BASIC CONCEPT IN ORGANIC CHEMISTRY

1. Electrical effects

The electrical (or electronic) effects are mainly divided into following categories :

1.1 Inductive Effect
1.2 Resonance (or mesomeric) Effect
1.3 Electromeric Effect
1.4 Hyperconjugation

1.1 Inductive Effect (Polar nature of covalent bonds)

The displacement of an electron (shared) pair along the carbon chain due to the presence of an electron withdrawing or electron releasing groups in the carbon chain is known as Inductive Effect **(I–effect)**.

➢ $C\text{--}\overset{\delta\delta+}{\rightarrow}\text{--}C\text{--}\overset{\delta+}{\rightarrow}\text{--}\ C\ \text{--}\rightarrow G$ (G : functional group)

$C\ \text{--}\overset{\delta\delta-}{\leftarrow}\text{--}\ C\ \text{--}\overset{\delta-}{\leftarrow}\text{--}\ C\ \ \text{--}\leftarrow\ G$

But the effect is insignificant beyond third carbon atom.

➢ This effect is transmitted through the chain of σ bonds and diminishes. with increasing chain length.

Inductive effect is thus
(i) A permanent effect
(ii) The electrons never leave their original atomic orbital.
(iii) Operates through σ bonds
(iv) Polarisation of electrons is always in single direction.
(v) It is generally observed in saturated compounds.
(vi) Its magnitude (i.e., electron withdrawing or donating power) decreases with increase in distance.

On the basis of inductive effect, groups can be of two types.

***– I* group :** The group which withdraws electrons is known as – *I* group and its effect is known as – *I* effect.

– I power of various group & cation.

$\overset{\oplus}{N}F_3 > \overset{\oplus}{N}H_3 > NO_2 > CN > SO_3H > CHO > CO > COOH > COCl > COOR > CONH_2 > F > Cl > Br > I > OH > OR > NH_2 > C \equiv CH > C_6H_5 > CH = CH_2 > H$

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

+ *I* group : The group which donates or gives electron is known as + *I* group and effect is known as + *I* effect.

Alkyl groups, $\overset{\ominus}{O}$, $CO\overset{\ominus}{O}$ are + *I* groups.

(a) + *I* power of different type groups and anions :

$NH^{-} > O^{-} > COO^{-} >$ ter alkyl > sec.alkyl > p-alkyl $> CH_3 > H$

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+ *I* power in decreasing order with reference to H

(b) + *I* power of same type of alkyl groups :

+ *I* power ∝ number of C's in same type of alkyl group

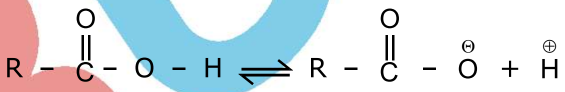
For example

$CH_3 - CH_2 -$
$CH_3 - CH_2 - CH_2 -$
$CH_3 - CH_2 - CH_2 - CH_2 -$

+ *I* power in increasing order ↓

APPLICATIONS OF INDUCTIVE EFFECT

(A) Strength of Carboxylic Acid : Acid strength is measured by the position of equilibrium of ionisation in water.



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

The further the ionisation go to the right, the greater the acid strenth. In other words.

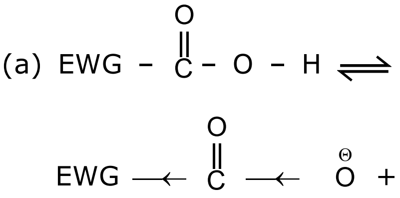
$$Ka = \frac{\left[R - \overset{O}{\overset{\|}{C}} - \overset{\ominus}{O}\right]\overset{\oplus}{[H]}}{[RCOOH]}$$

$$\text{Acid strength} \propto Ka \propto \frac{1}{pKa}$$

or Acid strength ∝ concentration of acid anion
or Acid strength ∝ stability of acid anion

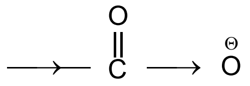
Thus strength of acid is the function of stability of acid anion.

The influence of the inductive effect on acidity can be summarised as follows :



$$\text{(a) } EWG - \overset{O}{\overset{\|}{C}} - O - H \rightleftharpoons EWG \longleftarrow \overset{O}{\overset{\|}{C}} \longleftarrow \overset{\ominus}{O} + \overset{\oplus}{H}$$

Electron withdrawing group (– I gp) stabilises group (– I gp) stabilises acid anion and strengthens the acid or, –I group increases strength of acid and thus: Strength of acid ∝–I power of the group present on – COOH

(b) EDG 
$\longrightarrow \overset{O}{\overset{\|}{C}} \longrightarrow \overset{\ominus}{O}$

Electron donating groups (i.e, + I gp) destablise acid anion and weaken the acid.

or, +I group decreases strength of acid and thus :

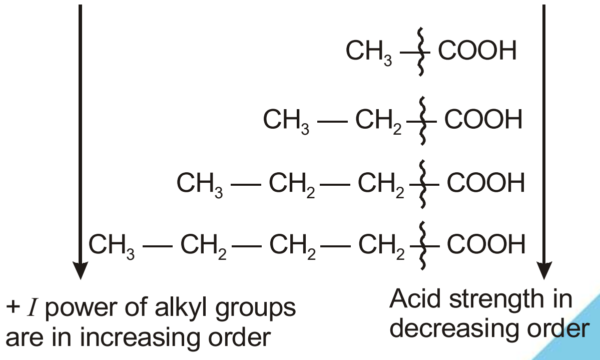
strength of acid ∝

$$\frac{1}{+I \text{ power of the group present on} - COOH} \propto - I$$

power of group

Consider the following homologous aliphatic acids.

Example 1.

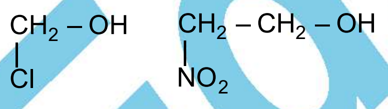


(B) Acidity of Alcohols : Acidity of alcohol depends on the stability of alkoxide ion (i.e., conjugate base of alcohol) which is obtained by the dissociation of alcohols.

$$R - O - H \rightleftharpoons R - \overset{\ominus}{O} + \overset{\oplus}{H}$$

Acid strength of alcohol ∝ stability of alkoxide ion

Note : As we know that as the distance from source increases, intensity of effect decrease also **(distance prefer on power)**.

Ex. 
$\underset{Cl}{\underset{|}{CH_2}} - OH \qquad \underset{NO_2}{\underset{|}{CH_2}} - CH_2 - OH$

I II

I is more acidic than II even power of NO_2 (–I) is more, but in case of Cl distance is less.

(C) Basicity of Amines :

Basicity is defined as the tendency to donate an electron pair for sharing. The difference in the base strength in various amines can be explained on the basis of +I - effect.

The groups producing +I effects (alkyl groups) tends to intensity electron density over N in amines thereby producing a base strengthening effect.

Thus, strength of base ∝ + I power of group present on – NH_2 ∝ K_b ∝ $\frac{1}{pKb}$

Whereas, a group producing -I effect [–Cl,–NO_2] tends to decrease electron density over N -atom in amines, thereby producing a base weaking effect.

Thus, strength of base ∝

$$\frac{1}{-I \text{ power of group present on} - NH_2} \propto K_b$$

The order of basicity is as given below :

Alkyl groups (R—)	**Relative base strength**
(i) CH_3	$R_2NH > RNH_2 > R_3N > NH_3$
(ii) C_2H_5	$R_2NH > RNH_2 > NH_3 > R_3N$
(iii) $(CH_3)_2CH$	$RNH_2 > NH_3 > R_2NH > R_3N$
(iv) $(CH_3)_3C$	$NH_3 > RNH_2 > R_2\ NH > R_3N$

Comparing with increasing + I effect, trend is rather surprising. This is due to the inability of 3° amines to give up their electrons due to presence of three bulky alkyl groups over N (steric effect).

(D) Stability of Non-conjugated Cations and Anions : Stability of non-conjugated charge species can be compared by the following rules:

Rule 1 : Less is the magnitude of charge, more will be stability of charge species.

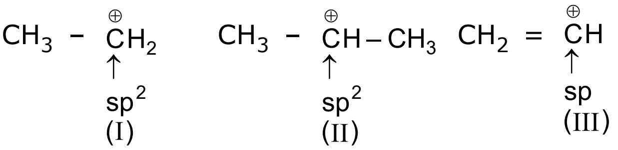
Stability of simiar charge species (i.e. stability between cations or stability between anions) can be compared by this rule in those cases where:

Thus, stability $\propto \frac{1}{\text{magnitude of} + \text{ve or} - \text{ve charge}}$

(i) Charge is present on the same atoms in all species, and

(ii) Hybridisation of atom bearing the charge should be same in all species.

For example :


$CH_3 - \underset{sp^2}{\underset{\uparrow}{\overset{\oplus}{C}H_2}} \qquad CH_3 - \underset{sp^2}{\underset{\uparrow}{\overset{\oplus}{C}H}} - CH_3 \qquad CH_2 = \underset{sp}{\underset{\uparrow}{\overset{\oplus}{C}H}}$

(I) (II) (III)

Stability of cations I and II can be compared by rule -1 because positive charge in (I) and (II) is present on same atom (i.e. carbon) and hybridisation of $\overset{\oplus}{C}$ is same in both cases.

Stability of (I) and (III) cannot be compared by rule-1 because hybridisation of $\overset{\oplus}{C}$ in (I) and (III) is different.

Rule 2 : For maximum stability : positive charge should be present on electropositive atom in catrion or negative charge should be present on electrongative atom in anion.

This rule can be used in those cases where hybridisation of atoms bearing charge is different. Thus stability of cations (I) and (III) or (II) and (III) can be compaired by this rule.

(1) Stability of Alkyl Carbocation :

Stability of alkyl carbocation ∝

$$\frac{1}{\text{magnitude of positive charge}} \quad ....(i)$$

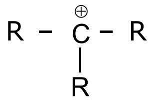
Magnitude of positive charge ∝

$$\frac{1}{+I \text{ power of group (i.e., alkyl group)}} \quad ....(ii)$$

From (i) and (ii)

Stability of alkyl carbocation ∝ + I power of the group present on $\overset{\oplus}{C}$. Thus tertiary alkyl carbocation is more stable than secondary which is more stable than primary carbocations.

$H-\overset{\oplus}{C}H_2$ $R-\overset{\oplus}{C}H_2$ $R-\overset{\oplus}{C}H-R$



$R-\overset{\oplus}{C}(R)-R$

methyl carbocaton 1o- 2o-carbocation 3o-carbocation

——————————————————————

(i) Number of + I groups on $\overset{\oplus}{C}$ is in increasing order

(ii) + I power on $\overset{\oplus}{C}$ is in increasing order

(iii) Magnitude of positive charge is in decreasing order

(iv) Stability is in increasing order

Note : Stability of free redical varies in same order as carbocation.

(2) Stability of Alkyl Carbanion

Stability of alkyl carbanion ∝

$$\frac{1}{\text{magnitude of negative charge}} \quad ....(i)$$

Magnitude of negative charge ∝ + I power of the group (i.e., alkyl group) ....(ii)

Stability of alkyl carbanion ∝

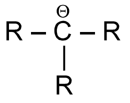
$$\frac{1}{+I \text{ power of the alkyl group present on } \overset{\oplus}{C}}$$

For examples :

$H-\overset{\ominus}{C}H_2$
Methyl carbanion

$R-\overset{\ominus}{C}H_2$
1o-carbanion

$R-\overset{\ominus}{C}H-R$
2o-carbanion



$R-\overset{\ominus}{C}(R)-R$
3o-carbanion

$\longrightarrow$

(i) Number of alkyl groups on $\overset{\ominus}{C}$ is in increasing order.

(ii) + I power on $\overset{\ominus}{C}$ is in increasing order

(iii) Negative charge on $\overset{\ominus}{C}$ is in increasing order

(iv) Stability is in decreasing order

(3) Stability of Alkyl and Vinyl Carbocation :

Stability of these two type of species can be compared by rule 2.

$CH_3-\overset{\oplus}{C}H_2$

→ sp^2-hybrid carbon

→ sp^2-hybridised carbon is less EN

⇓

Positive charge is present on less E.N. carbon.

$CH_2=\overset{\oplus}{C}H$

→ sp-hybrid carbon

→ sp-hybrid carbon is more electronegative

⇓

Positive charge is present on electropositive carbon

Hence alkyl carbocation is always more stable than vinyl carbocation.

Note :

(A) Order of electronegativity of different type of hybridised orbital is sp > sp^2 > sp^3

(B) Less E.N. carbon consist of +ve charge is more stable.

(4) Stability of Alkyl, Vinyl and Acetylenic Carbanions : Stability of these three species can be compared by rule 2.

(I) $CH_3-\overset{\ominus}{C}H_2$

→ sp^3-hybrid carbon

→ sp^3-hybrid carbon is electropositive

⇓

Negative charge is present on electropositive carbon

(II) $CH_2=\overset{\ominus}{C}H$

→ sp^2-hybrid carbon

→ It is electronegative carbon (% s-character is 33.33)

⇓

Negative charge is present on electronegative carbon (less electronegative)

(III) $CH\equiv\overset{\ominus}{C}$

→ sp-hybrid carbon

→ It is more electronegative than-II because % s-character is 50 %

⇓

Negative charge is present on more electronegative carbon

Hence, acetylenic carbanion is more stable than vinylic carbanion which is more stable than alkyl-carbanion.

Note :

More E.N. carbon consist –ve charge is more stable.

1.2 Resonance (or Mesomeric Effect)

When a molecule or ion can be represented by two or more structures which have the same arrangement of atomic nuclei but differ in distribution of electrons, the phenomenon is called as Resonance. The various structures are called contributing or resonating structures. None of these structures truly represents all the properties of that molecule or ion. The actual structure is a resonance hybrid of several contributing structures.

In the molecule if resonance is present then mesomeric effect may be present or may not be present. Resonance generally occurs when there is a conjugation of π-bonds (alternate double - single - double bond arrangement) known as conjugated system.

Conjugate positions of the molecule :

Alternate positions of the molecule having π bond, positive charge, negative charge, odd electron or lone pari of electrons are known as conjugative positions.

$CH_3-CH_2-\underset{1}{CH}=CH-\underset{3}{CH}=CH-\underset{5}{CH}=CH_2$

1, 3, 5 are alternate positions having π bonds. Hence these positons are known as conjugate positions.

$\underset{1}{CH_2}=CH-\underset{3}{CH}=CH-\underset{5}{\overset{\oplus}{CH}}-CH_3$

1, 3 and 5 are conjugate positons.

$\underset{1}{CH_2}=CH-\underset{3}{CH}=CH-\underset{5}{CH}=CH-\underset{7}{\ddot{N}H_2}$

Conjugate positions

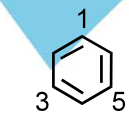
Note : Compound having at least two conjugate positions is known as conjugated compound.

Type of Conjugates

(1) π, π conjugation : If all conjugate positions have π bonds, then conjugation is known as π, π conjugation

$\underset{1}{CH_2}=CH-\underset{3}{CH}=CH_2$

$CH_3-CH_2-\underset{1}{CH}=CH-\underset{3}{CH}=CH-\underset{5}{CH}=CH_2$



All of the above compounds have π, π conjugation.

(2) Positive charge, π conjugation : In this case all conjugate positions have π bonds and only one conjugate positon has positive charge. If this is the case, then conjugation is known as positive charge, π conjugation.

$\underset{1}{CH_2}=CH-\underset{3}{\overset{\oplus}{CH_2}}$

It has positive charge, π conjugation.

$CH_2=CH-CH=CH-\overset{\oplus}{CH_2}$

This species has two type of conjugation π, π conjugation and positive charge, π conjugation.

(3) Negative charge, π conjugation : If all conjugate positions have π bonds and only one conjugate position has negative charge, then conjugation is known as negative charge, π conjugation

$CH_2=CH-\overset{\ominus}{CH_2}$

$CH_2=CH-CH=CH-\overset{\ominus}{CH_2}$

(4) Odd electron, π conjugation : If all conjugate positions have π bonds and one conjugate position has odd electron, then conjugation is known as odd electron, π conjugation.

$CH_2=CH-\dot{C}H_2$

$CH_2=CH-CH=CH-\dot{C}H_2$

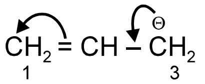
(5) Lone pair, π conjugation : If all conjugate positions have π bonds and only one conjugate position has ℓp then conjugation is known as ℓp, π conjugation.

$CH_2=CH-\ddot{N}H_2$ $\qquad CH_2=CH-\ddot{\underset{..}{X}}:$

$\underset{1}{CH_2}=CH-\underset{3}{CH}=CH-\underset{5}{CH}=CH-\underset{7}{\ddot{N}H_2}$

(A) Properties of conjugated compounds :

1. Conjugated electrons migrate from one conjugate positon to the other conjugate position



$\underset{1}{CH_2}=CH-\underset{3}{\overset{\ominus}{CH_2}} \qquad \underset{1}{\overset{\ominus}{CH_2}}-CH=\underset{3}{CH_2}$

Thus conjugated electrons are delocalised electrons and conjugated compounds are delocalised compounds.

2. Conjugated compounds can be represented by two or more than two possible structures due to the delocalisation of conjugated electrons. These possible structures are known as resonating structures.

Thus

$CH_2=\underset{I}{CH}-\overset{\ominus}{CH_2}$ and $\overset{\ominus}{CH_2}-\underset{II}{CH}=CH_2$

I and II are resonating structures of allyl carbanion.

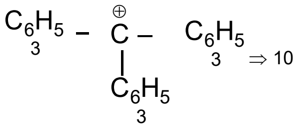
3. (a) Number of resonating structures of conjugated compound = Number of conjugate positions.

Note : This formula is not valid for benzene and fused benzene system, i.e., naphthalene, anthracene etc.

Structure	**Number of resonating structures**
$\underset{1}{CH_2} = CH - \underset{3}{\overset{\oplus}{CH_2}}$	2
$\underset{1}{CH_2} = CH - \underset{3}{CH} = CH - \underset{5}{\overset{\ominus}{CH_2}}$	3

(b) Number of resonating structures of benzene derivatives in which key atom is in conjugation to benzene ring = Three resonating structures for per benzene ring and one resonating structure corresponding to key atom. For examples :

$\underset{3}{C_6H_5} - \underset{1}{\overset{\ominus}{CH_2}} \Rightarrow 4$ $\quad \underset{3}{C_6H_5} - \underset{1}{\overset{\oplus}{CH}} - \underset{3}{C_6H_5} \Rightarrow 10$

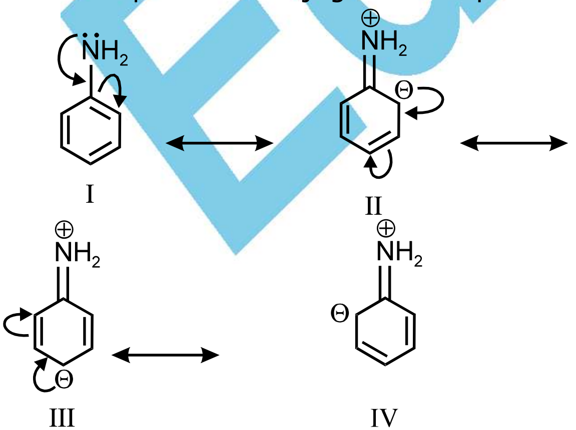


$\underset{3}{C_6H_5} - \overset{\oplus}{C}(\underset{3}{C_6H_5}) - \underset{3}{C_6H_5} \Rightarrow 10$

4. Resonating structures are not the real structures of conjugated compounds.

5. The real structure of conjugated compounds is a hybrid of all resonating structures.
This phenomenon is known as **resonance**, **mesomeris** or **delocalisaton**.

Thus, during resonance if one cannonical form has two real opposite poles, means at one terminal there is accomotation of charge & at another terminal there is depletion of charge takes place. Such type of resonance is called as mesomeric resoance & effect is called as mesomeric effect.
Thus resonance is nothing but hydridisation of resonating structrues and resonance phenomenon will take place in conjugated compounds.



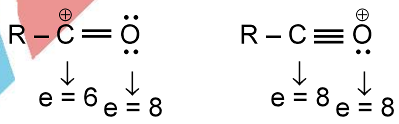
two real opposite poles

I to IV are the resonating structures of aniline. The real structure of aniline will be a resonance hybrid of all these four structures.

5. **Effect of resonance on the resonating structures :** Consider structures of benzene:

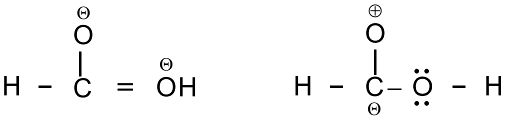
I and II are resonating structures of C_6H_6.
(a) According to resonating structure I, C, C bond length between C_1 and C_2 will be 1.33 Å.
(b) According to reasonating structure II, C, C bond bond length between C_1 and C_2 will be 1.54 Å.
(c) According to resonance, bond length between C_1 and C_2 will neither be 1.33 nor 1.54 Å but will be in between 1.33 and 1.54 Å, i.e., bond length between C_1 and C_2 is > 1.33 and < 1.54 Å.
(d) Experimental value is 1.40 Å, this result coincides with the result obtained by resonance, hence resonance theory or concept is correct.

(B) Contribution of Resonating structures : The contribution of an individual resonating structure depends upon its stability and stability depends on the followign factors :
(i) Neutral species is more stable than the charged (or dipoler species).
(ii) Species having complete octet is more stable than the species having incomplete octet.

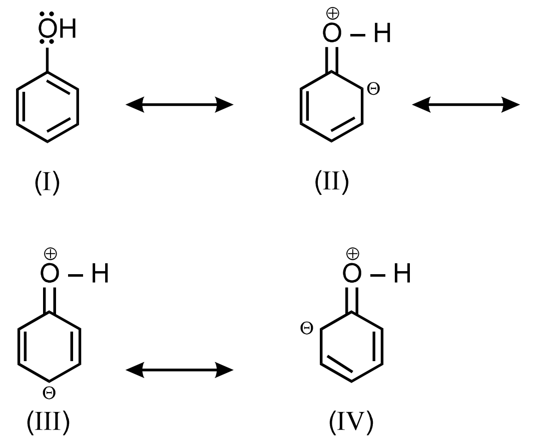


(I) (II)

(I) and (II) are resonating structures of acyl cation. (II) will be more stable than (I).
(III) If all structures have formal charge, the most stable one is that in which the positive and negative charges reside on the most electropositive and most electronegative atoms of the species respectively.



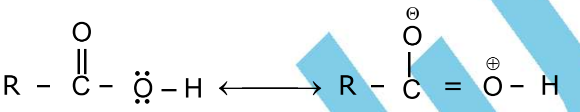
(I) and (II) are resonating structures of formic acid. All atoms in (I) and (II) have their complete octets. In (I) negative charge is on oxygen but in (II) negative charge is on carbon therefore (I) will be more stable than the (II).
(iv) Resonating structure with a greater number of covalent bonds is more stable.
(v) Increase in charge separation decreases the stability of resonating structure.



Hence stability of II and IV will be the same and both will be more stable than III. The order of stability of resonating structures in decreasing order will be as follows :
I > II ≡ IV > III

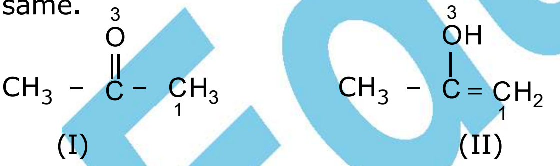
Note :
All the resonating structures do not contribute equally to the real molecule. Their contribution is a direct function of their stability.

(C) Conditions of Resonating structures : Resonance structures should fulfil following conditions:
(1) All resonating structures must have the same arrangement of atomic nuclei. Resonance differs from tautomerism in this very important aspect.



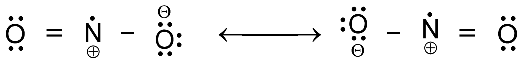
$$R-\overset{\overset{\Large O}{\|}}{C}-\ddot{O}-H \longleftrightarrow R-\overset{\overset{\ominus}{O}}{\overset{|}{C}}=\overset{\oplus}{O}-H$$

Position of atomic nuclei in (I) and (II) are same.



$$\underset{(I)}{CH_3-\overset{\overset{3}{O}}{\overset{\|}{C}}-\underset{1}{CH_3}} \qquad \underset{(II)}{CH_3-\overset{\overset{3}{OH}}{\overset{|}{C}}=\underset{1}{CH_2}}$$

Position of hydrogen nuclei in (I) and (II) are different hence (I) and (II) are not the resonating structures.
(2) The resonating structures must have the same numbers of paired and unpaired electrons. However, they differ in the way of distribution of electrons.

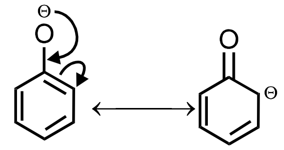


$$\ddot{O}=\underset{\oplus}{\dot{N}}-\overset{\ominus}{\ddot{O}}: \longleftrightarrow :\underset{\ominus}{\ddot{O}}-\underset{\oplus}{\dot{N}}=\ddot{O}$$

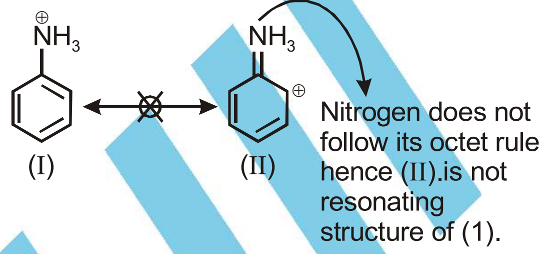
Total number of	Total number of
paired electrons = 16	paried electrons = 16
unparied electron=one	unpaired electron=one

(3) The energies of the different remaining structures must be the same or nearly the same.

(4) All atoms that are part of the delocalisation system must be in a plane or be nearly planar.
(5) All aotms of the resonating structure should follow the octet rule. For example :



All atoms follow octet rule.

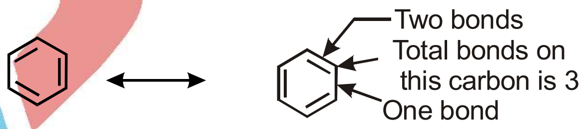


Nitrogen does not follow its octet rule hence (II).is not resonating structure of (1).

(D) Resonance and Bond order : Bond order in conjugated compound or bond order in compounds which exhibit resonance

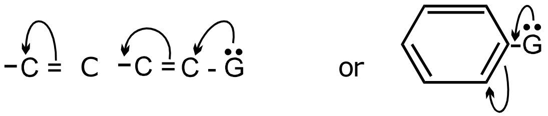
$$= \frac{\text{Total number of bonds on central atom}}{\text{Number of resonating structures}}$$

For examples :



Bond order of carbon in benzene $= \frac{2+1}{2} = 1.5$

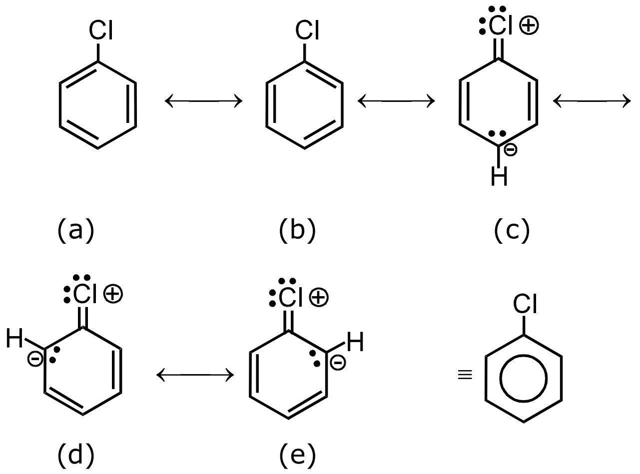
(E) + M effect (+R) :

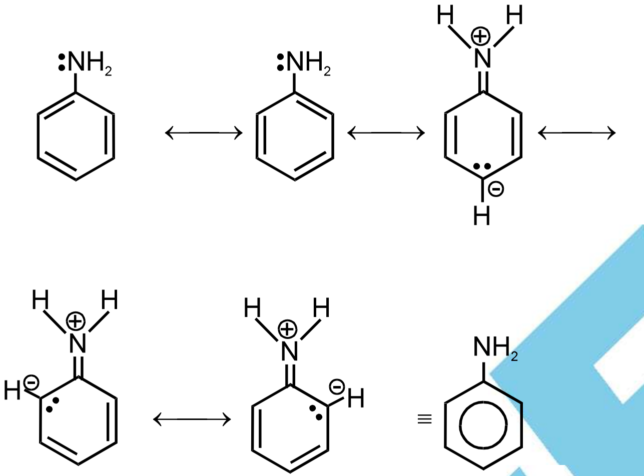


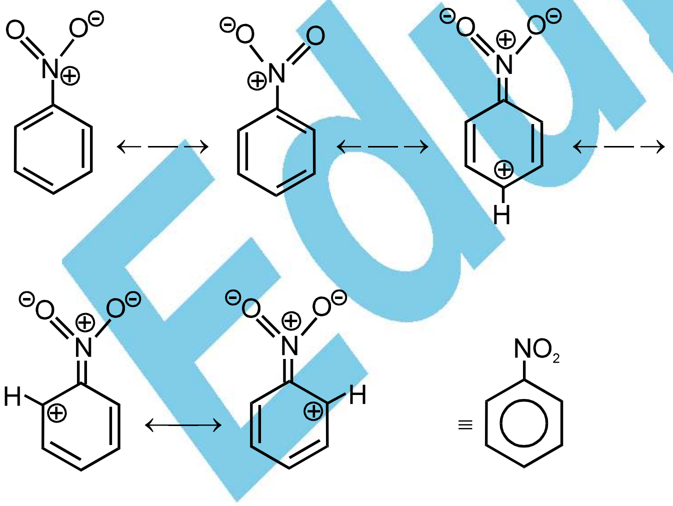
When flow of e⁻ pair (movement) starts from the group (G). It takes place when G has a lone pair or an extra electron (in ion).
e.g. $-NH_2$, $-OH$, $-Cl$, $-OR$ etc.

– M effect (– R) :

When e⁻ pair movement takes place towards G from the molecule.
e.g. $-NO_2$, $-C=O$, $-C\equiv N$, $-SO_3H$ etc. The various resonating structures of chlorobenzene, aniline and nitrobenzene are illustrated in following diagrams. Note that – Cl and $-NH_2$ show + M effect and $-NO_2$ show–M effect.







Thus, mesomeric effect works at only ortho & para position, it is absolutely absent on meta position, while inductive effect works at all three position o⁻, m⁻, p however intensity of effect decreases as the distance increases.

Note :

Mesomeric effect always dominant on inductive effect except halogen (Cl, Br, I only)

Application of Mesomeric effect :

(a) Stability of conjugated species :

(1) Stability of a conjugated compound is more than the corresponding non-conjugated compound.

For example :

$CH_2 = CH{-}CH = CH - CH_3$

(I)

Conjugated compound

$CH_2 = CH - CH_2 - CH = CH_2$

(II)

Non - Conjugated compound

Hence (I) will be more stable than (II)

(2) Stability of an aromatic compound is more than the corresponding non-aromatic conjugated compound. For example (III) is more stable than (IV)

$CH_2{=}CH{-}CH_2{=}CH{-}CH{=}CH_2$

(III) (IV)

Aromatic compound — Conjugated non-aromatic compound

Thus stability series of different compounds in decreasing order is as follows :

Aromatic compound > conjugated non-aromatic compound > non-conjugated compound

(3) Stability of allyl carbocation and benzyl carbocation :

Allyl and benzyl carbocation are conjugated species hence their stability can be compound by the number or resonating structures.

$CH_2 = CH - \overset{\oplus}{C}H_2$ $C_6H_5 - \overset{\oplus}{C}H_2$

Number of resonating Structures = 2 — Number of resonating Structures = 4

Hence the benzyl carbocation is more stable than the allyl carbocation.

(4) Stability of Substituted Benzyl Carbocations

: Stability of substituted benzyl carbocation depnds on the nature of group present in the benzene ring : The group may be +I, –I, +R or – R

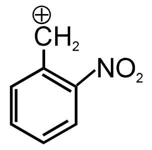
Case I : When ring has group which is – I and –R group.

$$\text{Stability} \propto \frac{1}{\text{Magnitude of charge}}$$

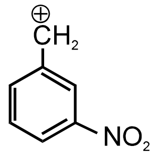
$$\text{P.E.} = K\frac{q^2}{r}$$

P.E. ↑ = charge ↑ = Stability ↓

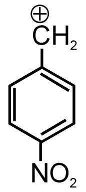
Example :



(I)
(i) Increase in the magnitude of positive charge by –I and – R effect
(ii) –I and –R power is maximum



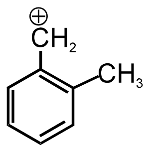
(II)
Increase in Positive charge only by –I effect



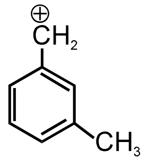
(III)
(i) Increase in Positive charge by –I and – R effect
(ii) –I and – R power is minimum

Hence (II) is more stable than (III) which is more stable than (I)

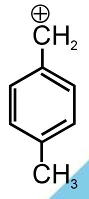
Case II : When ring has a group which is + I and + R group.



(I)
Positive charge is decreased by + I and + R group or stabilised by + I and + R group



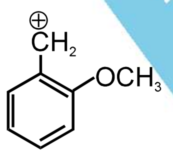
(II)
Stabilised by+I group only



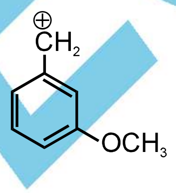
(III)
Stabilised by + I and + R effect

Hence (I) is more stable than (III) which is more stable than (II).
Thus o - derivative is more stable than p-derivative which is more stable than m-derivative.

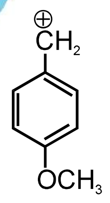
Case III : When group has + R effect and – I effect.



Stabilised by + R effect destabilised by –I effect –I power is maximum (due to distance)



Stabilised by –I effect only



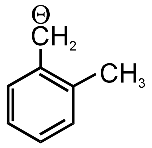
Stabilised by + R effect destabilised by –I effect –I power is minimum (due to distance)

Hence p-derivative is more stable than o-derivative which is more stable than m-derivative.

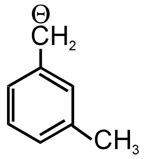
Note :
Stability of free radical have same order of arrangement.

(5) Stability of Substituted Benzyl carbanions

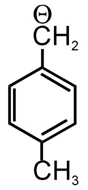
When group has + R and + I



+R effect decrease stability
+I effect also decrease stability
+I power is maximum



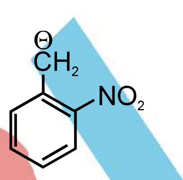
Destabilised only by+I effect only



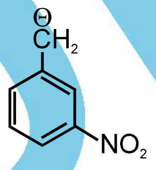
Destabilised only by+ R and + I effect (+ I power is minimum)

Hence m -derivative is more stable than p-derivative which is more stable than o-derivative.

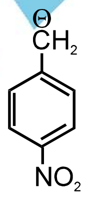
Case II : When group has – R and – I effect.



Stabilised by –R and–I effect (–I power is minimum)



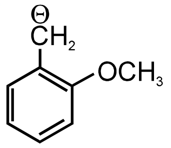
Stabilised by –I effect



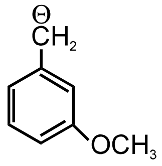
Stabilised by–R and –I effect (–I power is maximum)

Thus o-derivative is more stable than p-derivative which is more stable than m-derivative.

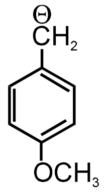
Case III : When group has + R and – I effect.



Destabilised by+R effect and stabilised by –I effect –I power is maximum



Stabilised by –I effect



Destabilised by +R effect stabilised by–I effect and–I power is minimum

Thus m-derivative is more stable than o-derivative which is more stable than p-derivative.

Note :
In case of halo derivative, result depends only on inductive effect.

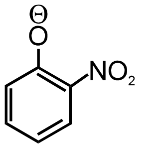
(B) Acidity of Phenol

$$C_6H_5OH \longrightarrow C_6H_5\overset{\ominus}{O} + \underset{\downarrow}{\overset{\oplus}{H}}$$

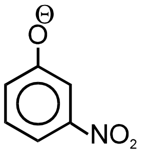
more is the stability of phenoxide ion more will be the acidity of phenol

Acidity of Substituted Phenols : Acidity of substitued phenols depend on the stability of the phenoxide ion because acidity is the function of acid anion.

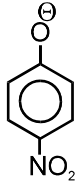
Case I : When group is –R and –I group.



Phenoxide ion is stabilised by –R and–I effect and –I power is maximum –R power is maximum



Stabilised by –I effect only



Stabilised by –R and–I effect and–I power is minimum–R power is minimum.

Thus according to stability of anions o-derivative will be more acidic than p-derivative which will be more acidic than m-derivative. But result is as follows in case of nitrophenols, p-derivative is more acidic than o-derivative which is more acidic than m-derivative. In o-derivative , there is hydrogen bonding which decrease acidity. Thus order of acidity is as follows :

p-derivative>o-derivative>m-derivative>phenol.

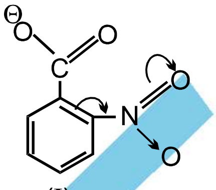
$$\xrightarrow{\hspace{6cm}}$$

Acidity in decreasing order

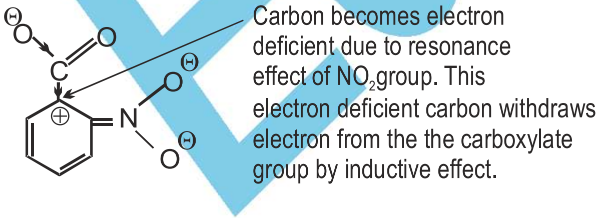
(C) Acidity of aromatic acids

Acidity of substituted acids Ortho substituted banzoic acid is always a stronger acid than m- and p-derivative due to the ortho effect.

Case I : When group is –R and – I group.

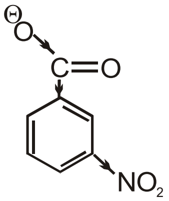


(I)



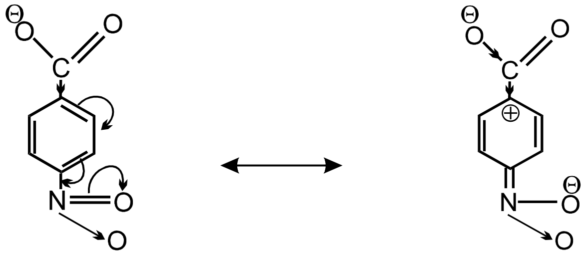
Carbon becomes electron deficient due to resonance effect of NO_2 group. This electron deficient carbon withdraws electron from the the carboxylate group by inductive effect.

Thus, anion is stabilised by –R and –I effect and – I power is maximum.



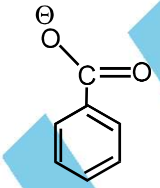
(II)

Anion is stabilised only by –I effect of NO_2 group



(III)

Anion is stabilised by -R and –I effect of NO_2 group



(IV)

Thus decreasing order of the stability of these anions is follows : I > III> II > IV

We know that ortho derivative is the most acidic therefore decreasing order of acidity of these acids is as follows :

o - derivative > p - derivative > m - derivative > benzoic acid

$$\xrightarrow{\hspace{6cm}}$$

Acidity in decreasing order

(D) Basicity of nitrogen containing compounds :

(i) Basicity of Aromatic Amines : Basicity of nitrogen containing compounds ∝ Electron density on nitrogen.

In aromatic amines, lone pair of elecrons present on nitrogen is delocalised, hence electron density decrease due to resonance.

Thus :

$$\text{Basicity} \propto \frac{1}{\text{Number of resonating structures}}$$

Structure	Number of resonating structures
$C_6H_5\ddot{N}H_2$	4
$C_6H_5-\ddot{N}H-C_6H_5$	7
$C_6H_5-\underset{C_6H_5}{\underset{\mid}{\ddot{N}}}-C_6H_5$	11

Basicity in decreasing order

(ii) Basicity of other Nitrogen Containing Compounds : Basicity depends on the following factors :

(1) Electronegativity of nitrogen

$$\text{Basicity} \propto \frac{1}{\text{Electronegativity of nitrogen}}$$

Example :

(a)

(II) is more basic than (I)

$R-\ddot{N}H_2$ $\quad R-CH=\ddot{N}H$ $\quad R-C\equiv\ddot{N}$

(b) $\xrightarrow{sp^3 \qquad sp^2 \qquad sp}$

Electronegativity in increasing order Basicity in decreasing order

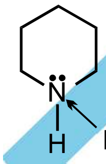
(c) $CH_3-CH_2-\overset{sp^3}{CH_3}-\ddot{N}H_2$

$CH_3-CH=\overset{sp^2}{CH}-\ddot{N}H_2$

$CH_3-C\equiv\overset{sp}{CH}-\ddot{N}H_2$

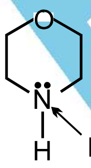
Electronegativity of carbons attached to amino group is in increasing order hence basicity is in decreasing order.

(d)



I

Less electronegative



II

More electronegative due to oxygen

Hence I is more basic than II

(2) Inductive effect

Basicity ∝ + I power of the group on nitrogen

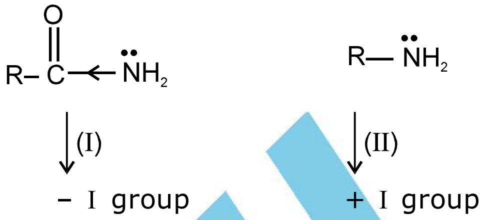
$$\text{Basicity} \propto \frac{1}{-\text{I power of the group on nitrogen}}$$

$R-\ddot{N}H_2$ $\qquad \ddot{N}H_2-OH$

$\downarrow \qquad\qquad \downarrow$

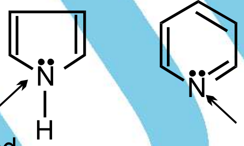
+ I group (I) $\qquad$ (II) – I group

hence amines are more basic than hydroxyl amines.



hence (II) is more basic than (I)

(3) Resonance : Delocalisation of lone pair of electrons present on nitrogen decreases basicity.



Lone pair delocalised

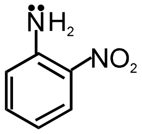
Lone pair is not delocalised

(I) $\qquad$ (II)

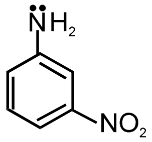
hence (II) is more basic than (I)

(iii) Basicity of substituted Anilines : Para substituted aniline is more basic than ortho substituted aniline and the effect is known as para effect.

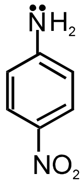
Case I : When group has –R has –I effect.



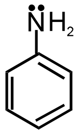
Decrease in electron density on nitrogen by – R and – I effect and – I effect is maximum (minimum electron density on nitrogen)



Decrease in electron density on nitrogen by – I effect only



Decrease in electron density on nitrogen by – R and – I effect and – I power is minimum



no group (maximum electron density on nitrogen)

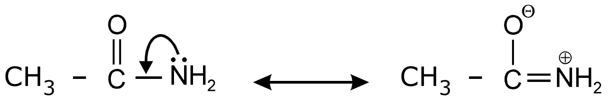
Thus order of basicity is as follows :

aniline>m-derivative>p-derivatives>o-derivative

$\xrightarrow{\hspace{8em}}$

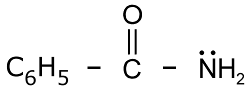
Basicity in decreasing order

Case-II Effect of cross conjugation on basicity :



$CH_3-\overset{O}{\overset{\|}{C}}-\ddot{N}H_2 \longleftrightarrow CH_3-\overset{O^{\ominus}}{\overset{|}{C}}=\overset{\oplus}{N}H_2$

Due to delocalisation and – I effect of CO group, amides are less basic than amines.



$C_6H_5-\overset{O}{\overset{\|}{C}}-\ddot{N}H_2$

In this amide there is cross conjugation which increases basicity; thus $C_6H_5CONH_2$ is more basic than CH_3CONH_2. π bond of C = O group is in conjugation to benzene ring as well as lp of NH_2 group.

Case-III Basicity of different nitrogen compounds in decreasing order :

Guanidine > Aliphatic amines > NH_3 > Aromatic amines > Imine > Amide > Cyanide

$\xrightarrow{\hspace{6cm}}$

Basicity in decreasing order

1.3 Electromeric Effect

It is temporary effect and operates only in π - electrons (i.e. multiple bonded compounds) in presence of some attacking reagents. It means, it is externally induced in a molecule. In polar bonds, in presence of attacking reagents, a complete transfer of electron (one of π e⁻ pair) to more electronegative atom takes place. e.g. in $>C^{\delta+}=O^{\delta-}$ in presence of nucleophile like CN^-, HSO_3^-, π electrons shifts over to O.

$>C^{\delta+}=O^{\delta-} + CN^- \dashrightarrow >C^+-O^-$

or

$>C=C< + H^{\delta+} + Br^{\delta-} \dashrightarrow >C^+-C^-<$

(H^+ ion presence results in polarisation)

1.4 Hyperconjugation

When (C – H) sigma electrons are in conjugation to pi bond, this conjugation is known as σ (C – H), π conjugation, excessive conjugation or hyperconjugatioon.

Structural requirement for hyperconjugation:

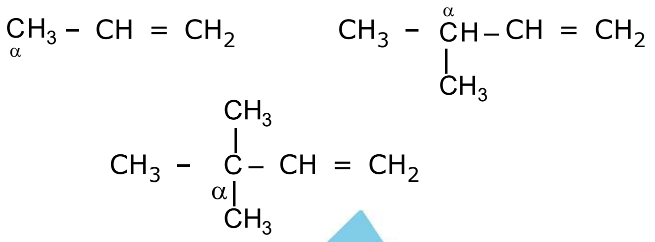
(A) Compound should have at least one sp^2-hybrid carbon of either alkene alkyl carbocation or alkyl free radical.

(B) 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 moelucle.

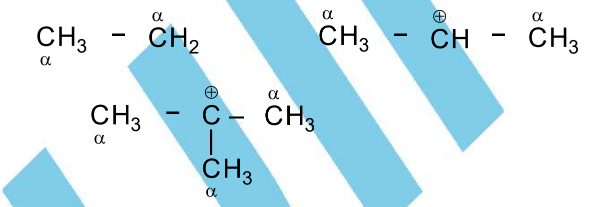
(C) Hyperconjugation is of three types :

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



$\underset{\alpha}{CH_3}-CH=CH_2 \qquad CH_3-\overset{\alpha}{C}H(CH_3)-CH=CH_2 \qquad CH_3-\underset{\alpha}{C}(CH_3)_2-CH=CH_2$

(ii) σ (C – H), positive charge conjugation : This type of conjugation occurs in alkyl carbocation.

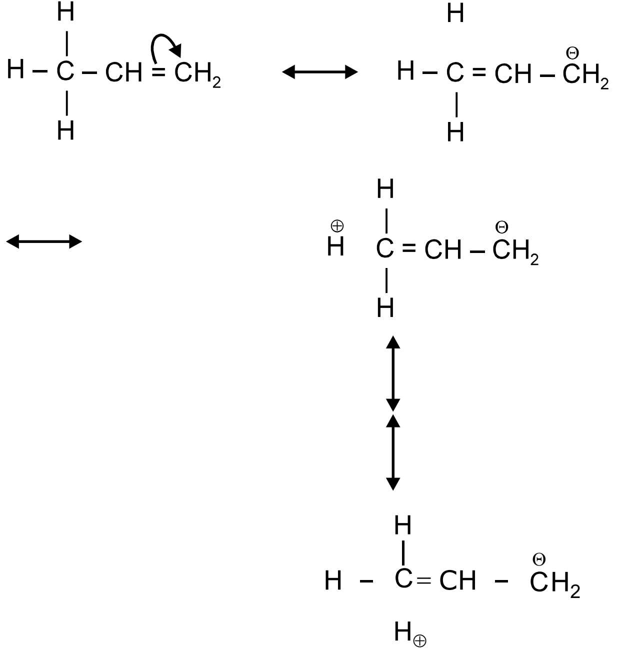


$\underset{\alpha}{CH_3}-\overset{\alpha}{C}H_2 \qquad \overset{\alpha}{CH_3}-\overset{\oplus}{C}H-\overset{\alpha}{CH_3} \qquad \underset{\alpha}{CH_3}-\overset{\oplus}{C}(\underset{\alpha}{CH_3})-\overset{\alpha}{CH_3}$

(iii) σ (C – H), odd electron conjugation : This type of conjugation occurs in alkyl free radicals -

$\underset{\alpha}{CH_3}-\underset{sp^2}{\dot{C}H_2} \qquad \overset{\alpha}{CH_3}-\dot{C}(\underset{\alpha}{CH_3})-\overset{\alpha}{CH_3}$

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



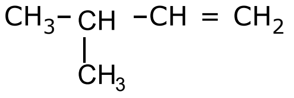
In the above resonating structures there is no covalent bond between carbon and hydrogen. From this point of view, hyperconjugation may be regarded as **" no bond resosnance "**.

Application of Hyperconjugation :

(A) Stability of Alkenes : Hyperconjugation explains the stability of certain alkenes over other alkenes:

(i) Stability of alkenes ∝ Number of alpha hydrogens ∝ Number of resonating structures

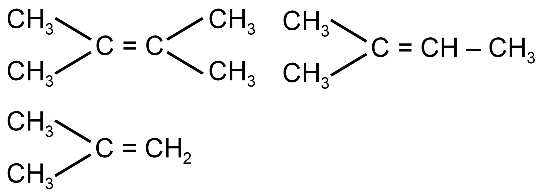
$CH_3-CH=CH_2$ $CH_3-CH_2-CH=CH_2$



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

⟶

Stability in decreasing order



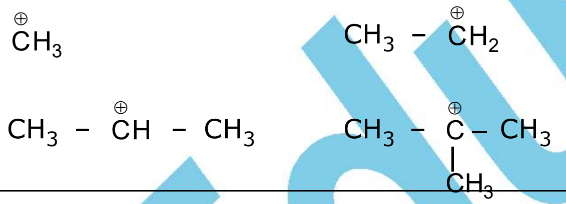
⟶

Number of alpha hydrogens in decreasing order stability of alkenes in decreasing order

(B) 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.

The bond length between carbon-carbon double bond ∝ number of resonating structures.

(C) Stability of Alkyl Carbocations : Stability of alkyl carbocations ∝ number of resonating structures ∝ number of hydrogens.



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

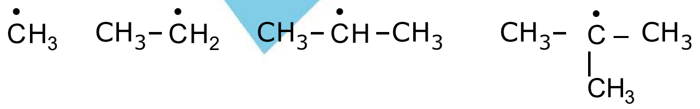
⟶

(i) Number of α-hydrogens in increasing order

(ii) Stability in increasing order

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

structure



$\dot{C}H_3$ $CH_3-\dot{C}H_2$ $CH_3-\dot{C}H-CH_3$ $CH_3-\underset{CH_3}{\underset{|}{\dot{C}}}-CH_3$

0 4 7 10

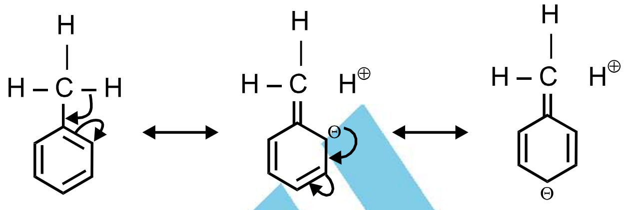
No of resonating structures

⟶

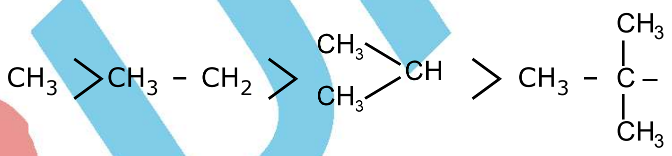
(i) Number of resonating structures in increasing order

(ii) Stability is in increasing order

(E) 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 -

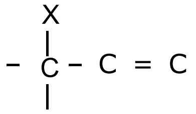


⟶

Electron donatnig power in decreasing order due to the hyperconjugation

Reverse Hyperconjugation :

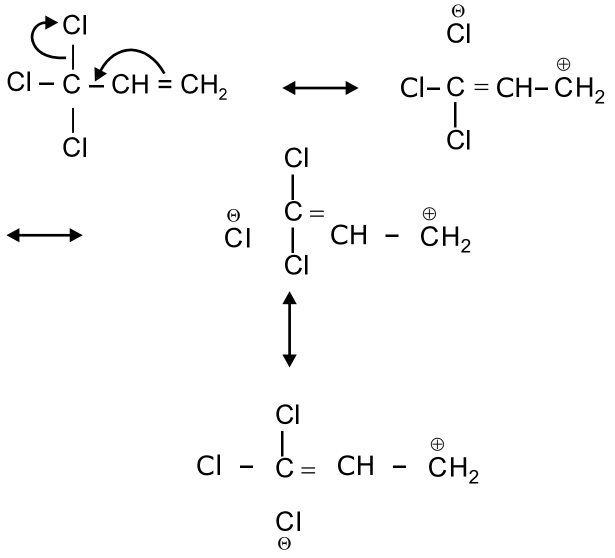
The phenomenon of hyperconjugation is also observed in the system given below :



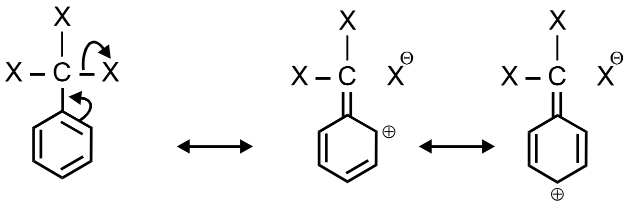
$-\underset{|}{\overset{X}{\overset{|}{C}}}-C=C$

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.



2. BOND FISSION

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

2.1 Homolytic Fission :

Occurs in gas phase or in non-polar solvents and is catalysed by reagents. In such fission free radicals are formed. Here the bond pair is equally shared after the fission.

$AB \rightarrow A^{\circ} + B^{\circ}$ (free radicals)

Condition for Homolytic Bond Fission : Homolysis takes place in the presence of peroxide, UV light, heat (≥ 500°C), electricity and free radical. The process is known as initiation of free radical reaction.

$$A : B \xrightarrow[\substack{\text{(ii) } h\nu \\ \text{(iii) } \Delta \\ \text{(iv) Electricity} \\ \text{or} \\ \text{(v) Free Radical}}]{\text{(i) Peroxide}} A^{o} + B^{o}$$

$$CH_3 - H \xrightarrow{h\upsilon} \dot{C}H_3 + \dot{H}$$

$\downarrow$

methyl free radical

(i) Homolytic bond fission gives free radical as the reaction intermidiate.

(ii) Reaction mechanism of the reaction is known as free radical or homolytic mechanism.

2.2 Heterolytic fission :

Occurs in polar solvents, catalysed by acids or bases, greatly influenced by polarity of solvents. Here, the ions are formed. In an organic compound such as R - G, two types of ions are formed.

$R - G \rightarrow R^{+} + G^{-}$

(R^{+} is known as carbonium ion)

$R - G \rightarrow R^{-} + G^{+}$

(R^{-} is known as carbanion ion)

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

Thus

(A) Heterolytic bond fission gives carbocation or carbanion as reaction intermediate.

(B) Mechanism of the reaction in which heterolytic bond fission takes place is known as heterolytic mechanism or ionic mechanism.

(C) The energy required for heterolytic bond fission is always greater than that for homolytic bond fission due to electrostatic force of attraction between ions.

3. REACTION INTERMEDIATES

Reaction intermediates are generated by the breaking of covalent bond of the substance. They are short -lived species and are highly reactive. There are six important types of reaction -intermediates.

(1) Carbocation (2) Carbanion
(3) Free radical (4) carbene
(5) Nitrene

3.1 Carbocations

(1) An organic species which has a carbon atom bearing six electrons in its outermost orbit and has a positive charge is called a carbocation.

(2) Carbocations can be classified into the following groups :

(A) Alkyl carbocations : When positive charge is present on the alkyl carbon, carbocation is known as alkyl carbocation.

⇒ Stability of alkyl carbocations can be explained by

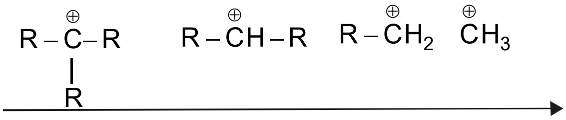
(i) Inductive effect and

(ii) Hyperconjugation

Stability of carbocation depend on the +I & –I group as follows :

Stability ∝ + I power of group

⇒ According to these two effects the stability order is as follows :



$$R-\overset{\oplus}{C}(R)-R \quad R-\overset{\oplus}{C}H-R \quad R-\overset{\oplus}{C}H_2 \quad \overset{\oplus}{C}H_3$$

Stability in decreasing order

$$\text{Stability} \propto \frac{1}{-\text{I power of group}}$$

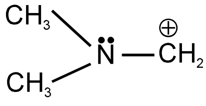
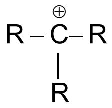
$$I-\overset{+}{C}H_2 \qquad Br-\overset{+}{C}H_2 \qquad Cl-\overset{+}{C}H_2 \quad F-\overset{+}{C}H_2$$

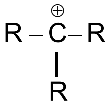
–I power of halo group increases

Stability increases (due to pπ-pπ overlapping)

⇒ 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 cabocation due to the delocalisation.

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

 is more stable than 

$CH_3-\ddot{\underset{..}{O}}-\overset{\oplus}{C}H_2$ is more stable than 

(B) 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.

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

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

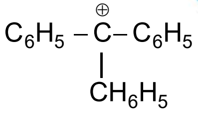
(ii) Allyl carbocations are more stable than the alkyl carbocations due to the resonance. Allyl carbocations are stabilised by delocalisation (or resonance).

(D) Phenyl methyl carbocations :

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

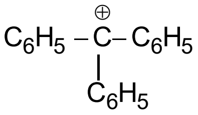
(ii) Phenyl methyl carbocations are of three types:

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



Triphenyl methyl
carbocation
(3°–carbocation)

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

Structure :		$C_6H_5-\overset{\oplus}{C}H-C_6H_5$	$C_6H_5-\overset{\oplus}{C}H_2$
No of resonating Structures	10	7	4

$\longrightarrow$

(i) Number of resonating structures in decreasing order.

(ii) Stability in decreasing order

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

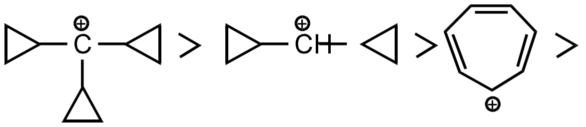
(E) Aromatic Carbocations :

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

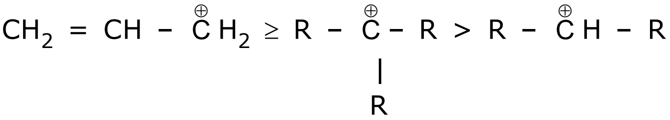
(ii) Aromatic carbocations are so stable that even their solid states are known. For example tropolium carbocation as tropolium bromide is a yellow solid. It fact tropolium carbocation is about 10^{11} times more stable than triphenyl methyl carbocation.

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

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



$(C_6H_5)_3\overset{\oplus}{C} > (C_6H_5)_2\overset{\oplus}{C}H > C_6H_5 - \overset{\oplus}{C}H_2 \geq$



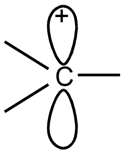
$CH_2 = CH - \overset{\oplus}{C}H_2 \geq R - \underset{R}{\overset{\oplus}{C}} - R > R - \overset{\oplus}{C}H - R$

$> R - \overset{\oplus}{C}H_2 > CH_2 = \overset{\oplus}{C}H$

(4) Characteristics of carbocations (except vinyl carbocation) :

(i) It has three pairs with empty p-orbital. Its hybridisation is sp^2.

(ii) Shape of carbocation is trigonal planar.



Note : Triphenyl methyl carbocation has propeller shape.

(iii) There are six electrons in the outermost orbit of carbocationic carbon hence its octet is incomplete. All the six electrons are paired.

(iv) It is charged electrophile.

(v) It is diamagnetic in character.

(vi) It is formed by heterolytic bond fission.

(vii) It reacts with nucleophiles.

(5) Reactions which take place by the formation of carbocation as reaction intermediate : In the following type of reactions product formation takes place by the formation of carbocation as reaction intermediate.

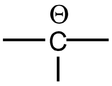
(i) SNI reactions

(ii) EI reactions

(iii) Electrophilic addition reaction of alkenes and alkynes.

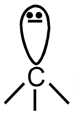
3.2 Carbanions

Anion of carbon is known as carbanion. Carbanion carries three bond pairs and one lone pair, thus making the carbon atom negatively charged. So carbanion may be represented as



(1) Characteristic of Carbanions :

(i) Hybridisation and geometry : Alkyl carbanion has three bond pairs and one lone pair. Thus hybridisation is sp^3 and geometry is pryamidal.



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

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

(iii) It behaves as charged nucleophile.

(iv) It is diamagnetic in character because all eight electrons are paired.

(v) It is formed by heterolytic bond fission.

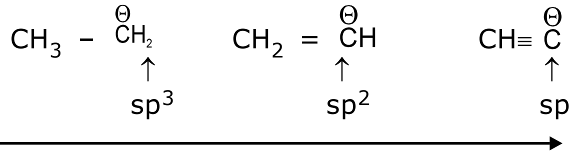
(vi) It reacts with electrophiles.

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

(A) Electronegativity of carbanionic carbon :

Stability$\propto$Electronegativity of carbaionic carbon

$\propto$ % s-character of carbanionic carbon

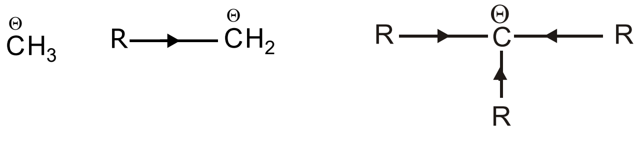


(i) % s-character in increasing order

(ii) Stability in increasing order.

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

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



(i) +I power in increasing order

(ii) Stability in decreasing order.

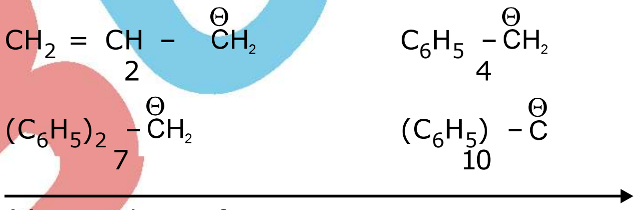
(b) Stability of carbanions $\propto$ –I power of the group

For example :

(i) –I power of halo group is in increasing order

(ii) Stability in increasing order.

(C) Delocalistion or Resonance : Allyl and banzyl carbanions are stabilised by delocalisation of negative charge.



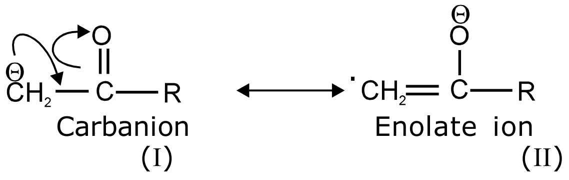
(i) Number of resonating structures is in increasing order

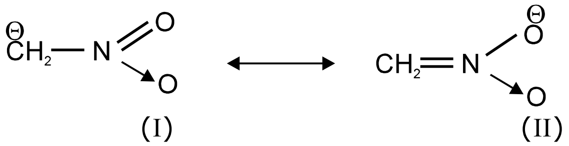
(ii) Stability is in increasing order

(D)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.

(E) Stabilisation by >C=O, $-NO_2$ and CN groups present on carbanionic carbon : These groups stabilise carbanion by resonance effect





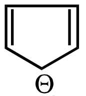
Contribution of structure (II) will be more than (I) because in (II) negative charge is present on electronegative oxygen.

(F) Stability of Aromatic Carbanions :

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

(ii) Aromatic carbanions are most stable carbaions.

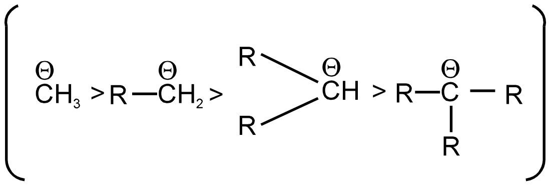
(iii) Anions obeying Huckel rule are stable because they are aromatic and there is complete delocalisation of negative charge.



Cyclopentadienyl anion

(3) Stability of different type of carbanions in decreasing order :

Aromatic carbanion > Benzyl carbanion > Allyl carbanion > $CH \equiv \overset{\Theta}{C} > CH_2 = \overset{\Theta}{CH}$ > Alkyl carbanion



(D) Reactions in which product formation takes place by formation of carbanion as reaction intermediate : In the following reactions product formation takes place by the formation of carbanion as reaction intermediates:

(i) Condensation reactions of carbonyl compounds, i.e., aldol condensation, Perkin reaction, reformatsky reaction etc.

(ii) Condensation reactions of ester; Claisen condensation.

(iii) Wittig reaction.

3.3 Carbon Free Radical

(1) Carbon free radicals are odd electron species in which carbon atom bears the odd electron.

(2) Homolytic bond fission of a covalent single bond gives rise to free radicals.

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

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

(5) The structure of the carbon free radicals are very difficult to predict. They have planar to pyramidal geometry depending upon the groups and atoms attached to the carbon atom having odd electron. For example, methyl free radical is planar. On the other hand trifluoro methyl free radicals is pyramidal. Alkyl free radicals have also pyramidal geometry.

(6) Free radicals are neutral electrophiles.

(7) Free radical generally reacts with free radical.

(8) Stability :

(A) Stability of Alkyl free redicals : Stability of alkyl free radicals can be explained by hyperconjugation and number of resonating structures due to the hyperconjugation. The decreasing order of stability of alkyl free radicals is as follows :

tertiary > secondary > primary > CH_3

Both electron withdrawing group such as carbonyl, cyano and nitro and electron-donating groups such as methoxy and dimethyl amino have a stabilising effect on a radical at an adjecent carbon due to resonance.

(B) Stability of Allyl and Benzyl free radicals:

(i) Stability of these radicals can be explained by delocalisation or resonance.

Structure :

$$\underset{10}{(C_6H_5)_3\dot{C}} > \underset{7}{(C_6H_5)_2\,\dot{C}H} > \underset{4}{C_6H_5-\dot{C}H_2} >$$

$$\underset{2}{CH_2 = CH - \dot{C}H_2}$$

No. of resonating structure :

$\longrightarrow$

(i) Number of resonating structures in decreasing order

(ii) Stability in decreasing order

(ii) Allyl and benzyl radical are more stable than alkyl radicals. Triphenyl methyl radical and similar radicals are stable enough to exist in solution at room temperature.

Stability of different free radicals in decreasing order :

$$(C_6H_5)_3 - \dot{C} > (C_6H_5)_2 - \dot{C}H > C_6H_5 - \dot{C}H_2 >$$

$$CH_2 = CH - \underset{\underset{CH_3}{|}}{\dot{C}} - CH_3 > CH_2 = CH - \dot{C}H - CH_3 > CH_2$$

$= CH - \dot{C}H_2$ > Ter alkyl free radical > See alkyl free radical > P-alkyl free radical > $\dot{C}H_3$

Stability of the same type of alkyl free radical $\propto$ Number of carbons in alkyl free radical

Free radical reactions : Chemical reaction which takes place in the presence of peroxide, heat hυ, electricity or free radical is known as free radical reaction.

⇒ Amount of energy needed for homolysis of a covalent bond depends upon the stability of resulting free radical as reaction intermidiate (RI)

$$\text{Energy needed} \propto \frac{1}{\text{Stability of free radical as RI}}$$

4. REACTION REAGENTS

Organic reagents can be classified in two categories :

(A) Electrophile : Electron deficient species or electron acceptor is electrophile.

(B) Nucleophile : Electron rich species or electron or electron donor is nucelophile.

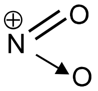
4.1 Electrophiles

It can be classified into two categories :

(A) Charged electrophiles ($E^{\oplus}$)

(B) Neutral electrophiles (E)

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

$H^{\oplus}$, $X^{\oplus}$, $R^{\oplus}$,  , $\overset{\oplus}{\underset{\cdot\cdot}{N}} = O$, $\overset{\oplus}{S}O_3H$

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

(B) Neutral electrophiles : It can be classified into three categories :

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

$BrCl_2$, BH_3, $ZnCl$, AlX_3, FeX_3, $\dot{C}H_3$, $\ddot{C}H_2$, $\ddot{C}X_2$

(IIB) Neutral covalent compound in which central atom has complete or expended octet and central atom has unfilled -d-shell is neutral electrophile

$SnCl_4$, $SiCl_4$, PCl_5, SF_6, IF_7

(IIIB) 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

PCl_5, NF_3, $\ddot{C}X_2$, CO_2, SO_3, CS_2, CX_4

Note :

(i) Cl_2, Br_2 and I_2 also behave as neutral electrophiles.

(ii) Electrophiles are Lewis acids.

4.2 Nucleophiles

Nucleophiles can be classified into three categories:

(A) Charged nucleophiles : Negatively charged species are charged nucleophiles.

$\overset{\ominus}{H}$, $\overset{\ominus}{O}H$, $R-\overset{\ominus}{O}$, $\overset{\ominus}{C}H_3$, $\overset{\ominus}{X}$, $\overset{\ominus}{S}H$, $R-\overset{\ominus}{S}$

(B) Neutral nucleophiles : It can be classified into two categories :

(IB) Neutral covalent compound, in which central atom has complete octet, has at least one lone pair of electrons and all atoms present on central atom should not be electronegative, is neutral nucleophile.

$\ddot{N}H_3$, $R-\ddot{N}H_2$, $R_2\ddot{N}H$, $R_3\ddot{N}$, $\ddot{N}H_2-NH_2$

(Nitrogen nucleophile)

$H-\underset{\cdot\cdot}{\ddot{O}}-H$, $R-\underset{\cdot\cdot}{\ddot{O}}-H$, $R-\underset{\cdot\cdot}{\ddot{O}}-R$

(Oxygen nucleophiles)

$H-\underset{\cdot\cdot}{\ddot{S}}-H$, $R-\underset{\cdot\cdot}{\ddot{S}}-H$, $R-\underset{\cdot\cdot}{\ddot{S}}-R$

(Sulphur nucleophiles)

$\ddot{P}H_3$, $R\ddot{P}H_2$, $R_2\ddot{P}H$, $R_3\ddot{P}$

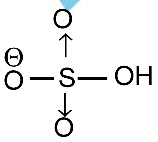
(Phosphorus nucleophiles)

(IIB) Organic compound containing carbon, carbon multiple bond/bonds behave as nucleophile.

Alkenes, Alkynes, Benzene,

$CH_2 = CH - CH = CH_2$, $CH_2 = CH - C \equiv CH$

(C) Ambident nucleophile : Species having two nucleophilic centres, one is neutral (complete octet and has at least one lone pair of electrons) and other is charged (negative charge) behaves as ambident nucelophile.

$\overset{\ominus}{C} \equiv \ddot{N}$, $\overset{\ominus}{O} - \ddot{N} = O$, 

$\overset{\ominus}{O}-\underset{\downarrow \atop O}{\overset{O \atop \uparrow}{S}}-OH$

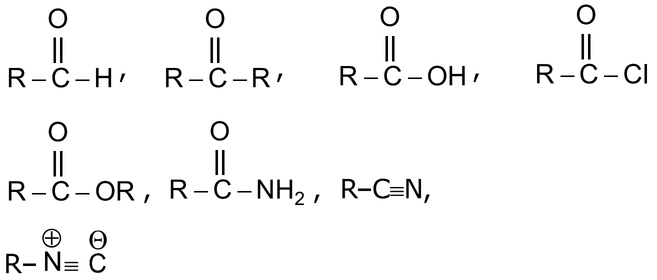
Note :

(A)Organometallic compounds are necleophiles.

(B)Nucleophiles are Lewis bases.

Organic compounds which behave as electrophile as well as nucleophile :

Organic compound in which carbon is bonded with electronegative atom (O, N, S) by multiple bond/bonds behaves as electrophile as well as nucleophile.



$R-\overset{O \atop \|}{C}-H$, $R-\overset{O \atop \|}{C}-R$, $R-\overset{O \atop \|}{C}-OH$, $R-\overset{O \atop \|}{C}-Cl$

$R-\overset{O \atop \|}{C}-OR$, $R-\overset{O \atop \|}{C}-NH_2$, $R-C\equiv N$,

$R-\overset{\oplus}{N}\equiv \overset{\ominus}{C}$

Note : During the course of chemical reaction electrophile reacts with nucleophile.

Nucleophilicity versus basicity

⇒ If the nucleophilic atoms are from the same period of the periodic table, strength as a nucleophile parallels strength as a base. For example :

$$H_2O < NH_3$$

$$CH_3OH \approx H_2O < CH_3CO_2^{\ominus} < CH_3O^{\ominus} \approx OH^{\ominus}$$

$$\xrightarrow{\hspace{12em}}$$

increasing base strength

increasing nucleophile strength

⇒ Nucleophile strength increases down a column of the periodic table (in solvents that can have hydrogen bond, such as water and alcohols). For example :

$$\overset{\Theta}{RO} < \overset{\Theta}{RS}$$

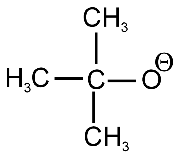
$$R_3N < R_3P$$

$$\overset{\Theta}{F} < \overset{\Theta}{Cl} < \overset{\Theta}{Br} < \overset{\Theta}{I}$$

$$\xrightarrow{\hspace{10em}}$$

increasing nucleophilic strength
decreasing base strength

⇒ Steric bulk decreases nucleophilicity . For example :



$<$ HO^{Θ}

weaker nucleophile Stronger base	stronger nucleophile weaker base

5. REACTION MECHANISM

There are mainly three categories into which major organic reactions are classified(for understanding of the reaction mechanisms).

3.1 Substitution Reactions
3.2 Addition Reactions
3.3 Elimination Reactions

5.1 Substitution (Displacement) Reaction :

The replacement of an atom or group from a molecule by a different atom or group is called as substitution reaction.

e.g. $RX + NaOH\ (aq) \rightarrow ROH + NaX$

$$C_6H_6 + RX \xrightarrow{AlCl_3} C_6H_5R + HCl$$

These reactions are further divided into three types depending upon the mechanism.

(a) Free - radical (b) Nucleophillic
(c) Electrophillic

Mechanism of Substitution Reactions

(a) Free radical substituion :

Halogenation in alkanes

$CH_4 \xrightarrow{Cl_2\ (h\upsilon)} CH_3Cl + HCl$

(Cl° free radical is generated & attacks methane)

$Cl_2 \xrightarrow{(h\upsilon)} 2\ Cl°$

($CH_3°$ free radical is produced and forms CH_3Cl by attacking Cl_2)

$Cl° + CH_4 \rightarrow CH_3° + HCl$

$CH_3^{\circ} + Cl_2 \rightarrow CH_3Cl + Cl°$

(Cl° free radical attacks again and a sort of chain reaction occurs)

$Cl° + CH_3Cl \rightarrow Cl\ CH_2° + HCl$

$ClCH_2° + Cl_2 \rightarrow CH_2Cl_2 + Cl°$

(The chain propagates like this till the formation of CCl_4)

NOTE 1 :

The chlorination of ethane, C_2H_6 gives two isomers in presence of sunlight.

$C_2H_6 \xrightarrow{Cl_2\ (h\upsilon)} C_2H_5Cl + HCl$

$C_2H_5Cl \xrightarrow{Cl_2\ (h\upsilon)} CH_3CHCl_2 + CH_2\ Cl - CH_2Cl$

The Bromine is **less reactive** toward alkanes (in general) than chlorine. But bromine shows ability to identity among different types of hydrogen atom (i.e. primary, secondary and tertiary). It gives exclusive replacement of tertiary hydrogen atom. Chlorine, on the other hand is **less selective** than bromine Fluorine is even **less selective** than chlorine and gives equal % age of substituted products. (Refer to reactions of alkanes in next chapter)

Wurtz reaction

$2\ C_2H_5Br + Na \rightarrow 2C_2H_5° + NaBr$

$C_2H_5° + C_2H_5° \rightarrow C_4H_{10}$

(b) Nucleophillic Substitution

They are divided into two categories

(i) $S_N{}^2$ mechanism :

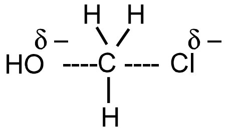
These are Biomolecular reactions. When rate of reaction depends upon concentration of both substrate (organic compound) and the nucleophile, the reaction is said to follow S_N2 (2nd order) mechanism

e.g. consider the hydrolysis of CH_3Cl

$H_3C^{\delta+} - Cl^{\delta-} + OH^- \rightarrow H_3C - OH + Cl^-$

The nucleophile OH^- attacks from the opposite side of Cl atom, and a transition state results where both OH^- & Cl^- are partially bonded to carbon atom.

Transition state :



$\rightarrow HO - CH_3 + Cl^-$

(ii) S_N1 mechanism :

These are Unimolecular reactions. When the rate of nuceleophillic substitution depends only on the concentration of the substrate, the reaction is first order and is respresented by S_N1.

e.g. : hydrolysis of tertiary butyl bromide

It follows two step process :

➢ heterolytic fission forming carbonium ion.

$$(CH_3)_3 - C - X \longrightarrow (CH_3)_3 - C^+ + X^-$$

(Slow step)

➢ Attack of nucleophile on planar carbonium ion.

$$(CH_3)_3 - C^+ + OH^- \longrightarrow (CH_3)_3 - C - OH$$

(fast step)

NOTE: 1

➢ Stronger is the nucleophile, more is the chance of S_N2 mechanism.
(large & easily polarised groups are stronger nucleophiles)

➢ more is the concentration of nucleophile, more is the chance of S_N2 mechanism.

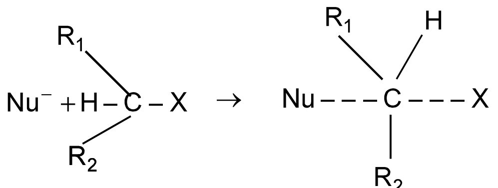
➢ presence of a polar medium, favours S_N1 mechanism.
(polar medium favours heterolytic fission)

➢ ease of S_N1 mechanism : benzyl > allyl > $3^0 > 2^0 > 1^0$ > methyl > phenylhalide
(depends upon stability of carbonium ion)

➢ ease of S_N2 mechansim : Phenyl > methyl > 1° > 2° >3°>allyl>benzyl halides.

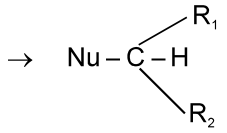
NOTE: 2

In S_N2 mechanism, Nu^- attacks from back side i.e. side opposite to halide atom.



optically active (+) configuration

Transition state



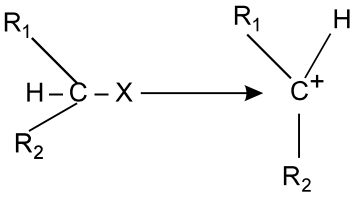
optically active (–) configuration

This means in S_N2 mechanism, the inversion of molecules takes place i.e.if the original reactant molecules is dextro–rotatory (+), the product formed is levo–rotatory (–).

So in S_N2 mechansim, the nucleophile attacks the substrate from back side and forms an intermediary transition state and forms a molecule with opposite configuration. This means that there is complete inversion which is also refers to a Walden Inversion.

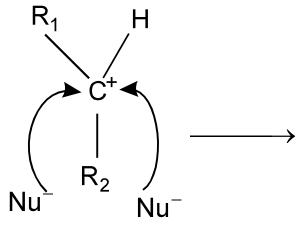
NOTE : 3

➢ In S_N1, first carbonium ion is formed which is sp^2 hybridised & planar.

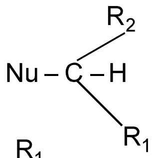


(planar)

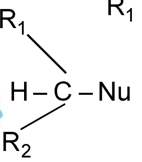
➢ Now Nu^- can attack from either side (as carbonium ion R^+ is planar)



50% of configurations are (+) type



50% of configurations are (-) type :



Hence in S_N1 mechanism, a racemic mixture is formed. The above discussion provides an evidence for S_N1 & S_N2 mechanisms.

NOTE : 4

The nature of solvent also affects the mechanism of the reaction e.g. more polar solvent favours S_N1 mechanism because of :

➢ The formation of carbonium ions is easy

➢ The ions formed are easily solvated.

The ionising power of solvent depends upon its dielectric constant. e.g. the order of ionising power of some solvents is :

$H_2O > HCOOH > CH_3OH > C_2H_5OH > CH_3COOH$

(c) Electrophillic Substitution :

Substitution in benzene ring follows electrophillic substitution.

e.g. bromination of benzene.

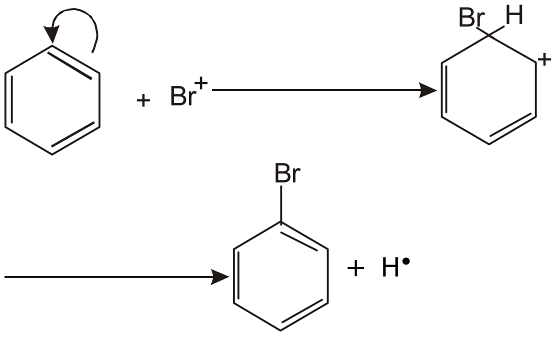
$$C_6H_6 + Br_2 \xrightarrow{FeBr_3} C_6H_5Br + HBr$$

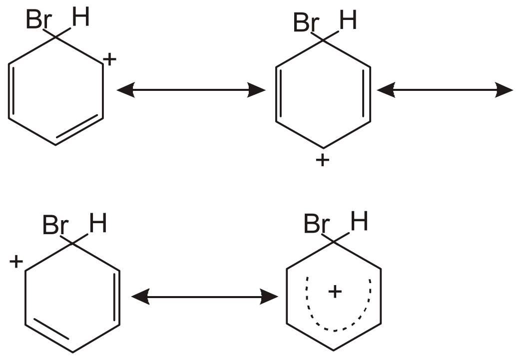
Mechanism :

➢ Formation of electrophile :

$$Br - Br + FeBr_3 \longrightarrow Br^+ + FeBr_4^-$$

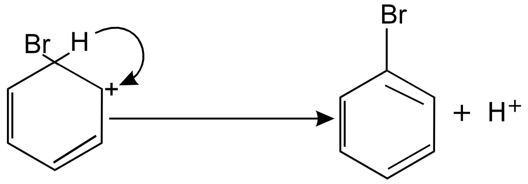
➢ Br^+ attacks benzene due to nucleophillic character of ring :





aromatic carbonium ion is resonance stabilised

- elimination of proton :



NOTE : 1

In benzene derivatives (C_6H_5 – G), the functional group G can also be classified on basis of their polar nature as : **Activating or Deactivating**.

An activating group (or an electron donating group) is one which makes benzene more reactive than benzene itself. Such groups are :

– NH_2, –OH, –OR. etc.

A de–activating group is one which makes benzene less reactive than benzene itself. Such groups –COOH, –C=O, –CHO, NO_2, –CN etc.

NOTE: 2

The presence of activating groups in benzene ring increases the ease of electrophillic substitution, whereas the deactivating groups do just the opposite.

NOTE: 3

Directive influence of substituents on Benzene

The various groups are classified as electron donating and electron withdrawing. Those that withdraw electrons inductively (polar effect) are said to exert an – I effect and those withdraw electrons conjugatively are said to exert a – M effect. Similarly + I and + M effect terms are used for electron donating. The following table illustrates the directive influence of various functional groups over benzene for second substitution.

Very strong	$-O^-$	(+) I, (+) M	
Strong (activating)	$-NR_2$ –NHR $-NH_2$ –OH –OR	(–) I < (+)M	o,p – Directors
Moderately strong (activating)	–OCOR –NHCOR $-C_6H_5$	(–) I<(+) M	o,p – Directors
Weak (activating)	$-CH_3$ $-CR_3$	(+)I	o,p – Directors
Weak (de – activating)	–F(~H) –Cl,Br,I $-CH_2Cl$ –CH = CH – COOH $-CH=CH-NO_2$	(–) I (+) M	o,p – Directors
Strong (de – activating)	–COR –CHO –COOR $-CONH_2$ –COOH $-SO_3H$ –CN $-NO_2$	(–) I > (–) M	m – Directors
Very strong (de – activating)	$-\overset{+}{N}H_3$ $-\overset{+}{N}R_3$	(–) I	m – Directors

5.2 Addition Reactions

Reactions in which atoms or groups of atoms are added to a molecule are called addition reactions.

These are also classified into three types depending upon mechanism

(a) Electrophillic (b) Nucleophillic
(c) Free radical

Mechanism of Addition Reactions :

(a) Electrophillic Addition Reactions :

Addition of HBr on ethylene

- $HBr \rightarrow H^+ + Br^-$
- electrophile (H^+) attacks the " = " bond

$$CH_2=CH_2 + H^+ \rightarrow CH_3 - C^+H_2$$

(carbonium ion)

Seeing incoming electrophile (H^+) electromeric effect occurs, and π electron cloud is displaced towards one of the carbon atoms.

- nucleophile (Br^-) attacks carbonium ion.

  $CH_3-C^+H_2+Br^- \rightarrow CH_3CH_2Br$

In case of $CH_3CH=CH_2$

$$CH_3CH=CH_2 + H^+ \longrightarrow \begin{cases} CH_3-HC^+-CH_3 \ \text{(2° carbonium, more stable)} \\ CH_3-CH_2-H_2C^+ \ \text{(1° carbonium, less stable)} \end{cases}$$

So the major product formed is CH_3–HC(Br)–CH_3 (Markonikoff's addition). In all addition reactions, same mechanism is followed.

- ➢ reactivity of Halogen acids for addition reaction: HI > HBr > HCl
- ➢ reactivity of Halogen : $Cl_2 > Br_2 > I_2$

NOTE :

If an electron withdrawing group is present at one end of alkene, then the addition is reversed. For example consider addition of

HCl to 3,3,3 –trichloro propene.

$Cl_3{-}C{-}CH{=}CH_2 + HCl \rightarrow$

$Cl_3CH_2CH_2Cl + Cl_3{-}C{-}CH(Cl)CH_3$

(major) (minor)

The reason for this is the stability of intermediate carbonium ion.– I effect producing group decreases stability of carbonium (C^+) ions. Try to compare the two possible carbonium ions formed.

(I) $Cl_3{-}C{-}CH_2{-}C^+H_2$ (II) $Cl_3{-}C{-}C^+H{-}CH_3$

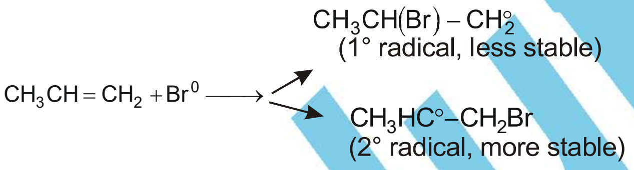
In (I) three Cl atoms are at a greater distance from C^+ site, whereas in (II), three Cl atom are near to C^+ site. Hence –I effect de–stabilises the carbonium ion (II) to a much greater extent than it does in (I).

(b) Free radical addition :

In presence of peroxide, addition of HBr follows anti–Markonikoff's addition (peroxide effect).

HBr + peroxide → Br°

(free radical addition takes place)



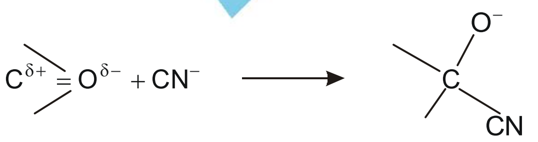
So the major product is $CH_3{-}CH_2{-}CH_2{-}Br$ (anti–markonikoff's addition).

NOTE :

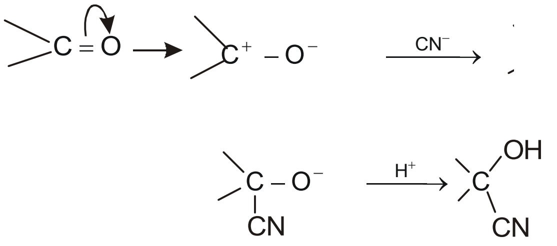
HCl and HI do not add similarly in presence of peroxides. The reaction with HCl fails because of high H–Cl bond energy. It is not possible to extract Cl° (radical in this manner). HI does not add because C–I bond is not of suffcient energy to promote attack of 1° radical.

(c) Nucleophillic addition reaction :

Addition of CN^- to aldehydes & ketones



In presence of CN^- (nucleophile) π e's of >C=O bond are shifted towards more electronegative oxygen atom (electromeric effect).



5.3 Elimination Reactions :

These reactions involve loss of atoms or group of atoms from a molecule to form multiple bonds.

CH_3CH_2X + (alc.) KOH → $CH_2{=}CH_2$ + HCl

$CH_3CH_2OH + H_2SO_4 \rightarrow CH_2{=}CH_2 + H_2O$

In general, loss of atoms or group occurs from adjacent carbon atoms to yield an alkene.

Mechanism of elimination reactions :

Elimination reactions are divided into two classes based on their mechanisms.

E2 : bimolecular elimination

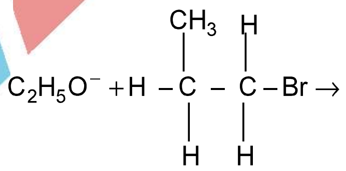
E1 : unimolecular elimination

Dehydrohalogenation of alkyl halides :

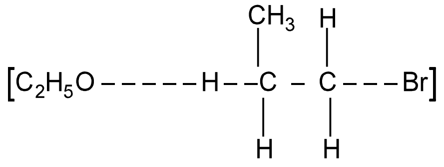
- ➢ dehydrohalogenation of 1° halides follows E2 mechanism.

(similar to S_N2 mechanism)

Nucleophile in this case is $C_2H_5O^-$ (ethanolic KOH) which forms a transition state with (1°) alkyl halides.



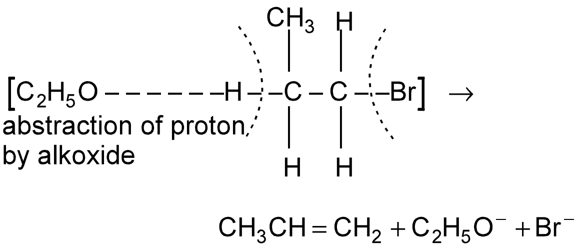
$C_2H_5O^- + H{-}C(CH_3)(H){-}C(H)(H){-}Br \rightarrow$



$[C_2H_5O{-}{-}{-}{-}{-}H{-}{-}C(CH_3)(H){-}C(H)(H){-}{-}{-}Br]$

Transition state

The reactions follows E2 mechanism, just like S_N2 mechanism and follows saytzeff rule



$CH_3CH=CH_2 + C_2H_5O^- + Br^-$

NOTE :

- The reaction rate increases with increasing strength of the base :

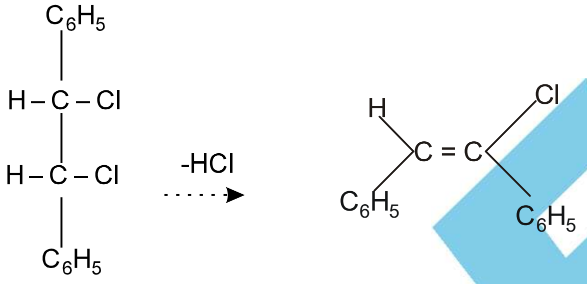
$$CH_3COO^- < HO^- < C_2H_5O^- < (CH_3)_3CO^- < NH_2^-$$

- The ease of elimination follows :

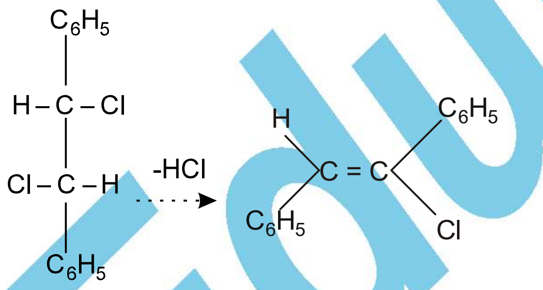
  C – I > C – Br > C – Cl > C – F
- The order of reactivity is : 3° > 2° > 1°
- The elimination occurs more easily when the halides are already unsaturated. e.g. elimination occurs readily in

  $CH_2=CH-CH_2CH_2Br$ than in

  $CH_3CH_2CH_2CH_2Br$.
- The nature of products of E_2 elimination of a compound having two chiral carbons depends upon stereochemistry of starting isomers. Consider dehydrohalogenation of meso compound diphenyl dichloro ethylene.



Optically Inactive meso cis isomer



optically active trans isomer

(d ℓ configuration)

- dehydrohalogenation of 3° halides follows E_1 mechanism

(similar to SN^1 mechanism)

1st Step :

heterolytic fission forming 3° carbonium ion (highly stable).

$(CH_3)_3-C-X \rightarrow (C_3)_3-C^+ + X^-$ (slow step)

2 nd step :

loss of proton (H^+) from carbonium ion.

$(CH_3)_2-C^+-CH_2-H \rightarrow (CH_3)_2-C=CH_2$ (fast step)

NOTE:

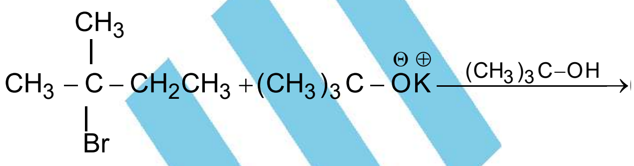
When two different alkenes may be formed, the one having more alkylation about double bond is formed *consider 2–bromobutane :*

$CH_3CH_2CH(Br)CH_3 + alc.KOH \rightarrow$

$CH_3CH=CHCH_3$ is major product.

$\rightarrow CH_3CH_2CH=CH_2$ is minor product.

This is referred to as Saytzeff Rule. The exception to Saytzeff rule comes when the proton to be removed is sterically hindered. e.g. consider 2–bromo – 2 – methyl butane :



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{Br}{|}}{C}}-CH_2CH_3+(CH_3)_3C-\overset{\ominus\,\oplus}{OK}\xrightarrow{(CH_3)_3C-OH}$$

$(CH_3)_2-C=CHCH_3 + CH_2=C(CH_3)-CH_2CH_3$

Minor Major

6. INTERMOLECULAR FORCES OF PHYSICAL PROPERTIES

In organic compounds, there exists only covalent bonds. The molecules in organic compounds are held together through very weak forces which are of three types : –

6.1 Dipole–Dipole :

In a molecule having polar bonds $(A^{\delta+}-B^{\delta-})$, there is an interaction among bond dipole. These interactions are called as dipole–dipole interactions. Due to these molecules are held quite strongly.

6.2 Hydrogen Bond : (H–F,H–O,H–N)

When Hydrogen is bonded with F,O,N the polarisation of H–F,H–O & H–N bond is strong, hence the dipole–dipole interaction is very–very strong. Hence the molecules having H–bonding have abnormally high intermolecular forces.

6.3 Vander waal forces :

The charge distribution in non–polar molecules can be symmetrical at one particular instant and un–symmetrical at some other, since the electrons are always in motion. At that instant, a non polar molecules (s) may be a weak–dipole. At the moment, the momentary dipole induces another short–lived dipole in a nearby molecule and both dipoles will be attracted to each other. Such interactions are called Vander waal Interactions (forces). Vander waal forces are proportional to -

(a) **Surface area of a molecule** : Greater is the surface area, greater is the number of interactions & hence stronger Vander waal forces.

(b) **Molecular weight of a molecule** : Due to greater number of electrons, greater is Vander waal force.

The physical properties like M.P. (melting points) B.P. (boiling points) and solubilities depend mainly on nature of bond present in the molecule, nature of intermolecular forces & molecular weight of molecule.

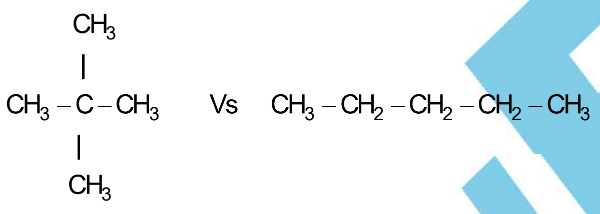
6.4 Melting Point :

➢ Organic solids, having molecules which are covalently bonded, and are held together by vanderwaals molecular forces and by dipole–dipole interactions, are generally low melting solids.

➢ The size and shape of a solid is also a factor determining its melting point.

(a) Solids composed of large molecules have high M.Ps. In large molecules, vanderwaal forces are also stronger.

(b) more symmetric a molecule is, the higher is its m.p.e.g. neopentane Vs n–pentane.



$$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C}}-CH_3 \quad Vs \quad CH_3-CH_2-CH_2-CH_2-CH_3$$

neo–pentane n–pentane

As neo–pentane is more symmetric & compact, its, m.p. is high. neo–pentane packs more efficiently in its crystal lattice and hence has higher lattice energy as compared to non-symmetric n-pentane.

(c) In case of geometric isomers, greater symmetry of trans isomers results is high m.p. for them.

e.g.(cis) maleic acid Vs (trans) fumaric acid

$$\begin{array}{l} H-C-COOH \\ \quad\ \| \\ H-C-COOH \end{array} \qquad \begin{array}{l} \qquad\quad H-C--COOH \\ \qquad\qquad\quad \| \\ HOOC-\ \ C-H \end{array}$$

maleic acid (m.p. = 150°C)

fumaric acid (m.p. = 250°C)

In carboxylic acids, even number of carbon atoms results in higher melting point than in molecules having odd number of carbon atoms. The cause is the symmetry of even' members.

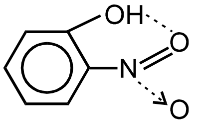
6.5 Boiling Points :

➢ In organic liquids, the intermolecular forces (cohesive forces) are Vander waal forces, dipole–dipole interactions which are generally weak and hence are low boiling liquids.

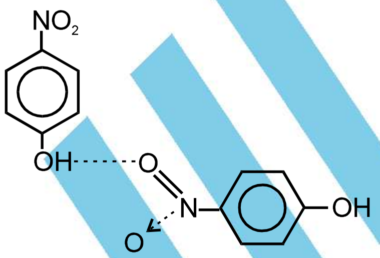
➢ In liquids having H–bonding show abnormally high boiling points. Actually Hydrogen bonding influences b.p. in two different manners.

(a) Intermolecular H–bonding :

Such H–bonding enhances the intermolecular forces & hence high boiling points.



(b) Intra–molecular H–bonding :



Such H–bonding occurs between different atoms with–in the same molecule (generally in ring structures). This bonding is also called as Chelation. It lowers the melting & boiling points and solubility. As interaction exist in molecules with–in, intermolecular forces weakens, e.g., compare H–bonding in o–nitrophenol and p-nitrophenol. In o–nitrophenol, intramolecular H–bonding occurs, which lowers the boiling point. In p–nitrophenol, intermolecular H–bonding occurs, which increases the boiling point.

➢ Shape also effects the B.P. e.g., branching always lowers the boiling point. Among the isomers of pentane, n-pentane has highest B.P. due to larger surface area of zig–zag chain of carbon atoms.

7. SOLUBILITY

The solubility of a compound depends not only on the polarities of solute & solvent, but also on temperature & pressure. Solubility follows the rule of " like dissolves like."

➢ The compounds containing –OH groups, $-NH_2$, –COOH are soluble is H_2O due to H-bonding. Not only alcohols, acids and amines are soluble in water, but to some extent, ethers are also soluble in water.

➢ Another factor important in solubility is the size of solute molecule e.g. alkanes are almost insoluble in water, but lower ones (CH_4) are sparingly soluble in water due to their molecular size being similar to that of water molecules.

➢ In general, one can say that the functional group favours solubility whereas the hydrocarbon part opposes solubility. The larger is the hydrocarbon part, lower is the solubility of a compound.

SOLVED EXAMPLE

Ex.1 Most stable carbanion–

(A) $(CH_3)_3C^-$ (B) $(CH_3)_2CH^-$

(C) $CH_3CH_2^-$ (D) $(C_2H_5)_3C^-$

Sol. C

Primary carbanion is most stable

Ex.2 Which one of the following is strongest acid -

(A) 2-chloropentanoic acid

(B) 3-chloropentanoic acid

(C) 5-chloropentanoic acid

(D) 4-chloropentanoic acid

Sol. A

2-chloropentanoic acid, due to more effective – I effect.

Ex.3 The most stable carbanion is–

(A) $CH_3CH_2C\bar{H}_2$ (B) $CH_3—C≡C^-$

(C) $CH_3CH=C\bar{H}$ (D) $CH_3—\bar{C}=CH_2$

Sol. B

When highly electronegative atom carry –ve charge than it is highly stable.

Ex.4 Correct order of nucleophilicity–

(A) $CH_3^- < NH_2^- < OH^- < F^-$

(B) $F^- < OH^- < CH_3^- < NH_2^-$

(C) $OH^- < NH_2^- < F^- < CH_3^-$

(D) $F^- < OH^- < NH_2^- < CH_3^-$

Sol. D

For same periods nucleophilicity $\propto$ Basic Strength. Thus if more E.N. atom consist –ve Charge than stability ↑ & basic strength ↓. Thereby nucleophilicity ↓.

Ex.5 Hydrogen bonding is maximum in–

(A) Ethanol (B) Diethyl ether

(C) Ethyl chloride (D) Triethylamine

Sol. A

Due the presence of O–H bond.

Ex.6 Benzoic acid is less acidic than salicylic acid because of–

(A) Hydrogen bond (B) Inductive effect

(C) Resonance (D) none of these

Sol. D

It is due to ortho effect.

Ex.7 In a reaction of C_6H_5Y, the major product (>60%) is m-isomer, so the group Y is–

(A) –COOH (B) –Cl

(C) –OH (D) $–NH_2$

Sol. A

–COOH have (–M effect)

Ex.8 Which one of the following orders is correct regarding the –I effect of the substituents ?

(A) $–NR_2 < –OR > –F$

(B) $–NR_2 > –OR > – F$

(C) $–NR_2 < –OR < –F$

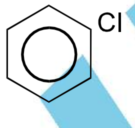
(D) $–NR_2 > –OR < –F$

Sol. C

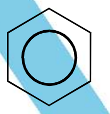
see series of –I effect

Ex.9 Which one of the following compounds will be most easily attacked by an electrophile ?

(A)

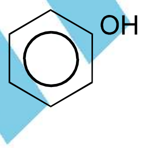


(B)



(C)

(D)



Sol. D

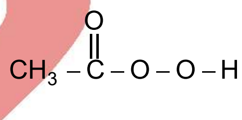
–OH group show (+M) effect and also +m effect is greater from $(–CH_3)$ group.

Ex.10 The weakest acid among the following–

(A) CH_3COOH (B) CH_3CO_2OH

(C) $ClCH_2COOH$ (D) CH_3CH_2COOH

Sol. B



$CH_3-\overset{\overset{O}{||}}{C}-O-O-H$ peroxide is week acid.

Ex.11 The correct order of boiling point for primary (1º), secondary (2º) and tertiary (3º) alcohols is–

(A) 2º > 1º > 3º (B) 3º > 2º > 1º

(C) 1º > 2º > 3º (D) 2º > 3º > 1º

Sol. C

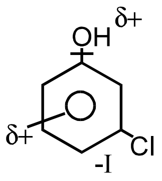
On increase branching surface area decrease, thus boiling point decrease.

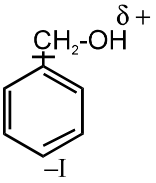
Ex.12 Which of the following is most acidic ?

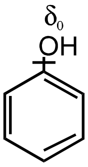
(A) m-chlorophenol (B) benzyl alcohol

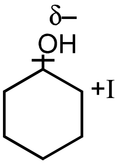
(C) phenol (D) cyclohexanol

Sol. A









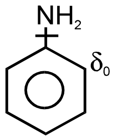
–I (Cl) > – I $(–C_6H_5CH_2)$

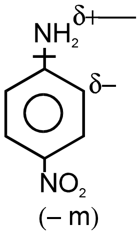
Ex.13 Among the following the strongest base is–

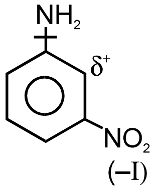
(A) $C_6H_5NH_2$ (B) p-NO_2–$C_6H_4NH_2$

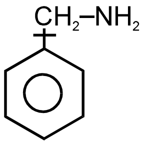
(C) m–NO_2–$C_6H_4NH_2$ (D) $C_6H_5CH_2NH_2$

Sol. **D**









lone pair localised

(+I) Primary amine

Aromatic primary amine is more basic than aniline. Because lone pair delocalised..

Ex.14 Strongest acid out of the following–

(A) CH_3COOH (B) $ClCH_2COOH$

(C) CH_3CH_2COOH (D) $(CH_3)_2CHCOOH$

Sol. **B**

Acidic strength ∝ –I power of Cl group.

Ex.15 Increasing order of acid strength among p-methoxyphenol, p-methylphenol, and p-nitrophenol is–

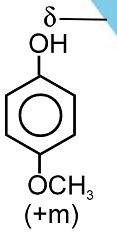
(A)p-nitrophenol, p-methoxyphenol, p-methylphenol

(B)p-methylphenol, p-methoxyphenol, p-nitrophenol

(C)p-nitorphenol, p-methylphenol, p-methoxyphenol

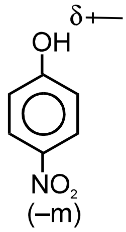
(D)p-methoxyphenol, p-methylphenol, p-nitorphenol

Sol. **D**



(i)

(ii)



(iii)

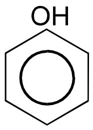
+ m ($-OCH_3$) > + m ($-CH_3$)

(i) < (ii) < (iii)

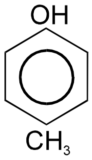
$\xrightarrow{\hspace{2cm}}$

↑ of acidic strength

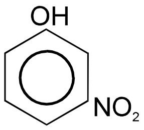
Ex.16 In the following compounds–



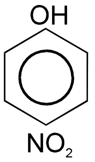
(I)



(II)



(III)



(IV)

the order of acidity is–

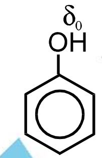
(A) III > IV > I > II

(B) I > IV > III > II

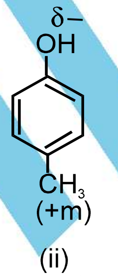
(C) II > I > III > IV

(D) IV > III > I > II

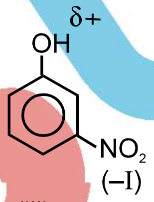
Sol. **D**



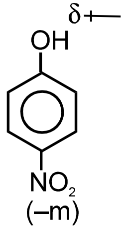
(i)



(ii)



(iii)



(iv)

at meto position +m effect absent thus only –I effect of $-NO_2$ is taken in (iii)

(iv) > (iii) > (i) > (ii)

Ex.17 Most powerful leaving group in following–

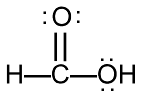
(A) NH_2^- (B) OH^-

(C) CH_3^- (D) F^-

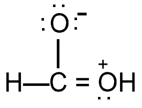
Sol. **D**

Weak base are always better leaving group.

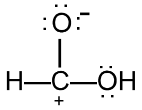
Ex.18



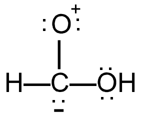
$H-\overset{\overset{\displaystyle :\ddot{O}:}{\|}}{C}-\ddot{O}H$ (I)



$H-\overset{\overset{\displaystyle :\ddot{O}:^-}{|}}{C}=\overset{+}{\ddot{O}}H$ (II)



$H-\underset{+}{\overset{\overset{\displaystyle :\ddot{O}:^-}{|}}{C}}-\ddot{O}H$ (III)



$H-\underset{\cdot\cdot}{\overset{\overset{\displaystyle :\dot{O}:^+}{|}}{C}}-\ddot{O}H$ (IV)

Increasing order of stability is–

(A) I < III < II < IV

(B) IV < III < II < I

(C) III < IV < II < I

(D) II < IV < III < I

Sol. **B**

(I) → have higher no of covalent bond

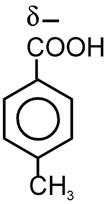
(II) → have complete octet

(III) → more E.N. atom consist –ve charge

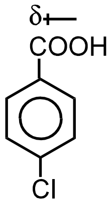
Ex.19 Increasing order of acidity in para methyl (I), chloro (II), amino (III), and nitro (IV) benzoic acids is–

(A) III < II < I < IV
(B) I < II < IV < III
(C) III < I < II < IV
(D) II < I < III < IV

Sol. **C**

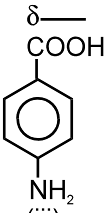


(i)

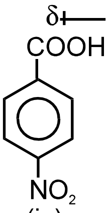


(ii)

Operating
group ⇒ +m – I



(iii)



(iv)

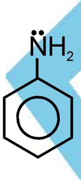
operating
group ⇒ +m –m
+ m (CH_3) < + m (NH_2)

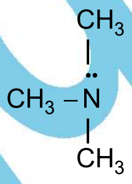
Ex.20 Increasing order of basic strength of following compounds is

$C_6H_5NH_2$, $(CH_3)_3N$, $(C_6H_5)_2NH$, $C_6H_5NHCH_3$
(I) (II) (III) (IV)

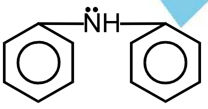
(A) III < IV < I < II
(B) III < I < IV < II
(C) I < III < II < IV
(D) II < IV < III < I

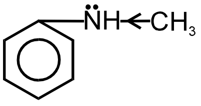
Sol. **B**





(a) lone pair delocalised
lone pair localised
(I) (II)





lone pair delocalised
lone pair delocalised
(III) (IV)

Thus II is more basic.

(b) Now than apply the theory of power of delocalisation which is highest in III, thus it is least basic.

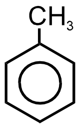
(c) 2° amine is more basic than 1° thus (IV) is more basic than (I) due to + I effect of $-CH_3$ group.

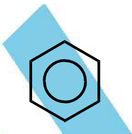
∴ (III) < (I) < (IV) < (II)

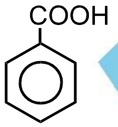
Ex.21 The compound that is most reactive towards electrophilic nitration is–

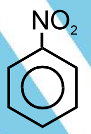
(A) Toluene (B) Benzene
(C) Benzoic acid (D) Nitrobenzene

Sol. **A**





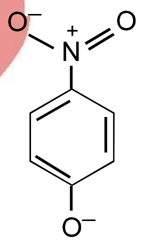


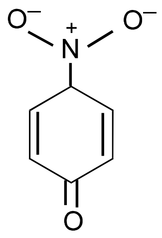


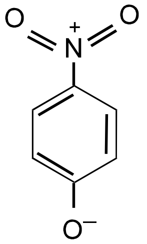
⇒ – COOH, & $-NO_2$ group are deactivating thus they are less reactive towards electrophile nitration then benzene.

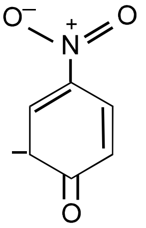
⇒ – CH_3 group is activating thus it is most reactive towards electrophic nitration then benzene.

Ex.22 The most unlikely representation of resonance structures of p-nitrophenoxide ion is–

(A)


(B)


(C)


(D)


Sol. **C**

In III structure, outermost orbit of N–atom have 10 e′, which is invalid condition for resonance, thus it most unlikely structure.

Ex.23 Consider the following three halides -

(1) $CH_3 - CH_2 - Cl$
(2) $CH_2 = CH - Cl$
(3) $C_6H_5 - Cl$

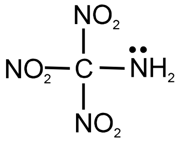
Arrange C – Cl bond length of these compound in decreasing order -

(A) 1 > 2 > 1 (B) 1 > 3 > 2
(C) 3 > 2 > 1 (D) 2 > 3 > 1

Sol. **A**

Ex.24 Arrange the following in increasing basic strength-

(a) CH_3NH_2 (b)

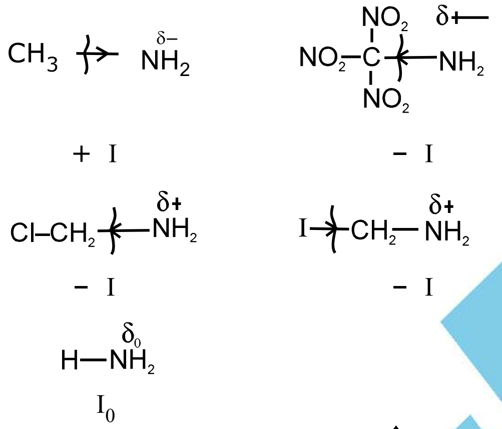


$C(NO_2)_3-\ddot{N}H_2$

(c) $Cl-CH_2-NH_2$ (d) $I-CH_2-NH_2$
(e) NH_3

Correct answer is -
(A) (a) < (b) < (c) < (e) < (d)
(B) (a) < (b) < (c) < (d) < (e)
(C) (b) < (c) < (d) < (e) < (a)
(D) (c) < (b) < (e) < (d) < (a)

Sol. **C**



As magnitude of +ve charge ↑ basic strength ↓

Ex.25 Arrange in increasing pK_a
(a) CH_3CH_2COOH
(b) $CH_3CH_2CH_2COOH$
(c) CH_3COOH

Correct answer is-
(A) (c) < (a) < (b)
(B) (b) < (a) < (c)
(C) (a) < (c) < (b)
(D) (b) < (c) < (a)

Sol. **A**

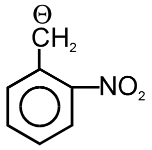
Ex.26 Arrange in increasing basic strength
(a) $Cl-CH_2-COOH$
(b) $Cl-CH_2-CH_2-CH_2-COOH$
(c) $Cl-CH_2\ CH_2\ COOH$

Correct answer is-
(A) (a) < (c)< (b)
(B) (b) < (a) < (c)
(C) (c) < (b)< (a)
(D) (a) < (b) < (c)

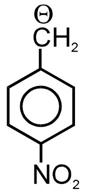
Sol. **A**

Ex.27 Which one of the carbaions is most stable?

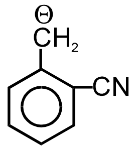
(A)



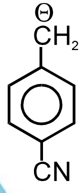
(B)



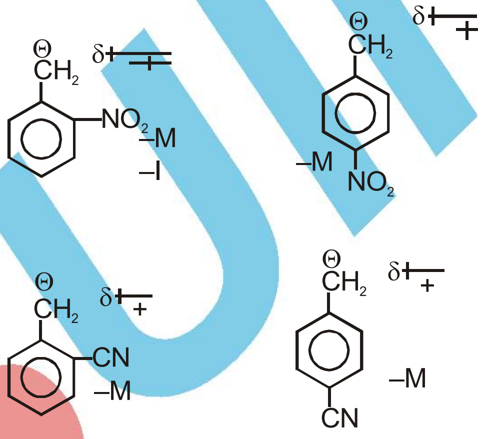
(C)



(D)



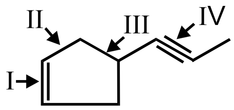
Sol. **A**



Stability $\propto \dfrac{1}{\text{Magnitude of charge}}$,

thus 1 is most stable.

Ex.28 What is the correct increasing order of bond lengths of the bonds indicated as I, II, III and IV in following coumpounds -



(A) I < II < III < IV
(B) II < III < IV < I
(C) IV < II < III < I
(D) IV < I < II < III

Sol. **D**

Ex.29 Which one of the following chlorides gives white precipitate with $AgNO_3$ most readily -
(A) $CH_2=CH-CH_2Cl$
(B) $CH_2=CH-Cl$
(C) CH_3-CH_2Cl
(D) $(C_6H_5)_2\ CH-Cl$

Sol. **D**