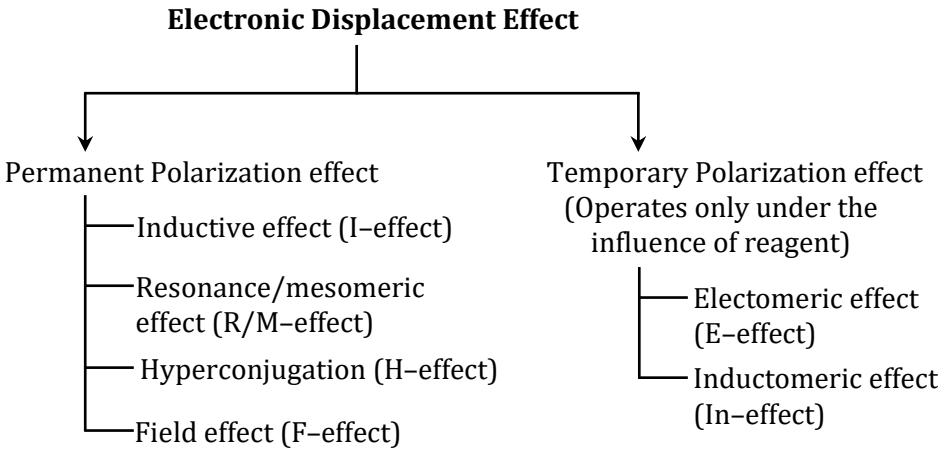
02 Electronic Displacement Effects (GOC)



Bond fission :

Any organic reaction cannot be completed without breaking or formation of a covalent bond. There are two types of bond breaking :-

(a) Homolytic bond breaking :

In such cases, bonding e^- are equally distributed between bonding atom so that electrically neutral intermediates are formed.

$$A\!-\!B \longrightarrow \dot{A} + \dot{B} \text{ (Free radical)}$$

(b) Heterolytic bond breaking :

In such cases, bonding e^- is transferred to any one of the atoms such that charged intermediates are formed.

$$A\!-\!B \longrightarrow A^{\oplus} + B^{\ominus}$$

Note :

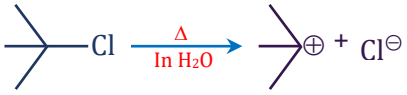
(i) Any covalent bond can break in both homolytic and heterolytic manner.

(ii) Heterolytic bond breaking takes place in polar solvent.

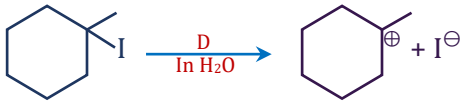
(iii) Homolytic bond breaking takes place in gas phase or in non-polar solvent.

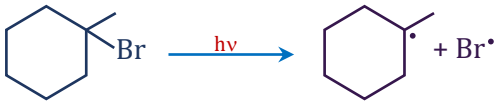
(iv) **Bond energy :** Minimum energy required to break a bond in homolytic cleavage.

$$\text{Bond Energy} \propto \frac{1}{\text{Stability of free radical obtained}}$$

Ex.I (i) 

(ii) 

(iii) 

(iv) 

(v) $Cl_2 \xrightarrow{h\nu} Cl^{\bullet} + Cl^{\bullet}$

(vi) $H{-}Cl \xrightarrow{H_2O} H^{\oplus}_{(aq)} + Cl^{\ominus}_{(aq)}$

(vii) $\ddot{N}H_3 + H^{\oplus}_{(aq.)} \longrightarrow NH^{\oplus}_{4(aq.)}$

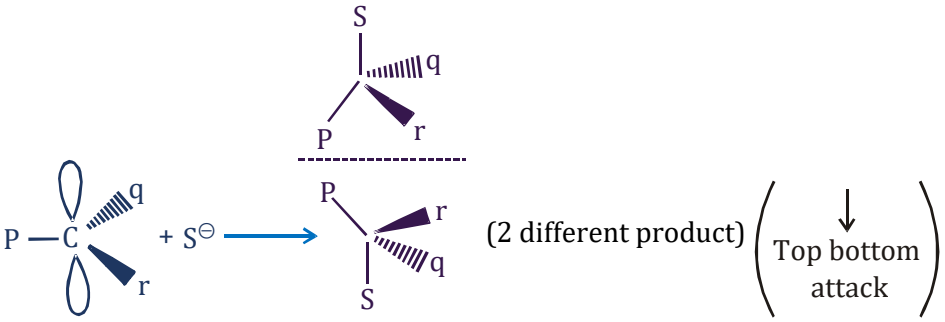
(viii) $CH_4 + H^{\oplus}_{(aq.)} \longrightarrow$ No reaction

(ix) $H{-}Cl \xrightarrow[\Delta]{gas} H^{\oplus}_{(g)} + Cl^{\ominus}_{(g)}$ (Radicals are formed, then on prolonged heating ions are formed)

Intermediates:

Species obtained between reactant and product during reaction.

(Carbocation) $^{\oplus}CH_3$	Carbanion $^{\ominus}CH_3$	Carbon free radical $\dot{C}H_3$
Highly unstable	Highly unstable	Highly unstable
Incomplete octet	Complete octet	Incomplete octet
Only $6e^{\ominus}$	$8e^{\ominus}$	$7e^{\ominus}$
Lewis Acid	Lewis Base	Neither
Bond Pair : 3	Bond Pair :3	Bond Pair : 3
Unpaird Pair (n) : 0	Unpaired $e^{\ominus}$: 0	Unpaired $e^{\ominus}$: 1
Lone Pair : 0	Lone Pair : 1	Lone Pair = 0
Magn. Moment : $\sqrt{n(n+2)} = 0$	Mag. moment = 0	Mag. moment = $\sqrt{3}$
Spin Multiplicity = 2|s| + 1 = 1	Spin Multiplicity = 1	Spin Multiplicity = 2
Hyb. = sp^2	Hyb. = sp^3	Hyb. = sp^2
Bond angle = 120°	Bond Angle = 107°	Bond Angle = 108°



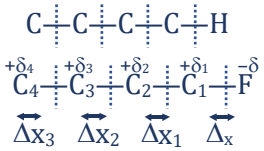
(2 different product) (↓ Top bottom attack)

Electron Displacement Effect : (EDE)

Effect because of displacement of electron is known as EDE.

Permanent Effect	Emporary Effect
(i) Inductive Effect (displacement of σ-e⊖)	(i) Inductomeric Effect displacement of σ-e⊖
(ii) Resonance/Mesomeric effect (displacement of p(π)e⊖)	(ii) Electromeric Effect temp. displacement of p-e⊖
(iii) Hyperconjugation effect (displacement of σ e⊖ in p-orbital)	

Inductive Effect :



(i) $\Delta x > \Delta x_1 > \Delta x_2 > \Delta x_3$

(ii) $\delta = (\delta_1 + \delta_2 + \delta_3 + \delta_4)$

(iii) $\delta > \delta_1 > \delta_2 > \delta_3 > \delta_4$

(iv) $\delta_4 \sim 0$ (experimentally)

Type of inductive effect :

–I-effect : (i) Permanent displacement of σ-e⊖ in a covalent bond because of any atom or group is known as I-effect of that atom. If the electron withdrawing power of group is higher than that of hydrogen then these groups are known as –I groups.

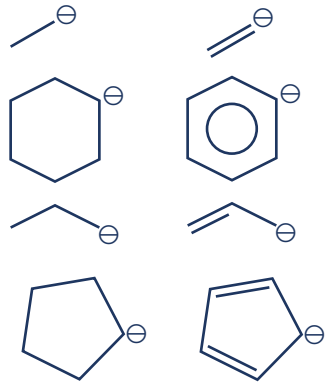
Decreasing order of e^- withdrawing tendency by inducting.

–I-Series :

$-\overset{\oplus}{N}F_3 > \overset{\oplus}{N}R_3 > -\overset{\oplus}{N}H_3 > -NO_2 > -CN > -SO_3H > -CHO > -COOH > -F > -Cl > -Br > -I > -OH > -NH_2 > -C \equiv CH > -Ph > -CH = CH_2 > (H)$

Hybridisation state of carbanion :

* sp^3 sp^2



+I effect :

If the electron donating power of group is higher than that of hydrogen, then these groups are known as +I groups.

+I series :

$$-CH_2^{\ominus} > -NH^{\ominus} > -O^{\ominus} > -COO^{\ominus} > -\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-CH_3 > -\ CH\begin{matrix}\diagup CH_3\\ \diagdown CH_3\end{matrix} > -CH_2-CH_3 > -CT_3 > -CD_3 > -CH_3 > -T > -D > -H$$

Note:

(i) For I-effect C–H bond is taken as reference.

(ii) It is permanent and weak effect.

(iii) During I-effect partial displacement takes place within orbitals.

(iv) I-effect is distance dependent effect.

(v) Practically, it is observed only up to C_3 atom.

(vi) Experimentally proved, that 10% effect is transferred to next atom.

Ex.1 $\overset{+\delta_1}{CH_2}-\overset{+\delta_2}{CH_2}-\overset{+\delta_3}{CH_2}-\overset{+\delta_4}{CH_2}$ (F with $-\delta_5$, Cl with $-\delta_6$)

I-effect of Cl: $C_1 - C_4$ ↑ , $C_4 - C_1$ ↑

I-effect of F: ↓ , ↓

Magnitude : $\delta_5 > \delta_6 > \delta_1 > \delta_4 > \delta_2 > \delta_3$

Ex.2 **(a)** –T,–D, –H (+I)

Heavier the molecule (atom), less is its oscillation frequency ⇒ Higher overlapping makes strong and small bond. So that as small displacement of e^- cause large I-effect. So

$\boxed{-T > -D > -H}$

(b) $-CH_3, -CH_2D, -CHD_2, -CD_3$ (+I)

$\boxed{-CH_3 < -CH_2D < -CHD_2 < -CD_3}$

(c) $-CH_3, -CD_3, -CT_3$ (+I)

$\boxed{-CH_3 < -CD_3 < -CT_3}$

(d) $-CH_3, -SiH_3$(+I)

$-CH_3 < -SiH_3$

(e) $-CH_3, -CCl_3$ (+I)

$-CH_3 > -CCl_3$

Application of I-effect

(1) Stability of carbocation :

(a) If number of + I groups increases then stability of carbocation increases.

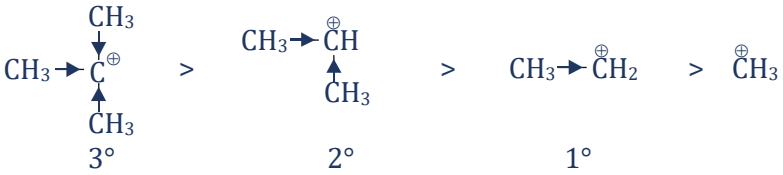
(b) If number of –I groups decreases then stability of carbocation increases.

Therefore

$$\text{Energy} \propto \frac{1}{\text{Stability}}$$

$$\boxed{\text{Stability of Carbocation} \propto +\text{I effect}}$$

$$\text{Stability of Carbocation} \propto \frac{1}{\text{-I effect}}$$

Ex : Stability order : 

3° > 2° > 1°

Sol. Reason : More no. of +I group.
more stable carbocation.

(2) Stability of carbanion :

(a) If number of – I groups increases then stability of carbanion increases.

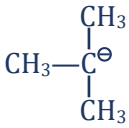
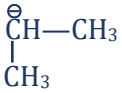
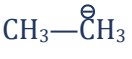
(b) If number of +I groups decreases then stability of carbanion increases.

Therefore

$$\boxed{\text{Stability of Carbanion} \propto -\text{I effect}}$$

$$\boxed{\text{Stability of Carbanion} \propto \frac{1}{+\text{I effect}}}$$

Example :

(1)  (2)  (3)  (4) 

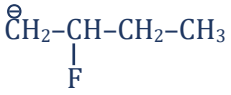
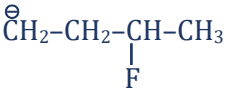
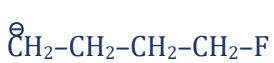
3° 2° 1°

More No. of +I group.

Less stable carbanion.

So stability order 1 < 2 < 3 < 4

Example :

(1)  (2)  (3) 

Minimum distance of –F.

Maximum –I of –F.

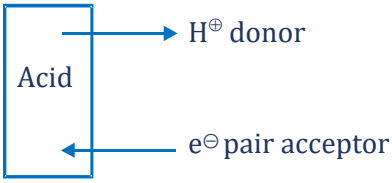
Minimum negative charge.

Maximum stable.

So stability order 1 > 2 > 3

Acidic and Basic Strength

Acidic strength :



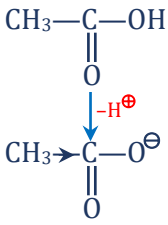
(i) If No. of – I groups increases then acidic strength increases.

(ii) If No. of + I groups increases then acidic strength decreases.

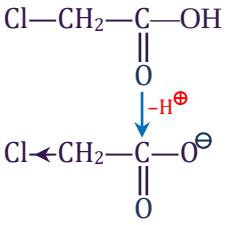
$$\text{acidic strength} \propto -\text{I effect} \propto \frac{1}{+\text{I effect}}$$

Example :

(i)



+I of $-CH_3$
So anion is less stable

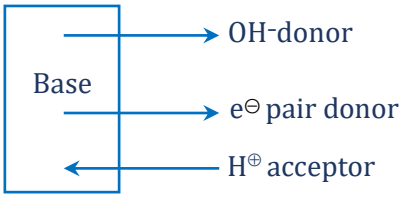


–I of –Cl, so anion is more stable
and corresponding acid is more acidic.

(ii) $CH_3—\underset{\underset{F}{|}}{CH}—CH_2—COOH > CH_3—\underset{\underset{F}{|}}{CH}—CH_2—COOH > CH_2—\underset{\underset{F}{|}}{CH_2}—CH_2—COOH$

minimum distance of F
from –COOH maximum –I
of F. So maximum acidic.

Basic strength :



(i) If No. of + I groups increases then basic strength increases.

(ii) If No. of – I groups increases then basic strength decreases.

$$\text{Basic strength} \propto +\text{I effect} \propto \frac{1}{-\text{I effect}}$$

Example :

$$\underset{\underset{CH_3}{|}}{\overset{CH_3}{|}}{}\!\!-\!\underset{\underset{CH_3}{|}}{C}\!-OH \;>\; CH_3—\underset{\underset{CH_3}{|}}{CH}—OH \;>\; CH_3—CH_2—OH$$

Maximum +I.
Maximum tendency to donate l.p.
Maximum basic.

Illustration 1:

Ethyl amine is more basic then aniline, why ?

Solution:

Due to the + I effect of ethyl group.

Illustration 2:

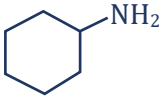
$Cl–NH_2$ is less basic then methyl amine, why ?

Solution:

Due to – I effect of –Cl group and $p_\pi–d_\pi$ conjugation.

Illustration 3:

Correct basic order of the following different amine in chlorobenzene medium is -

(A) $CH_3–CH_2–NH_2$ (B)  (C)  (D) 

Solution:

(C > D > B > A)

Illustration 4:

Which is most basic among the following :

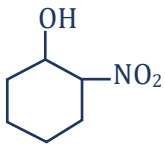
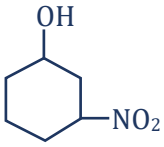
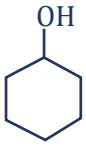
(A) CH_3NH_2 (B) $CH_3CH_2NH_2$ (C) NH_3 (D) $(CH_3)_2CHNH_2$

Solution:

(D)

Illustration 5:

Which is most acidic compound –

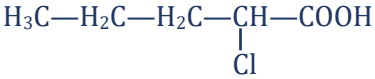
(A)  (B)  (C)  (D) 

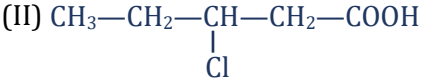
Solution:

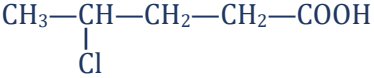
(A)

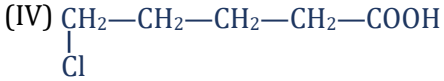
(a) Strength of aliphatic carboxylic acids

Example :

(I) 

(II) 

(III) 

(IV) 

Acid strength order is : I > II > III > IV

Explaination : We know that – I effect increases acidic strength. But it is distance dependent effect so where the – I group is nearest to – COOH, it exerts strong effect and makes acid stronger.

(b) Acidic strength of alcohol : Greater - I effect results in greater acidic character.

Similarly greater + I effect lowers acidic character.

Example : Acidic strength order is :

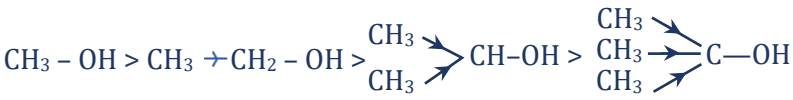


Illustration 6:

Find out the strongest acid of the following :

(A) $O_2N–CH_2–COOH$ (B) $F–CH_2–COOH$

(C) $H_3CO–CH_2–COOH$ (D) $CH_3–CH_2–COOH$

Solution:

(A) Since, $–NO_2$ has strong – I effect its influence will make corresponding acid strongest.

Illustration 7:

Which is most basic among the following :

(A) CH_3NH_2 (B) $CH_3CH_2NH_2$ (C) NH_3 (D) $(CH_3)_2CHNH_2$

Solution:

(D) Isopropyl group has maximum +I effect in the given alkyl group so corresponding nitrogen atom is most electron dense.

Resonance

If a single structure cannot explain all of the properties of a molecule then more than one structures are required then it is said that molecule is showing resonance. It is due to the delocalization of electrons within the molecule.

All the contributing structures in the resonance are called **resonating structures** or **canonical structures.**

These structures are helpful in explanation of chemical reactivity or the chemical reaction of the compound.

(i) Resonating structure are not the real structures.

(ii)The real structure is a hybrid of all resonating structures which is called as **resonance hybrid**.

Conditions for resonance

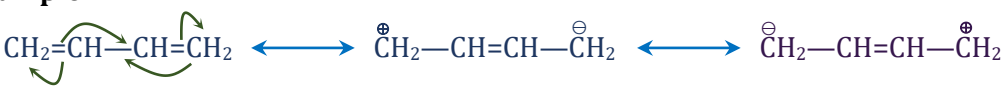
1. System must be planar.
2. System must be in conjugation (i.e. parallel p orbitals are required)

Following type of conjugation may be present in a molecule :-

1. $\pi \rightarrow \pi$ conjugation :

If there are two π bonds at alternate position then $e^{\ominus}$ of one π bond are transferred towards another π bond. (According to I–effect).

Example :

(i) 

(ii) 

(iii) 

2. Lone pair → π conjugation :

If there is one lone pair and one π bond are in parallel orbital then electrons of lone pair are delocalised through π bond.

Example :

(i) 

(ii) 

(iii) 

(iv) 

3. π → vacant orbital conjugation :

If there is one vacant orbital and one π bond are in parallel orbital then electrons of π bond are delocalised towards vacant orbital.

Example :

4. π → unpaired e⊖ conjugation :

If there is one free e⊖ and one π bond are at alternate position.

Example :

(i) 

(ii) 

5. Lone pair → +ve charge conjugation :

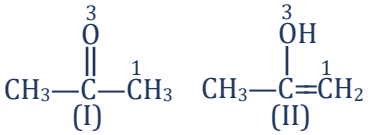
If there is one lone pair or negative charge and one positive charge are at adjacent atoms then e⊖ of lone pair or negative charge are transferred towards positive charge.

Example : 

Conditions of Resonating Structures : Resonance structures should fulfil following conditions :

(a) All resonating structures must have the same arrangement of atomic nuclei. Resonance differs from tautomerism in this very important aspect.

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

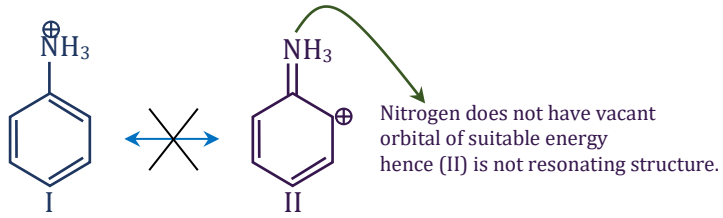


Position of hydrogen nuclei in (I) and (II) are different, hence (I) and (II) are not resonating structures, they are tautomer.

(b) The resonating structures must have the same numbers of paired and unpaired electrons. However, they differ in the way of distribution of electrons.

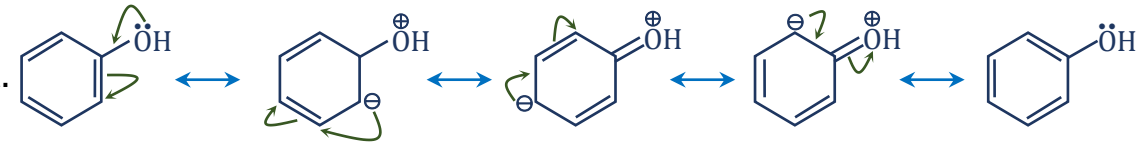
Total number of paired electrons =16, unpaired electron = 1 ⟷ Total number of paired electrons =16, unpaired electron = 1

- The energy of the different resonating structures must be the same or nearly the same.
- All atoms that are part of the delocalisation system must be in a plane or be nearly planar.



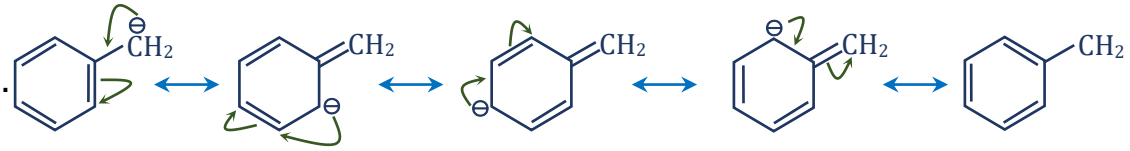
Examples of drawing resonating structures :

1.



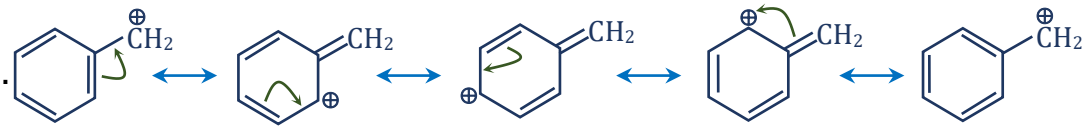
5-Resonating structure

2.



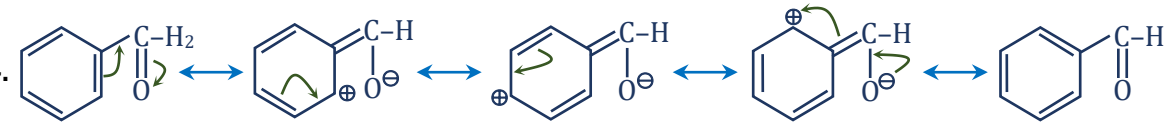
5-Resonating structure

3.



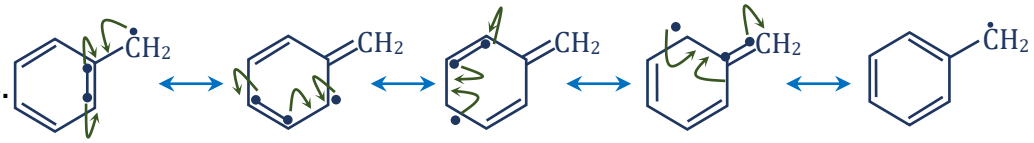
5-Resonating structure

4.



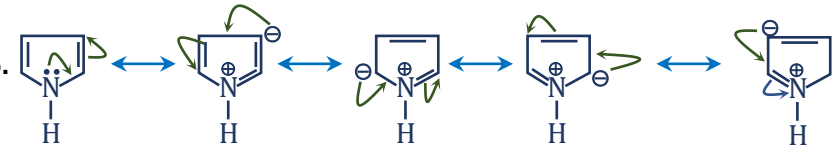
5-Resonating structure

5.

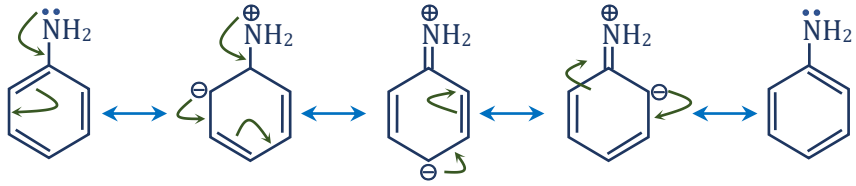


5-Resonating structure

6.



5-Resonating structure

7. 

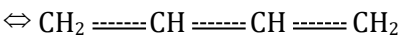
5-Resonating structure

Hybrid resonating structure :

(I) (II) (III)

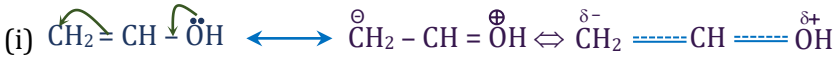
In the structure I C_1–C_2 has double bond while in II and III C_1–C_2 has single bond, so C_1—C_2 shows bond length in between single and double bond similarly in structure I C_2—C_3 has single bond. While in structure II and III C_2—C_3 has double bond, so C_2–C_3 shows bond length in between single and double bond.

So hybrid resonating structure from all its resonating structures is :

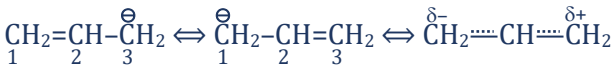


Hybrid structure

Example :

(i) 

I (Resonating structure) II (Hybrid structure)

(ii) 

(Resonating structure) (Hybrid structure)

Rules for stability of R.S.

1. R.S. having complete octet is relatively more stable.

I II II > I

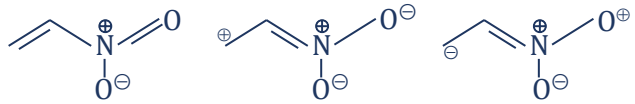
II > I

II > I

2. R.S. having higher no. of covalent bond/(less charge) is more stable.

I > II

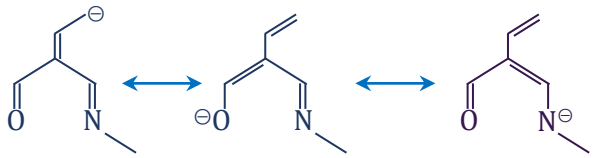
3. R.S. having –ve charge on E.N. atom and +ve charge on Electropositive atom is stable.

(i) 

I > II > III

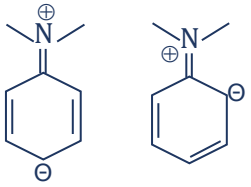
(ii) 

II > I

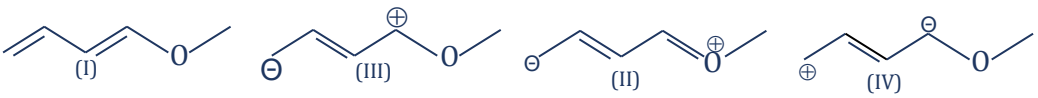
(iii) 

II > III > I

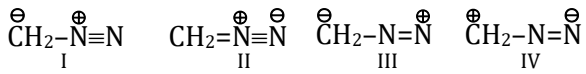
4. R.S. having unlike charges closer and like charges away are relatively more stable.

(i) 

II > I

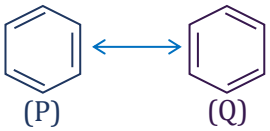
(ii) 

I > II > III > IV

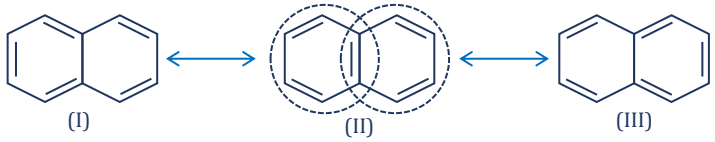
(iii) 

II > I > IV > III

5. R.S. having higher no. of benzenoid structure is more stable.

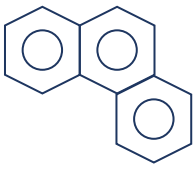
(i) 

I = II

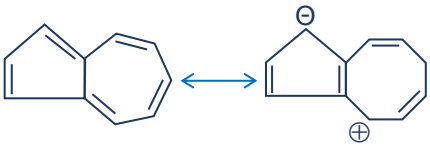
(ii) 

II > I = III

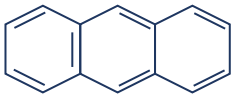
(iii) Anthracene 

(iv) Phenanthracene 

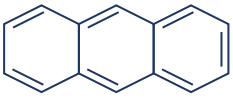
(v) (a) Napthalene is insoluble in aq. acid

(b) Azulene is soluble in aq. acid, 

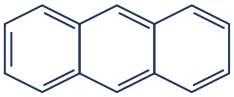
6. Anthracene:



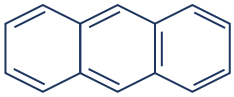
(I)



(II)



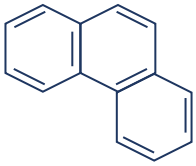
(III)



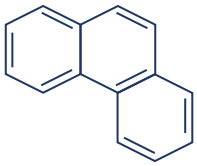
(IV)

I = IV > II = III

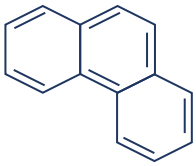
7. Phenanthrene :



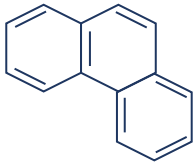
(I)



(II)



(III)



(IV)

I > II = IV > III

Aromaticity :

Order of stability for prototype structure

Aromatic > Non Aromatic > Anti Aromatic

Aromatic :-

Extra stable molecules/ions

→ Cyclic, planar, conjugated,

$(4n + 2)\ \pi e^{\ominus}$ [Huckel's Rule]

n = integer

$2\pi e^{\ominus}, 6\pi e^{\ominus}, 10\pi e^{\ominus}, 14\pi e^{\ominus}$

Antiaromatic :

→ Extra unstable molecules/ions

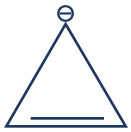
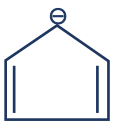
Cyclic, planar, conjugated,

$4n\pi e^{\ominus}$

n = integer

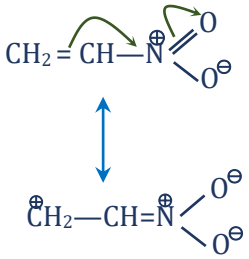
$4\pi e^{\ominus}, 8\pi e^{\ominus}, 12\pi e^{\ominus}, 16\pi e^{\ominus}$

Aromatic	Cyclic	Planar (Nearly)	Conjugated
	✓	✓	✓ $\pi e^{\ominus}$ $6\pi e^{\ominus}$
Antiaromatic			
 Antiaromatic	✓	✓	✓ $4\pi e^{\ominus}$
Non Antiaromatic			
 Non-aromatic	✓	✓	× $4\pi e^{\ominus}$

No.	Compound	Cyclic	Planar	Conjugated	$\pi e^{\ominus}$	decision
1.		✓	×	×	$2\pi e^{\ominus}$	Non–aromatic
2.		✓	✓	✓	$2\pi e^{\ominus}$	Aromatic
3.		✓	✓	✓	$4\pi e^{\ominus}$	Anti–aromatic
4.		✓	✓	✓	$4\pi e^{\ominus}$	Anti–aromatic
5.		✓	✓	✓	$2\pi e^{\ominus}$	Aromatic
6.		✓	✓	✓	$6\pi e^{\ominus}$	Aromatic
7.		✓	×	×	$6\pi e^{\ominus}$	Non–Aromatic
8.		✓	✓	✓	$4\pi e^{\ominus}$	Anti–Aromatic
9.		✓	✓	✓	$6\pi e^{\ominus}$	Aromatic
10.		✓	✓	✓	$6\pi e^{\ominus}$	Aromatic

Mesomeric effect or Resonance effect

- Polarity developed in conjugated system by interaction of parallel orbitals is known as mesomeric effect.
- If transfer of pi-bond electron takes place from conjugate system to group then it is known as **negative mesomeric (–M)** effect.

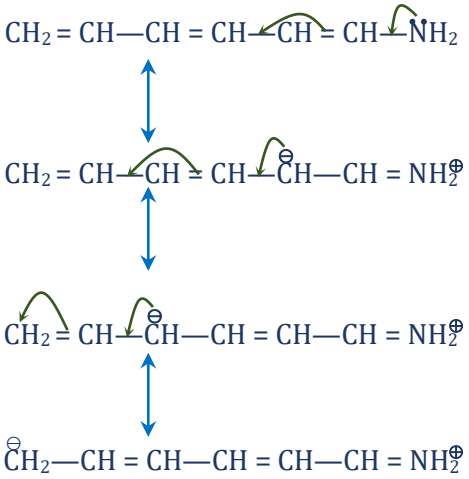


- For –M effect, group should have either be positive charge or should have vacant orbital.
- Due to –M effect positive charge comes over conjugate system or due to –M effect electron density decrease in conjugate system, such type of conjugate system will be more reactive towards nucleophile or will be less reactive towards electrophile.

Group which shows –M effect are -

$-NO_2$, –CN, $-SO_3H$, – CHO, –COR, –COOH, –COOR , –COX, $-CONH_2$ etc.

If transfer of non-bonding electron takes place from group to conjugate system then it is known as **positive mesomeric (+M)** effect.



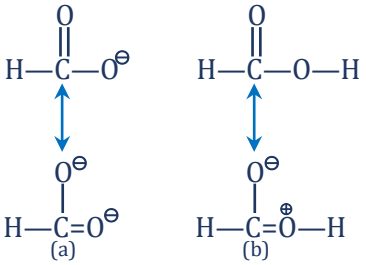
- For +M effect, group should have either be lone pair of electrons or should have negative charge.
- Due to +M effect negative charge comes over conjugate system or electron density increase on conjugate system such type of conjugate system will be more reactive towards electrophile or will be less reactive towards nucleophile.
- **Group which shows + M effect are -**

  $-\ddot{O}$, $-\ddot{N}H$, $-NR_2$, –NHR, $-NH_2$, – OH, –OR, –SH – SR, – F, – Cl, – NHCOR , –O–COR etc.
- In mesmeric effect polarity or charge migrate from one end to another end. During charge transfer, energy releases from the conjugate system which increase the stability of conjugate system also.

Resonance Energy :

Difference in energy between most stable resonating structure resonance hybrid.

Resonance energy ↑ with better overlapping.

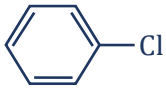


(a) has more R.E. than (b)

(a) has more R.E. than (b)

Applications :

(1) Comparison of bond length C–Cl bond length

(a) $CH_2 = CH—\ddot{Cl}:$ (b) $CH_3 –CH_2 –CH_2 –Cl$ (c) 

Ans. (b) > (a) > (c) (C – Cl bond length)

(2) Compare C = C bond length

(a) $CH_2 = CH_2$ (b) $CH_2 = CH_2 – NH_2$

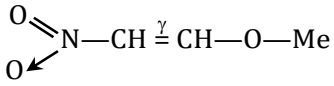
Ans. (b) > (a)

Compare bond length of α, β and γ

$CH_2 \overset{\alpha}{=} CH_2$ $CH_2 = CH\overset{\beta}{—}CH = CH_2$ $CH_3\overset{\gamma}{—}CH_3$

$\boxed{\gamma > \beta > \alpha}$

Compare bond length in α, β and γ

(a) $CH_2 \overset{\alpha}{=} CH_2$ (b) $CH_2 \overset{\beta}{=} CH—O—Me$ (c) 

$\boxed{\gamma > \beta > \alpha}$

amount of energy required to rotate the bond (it. energy barrier) decreases with the increase in bond length or single bond character.

$$\text{Bond order} \propto \frac{1}{\text{Bond length}}$$

$$\propto \frac{1}{\text{single bond character}}$$

$\propto$ Bond energy

$\propto$ Bond Stability

Stability of Intermediates:

Stability of carbocation ∝ EDG (+R / +H / +I)

Stability of carbon free radical ∝ EDG (+R / +I)

EWG (–R)

Stability of carbonion ∝ EWG (–R / –I)

1. $+CH_3$, $+CH_2-CH_3$, $\overset{\oplus}{C}H(CH_3)_2$, $H_3C-\overset{\oplus}{C}(CH_3)-CH_3$

(I) (II) (III) (IV)

(I)<(II)<(III)<(IV)

2. $\dot{C}H_2$, $-CH_3$, $\dot{C}H(CH_3)_2$, $H_3C-\dot{C}(CH_3)-CH_3$

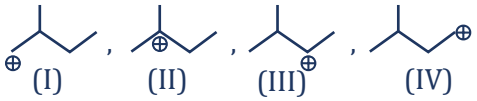
(I) (II) (III) (IV)

IV > III > II > I

3. $-CH_3$, $-CH_2-CH_3$, $\overset{\ominus}{C}H(CH_3)_2$, $H_3C-C^{\ominus}(CH_3)-CH_3$

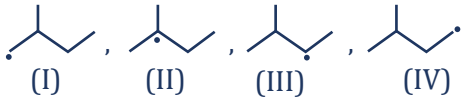
(I) (II) (III) (IV)

I > II > III > IV

4. 

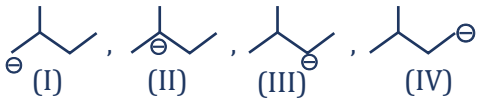
(I) (II) (III) (IV)

II > III > IV > I

5. 

(I) (II) (III) (IV)

IV < I < III < II

6. 

(I) (II) (III) (IV)

IV > I > III > II

7. $CH_3-\overset{\oplus}{C}H_2$, $CH_2=\overset{\oplus}{C}H$, $CH\equiv C^{\oplus}$

(I) (II) (III)

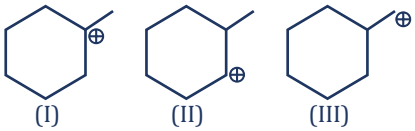
I > II > III

8. $\underset{(I)}{CH_3}-\underset{}{\overset{\bullet}{C}H_2}$, $\underset{(II)}{CH_2}=\overset{\bullet}{C}H$, $\underset{(III)}{CH}\equiv C^{\bullet}$

I > II > III

9. $\underset{(I)}{CH_3}-\overset{\ominus}{C}H_2$, $\underset{(II)}{CH_2}=C^{\ominus}H$, $\underset{(III)}{CH}\equiv C^{\ominus}$

III > II > I

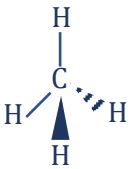
10. 

(I) (II) (III)

I > II > III

Baeyer's Angle Strain Theory :

→ For any sp^3 carbon maximum stability is attained when B.A. is 109°.28'.



According to Baeyer's :

$\delta = \frac{1}{2}[109°28' - \alpha]$

$\alpha = 60°, \delta = 24.5°$

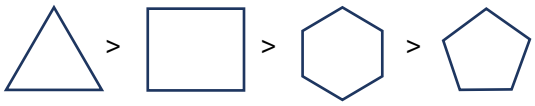
$\alpha = 90°, \delta = 9.5°$

$\alpha = 108°, \delta = 0.5°$

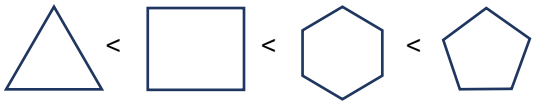
$\alpha = 120°, \delta = -5.5°$

$$\text{Stability} \propto \frac{1}{\text{strain}}$$

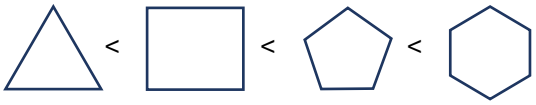
$\Rightarrow$ Strain order :



$\Rightarrow$ Stability order : (Ace. to Baeyer)



Now six-member ring shows flipping which results six-member ring more stable than five-member ring. overall stability order



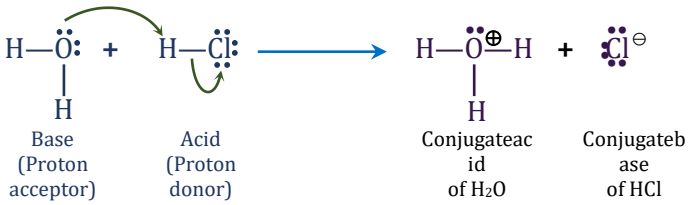
Acidic strength :

It can be explained by Bronsted -Lowry of Lewis concept.

(1) The Bronsted - Lowry concept of Acids and Bases

According to it - an acid is a substance that can donate a proton, and a base is a substance that can accept a proton.

Consider, that gaseous hydrogen chloride dissolves in water :

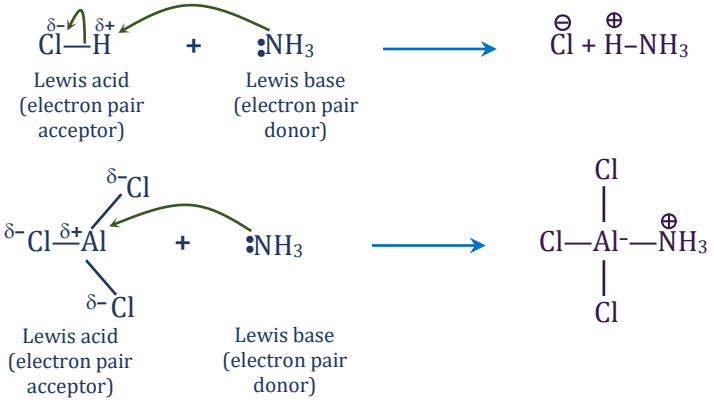


Hydrogen chloride, a very strong acid, transfer its proton to water. Water acts as a base and accept the proton. The products that result from this reaction are hydronium ion ($H_3O^{\oplus}$) and chloride ion ($Cl^{\ominus}$).

The molecule or ion that forms when an acid donates its proton is called the **conjugate base** of that acid. (The chloride ion is the conjugate base of HCl). The molecule or ion that is formed when a base accept a proton is called the **conjugate acid** of that base ($H_3O^{\oplus}$ is conjugate acid of H_2O).

(2) The Lewis concept of Acids and Bases

Lewis proposed that acids are electron pair acceptors and bases are electron pair donors. For example, aluminium chloride, reacts with ammonia in the same way that a proton donor does. Using curved arrows to show the donation of the electron pair of ammonia (the Lewis base), it can be given as :



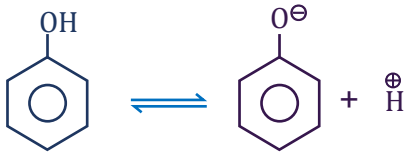
(I) Relative acidic strength of hydrocarbons

Being most electronegative the sp hybridised carbon atom of ethyne or terminal alkyne polarizes its C–H bond to the greatest extent causing its H to be most positive therefore ethyne is most acidic. Hence acidic strength order is

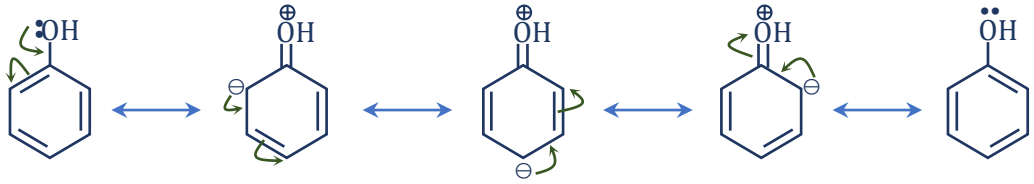
$HC \equiv CH > H_2C = CH_2 > H_3C - CH_3$

(II) Acidic Strength of Phenols :

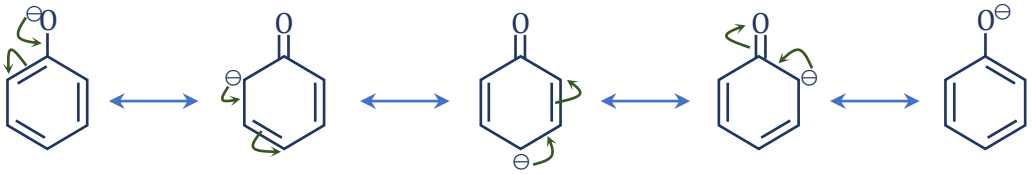
When phenol ionises, the phenoxide ion is more stabilised by resonance than the unionised phenol.



Resonating structures of phenol are :

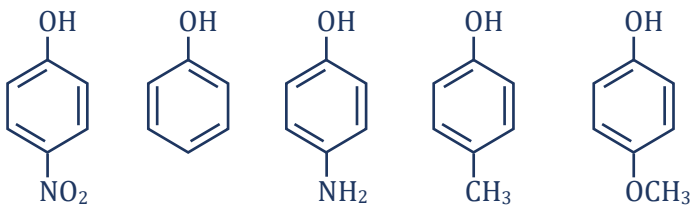


Resonating structures of phenoxide ion are :



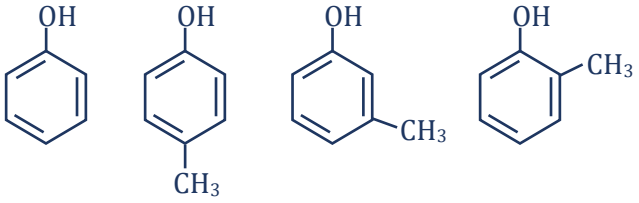
Groups which are – I, – M increases acidic character of phenol by effectively dispersing negative charge of phenoxide ion. However, +I and + M groups decreases acidic strength.

Example :



Acid strength order : I > II > IV > V > III ($-NO_2$ show –M & –I while $-OCH_3$, $-NH_2$ show –I and +M)
So nitrophenol will be most acidic followed by phenol. Amongst cresol and methoxyphenol, methoxyphenol has + M effect of – OCH_3 which increases electron density hence decrease acidic strength.

Example:

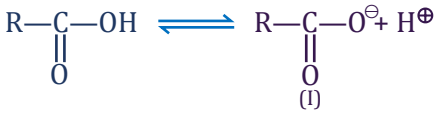


(I) (II) (III) (IV)

Acid strength order : I > III > II > IV

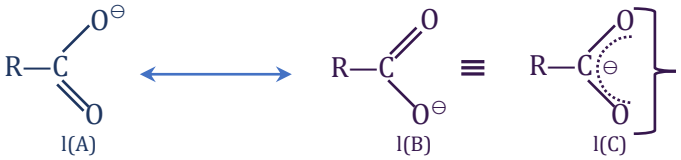
CH_3 have + I effect so all methylphenols (cresols) are less acidic than phenol (I). Amongst cresols, para and ortho CH_3 are increasing the electron density due to their hyper conjugation but ortho isomer has viable + I effect also, which will help in destabilising phenoxide ion therefore o- is least acidic. Since at meta position only + I works it has least electron density amongst the cresols

(III) Acidic strength of Carboxylic Acids :



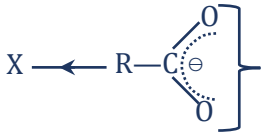
(I)

$RCOO^{\ominus}$ (I) exists as two equivalent canonical structures I(A) and I(B). This ion is resonance stabilised and resonance hybrid structure is I(C), while RCOOH has two non-equivalent resonating structures making it less stable.



I(A) I(B) I(C)

Electron withdrawing group (–I effect) stablises the anion and hence, increases acidic nature.

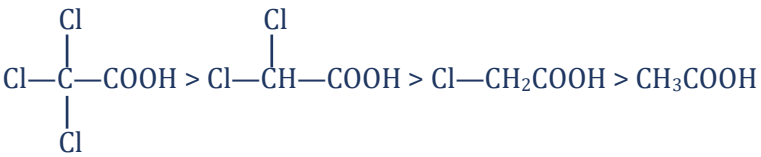


Ex. 1

$$F-CH_2-COOH > Cl-CH_2COOH > Br-CH_2COOH > I-CH_2COOH$$

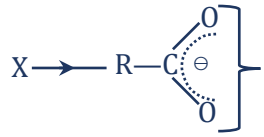
Increasing acid strength

Ex. 2



Increasing acid strength

Electron releasing group (+ I effect) destabilises the anion and hence decreases acidic nature.

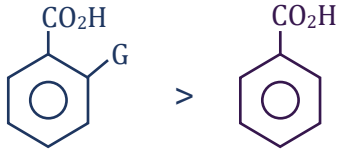


Ex. 3 $HCOOH > CH_3COOH > CH_3-CH_2-COOH$

Ex. 4 

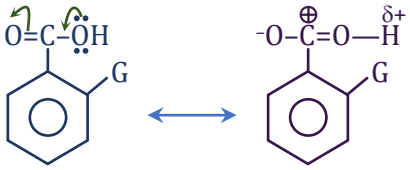
Ortho effect :

Ortho derivative of benzoic acid is generally more acidic than benzoic acid itself. It is called ortho effect.

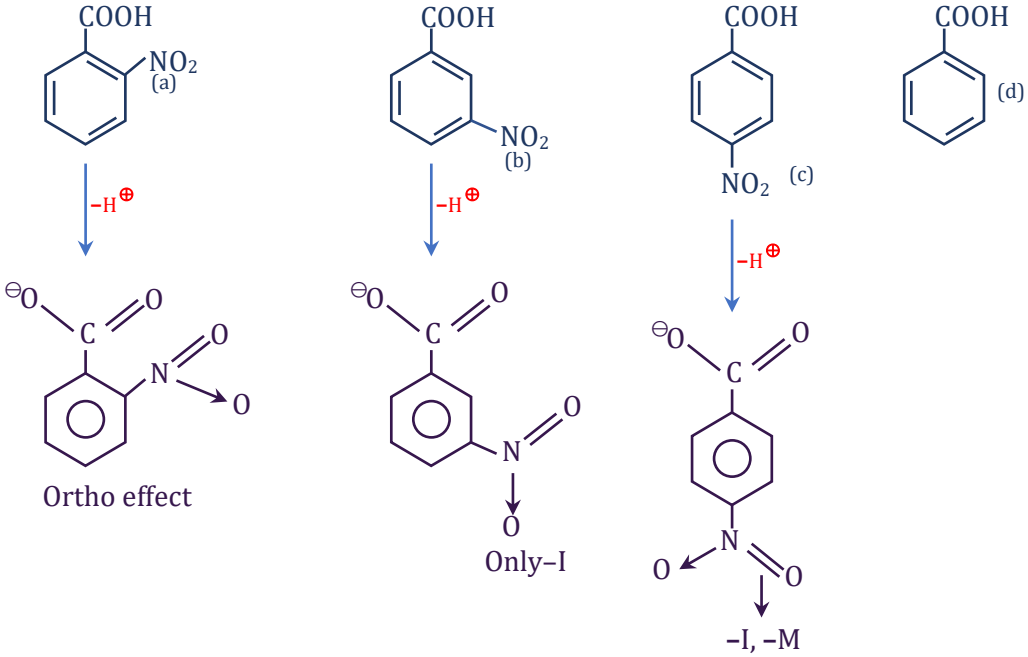


Explanation :

At ortho position when group G is attached, there will be steric repulsion between group G and $-CO_2H$ group, due to which $-CO_2H$ group is partially out of plane. So resonance of phenyl group w.r.t.  decreases and resonance of –OH group w.r.t.  increases, +ve charge on oxygen atom increases, –I effect increases, acidity increases.

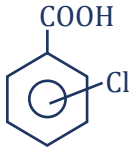


Example : If substitutent is –I and –M ($-NO_2$)



K_a order = ortho > para > meta > benzoic acid

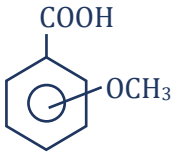
Example : If substitutent is (–I > +M) – Cl, Br, F, I



K_a order = ortho > meta > para > benzoic acid

acidity = a > c > b > d

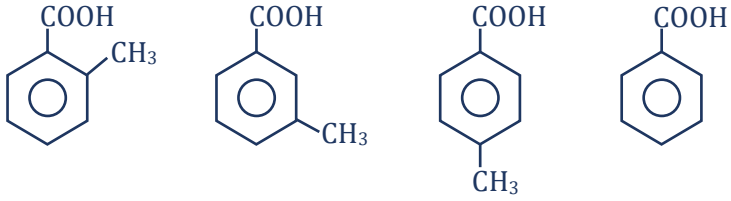
Example : If substitutent is (+M > –I) $-OCH_3$



K_a order = ortho > meta > benzoic acid > para

Acidity = ortho > meta > benzoic acid > para

Example : If substitutent is (+I, +H) – R (Alkyl group)



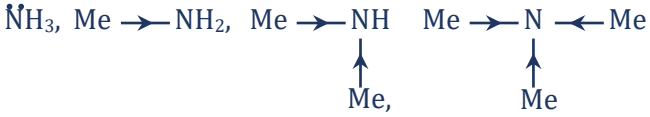
K_a order = ortho > benzoic acid > meta > para

Basic strength

(I) Aliphatic Amines

Ease of protonation is the basic nature. Increasing strength of nitrogenous bases is related to readiness with which they are prepared to take up protons.

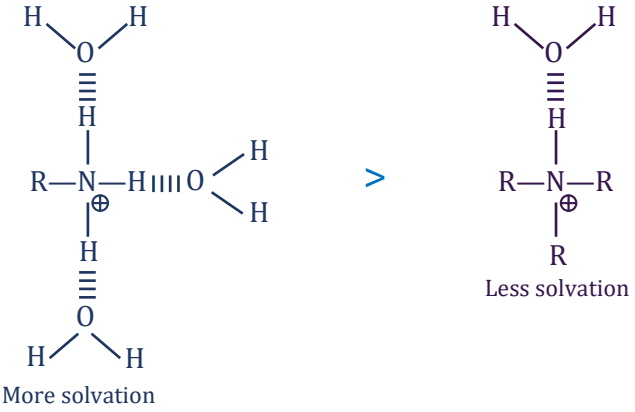
Consider the following molecules



By considering + I effect of methyl in above example we may expect basic nature as

$NH_3 < MeNH_2 < Me_2NH < Me_3N$ **(Which is not true always)**

This is due to the fact that basic strength of an amine in water is determined not only by ease of electron donation (protonation) of N atom but also by the extent to which cation so formed can undergo **SOLVATION** and become stabilised by H atom attached to N atom. Greater is possibility of solvation via H bonding by water more will be its basicity but Alkyl groups are hydrophobic and inhibits H bonding hence solvation decreases and basicity decreases.



Thus, due to two opposite effects i.e. solvation of cation and +I effect, the jumbled order comes to be

$Me_2NH > Me - NH_2 > Me_3N > NH_3$

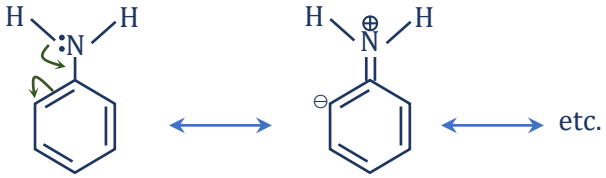
It is also interesting to note that in gas phase basicity order of amines follows the usual order of $Me_3N > Me_2NH > MeNH_2 > NH_3$ (Since only + I effect works and no solvation effect persists).

Similarly on the same reasons ethyl amines and other amine follows the following order for basic strength:

$Et_3N > Et_2NH > EtNH_2 > NH_3$ (gas phase)

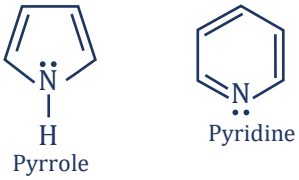
$Et_2NH > Et_3N > EtNH_2 > NH_3$ (water as solvent)

(II) Aromatic amines ($Ph-\ddot{N}H_2$) or Anilines :

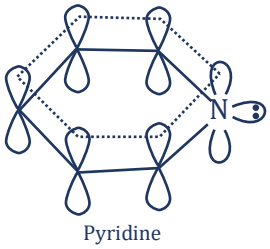


When the lone pair lies in conjugation with a multiple bond, system can get resonance stabilisation. Aniline is a weaker base than NH_3 because it has delocalised lone pair.

Example :

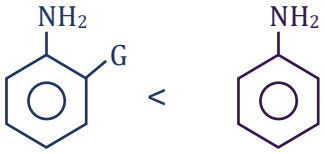


In pyrrole lone pairs are involved in resonance therefore it is less basic. But in pyridine lone pairs are in perpendicular plane of π orbitals therefore not involved in resonance

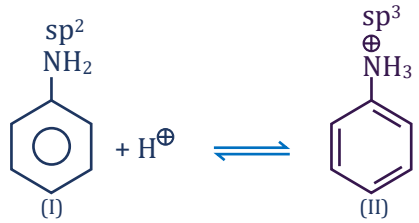


Ortho effect

Ortho derivative of aniline is generally less basic than aniline itself. It is called ortho effect.



during protonation N change its hybridisation from sp^2 to sp^3. Steric crowding around N increases. If G is occupied at ortho position then steric crowding further increases, stability of protonated product decreases, basicity decreases.

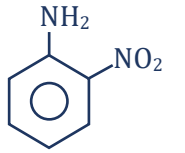


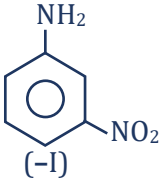
Change of hybridization causes steric repulsion.

steric crowding further increases, stability of II' further decreases basicity order to I' < I

Example : Arrange the following in their basic strength

(i) G = (–M, –I); NO_2

(A) 
(–I, –M ortho effect)

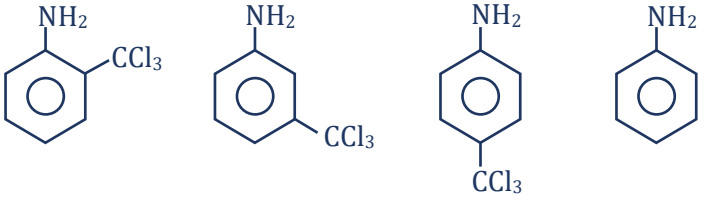
(B) 
(–I)

(C) 
(–I,–M)

(D) 

Solution : (Aniline > m > p > o).

(ii) G = (–I); CCl_3



Solution : (Aniline > m > p > o).

Basic Strength

* Acid amides are weaker bases
* Ability to donate $e^{\ominus}$
* Check stability of conjugate acid

1.

I	II	III	IV
$I^{\ominus}$	$Cl^{\ominus}$	$Br^{\ominus}$	$F^{\ominus}$
↓	↓	↓	↓
HI	HCI	HBI	HF

IV > III > II > I as the acidic character decreases from I→IV, the basic character ↑

2.

I	II	III	IV
$^{\ominus}CH_3$	$^{\ominus}NH_2$	$^{\ominus}OH$	$^{\ominus}F$
↓	↓	↓	↓
CH_4	NH_3	H_2O	HF

I > II > III > IV → as E.N. ↑ , –ve charge becomes more stable and basic ↓

3.

I	II
$RO^{\ominus}$ >	$RS^{\ominus}$
↓	↓
ROH	RSH

I > II as smaller the size, more will be the charge density.

4.

I	II
R_3N	R_3P
↓	↓
$^{\oplus}NR_3H$	$^{\oplus}PR_3H$

I > II , smaller the size, better the overlapping

5.

I	II	III
NH_2	NH	N
↓	↓	↓
$NH_3^{\oplus}$	$NH_2^{\oplus}$	$NH^{\oplus}$

I > II > III as s character ↑, acidity ↑ Basicity ↓

6.

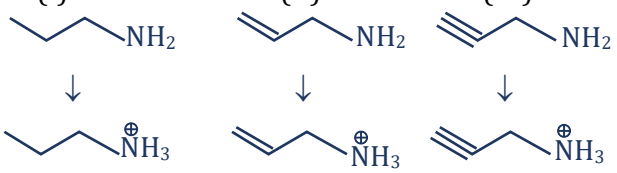
I	II	III
NH_2	O, NH	N
↓	↓	↓
$NH_3^{\oplus}$	O, $NH_3^{\oplus}$	$NH_3^{\oplus}$

I > III > II, I - Localized

II - Dispersed on O ⇒ highly delocalize lone pair

III - Dispersed on C ⇒ moderately localize.

7. (I) (II) (III)



> II > III as +I effect decreases from sp^3 C → sp C.

8. (I) (II) (III)

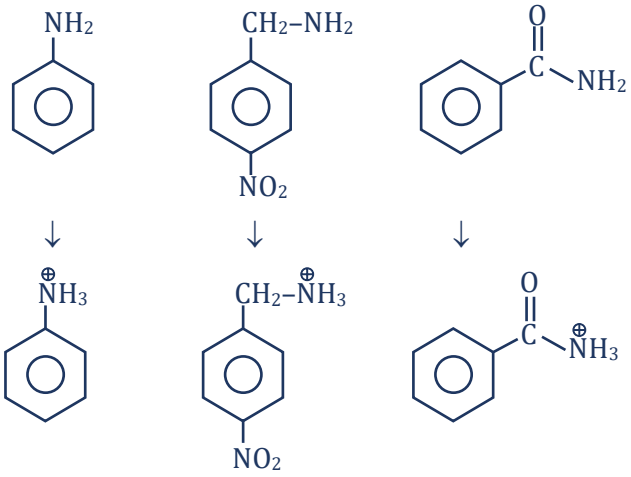
$HC \equiv C^{\ominus}$ $CH_2=CH^{\ominus}$ $CH_3-CH_2^{\ominus}$

↓ ↓ ↓

$HC \equiv CH$ $CH_2 = CH_2$ $CH_3- CH_3$

III > II > I as s corrector decreases from I → III.

9. (I) (II) (III)



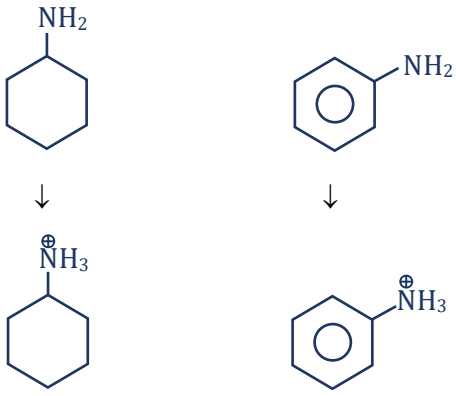
II > I > III

II–Localized L.P.

I–$e^{\ominus}$ dispersed on C

III–$e^{\ominus}$ dispersed on O

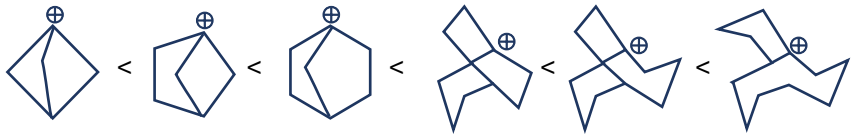
10. (I) (II)

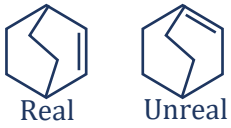


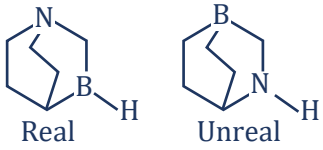
I > II due to localized L.P.

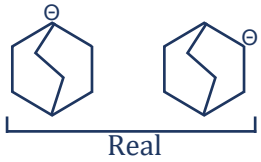
Bredt's Rule

According to this rule, planarity can't be acheived at bridge head centre of bicyclic compound having less than 8C. (* included). (* p-orbital can't be on bridge head)

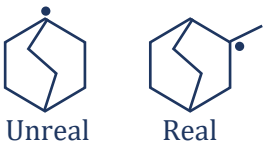
1. 

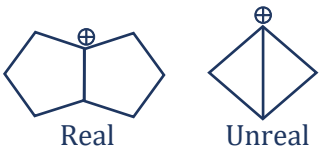
2. 

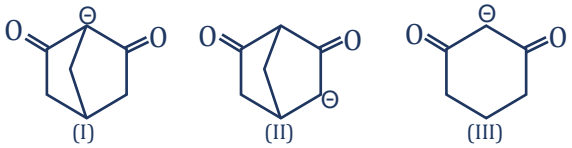
3. 

4. 

5. 

6. 

7. 

8. 

Stability (III) > (II) > (I)

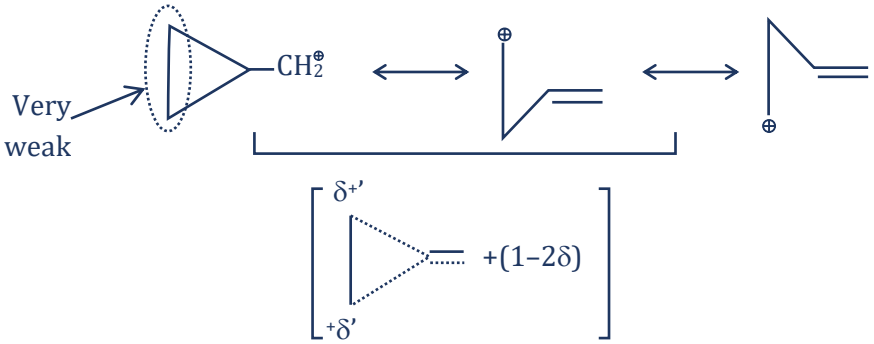
III → Resonance with two

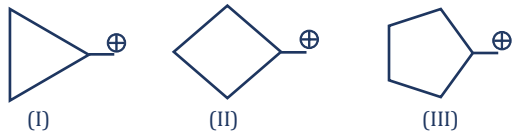
II → Resonance with one

I → No Resonance

Sigma Resonance

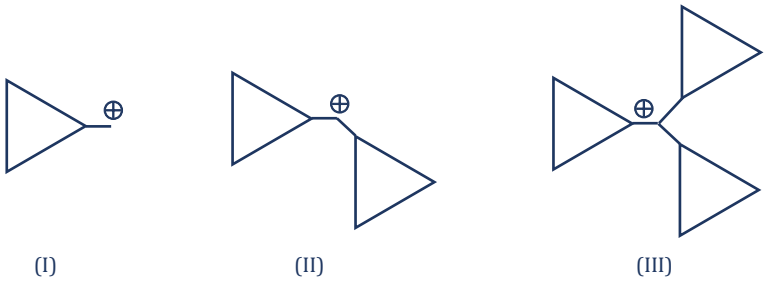
For cyclopropyl methyl carbocation



1. 

I > III > II , 1-σ-resonance, +I effect is higher in III than in II

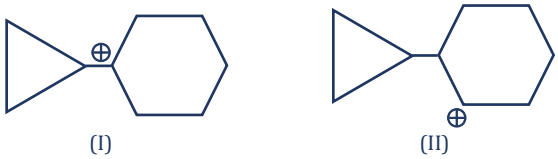
2.



(I) (II) (III)

III > II > I , σ-resonance increases

3.

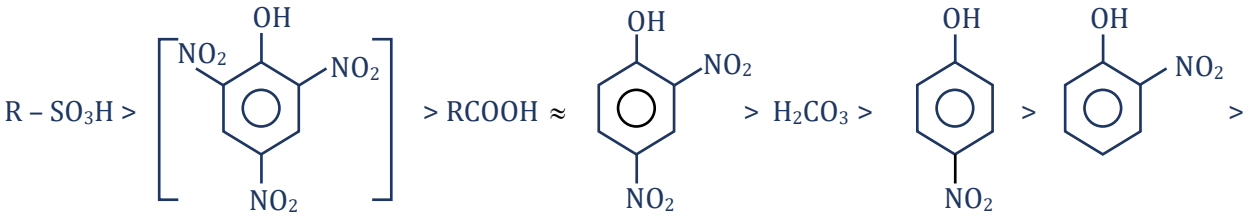


(I) (II)

I > II , σ-resonance possible in I effectively

Important acid strength order :

$> \underbrace{H_2O > R^*-OH}_{\text{Order is reversed in case of methanol}} > R-C\equiv CH > NH_3 > H_2$



Ex 1 : Feasible reaction is/are :

(a) $R-C\equiv CH + NaOH \longrightarrow RC\equiv C^{-}Na^{\oplus} + H_2O$

(b) $RC\equiv CH + KOH \longrightarrow R-C\equiv C^{-}K^{\oplus} + H_2O$

(c) $RC\equiv CH + NaNH_2 \longrightarrow R-C\equiv C^{-}Na^{\oplus} + NH_3$

(d) $RC\equiv CH + NaH \longrightarrow R-C\equiv C^{-}Na^{\oplus} + \frac{1}{2}H_2$

(e) $RC\equiv CH + NaHCO_3 \longrightarrow R-C\equiv C^{-}Na^{\oplus} + H_2CO_3$

Compare these. clearly c, d are feasible

Ex.2: Product when R–COOH reacts with aq. $NaHCO_3$:

$R-COOH + NaHCO_3 \longrightarrow R-\underset{\underset{O}{\|}}{C}-ONa + [H_2O + CO_2]$

Ex.3: Gases evolved when $NaH^{14}CO_3$ is added in a container having R–COOH and $R-SO_3H$:

(i) $R-COOH + NaH^{14}CO_3 \longrightarrow RCOO^{-}Na^{\oplus} + H_2O + {}^{14}CO_2$

(ii) $R-SO_3H + NaH^{14}CO_3 \longrightarrow R-SO_3HNa + H_2O + {}^{14}CO_2$

Ex.4: Reaction between p-nitrophenol and aq. $NaHCO_3$:

Ex.5 Find no. of compounds reacting with:

(i) aq. NaOH

(ii) aq. $NaHCO_3$

(iii) both in NaOH and $NaHCO_3$

(iv) give effervescence of CO_2 with $NaHCO_3$.

(a) 

(NaOH)

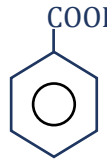
(b) 

(NaOH + $NaHCO_3$)

(c) 

(NaOH + $NaHCO_3$)

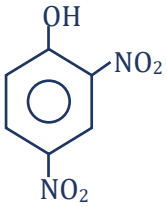
(d) 

(e) 

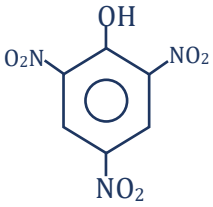
(NaOH + $NaHCO_3$)

(f) 

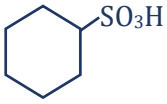
(NaOH + $NaHCO_3$)

(g) 

(NaOH + $NaHCO_3$)

(h) 

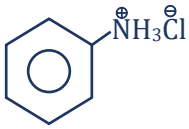
(NaOH + $NaHCO_3$)

(i) 

(NaOH + $NaHCO_3$)

(j) HCl
(NaOH + $NaHCO_3$)

(k) H_2SO_4c
(NaOH + $NaHCO_3$)

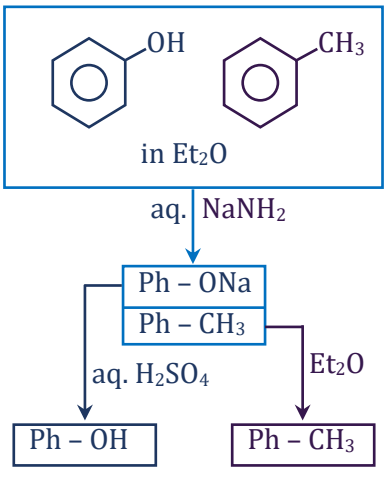
(l) 

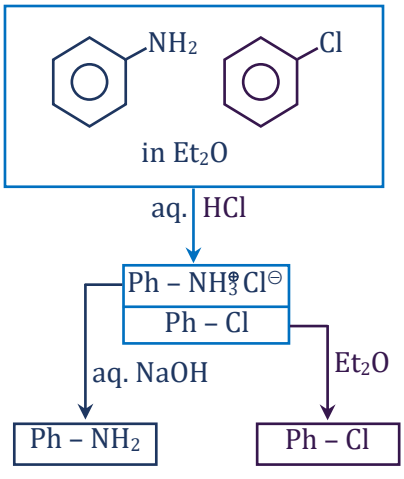
(NaOH + $NaHCO_3$)

(m) 

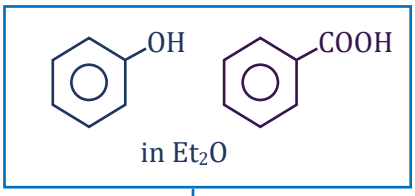
(n) 

Ex.6 How can we separate following binary mixture by acid-base extraction method.

(i) 

(ii) 

(iii)



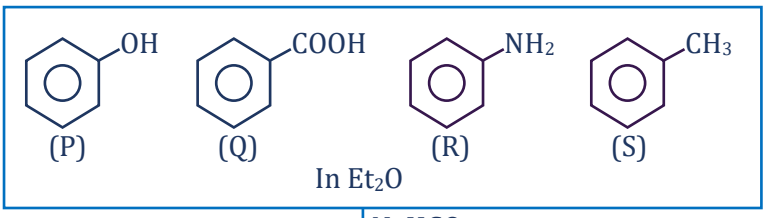
aq. $NaHCO_3$

Ph – COONa
Ph – OH

aq. HCl

Ph – COOH | Ph – OH

(iv)



aq. $NaHCO_3$

$PhCOO^{\ominus}Na^{\oplus}$
Ph – OH

H_2O | Et_2O

Ph – COONa | P,R,S

H_2SO_4 | Aq.NaOH

Q | PhONa / RS

H_2O | Et_2O

PhONa | R,S

H_2SO_4 | Aq.HCl

P | $PhNH_3^{\oplus}Cl^{\ominus}$ / S

H_2O | Et_2O

$PhNH_3^{\oplus}Cl^{\ominus}$ | S

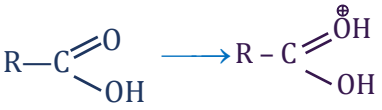
NaOH

P

Ex.7 Write conjugate acid of following :

(i) $H_2O \longrightarrow H_3O^{\oplus}$

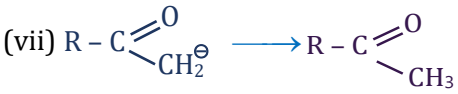
(ii) $OH^{\ominus} \longrightarrow H_2O$

(iii)  ← as $e^{\ominus}$ is localized in this C not in the other.

(iv) $S^{2\ominus} \longrightarrow HS^{\ominus}$

(v) $HPO_4^{2\ominus} \rightarrow H_2PO_4^{\ominus}$

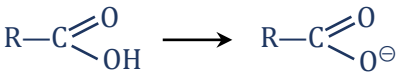
(vi) $NH_2{-}NH_2 \longrightarrow NH_2 - NH_3^{\ominus}$

(vii) 

Ex.8 Write conjugate base of following:

(i) $H_2O \longrightarrow OH^{\ominus}$

(ii) $NH_3 \longrightarrow NH_2^{\ominus}$

(iii) 

(iv) 

(v) 

(vi) 

(vii) $H_2S \longrightarrow HS^{\ominus}$

Ex.9 A container with acid HA_1, HA_2, and HA_3 with pk_a : x, y, z respectively if y > z > x then.
$[HA_1 > HA_3 > HA_2]$

(a) $HA_1 + HA_2 \longrightarrow H_2A_1^{\oplus} + A_2^{\ominus}$

(b) $HA_1 + HA_3 \longrightarrow H_2A_3^{\oplus} + A_1^{\ominus}$

(c) $HA_2 + HA_3 \longrightarrow H_2A_2^{\oplus} + A_3^{\ominus}$

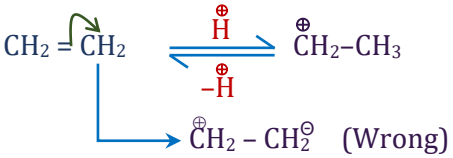
(d) $HA_2 + HA_3 \longrightarrow H_2A_3^{\oplus} + A_2^{\ominus}$

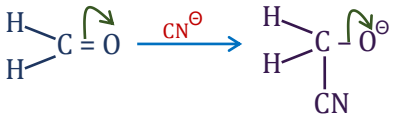
Option b & c are correct.

Temporary effect

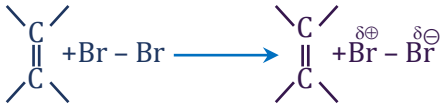
1. Electromeric effect :

Complete shift of π-electron under the influence of reagent.Temporary effect Operates only in the presence of reagent, vanishesh as reagent removed.

Ex.1 

Ex.2 

2. Inductomeric effect : Complete shift of σ-electron in the influence of reagent.

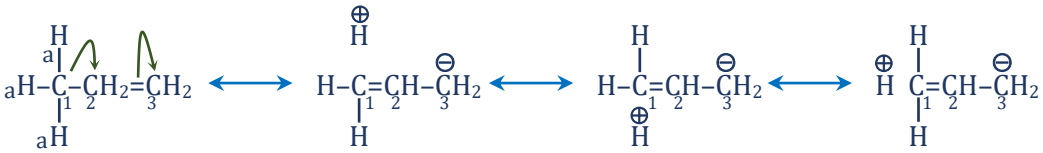


It is delocalisation of σ electron with p-orbital. Also known as σ –π conjugation or no bond resonance. It may take place in alkene, alkyne, carbocation, free radical, alkyl benzene nucleus. It was given by Nathan and Baker.

Necessary Condition of H effect : Presence of at least one hydrogen at saturated carbon which is α with respect to alkene, alkynes, carbocation, free radical, alkyl benzene nucleus. Carbon which is attached to sp^2 C is called as α –C and H which are attached to α-C are called as α-H.

1 Hyperconjugation in alkene :

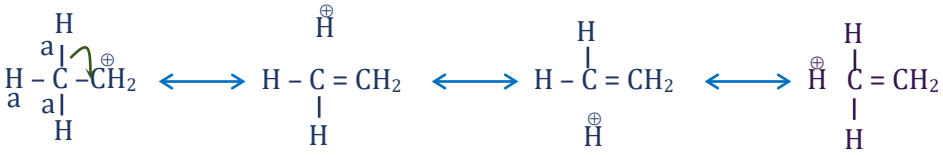
If there is one C–H σ bond and π bond are at alternate position then there will be H-effect.



These resonating structures only suggest that there is some ionic character between C–H bond. Carbon–carbon double bond acquires some single bond character.

2 Hyperconjugation in carbocation :

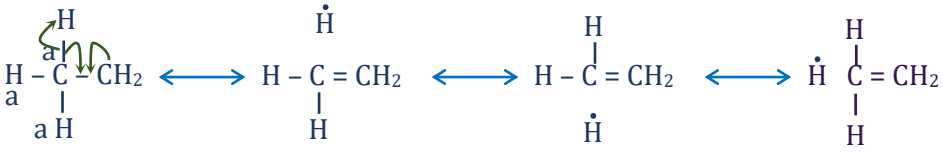
If there is one C–H σ bond and one positive charge are at alternate position then there will be H–effect. All the structures are called as hyperconjugation structures.



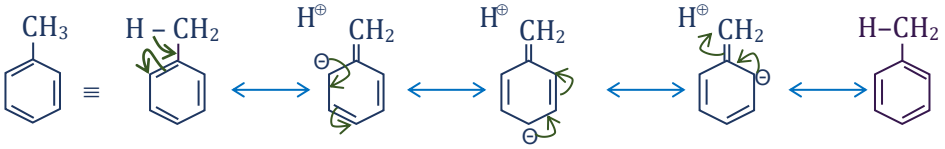
If number of α – H are more then there will be more number of hyperconjugation structures, results more stable carbocation.

3 Hyperconjugation in free radical :

If there is one C–H σ bond and one free electron are at alternate position then there will be H-effect.



4. Hyperconjugation in toluene :



Example :

Structure	Number of α-hydrogens	Total number of Hyperconjugative structure	Number of Hyperconjugative structure (involving C–H bond)
$CH_3–CH=CH_2$	3	4	3
$CH_3–CH_2–CH=CH_2$	2	3	2
$CH_3–CH=CH–CH_3$	6	7	6
$CH_3–\overset{\oplus}{C}H_2$	3	4	3
$CH_3–\overset{\oplus}{C}(CH_3)–CH_3$	9	10	9

5. Applications of hyperconjugation :

(I) Stability of Alkenes :- More is the number of hyperconjugative structures, more stable is the alkene. So **"More alkylated alkenes are more stable".**

Example : $(H_3C)_2C=C(H)CH_3$ $(H_3C)_2C=CH-CH_3$ $(H_3C)_2C=CH_2$ → Stability in decreasing order

Example : $CH_3–CH=CH_2 > CH_2=CH_2$

3 α-H 0 α-H

more stable

Example : Stability order of alkenes is

$(CH_3)_2C=C(CH_3)_2 > (CH_3)_2C=C(H)CH_3 > (CH_3)_2C=CH_2 > H(CH_3)C=C(H)CH_3$

$(CH_3)_2C=C(H)CH_3 > H(CH_3)C=C(H)CH_3 > H_2C=C(H)_2$

(II) Heat of hydrogenation : Greater the number of α hydrogen results in greater stability of alkene. Thus greater extent of hyperconjugation results lower value of heat of hydrogenation. So order for heat of hydrogenation of some alkene can be given as

$CH_2=CH_2 > CH_3–CH=CH_2 > CH_3–CH=CH–CH_3$

(III) Bond Length : Bond length is also affected by hyperconjugation

Example: $H_2C^{III}=HC^{II}-CH_2^{I} \longrightarrow H_2C^{III}=CH^{II}-\overset{\ominus}{C}H_2^{I}$ (H on C(III) becomes $\overset{\oplus}{H}$)

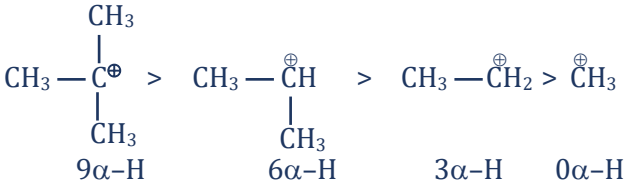
(i) Bond length of C(II) – C(III) bond is less than normal C–C bond.

(ii) Bond length of C(II) – C(I) bond is more than normal C=C bond.

(IV) Dipole moment : Since hyperconjugation causes the development of charge, it also affects the dipole moment of the molecule.

Example : $CH_2 = CH_2$ < $CH_3 - CH = CH_2$ (Dipole moment)

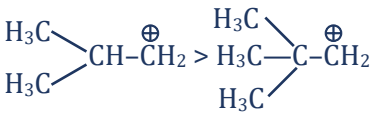
(V) Stability of carbocation : If hyperconjugation structures are more then more is the stability.

Example: 

9α–H 6α–H 3α–H 0α–H

Maximum stable

Example: 

Example: $CH_3\overset{\oplus}{C}H_2 > CH_3-CH_2-CH_2-\overset{\oplus}{C}H_2 >$  >

(VI) Stability of free radical : Greater the number of α-hydrogen results greater stability of carbon free radical.

Example : $\dot{C}H_3 < CH_3 - \dot{C}H_2 < CH_3 - \dot{C}H - CH_3 <$ 

Heat of Combustion (HOC) :

Enthalpy change when 1 mole of compound is oxidized.

$HOC \propto$ No. of C-atom $\propto \frac{1}{\text{stability}} \propto$ strain

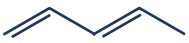
Arrange in decreasing order of HOC

1. (I)  (II)  (III)  (IV)

IV > III > II > I , ↑ no. of C-atom

2. (I)  (II) 

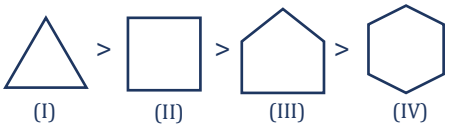
I > II , II is more stable due to +H effect

3. (I)  (II) 

I > II , II is more stable due to +H effect

4. (I)  (II)  (III)  (IV) 

IV > III > II > I , increase in no. of carbon.

5. Per CH_2 in 

(I) (II) (III) (IV)

I > II > III > IV the strain decrease from I → IV

6. (I)  (II) 

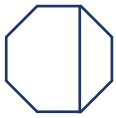
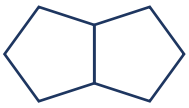
II > I , more no. of C, more is H.O.C.

7. (I)  and (II) 

II > I more no of c, more is H.O.C

8. (I)  (II)  (III) 

III > I > II, no. of C-atom increases increasing H.O.C.

9. (I)  (II)  (III) 

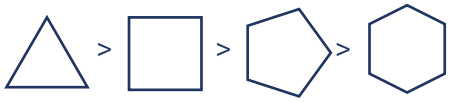
I > II > III, segment attached ring of 3, 4 and 5

10. (I)  (II)  (III) 

I > II > III, by stability

11. From HOC data,

strain order :



Stability order :