General Organic Chemistry (I & II)

(Electronic Effects and Applications)

Part A : GOC- I

Electron displacement in organic compounds :

The electron displacement in an organic molecule may take place under the influence of an atom or a substituent group or in the presence of an appropriate attacking reagent.

Types of electronic displacement

1. Inductive effect2. Resonance effect3. Mesomeric effect

4. Hyperconjugation 5. Electromeric effect (temporary effect)

1. Inductive effect :

When a covalent bond is formed between the two atoms of different electronegativity then sigma bond pair of electrons are shifted towards more electronegative atom as a result dipole is created between two atoms. Due to this dipole, sigma bonded electrons in the carbon chain becomes polarised. Such polarisation of σ bond caused by the polarisation of adjacent σ bond is referred to as the **inductive effect**.

Ex.
$$\overset{\delta\delta^+}{CH_3} \xrightarrow{\delta^+} \overset{\delta^-}{CH_2} \xrightarrow{\delta^-} \overset{\delta^-}{CH_3} \xrightarrow{\delta^-} \overset{\delta^-}{CH_2} \xrightarrow{\delta^+} \overset{\delta^+}{MgCl}$$

Note: (i) It is a permanent effect

(ii) It is distance dependent

(iii) It is operated through σ bond not through π -bond (iv) It is negligible after third carbon atom

(v) C–H bond is the reference of inductive effect i.e. polarity of C–H bond is considered to be negligible.

Inductive effects are of two types :

(i) -I effect :

The atom or group which withdraws electron clouds is known as -I group and effect is called -I effect.

Decreasing order of –I effect :

 $-\overset{\oplus}{\mathsf{NR}}_{3} > -\overset{\oplus}{\mathsf{SR}}_{2} > -\overset{\oplus}{\mathsf{NH}}_{3} > -\mathsf{NO}_{2} > -\mathsf{SO}_{2}\mathsf{R} > -\mathsf{CN} > -\mathsf{CHO} > -\mathsf{COOH} > -\mathsf{F} > -\mathsf{CI} > -\mathsf{Br} > -\mathsf{I} > -\mathsf{OR} > -\mathsf{OH} > -\mathsf{C} \equiv \mathsf{CH} > -\mathsf{NH}_{2} > -\mathsf{C}_{6}\mathsf{H}_{5} > -\mathsf{CH} = \mathsf{CH}_{2} > -\mathsf{H}.$

(ii) +I effect :

The group which releases or donates electron clouds is known as +I group & effect is called +I effect.

Decreasing order of +I effect :

 $-\overset{...\Theta}{\mathsf{NH}} - \overset{O}{\mathsf{O}} > - \overset{O}{\mathsf{COO}} > - \mathsf{C}(\mathsf{CH}_3)_3 > - \mathsf{CH}(\mathsf{CH}_3)_2 > - \mathsf{CH}_2 - \mathsf{CH}_3 > - \mathsf{CH}_3 > \mathsf{T} > - \mathsf{D} > - \mathsf{H}_3 > \mathsf{CH}_3 > \mathsf{T} > - \mathsf{D} > - \mathsf{H}_3 > \mathsf{C} > \mathsf{C}$

Direction of electron displacements



Applications of Inductive effect :

(i) Acidic strength : Presence of – I groups increases acidic character.

Acidic strength $\infty - I$ effect groups

 $O_2N-CH_2-COOH > F-CH_2-COOH > H_3CO-CH_2-COOH > CH_3-CH_2-COOH$

Since NO_2 has strong – I effect, its influence will make corresponding acid stronger.

(ii) Basic strength : Presence of + I groups increases basic character.

Basic strength ∞ + I effect

 $\mathsf{CH}_{3}-\mathsf{NH}_{2} > \mathsf{NH}_{3} \hspace{0.2cm} ; \hspace{0.2cm} \mathsf{NH}_{3} > \mathsf{C}_{6}\mathsf{H}_{5}\mathsf{NH}_{2}$

(iii) Stability of carbocations :

Carbocations are electron deficient species and they are stabilised by + I effect and destablised by - I effect. Because + I effect tends to decrease the positive charge and - I effect tends to increases the positive charge on carbocation

Stability :
$$\overset{\oplus}{C}H_3 < CH_3\overset{\oplus}{C}H_2 < (CH_3)_2\overset{\oplus}{C}H < (CH_3)_3\overset{\oplus}{C}$$

 $CH_3\overset{\oplus}{C}H_2 > CI - CH_2 - \overset{\oplus}{C}H_2 > \overset{\oplus}{C}H_2 - CH_2 - NO_2$

(iv) Stability of carbanion :

Carbanions are stabilised by -I effect and destabilised by +I effect.

Stability : $\overset{\circ}{\mathsf{C}}\mathsf{H}_3 > \mathsf{CH}_3 \overset{\circ}{\mathsf{C}}\mathsf{H}_2 > (\mathsf{CH}_3)_2 \overset{\circ}{\mathsf{C}}\mathsf{H} > (\mathsf{CH}_3)_3 \overset{\circ}{\mathsf{C}}$

(v) Stability of carbon free radical :

Carbon free radicals are stabilised by + I effect.

Stability :
$$CH_3^{\bullet} < CH_3 \rightarrow CH_2^{\bullet} < CH_3 \rightarrow \dot{C}H < CH_3 \rightarrow \dot{C}H_3 - CH_3$$

(vi) Dipole moment : Greater I effect results in greater dipole moment.

 μ : CH₃NO₂ > CH₃COOH > CH₃F > CH₃OH

2. Resonance Effect :

It is a phenomenon in which a particular compound can be written in two or more structures with identical position of atoms. These lewis structures are called resonating structure or canonical structure or contributing structures.



Note :-

- (i) The resonance structures are hypothetical and individually do not represent any real molecule. But they all contribute to a real structure which is called resonance hybrid.
- (ii) The resonance hybrid is more stable than any resonating structure.

(iii) The most stable resonating structure contribute maximum to the resonance hybrid and least stable resonating structure contribute minimum to resonance hybrid.

Resonance energy :

The P.E. difference between the most stable resonating structure and resonance hybrid is called resonance energy. The stability of molecule is directly proportional to resonance energy.

Conditions for resonance :

- 1. All atoms participating in resonance must be sp or sp² hybridised.
- 2. The parallel p-orbitals overlap to each other.
- 3. Molecule should have conjugated system (parallel p-orbitals system is called conjugate system)

Types of Conjugation :

1. Conjugation between C = C and C = C (CH₂ = CH – CH = $CH_2 \leftrightarrow CH = CH = CH - CH = CH - CH_2$)

2. Conjugation between +ve charge and C = C (CH₂ = CH – CH₂ \longleftrightarrow $CH_2 - CH = CH_2$)

- **3.** Conjugation between lone pair and C = C (: $\ddot{C}I CH = CH_2 \longleftrightarrow \ddot{C}I = CH \ddot{C}H_2$)
- **4.** Conjugation between odd electron and $C = C (CH_2 = CH \dot{C}H_2 \leftrightarrow \dot{C}H_2 CH = CH_2)$

5. Conjugation between negative charge and
$$C = C$$
 ($CH_2 = CH = CH_2 \longrightarrow CH_2 - CH = CH_2$)

Rules for writing resonating structure :

(i) In resonating structure only p-orbitals electron are shifted, σ bond electron are not involved in resonance, therefore the σ bond skeleton will remain same in between the resonating structures.

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

(ii) The movement of atoms are not allowed.

 $CH_2 = CH - CH = CH_2 \leftrightarrow CH_3 - CH = C = CH_2 \leftrightarrow CH_2 - C = CH_2$

(iii) The no. of paired electrons are same and no. of unpaired electrons are also same in two resonating structures.

$$CH_2 = CH - CH = CH_2$$
 \leftrightarrow $CH_2 - CH = CH - CH_2$
 2π electron and unpaired electrons = 2

(iv) The octet rule should not violate (for second period elements).

$$CH_{2} = CH - NH_{3} \leftrightarrow H_{2} - CH = NH_{3}$$

$$10e^{-1}$$

(v) High energy structures are rejected as resonating structure because their contribution to the resonance hybrid is negligible.

Similar charges on adjacent atoms and other given below cases are of high energy and least contributing structures.

$$CH_{2} = CH - CH = CH_{2} \longleftrightarrow GH - CH = CH_{2}$$

$$CH_{2} = CH - CH = CH_{2} \bigoplus GH - CH = CH_{2}$$

$$GH_{2} - CH - CH = CH_{2}$$

Examples : Resonating structures for the following molecules are :

(a)
$$CH_3 - CH = CH - C - CH_3 \Rightarrow CH_3 - CH = CH - C - CH_3 \Rightarrow CH_3 - CH = CH - C - CH_3 \leftrightarrow CH_3 - CH_$$



IMPORTANT POINTS :

(a) If any group has more than one π bond in conjugation, then only one π bond will take part in delocalisation.

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

Out of two π bonds only one π bond will take part in delocalisation.

(b) If any conjugate position has more than one lone pair then only one lone pair will take part in the delocalisation.

 $CH_2 = CH - O - CH_3$

Out of the two lone pair 's only one will take part in delocalisation.

(c) If any conjugate position has π bond and any of the positive charge, negative charge, odd electron, lone pair electrons then only π bond will take part in delocalisation on priority.

Nitrogen has π bond as well as lone pair, but only π bond of nitrogen will take part in delocalisation.

(d) Electrons of negative charge or lone pair behave as 2π electrons if it is in conjugation to π bond.

 $CH_2=CH-NH_2$ Behaves as 2π e's ; $CH_2=CH-CH_2$ Behaves as 2π e's ; $\langle H_2=CH-CH_2$ Behaves as 2π e's ;

H behaves as $2\pi e's$

Rules for stability of resonating structure :

(i) The resonating structure without any charge separation is more stable.

 $CH_{2} = CH - CH = O \longleftrightarrow CH_{2} - CH = CH - O$ (Stability order = I > II)

(ii) The resonating structure with more no. of π bonds is more stable and structure with complete octet at each atom is more stable.



(Stability order = II > I)

(iii) Negative charge on more electronegative atom and positive charge on less electronegative atom is more stable.





(Stability order = II > I)

Note : If the rule of electronegativity and rule of octet are contradictory to each other then priority is given to the octet rule.

$$CH_{3} - \overset{\oplus}{\underset{6e^{-}}{\overset{\oplus}{\otimes} e^{-}}} \overset{\bigoplus}{\underset{8e^{-}}{\overset{\oplus}{\otimes} e^{-}}} \overset{\oplus}{\underset{8e^{-}}{\overset{\oplus}{\otimes} e^{-}}} (Stability order = II > I)$$

$$H \overset{\oplus}{\underset{I}{\overset{\oplus}{\otimes}} - \overset{\bigoplus}{\underset{H}{\overset{\oplus}{\otimes}}} \overset{\bigoplus}{\underset{H}{\overset{\oplus}{\otimes}}} \overset{\bigoplus}{\underset{H}{\overset{\oplus}{\otimes}}} \overset{\bigoplus}{\underset{H}{\overset{\oplus}{\otimes}}} \overset{\bigoplus}{\underset{H}{\overset{\oplus}{\otimes}}} \overset{\bigoplus}{\underset{H}{\overset{\oplus}{\otimes}}} \overset{\bigoplus}{\underset{H}{\overset{\oplus}{\otimes}}} \overset{\bigoplus}{\underset{H}{\overset{\oplus}{\otimes}}} \overset{\bigoplus}{\underset{H}{\overset{\oplus}{\otimes}}} (Stability order = II > I)$$

$$I \qquad III \qquad III \qquad III$$

(iv) Between two different compounds more conjugated is more stable (provided nature of bonding is same).

$$CH_2=CH-CH=CH_2-CH=CH_2$$
 $CH_2=CH-CH=CH-CH=CH-CH_3$ (Stability order = II > I)

(v) In two compounds, if one is aromatic and another is non aromatic and conjugation is equal in both the compounds then aromatic compound is more stable.



(Stability order = I < II)

II (Aromatic)

(vi) Structure with linear conjugation is more stable than cross conjugation (nature of bonding is same). Cross conjugation : If two groups are in conjugation with a particular group but not conjugated with each other then the system is called cross conjugation.

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

 $H_2C = CH - C - CH = CH_2$ (Stability order
linear conjugation Cross conjugation

Note : Equivalent resonance structures make equal contributions to the hybrid and a system described by them has a large resonance stabilzation.



(Stability order : I = II)

= II < I)

3. Mesomeric effect :

Mesomeric effect is defined as permanent effect of π electron shifting from multiple bond to atom or from multiple bond to single bond or from lone pair to single bond.

This effect mainly operates in conjugated system of double bond. So that this effect is also known as conjugate effect. Mesomeric effect is **distance independent**.

Types of Mesomeric effect :

(i) + m effect (ii) – m effect

(i) + m group (Electron releasing group) :

A group, first atom of which bears -ve charge or lone pair always shows +m effect. Due to +m effect the electron density of benzene ring is increased particularly on ortho and para positions.

Relative order of +m group :



(ii) - m group (Electron withdrawing group) :

A group that contains double bond or triple bond between hetero atoms will show -m effect. Due to -m the electron density on benzene ring is decreased particularly on ortho and para positions.

Relative order of -m group :

 $-NO_2 > -CN > -SO_2R > -CHO > C=O > -C-O-C-R > -C-O-R > -COOH > -CONH_2$ $\| \quad \| \quad \| \quad \| \quad \| \quad \| \quad 0 \quad O$

(a)
$$O = CH - CH = CH_2 \longleftrightarrow O - CH = CH - CH_2$$

(b)
$$H_2C \stackrel{\checkmark}{=} CH \stackrel{\checkmark}{=} C\stackrel{\sim}{=} \stackrel{\sim}{N}: \longleftrightarrow H_2\stackrel{\leftrightarrow}{C} - CH = C = \stackrel{\sim}{N}:$$



4. Hyperconjugation :

When a sigma C–H bond of sp³ hybridised carbon is in conjugation with π -bond (p-orbital), half filled porbital or vacant p-orbital, then the bond pair e- of sigma C-H bond overlap with adjacent p-orbital. This phenomenon is called hyperconjugation. It may take place in alkene, alkynes, carbocations and carbon free radicals.

Like resonance hyperconjugation is also a stabilising effect but the effect of resonance is more dominating than hyperconjugation, since in resonance only p-orbital overlap while in hyperconjugation σ molecular orbitals overlap with p- molecular orbital.

* Hyperconjugation is also called no bond resonance or Baker Nathan Effect.

* Number of hyperconjugative structure = Number of α -hydrogen atoms at sp³ hybridised α -carbon atoms.

* **Condition :** sp^3 hybrid C–H or C–D must be present adjacent to the C+/C+/C=C/CC.

Important points :

(ii) Not applicable at carbanion.

(i) It is distance independent. (iii) Hybridisation of atoms remains unchanged. (iv) It is a permanent effect.

Structure	Number of α -hydrogens	Structure	Number of α -hydrogens
$CH_3 - CH = CH_2$	3	$H_3C - CH_3$	9
$CH_3 - CH_2 - CH = CH_2$	2	CH ³	
$CH_3 - CH = CH - CH_3$	6	H ₃ C-Č-CH ₃ -CH ₃	8
$CH_3 - CH_2$	3		0

(i) Hyperconjugation in carbocation :

$$\begin{array}{c} H \\ H \\ CH_{2} \end{array} \xrightarrow{\oplus} CH_{2} \end{array} \xrightarrow{\oplus} CH_{2} = CH_{2} \end{array} \qquad \begin{bmatrix} H \\ H \\ CH_{2} \end{array} \xrightarrow{\oplus} CH_{2} \\ Hybrid Structure \end{array}$$



(ii) Hyperconjugation in alkene :

$$\begin{array}{c} H \\ H \\ H^{\oplus} \\ CH_2 \end{array} - CH = CH_2 \\ \leftarrow \rightarrow \\ CH_2 = CH - CH_2 \\ \leftarrow \rightarrow \\ CH_2 = CH_2 \\ \leftarrow \rightarrow \\ CH_2 \\ \leftarrow \\ CH_2 = CH_2 \\ \leftarrow \rightarrow \\ CH_2 = CH_2 \\ \leftarrow \\ CH_2 \\ \leftarrow \\ CH_2 = CH_2 \\ \leftarrow \\ CH_2 \\ \leftarrow \\ CH_2 = CH_2 \\ \leftarrow \\ CH_2 = CH_2 \\ \leftarrow \\ CH_2 = CH_2 \\ \leftarrow \\ CH_2 \\ \leftarrow \\ CH_2 \\ \leftarrow \\ CH_2 = CH_2 \\ \leftarrow \\ CH_2 \\ \leftarrow \\$$

(iii) Hyperconjugation in radical :

$$\stackrel{\mathsf{H}}{\stackrel{\mathsf{I}}{\longrightarrow}} \stackrel{\bullet}{\stackrel{\bullet}{\longrightarrow}} \stackrel{\mathsf{H}}{\stackrel{\mathsf{I}}{\longleftarrow}} \stackrel{\mathsf{H}}{\overset{\mathsf{C}}{\longleftarrow}} \stackrel{\mathsf{H}}{\overset{\mathsf{C}}{\leftarrow}} \stackrel{\mathsf{H}}{\overset{\mathsf{C}}{\leftarrow} \stackrel{\mathsf{H}}{\overset{\mathsf{C}}{\leftarrow}} \stackrel{\mathsf{H}}{\overset{\mathsf{C}}{\leftarrow}} \stackrel{\mathsf{H}}{\overset{\mathsf{C}}{\leftarrow}} \stackrel{\mathsf{H}}{\overset{\mathsf{C}}{\leftarrow}} \stackrel{\mathsf{H}}{\overset{\mathsf{C}}{\leftarrow}} \stackrel{\mathsf{H}}{\overset{\mathsf{C}}{\leftarrow}} \stackrel{\mathsf{H}}{\overset{\mathsf{C}}{\leftarrow} \stackrel{\mathsf{H}}{\overset{\mathsf{C}}{\leftarrow}} \stackrel{\mathsf{H}}{\overset{\mathsf{C}}{\leftarrow}} \stackrel{\mathsf{H}}{\overset{\mathsf{C}}{\leftarrow}} \stackrel{\mathsf{H}}{\overset{\mathsf{C}}{\leftarrow}} \stackrel{\mathsf{H}}{\overset{\mathsf{C}}{\leftarrow}} \stackrel{\mathsf{H}}{\overset{\mathsf{C}}{\leftarrow}} \stackrel{\mathsf{H}}{\overset{\mathsf{C}}{\leftarrow}} \stackrel{\mathsf{H}}{\overset{\mathsf{C}}{\leftarrow} \stackrel{\mathsf{H}}{\overset{\mathsf{C}}{\leftarrow}} \stackrel{\mathsf{H}}{\overset{\mathsf{C}}{\leftarrow}} \stackrel{\mathsf{H}}{\overset{\mathsf{C}}{\leftarrow}} \stackrel{\mathsf{H}}{\overset{\mathsf{C}}{\leftarrow}} \stackrel{\mathsf{H}}{\overset{\mathsf{C$$

(iv) Hyperconjugation in toluene :



Applications of Hyperconjugation effect :

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

Stability of alkenes \propto no. of hyperconjugative structures $\propto \frac{1}{\Delta H_{\text{Hydrogenation}}}$



Stability in decreasing order

(ii) Heat of hydrogenation : Greater the number of α hydrogen atoms, greater will be stability of alkene. Thus greater extent of hyperconjugation results lower value of heat of hydrogenation ($\Delta H_{hydrogenation}$)

 $CH_2 = CH_2 > CH_3 - CH = CH_2 > CH_3 - CH = CH - CH_3$ (Heat of Hydrogenation)

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

$$\overset{H}{\overset{C}{\longrightarrow}} C \stackrel{C}{\overset{C}{\rightarrow}} C \stackrel{C}{\overset{C}{\longrightarrow}} C \stackrel{C}{\overset{H}{\longrightarrow}} C \stackrel{C}{\overset{C}{\longrightarrow}} C \stackrel{C}{\overset{C}{\to} C \stackrel{C}{\overset{C}{\to}} C \stackrel{C}{\overset{C}{\to}} C \stackrel{C}{\overset{C}{\to} C \stackrel{C}{\overset{C}{\to}} C \stackrel{C}{\overset{C}{\to} C \stackrel{C}{\overset{C}{\to}} C \stackrel{C}{\overset{C}{\to} C \overset{C}{\overset{C}{\to} C \overset{C}{\overset{C}{\to} C \overset{C}{\overset{C}{\to} C \overset{C}{\overset{C}{\to}$$

(a) Bond length of C(II) - C(III) bond is less than expected

(b) Bond length of C(II) - C(I) bond is more than expected

(c) C - H bond is longer than expected

(iv) Stability of carbocation : Greater number of ' α ' hydrogen atoms, greater will be stability of carbocations.

(a)
$$\overset{\oplus}{C}H_3 < CH_3\overset{\oplus}{C}H_2 < CH_3\overset{\oplus}{C}HCH_3 < (CH_3)_3\overset{\oplus}{C}$$

(b) $CH_3 - \overset{\oplus}{C}H_2 > CH_3 - CH_2 - CH_2 - \overset{\oplus}{C}H_2 > \overset{CH_3}{\underset{CH_3}{\overset{C}{\longrightarrow}}}CH - \overset{\oplus}{C}H_2 > \overset{CH_3}{\underset{CH_3}{\overset{C}{\longrightarrow}}}C - \overset{\oplus}{C}H_2$

(due to resultant of inductive effect and hyperconjugation)

(v) Stability of free radical :More the number of α-hydrogen atoms, more will be stability of carbon free radical

(a)
$$\dot{C}H_3 < CH_3 - \dot{C}H_2 < CH_3 - \dot{C}H - CH_3 < CH_3 - \dot{C} - CH_3$$

(b) $CH_3 - \dot{C}H_2 > CH_3 - CH_2 - \dot{C}H_2 > CH_3 - \dot{C}H_2 > CH_3 - \dot{C}H_2 > CH_3 - \dot{C}H_2 = CH_3 - \dot{C}H_3 = CH_3 + CH_3 = CH_3 + CH_3 +$

(due to resultant of inductive effect and hyperconjugation)

5. Electromeric effects :

It is a temporary effect. It is defined as the complete transfer of a shared pair of π -electrons to one of the atom joined by a multiple bond on the demand of an attacking reagent. The organic compound having a multiple bond (double or triple bond) show this effect in the presence of an attacking reagent only. It is represented by E and the shifting of the electrons is shown by a curved arrow.

There are two types of electromeric effect.

(i) **+E effect** : In this effect π -electron of the multiple bond transferred to that atom at which the reagent gets attached.

$$CH_2 = CH_2 \xrightarrow{\oplus} CH_2 - CH_2 - E$$

(ii) – **E effect :** In this effect the π -electron of the multiple bond transferred to that atom at which the attacking reagent does not get attached.

$$\stackrel{\Theta}{\subset}$$
N + >C = $\stackrel{\frown}{O}$ \longrightarrow NC \longrightarrow C - $\stackrel{\Theta}{O}$

Note: When inductive and electromeric effects operate in opposite directions then the electromeric effect dominates.

6. Aromatic Character : [The Huckel 4n + 2 rule]

Aromatic compounds have characteristic smell, have extra stability and burn with sooty flame.

Based on the properties of aromatic compounds there are four criteria about the π -system.

- (i) Complete conjugated system (all atoms must be sp² or sp hybridised).
- (ii) Cyclic.
- (iii) Planar.

(iv) Huckel rule: $(4n + 2) \pi$ electrons in the cyclic conjugated π -system. Where n = an integer 0,1,2,3....

Characteristics	Aromatic compounds (A)	Anti Aromatic compounds (B)	Non-Aromatic compounds (C)
Example			
1. Structure	Cyclic, planar all atoms of ring sp ² hybridised	Cyclic, planar all atoms of ring sp ² hybridised	Cyclic or acyclic, planar or non planar, sp or sp² or sp³
2. No. of π e ⁻ s in the ring	(4n + 2)πe⁻ (Huckel's rule)	(4n)πe	Any no. of πe ⁻ s
3. MOT	Unpaired e ⁻ s in B.M.O.	Some πe [—] s in non-bonding M.O.	B.M.O. / Non-bonding M.O.
4. Overlapping	Favourable over- lapping of p orbital	Unfavourable over- lapping of p orbital	Simple overlaping like alkenes
5. Resonance energy (R.E.)	Very high R.E. > 20-25 kcal/mol	Zero	4-8 kcal/mol like alkenes
6. Stability	Have extra stability due to close conjugation of πe^-s	Unstable, does not exist at room temperature	Normal stability like a conjugated system
7. Characteristic Reactions	Electrophilic substitution Reaction	Dimerisation reaction to attain stability	Electrophilic addtion reaction like alkenes

Comparision between aromatic, anti aromatic and non-aromatic compounds.

Stability of compounds = Aromatic compound > Non-Aromatic compound > Anti-Aromatic compound

Comparision between electronic effects :

Inductive effect	Mesomeric effect	Hyperconjugative effect	
(1) It is found in saturated and	(1) It is found in unsaturated	(1) It is found in carbocation,	
unsaturated compounds.	compounds especially having	carbon free radical and	
	conjugated system.	unsaturated compounds.	
(2) It involves partial shifting of	(2) It involves complete shifting	(2) It involves partial shifting of	
sigma electrons.	of pi-electrons of pi-bonds or	sigma-electrons into adjacent p-	
	lone pair of electrons.	orbital.	
(3) The electron pair is slightly	(3) The electron pair is	(3) The electron pair is partially	
displaced from its position and	completely transferred and	transferred.	
thus partial charges are	thus full positive and negative		
developed.	charges are developed.		
(4) It is transmitted over a	(4) It is transmitted from one	(4) It is transmitted from one	
quite short distance. The effect	end to other end of the chain	end to other end of the chain	
becomes negligible after third	provided conjugation is	provided conjugation is present.	
atom in the chain (distance	present. It is distance	It is distance independent.	
dependent).	independent.		

Part B : GOC- II

7. Reaction Intermediates :

A covalent bond can get cleaved either by : (i) Homolytic cleavage or (ii) Heterolytic cleavage (i) Homolytic bond dissociation : A bond dissociation in which a bond pair electron is equally distributed to the bonding atoms.

e.g., $A-B \longrightarrow A^{\bullet} + B^{\bullet}$

a homolytic bond dissociation generates radicals.

(ii) Heterolytic bond dissociation : A bond dissociation in which a bond pair electron is shifted to one atom only.

e.g., $A-B \longrightarrow A^{\oplus} + B^{\Theta}$

A heterolytic bond dissociation always generate a cation and an anion.

(A) Free Radicals :

Homolysis of covalent bond results into free radical intermediates possess the unpaired electrons.

$$A : B \xrightarrow{\text{homolysis}} \dot{A} + \dot{B}$$
Radicals

It is generated in presence of Sunlight, Peroxide or high temperature

$$\stackrel{\textbf{R}}{\rightharpoonup} X \xrightarrow[]{\text{or}} \stackrel{\textbf{h}_{\upsilon}}{\underset{\triangle}{\text{or}}} \stackrel{\textbf{h}_{\varepsilon}}{\underset{\text{free radical}}{\text{radical}}} \stackrel{\textbf{h}_{\varepsilon}}{\overset{\textbf{h}_{\varepsilon}}} + \stackrel{\textbf{h}_{\varepsilon}}{\overset{\textbf{h}_{\varepsilon}}{\underset{\text{free radical}}{\text{or}}}}$$

(i) It is a neutral species with odd electron.

- (ii) It is paramagnetic in nature due to odd electron.
- (iii) No rearrangement is observed generally.
- (iv) Carbon atom having odd electron is in sp² hybridised state and 7 e⁻ in its valence shell.
- (v) Usually O_2 is used as inhibitor to slow down the radical reaction.
- (vi) Any reaction if it is carried out in the presence of sunlight, peroxide or high temperature generally proceeds via free radical intermediate.

Stability of free radical: It is stabilised by resonance, hyperconjugation and + I groups.

stability order $(C_6H_5)_3C^{\bullet} > (C_6H_5)_2CH^{\bullet} > C_6H_5CH_2^{\bullet} > CH_2 = CH - CH_2^{\bullet} > 3^{\circ} > 2^{\circ} > 1^{\circ} > CH_3^{\bullet}$

(B) Carbocation :

A carbon intermediate which contain three bond pair & a positive charge on it, is called carbocation. It is a six electron having electrodeficient, diamagnetic species and rearrangement can be possible if stability increases.

Hybridisation	Example	
sp ²	$\overset{\oplus}{C}H_{3}$, CH_{3} – $\overset{\oplus}{C}H_{2}$	
sp	$H_2C = CH$, $HC \equiv C$	

Stability of carbocations : Followings factors increases the stability of carbocations (i) + m effect (ii) Resonance stabilization (iii) Hyperconjugation (iv) + I effect

General stability order :

$$Ph_{3}\overset{\oplus}{C} > Ph_{2}\overset{\oplus}{C}H > Ph - \overset{\oplus}{C}H - R > CH_{2} = CH - \overset{\oplus}{C}H - R > (CH_{3})_{3}\overset{\oplus}{C} > Ph\overset{\oplus}{C}H_{2} > CH_{2} = CH - \overset{\oplus}{C}H_{2} > (CH_{3})_{2}\overset{\oplus}{C}H > CH_{3} - \overset{\oplus}{C}H_{2} > CH_{2} = \overset{\oplus}{C}H_{2} \simeq \overset{\oplus}{\bigcirc} > R - C \equiv \overset{\oplus}{C}H_{2} = CH - CH - CH + CH + CH + CH +$$

Note : (1) The carbocation is not possible at following bridge head positions I and $\rm II$



(2) Carbocations showing aromatic behaviour are exceptionally more stable

) are aromatic carbocations

(3) Cyclopropylmethylcarbonium ion is also more stable due to σ bond overlapping with empty p-orbital.

Examples of stability order :

(a)
$$\overset{+}{\operatorname{CH}_3} \overset{+}{\operatorname{CH}_3} \overset{+}{\operatorname{CH}$$

(C) Carbanion :

A carbon intermediate which contain three bond pair and a negative charge on it, is called carbanion. **Hybridisation :** Carbanion carbon is in sp³ hybridised state if it is linked to sp³ hybridised carbon or hydrogen atoms, where as it will be in sp² hybridised state if it is linked to sp² hybridised C-atom due to resonance.

Hybridisation	Example	
sp ³	$\stackrel{\Theta}{CH}_3, CH_3 \stackrel{\Theta}{-CH}_2$	
sp ²	$H_2C = CH, CH_2 = CH - CH_2$; $\begin{array}{c} \Theta & \uparrow \\ \Theta & \uparrow \\ CH_2 - CH = CH_2 \longleftrightarrow CH_2 = CHCH_2 \\ \Psi & SP^2 \end{array}$
SD	Θ HC ≡C	ч ^у

Note: (i) Carbanion carbon is in sp³, sp² and sp hybridised state.
(ii) No rearrangement takes place.
(iii) It is diamagnetic (8e⁻) in nature.

Stability of Carbanions : Followings factors increases the stability of carbanions.

(i) – M effect (ii) Delocalisation of – ve charge (iii) – I effect

Note : If α -position of a carbanion has a functional group which contains multiple bond (C = C, C = O, C = N, NO₂ etc) then carbanions are stabilised by resonance.



(D) Carbenes (Divalent Carbon intermediates) :

Definition : There is a group of intermediates in which carbon forms only two bonds. These neutral divalent carbon species are called carbenes. Most carbones are highly unstable that are capable of only fleeting existence. Soon after carbones are formed, they usually react with another molecules.

Methods of preparation of carbene :

Ζ
$_{2}I_{2} + Zn \xrightarrow{\Delta} : CH_{2}$
$a = C = O \xrightarrow{\Delta} : CH_a + CO^{\uparrow}$

Types of carbene	Singlet Ċ	Triplet – C –
Shape	Bent	Linear
Hybridisation	sp ²	sp
Nature of reaction	stereospecific	None
State	Excited state	Ground state
Magnetic	Diamagnetic	Paramagnetic
Nature	Paired electrons	Diradical

(E) Nitrenes

The nitrogen analog of carbenes are nitrenes. They are very much reactive since in them octet of N is incomplete.

In nitrenes only one valency of N is satisfied.

(F) Benzyne

R

The benzene ring has one extra C – C π bond in benzyne



Clearly, we can see that the newly formed π bond cannot enter in resonance with other π orbitals of ring. since it is in perpendicular plane.

It is also important to note that hybridisation of each carbon involved in 'Benzynic bond' is sp² since the overlap between these sp² hybrid orbitals is not so much effective.

8. Tautomerism :

Definition :

Tautomerism is a phenomenon by which a single compound exists in two or more readily interconvertible structures that differ in the relative positions of at least one atomic nucleus, generally hydrogen.

These two isomers remain in dynamic equilibrium, can be isolated and also give different lab test.

Conditions :

1. Usually present in the following functional groups



2. Basic need for its existence is attachment of these groups with the sp^3 hybridised C-atom having atleast one hydrogen atom as –

To get tautomer of above structures α -hydrogen atom is shifting to more electronegative atom attached to double bond (i.e. hydrogen atom from 1st atom to 3rd atom) and double bond is developed between 1,2-atom from 2,3-atom. This can be represented as :

$$\begin{array}{c} CH \\ -C \\ -C \\ 1 \\ 1 \\ 2 \\ 3 \end{array} \xrightarrow{-C} -C = C - OH \\ -C \\ -C \\ -C \\ -C \\ -C \\ -C \\ -OH \\ -C \\ -OH \\ -C \\ -OH \\ -OH$$

These two forms (remain in equilibrium) are called tautomers of each other. The interconvertibility of tautomers is a chemical reaction which involves breaking and making of bonds.



% Enol content in the carbonyl compounds :

(i) For monocarbonyl generally it is very less.

(ii) Enol content increases with increase in the stability of enol by hyperconjugation, hydrogen bonding, resonance etc.



Decreasing order of enol content for above carbonyl compounds is : 3 > 2 > 1.

(iii) For a carbonyl compound having active methylene group percentage of enol content will be more because enolic form has intramolecular H-bonding and also it will be stabilised by resonance.



(iv) If active methylene group is more acidic, then enol content will be more.

For example in acetyl acetone (CH_3 –C– CH_2 – CH_3 enolic content is 75–76% while it is 7–8% in acetoacetic ester because ester group shows less electron withdrawing nature than keto group.

(v) Percentage of enol content is more in non-polar media while % of keto form is more in polar media.

(vi) A carbonyl compound having chiral α -hydrogen atom racemizes in aqueous solution.

$$\begin{array}{c} H & O \\ I & || \\ CH_{3}-C-C-CH_{3} & \underbrace{(aqueous)}_{(medium)} & H & O \\ I & || \\ C_{2}H_{5} & (medium) \end{array} \xrightarrow{(medium)} CH_{3}-C-C-CH_{3} + CH_{3}-C-C-CH_{3} \\ I & || \\ C_{2}H_{5} & H & O \end{array}$$

$$\begin{array}{c} H & O \\ CH_{3}-C-C-C-CH_{3} + CH_{3}-C-C-CH_{3} \\ I & || \\ C_{2}H_{5} & H & O \end{array}$$

$$\begin{array}{c} Optically active & (d\ell-mixture or racemic mixture) \end{array}$$

9. Acidic Strength :

Definitions:

(1) Arrhenius Acid : The compounds which furnish H⁺ ion in aqueous solution are called Arrhenius acids. Ex. H₂SO₄, HNO₃, HCI, HCIO₄ etc.

(2) Bronsted Acids : The species, which are proton (H⁺ ion) donors, are called Bronsted acids. Ex. NH⁺, H₂O⁺ etc. All Arrhenius acids are Bronsted acids.

(3) Lewis Acids : The lone pair acceptors are known as Lewis acids. They have vacant p or d orbitals. Ex. BX₃, AIX₃, ZnX₂ etc.

Scale for Measurement of Acid Strength :

$$\begin{array}{ccc} \mathsf{R}-\mathsf{COOH} & \underset{(\text{Conjugated base})}{\longleftrightarrow} & \mathsf{H}^{\bigoplus} \\ \mathsf{K}_{a} = & \underbrace{\left[\mathsf{RCOO}^{\Theta} \right] & \left[\mathsf{H}^{\oplus} \right]}_{\left[\mathsf{RCOOH} \right]} & \text{Where } \mathsf{K}_{a} \rightarrow \text{acid dissociation constant.} \end{array}$$

A compound is defined as the strong acid which furnish more number of H⁺ ion in aqueous solution. So, a stronger acid has higher value of K_a, or it has lower value of pK_a.

 $pK_a = -log K_a$ (More acidic nature means more K_a but less pK_a)

Note : (1) Generally conjugate base of stronger acid is more stable.

(2) Presence of EWG in the alkyl (-R) part of the acid increases stability of anion, and hence increases acidic strength.

 $\begin{bmatrix} EWG - R - C - O^{\Theta} & More stable \\ (-m, -I) & \parallel & conjugate base \end{bmatrix}$



(A) Acid Strength of Hydrides in periodic table :

(1) Along the period from left to right : As electronegativity increase, K $_{\rm a}\,\uparrow$

$$CH_4 < NH_3 < H_2O < HF.$$
 (Ka)

Conjugate base/Anion : ${}^{\Theta}_{CH_3} < {}^{\Theta}_{NH_2} < {}^{\Theta}_{OH} < {}^{\Theta}_{F}$ (stability)

(2) Along the group from top to bottom : As size of anion increases, K_a \uparrow

HF < HCl < HBr < HI

General acidic strength order is :

H₂SO₄ > HI > HBr > HCl > PhSO₃H > RSO₃H > HF > HCOOH > PhCOOH > RCOOH > H₂CO₃ >

$$\mathsf{NH}_4^+ > \mathsf{PhOH} > \mathsf{CH}_3\mathsf{OH} > \mathsf{H}_2\mathsf{O} > \swarrow > \mathsf{ROH} > \mathsf{RC} \equiv \mathsf{CH} > \mathsf{Ph}_3\mathsf{CH} > \mathsf{NH}_3 > \mathsf{RCH} = \mathsf{CH}_2 > \mathsf{RCH}_2 - \mathsf{CH}_3$$

(B) Relative acidity of hydrocarbons :

Being most electronegative the sp hybridised carbon atom of ethyne polarizes its C–H bond to the greatest extent causing its H to be most positive therefore ethyne is most acidic hydrocarbon.

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

(C) Acidity of Phenols :

The phenoxide ion is more stabilised by resonance than the unionised phenol.

- I, - m groups increases acidic character of phenol because effectively dispersing the negative charge of phenoxide ion. Alternatively + I and + m groups decreases acid strength.







 $\label{eq:Ans.acid strength order: I > II > IV > V > III$

Sol. Step 1. III will be least acidic as it has no dispersion of negative charge (No delocalisation of negative charge).

Ш

Step 2. Since -I, -m group will increase acid strength, Nitrophenol will be most acidic followed by phenol.

Step 3. Amongst cresol and methoxyphenol, methoxyphenol has +m effect of $- \text{OCH}_3$ which increases e^- density hence decrease acidic strength.



Ans. Acid strengh order : I > III > II > IV

Sol. Step 1 : Notice that CH₃ has + I effect so all methylphenols (cresols) are less acidic than phenol (I).

Step 2: Now amongst cresols p- and o- CH_3 are increasing the e⁻ 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, so it has least e⁻ density amongst the cresol.



- **Ans.** Acid strength order : II > IV > III > I
- **Sol.** Step 1. In nitrophenols I effect of NO₂ will help to increase acidic strength hence phenol is least acidic amongst all nitrophenols

Step 2. Only -I effect is applicable in meta nitrophenol so it will be number three. Now -o, -p have both -I and -m effect of NO₂ group over OH and in this particular case para isomer is more acidic than ortho nitro phenol because of intramolecular H–bond.

$$:O \rightarrow N = O$$

H is trapped by NO₂ group.

(D) Acidity of carboxylic acids :

Conjugate base of carboxylic acid exists as two equivalent cannonical structures (A) and (B). This ion is resonance stablised and resonance hybrid structure is (C).



Electron withdrawing group (–M, –I effect) **increases** acidic nature. Electron releasing group (+M, +I effect) **decreases** acidic nature.

Ex. (a)
$$F - CH_2 - COOH > CI - CH_2COOH > Br - CH_2COOH > I - CH_2COOH$$

Increasing acid strength

(b)
$$CI - COOH > CI - CH - COOH > CI - CH_2COOH > CH_3COOH$$

(c) HCOOH > $CH_3COOH > CH_3 - CH_2 - COOH$

(d)
$$\begin{array}{c} \text{COOH} \\ \text{COOH} \end{array} > \text{CH}_2 \xrightarrow{\text{COOH}} \end{array} > \begin{array}{c} \text{CH}_2 - \text{COOH} \\ \text{COOH} \end{array} > \begin{array}{c} \text{CH}_2 - \text{COOH} \\ \text{COOH} \end{array}$$

Comparison between two geometrical isomers



Now $\mathbf{K}_{1}^{m} > \mathbf{K}_{1}^{m}$

Since the conjugate base is stabilised by intramolecular H bonding.

But $K_2^{f} > K_2^{m}$ Since in maleate ion, after donation of H^{\oplus} two $-COO^{\Theta}$ groups faces each other and makes system unstable. In fumarate ion this repulsion is less.

Acidic strength of substituted benzoic acid :

(i) Formic acid is more acidic than benzoic acid while phenyl acetic acid is more acidic than acetic acid.

$$\begin{array}{rl} \mathsf{HCOOH} > \mathsf{PhCOOH} > \mathsf{C}_{6}\mathsf{H}_{5} &\longrightarrow \mathsf{CH}_{2} - \mathsf{C} - \ddot{\mathsf{O}} - \mathsf{H} > & \mathsf{CH}_{3} &\longrightarrow \mathsf{C} - \ddot{\mathsf{O}} - \mathsf{H} \\ \parallel & & \parallel \\ \mathsf{O} & & \mathsf{O} \end{array}$$

(ii) Electron withdrawing group attached to benzene ring will increase the acidic strength while electron releasing group decreases acidic strength.

(iii) If electron donating group present at para position then it is always less acidic than benzoic acid and also it is less acidic than meta substituted benzoic acid.



(v) On the other hand if e- withdrawing group is present at meta position than it is more acidic than benzoic acid.



Ortho effect :

It is common observation that generally ortho substituted benzoic acids are more acidic as compared to their isomers and benzoic acids itself. This is called **ortho effect** (which is combined effect of steric hindrance, crowding & electronic effect) in ortho substituted benzoic acid. However exceptions are seen.

CHEMISTRY FOR NEET

Ex.

(E)



соон

Remark : A stronger acid displaces the weaker acid from weak acid metal salt. The weaker acid is released out as a gas or liquid or precipitate out as a solid. The weaker acid cannot displace the stronger acid from the salt.

Salt of Strong acid

- (a) 2 NaCl + $H_2SO_4 \rightarrow Na_2SO_4 + 2HCl$ (feasible)
- $Na_2SO_4 + 2HCI \longrightarrow No reaction$ (b)

Salt of Weak acid

- $CH_{2}COONa + CH_{2}SO_{3}H \longrightarrow CH_{2}COOH + CH_{3}SO_{3}Na$ (feasible) (c)
- $CH_{3}COONa + PhOH \longrightarrow PhONa + CH_{3}COOH$ (not feasible) (d)

Strong Acid

ΗХ

Weak acid

CHEMISTRY FOR NEET

Que. Which of the following reaction is possible ?



Ans. (a) Not possible (reverse is possible)

10. Basic strength

Definitions:

(a) Arrhenius base : Those compound which furinishes OH° ions in aquous solutions are known as arrhenius base.

e.g. NaOH, KOH, Ca $(\mathbf{H}^{\oplus} \text{OH})_2$ etc.

(b) Bronsted base: Proton (ion) acceptor.

e.g. NH_{a} , $R\ddot{N}H_{a}$, $R_{a}\ddot{N}H$, $R_{a}\ddot{N}$, $H_{a}\ddot{O}$:, $R\ddot{Q}H$, $R-\ddot{Q}-R$

(c) Lewis base: e- pair donor to ion.

e.g.
$$\dot{N}H_3 + H^{\oplus} \longrightarrow \overset{\oplus}{N}H_4$$
; $R - \dot{Q} - R + H^{\oplus} \longrightarrow R - \overset{\oplus}{O} - R$

Basicity/Basic Strength(K $_{\rm b}$): It is the tendency to accept ion.

In aq. solution:-

$$\begin{split} & R - \dot{N}H_{2} + H_{2}O \Longrightarrow \qquad R - \overset{\bigoplus}{N}H_{3} + OH^{\Theta} \\ & \text{Base} \qquad \text{Conjugate Acid (C.A.)} \\ & K_{b} = \frac{[\overset{\bigoplus}{R}\overset{\bigoplus}{N}H_{3}][OH^{\Theta}]}{[RNH_{2}]} \quad [\text{where } K_{b} \text{ respresent Basic strength}]. \\ & pK_{b} = -\text{log}K_{b} \end{split}$$

Note : A stronger base always has a weaker conjugate acid and vice versa.

General basicity order :

 $R_{3}C^{\circ} > R_{2}C^{\circ}H > R-CH_{2} > CH_{3} > Ph > PhCH_{2} > NH_{2} > Ph_{2}C^{\circ}H > Ph_{3}C^{\circ} > H > R-C=C > RCCH_{2} > H$

$$\bigwedge^{\circ} \approx R - \overset{\circ}{O} \gtrsim \overset{\circ}{O} H \gtrsim CH_{3} \overset{\circ}{O} > CO_{3}^{2} > Ph \overset{\circ}{O} > R \overset{\circ}{S} > RCO \overset{\circ}{O} > OC \overset{\circ}{N} > H_{2}O > \overset{\circ}{C}$$

(A) Basic Strength in periodic table:-

(i) From left to right in a period, electronegativity of elements increases, so $K_{_{\rm b}}\downarrow$ (ii) From top to bottom in a group, size increases, so $K_{_{\rm b}}\downarrow$

Basic strength order is :

(a) $\overset{\circ}{C}H_3 > \overset{\circ}{N}H_2 > \overset{\circ}{O}H > F^{\Theta}$ (CH $_3^{\Theta}$ is strongest base in p-block) (b) $\overset{\circ}{C}H_3 > \overset{\circ}{P}H_2 > \overset{\circ}{S}H > \overset{\circ}{C}I$ (c) $F^{\Theta} > CI^{\Theta} > Br^{\Theta} > I^{\Theta}$ (d) $^{\Theta}OH > ^{\Theta}SH$ (e) $H_2 \\ \dot{O}: > H_2 \\ \dot{S}:$ (f) $:NH_3 > :PH_3$



(b) Possible (c) Not possible (d) Not possible

Stabilisation)



(E.N. \uparrow , K_b \downarrow)

(delocalised lone pair is less basic)

(better resonance due to -ve charge on 'O')

(C) Basic strength of aliphatic nitrogeneous base :

-ve charge)

In nitrogeneous compound basic strength is due to presence of lone pair of electrons at nitrogen atom which accept the proton.

$$\stackrel{\bullet\bullet}{\mathsf{NH}_3} + \mathsf{H}^{\oplus} \rightarrow \stackrel{\oplus}{\mathsf{NH}_4}$$

- Note: (1) Usually 1° amine is more basic than ammonia but if alkyl part of 1° amine is tertiary butyl then NH₃ is more basic due to steric hindrance caused by bulky nature of tertiary butyl group.
 RNH₂ > NH₃ ; (CH₃)₃ C–NH₂ < NH₃
 - (2) Basic strength of nitrogeneous compound depends upon the hybridised state of nitrogen. $R-CH_{a}-CH_{a}-NH_{a} > R - CH_{a} - CH = NH > R-CH = CH-NH_{a} > R-C=N$

(3) More electronegative atom will decrease the basic strength.

 $CH_{3}-CH_{2}-CH_{2}-NH_{2} > CH_{2}=CH-CH_{2}-NH_{2} > H-C=C-CH_{2}-NH_{2}$

(4) Cyclic amines are more basic than acyclic amines of same nature.

(5) Amidines are more basic in nature because their conjugate acid is more stable due to resonance.

$$\begin{array}{ccc} R-C=\dot{N}H & & & \\ I & (X) & & H^{\oplus} & \\ \vdots NH_{2} & & & \\ (Y) & & & (Y) & \\ \end{array} \xrightarrow{H^{\oplus}} & & R-C=\dot{N}H_{2} & \\ \vdots NH_{2} & & & H_{2} & \\ (Y) & & & (Y) & \\ \end{array}$$
 Nitrogen (X) is more basic than nitrogen (Y)

(D) Basic Strength of Aromatic Amines and substituted Anilines : (a) Aniline :

Lone pair of aniline lies in conjugation with a multiple bond, it resides in '2p' atomic orbital, so that it can get resonance stabilisation and hence, basic strength decreases. So, Aniline is a weaker base than NH_3



(b) Pyridine ($C_{s}H_{s}N$): 6- π electrons, aromatic



Lone pair of N in pyridine is localised so it is more basic than aniline.

(c) Pyrrole ($C_{A}H_{s}N$:): 6- π electrons, aromatic



Lone pair of N in pyrrole is delocalised in the aromaticity so it is very less basic than aniline.



(d) Substituted Anilines :

Electron releasing groups (ERG) +m, HC, +I increases the K_{b} Electron withdrawing groups (EWG) -m, -I decreases the K_{b}

Steric effect of ortho-substituent in Aniline (ortho effect) :



(i) Ortho-substituted anilines are mostly weaker bases than aniline itself.

- (ii) Ortho-substituent causes steric hinderance to solvation in the product (conjugate acid i.e. cation).
- (iii) The small groups like $-NH_2$ or -OH do not experience (SIR) due to small size.



CHEMISTRY FOR NEET



(E) Solvent Effect in bases :

The trend is not regular in the aqueous state as evident by their pK_b values given in Table.

Name of amine	рК _ь	Name of amine	рК _ь
Methanamine	3.38	N,N-Diethylethanamine	3.25
N-Metheylmethanamine	3.27	Aniline	9.38
N, N-Dimethylmethanamine	4.22	Phenylmethanamine	4.70
Ethanamine	329	N-Methylaniline	9.30
N-Ethylethanamine	3.00	N,N-Dimethylaniline	8.92

Table : pK_b Values of Amines in Aqueous Phase (Ref. NCERT)

In the aqueous phase, the substituted ammonium cations get stabilised not only by electron releasing effect of the alkyl group (+I) but also by solvation with water molecules. The greater the size of the ion (Alkyl groups are hydrophobic and inhibits H bonding and solvation.), lesser will be the solvation and the less stabilised is the ion.

The order of solvation of ions are as follows:



Greater is the stability of the substituted ammonium cation, stronger should be the corresponding amine as a base.

On the basis of above two sequences, we can say that the basic strength of amines is the combined effect of inductive effect, steric hindrance and solvation. So in aqueous phase K_{b} order is :

 $\begin{aligned} & R_2 NH > R NH_2 > R_3 N > NH_3 & (if R = CH_3) &(1) \\ & R_2 NH > R_3 NH > R NH_2 > NH_3 & (if R = C_2 H_5) &(2) \end{aligned}$

(F) Reaction of Bases :

(1) Nature of aqueous solution : Amines combine with water to form alkyl ammonium hydroxides. This gives hydroxide ions in solution, thus the aqueous solution of amines is basic in nature.

- (a) $RNH_2 + HOH \implies RNH_3OH^- \implies [RNH_3]^+ + OH^-$ 1° Amine
- (b) $R_2NH + HOH \Longrightarrow R_2^{+}NH_2OH^{-} \Longrightarrow [R_2NH_2]^{+} + OH^{-}$ 2° Amine

The aqueous solution of amines behave like NH₄OH and gives the precipitate of ferric hydroxide with ferric chloride.

(c) $3RNH_{3}OH + FeCI_{3} \longrightarrow Fe(OH)_{3} + 3RNH_{3}CI$

Brown ppt.

(ii) Aliphatic and aromatic amines form salt because of their basic nature:

(a)
$$RNH_2 + H_2O \longrightarrow RNH_3OH$$

Alkylammoniumhydroxide

(b)
$$RNH_2 + HCI \longrightarrow RNH_3 CI$$

Alkylammoniumchloride

(c)
$$\operatorname{RNH}_2 + \operatorname{H}_2 \operatorname{SO}_4 \longrightarrow (\operatorname{RNH}_3)_2 \operatorname{SO}_4^{-2}$$

(d)
$$C_6H_5NH_2 + HCI \longrightarrow C_6H_5NH_3CI \text{ or } C_6H_5NH_2:HCI$$

Aniliniumchloride or Anilinehydrochloride

Salts of amines are ionic compounds and hence water soluble. The amine salts react with base to give free amine –

$$RNH_3CI^-$$
 + $OH^- \longrightarrow RNH_2$ + H_2O + CI^-

(Soluble in water)