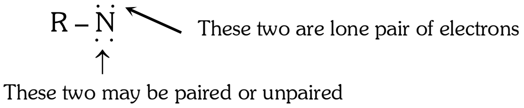
(ii) It reacts with strong nucleophile like $\overset{\ominus}{N}H_2$



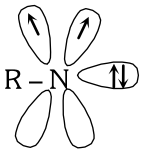
Nitrenes ($R-N:$)

(1) The nitrogen analogous of carbenes are called nitrenes.

(2) There is posibility of two spin states for nitrenes depending on whether the two non-bonding electrons (the normal nitrogen lone pair remains paired) have their spins paired or parallel.



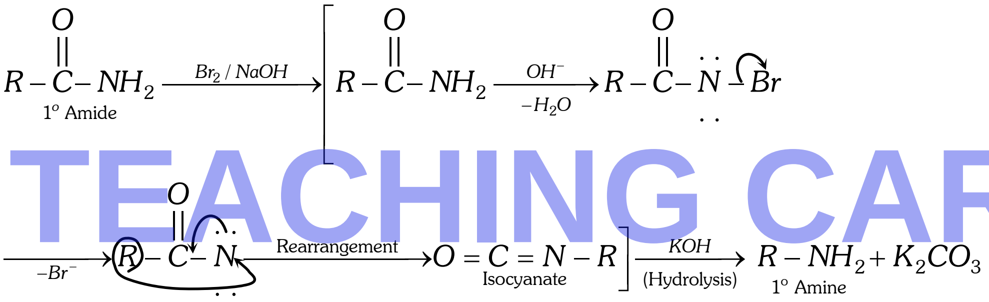
(3) In general nitrenes obey Hunds rule and are ground state triplet with two degenerate *sp*-orbitals containing a single electron each.



Sp-Triplet nitrene

(4) Nitrenes can be generated, in situ, by the following methods,

(i) ***By action of Br_2 in presence of a base on a 1° amide*** (Hofmann-bromamide reaction),



$$\underset{1^\circ\text{ Amide}}{R-\overset{O}{\overset{\|}{C}}-NH_2} \xrightarrow{Br_2/NaOH} \left[R-\overset{O}{\overset{\|}{C}}-NH_2 \xrightarrow[-H_2O]{OH^-} R-\overset{O}{\overset{\|}{C}}-\underset{..}{\ddot{N}}-Br \xrightarrow{-Br^-} R-\overset{O}{\overset{\|}{C}}-\underset{..}{\ddot{N}} \xrightarrow{\text{Rearrangement}} \underset{\text{Isocyanate}}{O=C=N-R} \right] \xrightarrow[\text{(Hydrolysis)}]{KOH} \underset{1^\circ\text{ Amine}}{R-NH_2} + K_2CO_3$$

(ii) ***By decomposition of azides in presence of heat or light.***

$$\underset{\text{Alkyl azide}}{R-\ddot{N}=\overset{+}{N}=\ddot{N}:^-} \xrightarrow{\Delta \text{ or } h\nu} \underset{\text{Alkyl nitrene}}{R-\ddot{N}:} + N\equiv N$$

(iii) Unsubstituted nitrene $(H-\ddot{N}:)$ can be obtained by photolysis of (or by passing electric discharge through) NH_3, N_2H_4 or N_3H.

Attacking reagents.

Most of the attacking reagents carry either a positive or a negative charge. The positively charged reagents attack the regions of high electron density in the substrate molecule while the negatively charged reagents will attack the regions of low electron density in the substrate molecule. The fission of the substrate molecule to create centres of high or low electron density is influenced by attacking reagents. Most of the attacking reagents can be classified into two main groups.

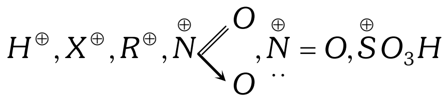
(1) Electrophiles or electrophilic reagents. (2) Nucleophiles or nucleophilic reagents.

(1) **Electrophiles :** Electron deficient species or electron acceptor is electrophile.

It can be classified into two categories :

(i) Charged electrophiles $(E^{\oplus})$, (ii) Neutral electrophiles (E)

(i) ***Charged electrophiles*** : Positively charged species in which central atom has incomplete octet is charged electrophile.



$$H^{\oplus}, X^{\oplus}, R^{\oplus}, \overset{\oplus}{N}\begin{matrix} O \\ O \end{matrix}, \overset{\oplus}{N}=O, \overset{\oplus}{S}O_3H$$

Note : ✸ All cations are charged electrophiles except cations of IA, IIA group elements, Al^{+++} and $\overset{\oplus}{N}H_4$

(ii) ***Neutral electrophiles*** : It can be classified into three categories,

(a) Neutral covalent compound in which central atom has incomplete octet is neutral electrophile,

$BeCl_2, BH_3, ZnCl_2, AlX_3, FeX_3, \dot{C}H_3, \ddot{C}H_2, \ddot{C}X_2$

(b) Neutral covalent compound in which central atom has complete or expended octet and central atom has unfilled –*d*-sub-shell is neutral electrophile,

$SnCl_4, SiCl_4, PCl_5, SF_6, IF_7$

(c) Neutral covalent compound in which central atom is bonded only with two or more than two electronegative atoms is neutral electrophile.

$BeCl_2, BX_3, AlX_3, FeX_3, SnCl_4, PCl_3; \quad PCl_5, \; NF_3, \; \ddot{C}X_2, \; CO_2, SO_3, \; CS_2,$

Note : ✸ Cl_2, Br_2 and I_2 also behave as neutral electrophiles.

✸ Electrophiles are Lewis acids.