General Organic Chemistry (GOC)-II

Applications of electronic effects :

Reaction intermediates :

A covalent bond can 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 between the bonding atoms.

$$A{-}B \longrightarrow A^{\cdot} + B^{\cdot}$$

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.

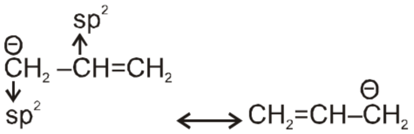
$$A{-}B \longrightarrow A^{\oplus} + B^{\ominus}$$

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

Section (A) : Carbanions

A carbon intermediate which contains three bond pair and a negative charge on it, is called carbanion.

Hybridisation : Carbanion carbon is in sp^3 hybridised state if it is linked to sp^3 hybridised carbon or hydrogen atoms, where as it will be in sp^2 hybridised state if it is linked to sp^2 hybridised C-atom due to resonance.

Hybridisation	**Example**
sp^3	$\overset{\ominus}{C}H_3$, $CH_3-\overset{\ominus}{C}H_2$
sp^2	$H_2C=\overset{\ominus}{C}H$, $CH_2=CH-\overset{\ominus}{C}H_2$; 
sp	$HC\equiv\overset{\ominus}{C}$

Note : (i) Carbanion carbon is in sp^3, sp^2 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.

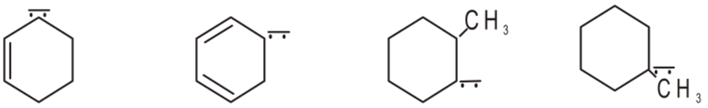
(i) – M effect (ii) Delocalisation of – ve charge (iii) – I effect

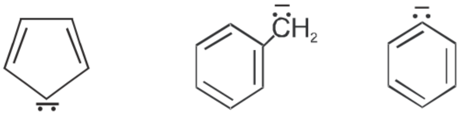
Note : If α-position of a carbanion has a functional group which contains multiple bond (C = C, C = O, C ≡ N, NO_2 etc) then carbanions are stabilised by delocalisation.

Examples of stability order :

(a) $\underset{1}{CH\equiv \bar{\ddot{C}}}$ $\underset{2}{CH_2=\bar{\ddot{C}}H}$ $\underset{3}{CH_3-\bar{\ddot{C}}H_2}$ (Stability order : 1 > 2 > 3)

(b)  (Stability order :1 > 2 > 3)

(c)  (Stability order : 2 > 1 > 3 > 4)

(d) 

1 2 3 (Stability order) : 1 > 2 > 3

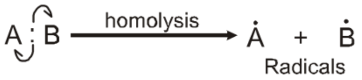
(e) $\bar{C}Cl_3$ $\bar{C}F_3$

1 2 (Stability order) : 1 > 2

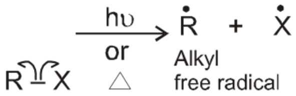
Section (B) : Carbon free radicals & carbocations

Free radicals :

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



It is generated in presence of sunlight, peroxide or high temperature



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

(ii) It is paramagnetic in nature due to odd electron.

(iii) Rearrangement is not observed generally.

(iv) Carbon atom having odd electron is in sp^2 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 : $(C_6H_5)_3\,C^\bullet > (C_6H_5)_2\,CH^\bullet > C_6H_5\,CH_2^\bullet > CH_2{=}CH{-}CH_2^\bullet > 3^o > 2^o > 1^\circ > \dot{C}H_3$

Carbocation :

A carbon intermediate which contains three bond pair & a positive charge on it, is called carbocation. It is six electrons containing electrodeficient,diamagnetic species.

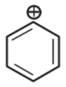
Hybridisation	**Example**
sp^2	$\overset{\oplus}{C}H_3$, $CH_3 - \overset{\oplus}{C}H_2$
sp	$H_2C = \overset{\oplus}{C}H$, $HC \equiv \overset{\oplus}{C}$

Stability of carbocations : Followings factors increases the stability of carbocations

(i) + m effect (ii) Resonance stabilization (iii) Hyperconjugation (iv) + I effect

General stability order :

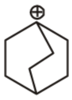
$Ph_3\overset{\oplus}{C} > Ph_2\overset{\oplus}{C}H > Ph-\overset{\oplus}{C}H-R > CH_2=CH-\overset{\oplus}{C}H-R > (CH_3)_3\overset{\oplus}{C} > Ph\overset{\oplus}{C}H_2 >$

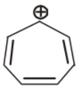
$CH_2=CH-\overset{\oplus}{C}H_2 > (CH_3)_2\overset{\oplus}{C}H > CH_3-\overset{\oplus}{C}H_2 > CH_2=\overset{\oplus}{C}H \simeq$  $> R-C\equiv\overset{\oplus}{C}$

Note : (1) Rearrangement can be possible if stability increases.

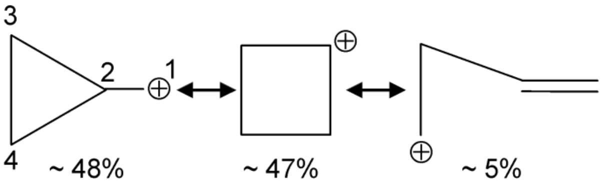
(2) The carbocation is not possible at following bridge head positions.


(I) ,

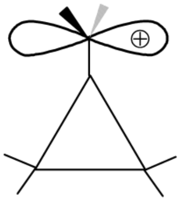

(II)

(3) Carbocations showing aromatic behaviour are exceptionally more stable (e.g.  and ).

(4) **Cyclopropylmethyl cation:** In solvolysis of simple primary cylcopropylmethyl systems the rate is enhanced because of the participation by the σ-bonds of the ring. The ion that forms initially is an unarranged cyclopropylmethyl cation that is symmetrically stabilized, that is, both the 2, 3 and 2, 4 σ-bonds help to stabilize the positive charge. Cyclopropyl group stabilizes on adjacent positive charge even better than a phenyl group.

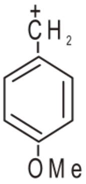


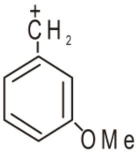
This special stability, which increases with each additional cyclopropyl group, is a result of conjugation between the bend orbitals of the cyclopropyl rings's and the vacant p-orbital of cationic carbon.

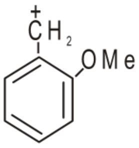


Examples of stability order :

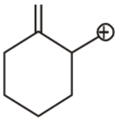
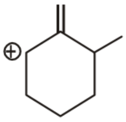
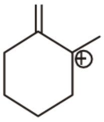
(a) $\overset{+}{C}H_3$ (1) $CH_3-\overset{+}{C}H-CH_3$ (2) $CH_3-\overset{+}{C}H-NH_2$ (3) $CH_3-\overset{+}{C}=\ddot{O}$ (4) (Stability order : 3 > 4 > 2 > 1)

(b) 





(Stability order : 1 > 3 > 2)

(c) 


(Stability order : 3 > 2 > 1)

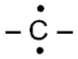
Carbenes (Divalent carbon intermediates) :

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

Methods of preparation of carbene :

$CHCl_3 + HO^{\ominus} \xrightarrow{-HCl} :CCl_2$ $\qquad$ $CH_2I_2 + Zn \xrightarrow[\Delta]{-ZnI_2} :CH_2$

$CH_2N_2 \xrightarrow{h\upsilon \text{ or } \Delta} N_2\uparrow + :CH_2$ $\qquad$ $CH_2{=}C{=}O \xrightarrow{\Delta} :CH_2 + CO\uparrow$

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

Nitrenes

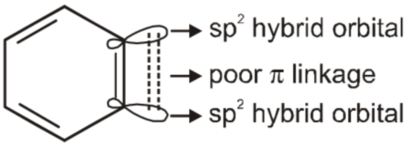
The nitrogen analog of carbenes are nitrenes. They are very much reactive since in them octet of N is incomplete.

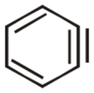
In nitrenes only one valency of N is satisfied.

$R-\underset{\cdot\cdot}{\ddot{N}}$ $\qquad$ $H-\underset{\cdot\cdot}{\ddot{N}}$

Benzyne

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 sp^2 since the overlap between these sp^2 hybrid orbitals is not so much effective.

Section (C) : Tautomerism

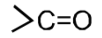
Definition :

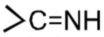
Tautomerism is a phenomenon by which a single compound exists in two or more readily interconvertible structures that differ in the relative positions of at least one atomic nucleus, generally hydrogen.

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


carbonyl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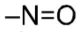
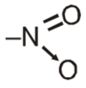
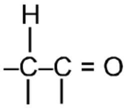
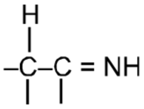
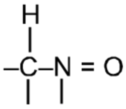

nitroso

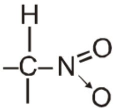

Nitro

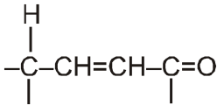
2. Basic need for its existence is attachment of these groups with the sp^3 hybridised C-atom having atleast one hydrogen atom as –



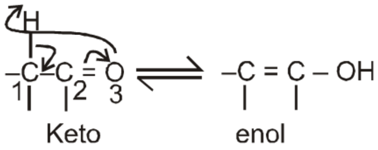






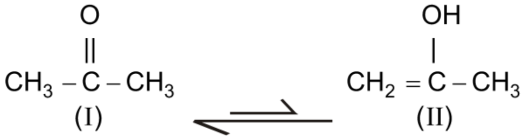


To get tautomer of above structures α-hydrogen atom is shifting to more electronegative atom attached to double bond (i.e. hydrogen atom from 1st atom to 3rd atom) and double bond is developed between 1,2-atom from 2,3-atom. This can be represented as :



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.

Ex. (a)



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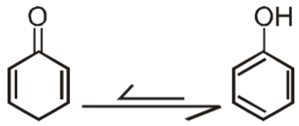

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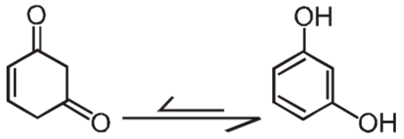
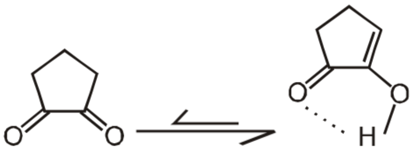


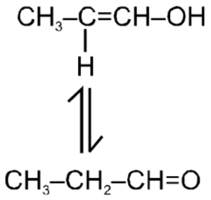
(d)

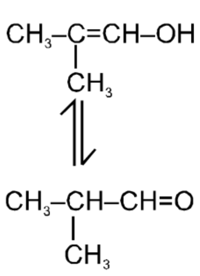


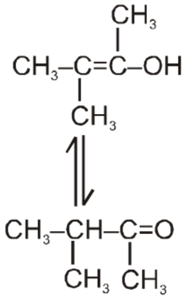
% Enol content in the carbonyl compounds :

(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.

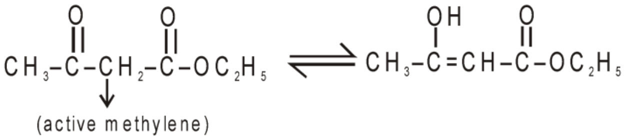

(1)


(2)

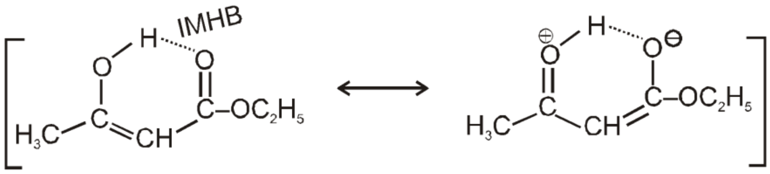

(3)

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

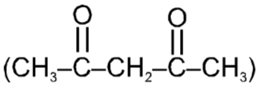
(iii) For a carbonyl compound having active methylene group percentage of enol content will be more because enolic form has intramolecular H-bonding and also it is stabilised by resonance.



Acetoacetic ester :

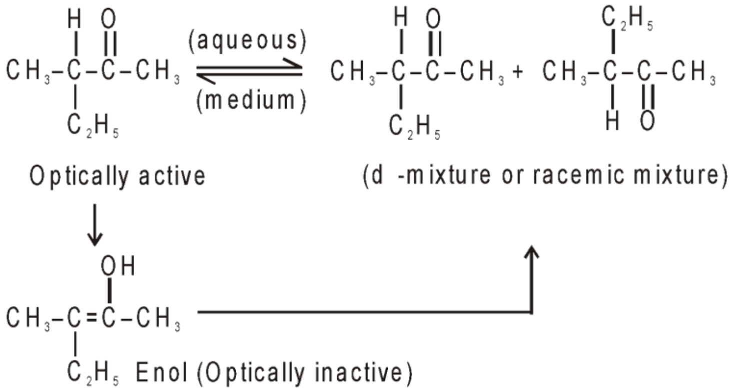


(iv) If active methylene group is more acidic, then enol content will be more.

For example in acetyl acetone  $(CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3)$ 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.



Section (D) : Acidic strength

Definitions :

(1) **Arrhenius Acids :** The compounds which furnish H^+ ion in aqueous solution are called Arrhenius acids.
Ex. H_2SO_4, HNO_3, HCl, $HClO_4$ etc.

(2) **Bronsted Acids :** The species, which are proton (H^+ ion) donors, are called Bronsted acids.
Ex. NH_4^+, H_3O^+ 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. BX_3, AlX_3, ZnX_2 etc.

Scale for measurement of Acid strength :

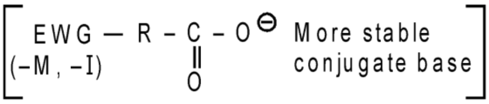
$$\underset{\text{(Acid)}}{R-COOH} \rightleftharpoons \underset{\text{(Conjugated base)}}{R-COO^{\ominus}} + H^{\oplus}$$

$$K_a = \frac{\left[RCOO^{\ominus}\right]\left[H^{\oplus}\right]}{\left[RCOOH\right]}$$ Where K_a → acid dissociation constant.

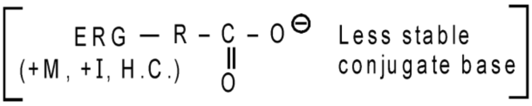
A compound is defined as the strong acid which furnish more number of H^+ ion in aqueous solution.
So, a stronger acid has higher value of K_a , or it has lower value of pK_a.
$pK_a = -\log K_a$ (More acidic nature means more K_a but less pK_a)

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.



$\left[\underset{(-M,\ -I)}{EWG} - R - \underset{\overset{\|}{O}}{C} - O^{\ominus}\ \text{More stable conjugate base}\right]$



$\left[\underset{(+M,\ +I,\ H.C.)}{ERG} - R - \underset{\overset{\|}{O}}{C} - O^{\ominus}\ \text{Less stable conjugate base}\right]$

Acid strength of hydrides in periodic table :

(1) **Along the period from left to right :** As electronegativity increase, K_a ↑

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

Conjugate base/Anion : $\overset{\ominus}{C}H_3 < \overset{\ominus}{N}H_2 < \overset{\ominus}{O}H < \overset{\ominus}{F}$ (stability)

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

$HF < HCl < HBr < HI$

General acidic strength order is :

$HI > HBr > HCl > PhSO_3H > RSO_3H > HF > HCOOH > PhCOOH > RCOOH > H_2CO_3 >$

$NH_4^+ > PhOH > CH_3OH > H_2O >$  $> ROH > RC{\equiv}CH > Ph_3CH > NH_3 > RCH{=}CH_2 > RCH_2{-}CH_3$

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.

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

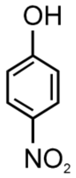
Acidity of phenols :

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

–I, –M groups increases acidic character of phenol.

Alternatively +I and +M groups decreases acid strength.

Ex. **(a)**



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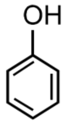
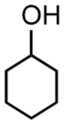


II



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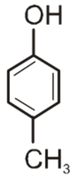
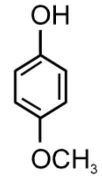


IV



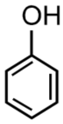
V

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).

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 $-OCH_3$ which increases e^- density hence decrease acidic strength.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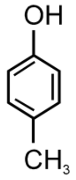
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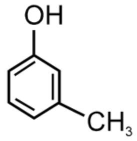
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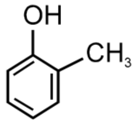
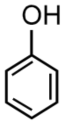

IV

Ex. **(b)**

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

Sol. **Step-1 :** Notice that CH_3 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.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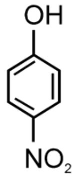
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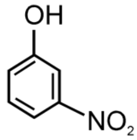
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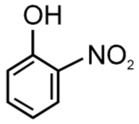
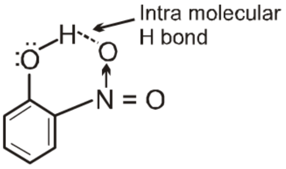

IV

Ex. **(c)**

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

Sol. **Step-1 :** In nitrophenols –I effect of NO_2 will help to increase acidic strength hence phenol is least acidic amongst all nitrophenols

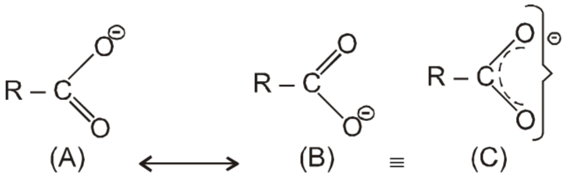
Step-2 : Only –I effect is applicable in meta nitrophenol so it will be number three. Now –o, –p have both –I and –M effect of NO_2 group over OH and in this particular case para isomer is more acidic than ortho nitro phenol because of intramolecular H–bond.



H is trapped by NO_2 group.

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).

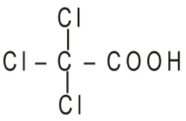
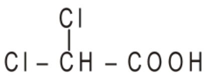


Electron withdrawing group (–M, –I effect) **increases** acidic nature.

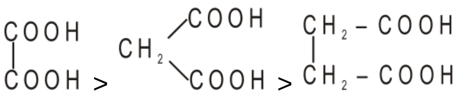
Electron releasing group (+M, +I effect) **decreases** acidic nature.

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

$$\xleftarrow[\text{Increasing acid strength}]{\qquad\qquad\qquad\qquad\qquad\qquad\qquad\qquad}$$

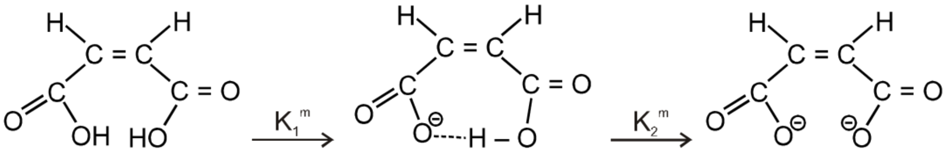
(b) 
$Cl-\underset{Cl}{\overset{Cl}{C}}-COOH$ > 
$Cl-\overset{Cl}{CH}-COOH$ > $Cl-CH_2COOH > CH_3COOH$

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

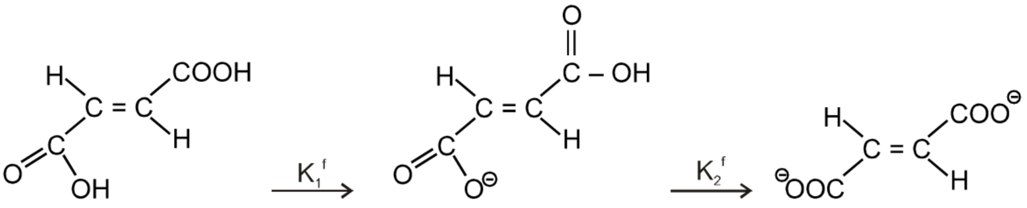
(d) 

Comparison between two geometrical isomers

Ex. **Maleic acid :**



Fumaric acid :



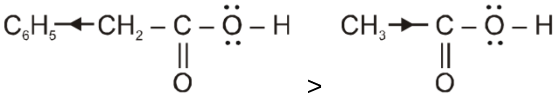
Now **K_1^m > K_1^f**

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 $-COO^{\ominus}$ groups faces each other and makes system unstable. In fumarate ion this repulsion is less.

Acidic strength of substituted benzoic acid :

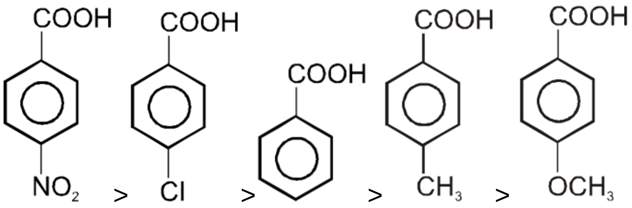
(i) Formic acid is more acidic than benzoic acid while phenyl acetic acid is more acidic than acetic acid.

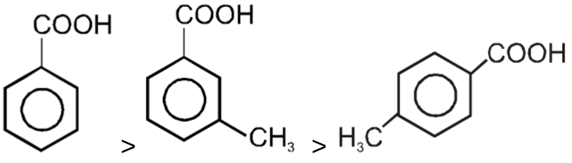
HCOOH > PhCOOH > 

$C_6H_5 \leftarrow CH_2 - \underset{\|}{\overset{}{C}} - \ddot{O} - H$ (C=O) > $CH_3 \rightarrow \underset{\|}{C} - \ddot{O} - H$ (C=O)

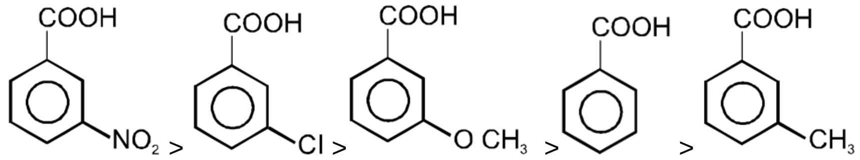
(ii) Electron withdrawing group attached to benzene ring will increase the acidic strength while electron releasing group decreases acidic strength.

(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.

(a) 

(b) 

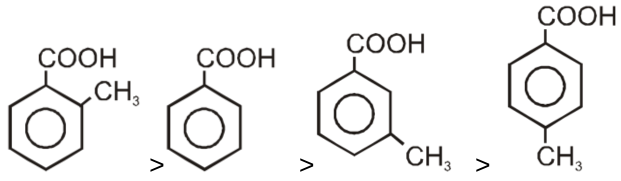
(iv) On the other hand if e⁻ withdrawing group is present at meta position than it is more acidic than benzoic acid.

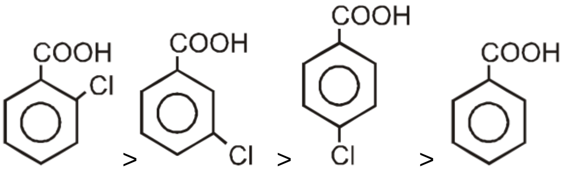
(c) 

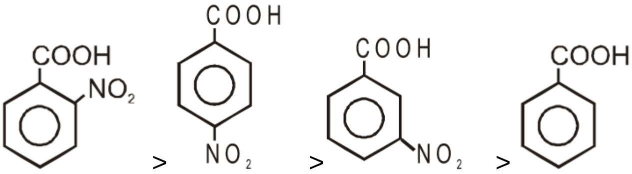
Ortho effect :

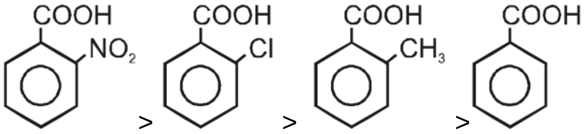
It is common observation that generally ortho substituted benzoic acids are more acidic as compared to their isomers and benzoic acid itself. This is called **ortho effect** (which is combined effect of steric hindrance, crowding & electronic effect) in ortho substituted benzoic acid. However exceptions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

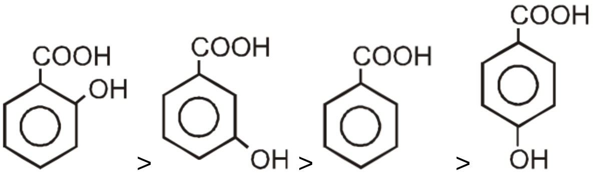
Acidic strength order of :

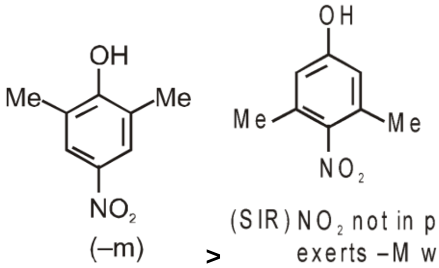
Ex. (a) 

(b) 

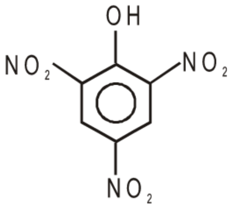
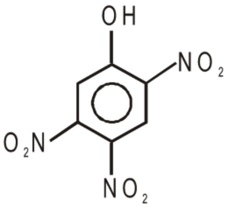
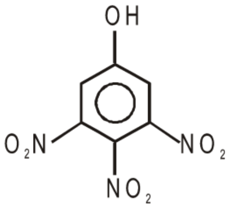
(c) 

(d) 

(e) 

(f) 

(SIR) NO_2 not in plane, so No_2 group does not exerts –M with benzene nucleus

(g)  >  > 

(picric acid)

Reaction of acids with salts :

NaX	+	HY	⟶	NaY	+	H X
Salt of Weak acid		Strong Acid		Salt of Strong acid		Weak acid

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.

(a) $2\ NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2HCl$ (feasible)

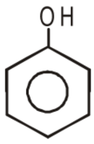
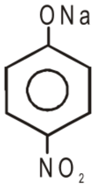
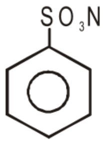
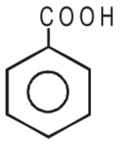
(b) $Na_2SO_4 + 2HCl \longrightarrow$ No reaction

(c) $CH_3COONa + CH_3SO_3H \longrightarrow CH_3COOH + CH_3SO_3Na$ (feasible)

(d) $CH_3COONa + PhOH \longrightarrow PhONa + CH_3COOH$ (not feasible)

Que. Which of the following reaction is possible ?

(a) $CH_3COOH + HCOONa \longrightarrow$ (b) $HC \equiv C - Na + H_2O \longrightarrow$

(c)  +  ⟶ (d)  +  ⟶

Ans. (a) Not possible (reverse is possible) (b) Possible (c) Not possible (d) Not possible

Section (E) : Basic strength

Definitions:

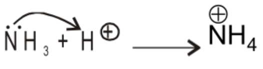
(a) **Arrhenius base :** Those compound which furinishes $OH^{\ominus}$ ions in aquous solutions are known as arrhenius base.

e.g. $NaOH$, KOH, $Ca(OH)_2$, $Ba(OH)_2$ etc.

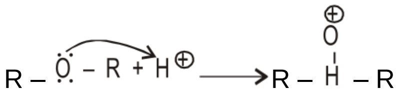
(b) **Bronsted base:** Proton ($H^{\oplus}$ ion) acceptor.

e.g. NH_3, $R\ddot{N}H_2$, $R_2\ddot{N}H$, R_3, $\ddot{N}$ $H_2\ddot{O}:$, $R\ddot{O}H$, $R-\ddot{O}-R$

(c) **Lewis base:** e^- pair donor to $H^{\oplus}$ ion.

e.g. 

$\ddot{N}H_3 + H^{\oplus} \longrightarrow \overset{\oplus}{N}H_4$

; 

$R-\ddot{O}-R + H^{\oplus} \longrightarrow R-\overset{\overset{\oplus}{O}}{H}-R$

Basicity (K_b) :

Basic Strength(K_b) is the tendency to accept $H^{\oplus}$ ion.

In aq. solution : $\underset{\text{Base}}{R-\ddot{N}H_2} + H_2O \rightleftharpoons \underset{\text{Conjugate Acid (C.A.)}}{R-\overset{\oplus}{N}H_3 + OH^{\ominus}}$

$K_b = \dfrac{[R\overset{\oplus}{N}H_3][OH^{\ominus}]}{[RNH_2]}$ [where K_b respresent Basic strength].

$pK_b = -\log K_b$

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

General basicity order :

$R_3\overset{\ominus}{C} > R_2\overset{\ominus}{C}H > R-\overset{\ominus}{C}H_2 > \overset{\ominus}{C}H_3 > \overset{\ominus}{P}h > Ph\overset{\ominus}{C}H_2 > \overset{\ominus}{N}H_2 > Ph_2\overset{\ominus}{C}H > Ph_3\overset{\ominus}{C} > \overset{\ominus}{H} > R-C\equiv\overset{\ominus}{C} > R\underset{\underset{O}{\|}}{C}\overset{\ominus}{C}H_2$

$>$  $\approx R-\overset{\ominus}{O} \gtrsim \overset{\ominus}{O}H \gtrsim CH_3\overset{\ominus}{O} > CO_3^{2-} > Ph\overset{\ominus}{O} > R\overset{\ominus}{S} > RCO\overset{\ominus}{O} > OC\overset{\ominus}{N} > H_2O > \overset{\ominus}{C}l$

Basic strength in periodic table :

(i) From left to right in a period, electronegativity of elements increases, so $K_b\downarrow$

(ii) From top to bottom in a group, size increases, so $K_b\downarrow$

Basic strength order is :

(a) $\overset{\ominus}{C}H_3 > \overset{\ominus}{N}H_2 > \overset{\ominus}{O}H > F^{\ominus}$ (b) $\overset{\ominus}{C}H_3 > \overset{\ominus}{P}H_2 > \overset{\ominus}{S}H > \overset{\ominus}{C}l$ (c) $F^{\ominus} > Cl^{\ominus} > Br^{\ominus} > I^{\ominus}$

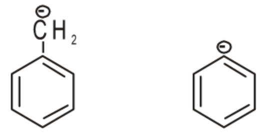
(d) ${}^{\ominus}OH > {}^{\ominus}SH$ (e) $H_2\ddot{O}: > H_2\ddot{S}:$ (f) $:NH_3 > :PH_3$

Carbanionic bases $(:C^{\ominus})$:

(a) $CH_3-\overset{\ominus}{C}H_2 > CH_2=\overset{\ominus}{C}H > CH\equiv\overset{\ominus}{C}$ (E.N. $\uparrow$, $K_b\downarrow$)

(b) $CH_3-CH_2-\overset{\ominus}{C}H_2 >> CH_2=CH-\overset{\ominus}{C}H_2$ (delocalised lone pair is less basic)

(c) $CH_2=CH-\overset{\ominus}{C}H_2 > CH_3-\overset{\overset{C}{\|}}{O}-\overset{\ominus}{C}H_2$ (better resonance due to –ve charge on 'O')

(d) 

(Resonance Stabilisation) < (localised –ve charge)

Basic strength of aliphatic nitrogeneous base :

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

$\ddot{N}H_3 + H^{\oplus} \rightarrow \overset{\oplus}{N}H_4$

Note : (1) Usually 1º amine is more basic than ammonia but if alkyl part of 1º amine is tertiary butyl then NH_3 is more basic due to steric hindrance caused by bulky nature of tertiary butyl group.

$RNH_2 > NH_3$; $(CH_3)_3C-NH_2 < NH_3$

(2) Basic strength of nitrogeneous compound depends upon the hybridised state of nitrogen.

$R–CH_2–CH_2–NH_2$ > $R–CH_2–CH=NH$ > $R–CH=CH–NH_2$ > $R–C≡N$

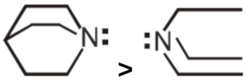
↓ ↓ ↓ ↓

sp^3 (localised) sp^2 (localised) sp^2 (delocalised) sp

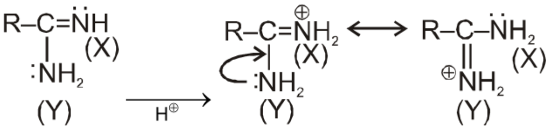
(3) More electronegative atom will decrease the basic strength.

$CH_3–CH_2–CH_2–NH_2 > CH_2=CH–CH_2–NH_2 > H–C≡C–CH_2–NH_2$

(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.

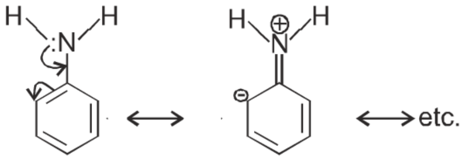


Nitrogen (X) is more basic than nitrogen (Y)

Basic strength of aromatic amines and substituted anilines :

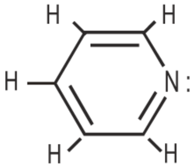
(a) Aniline :

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

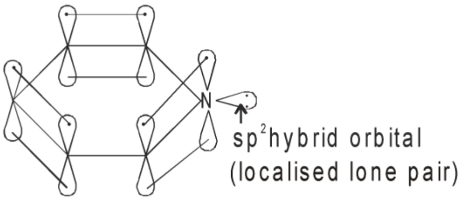


(b) Pyridine (C_5H_5N) : 6-π electrons, aromatic

S.F.:-



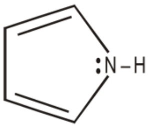
A.O. Diagram:



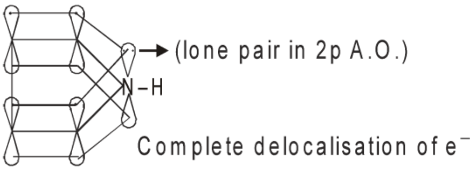
Lone pair of N in pyridine is localised so it is more basic than aniline.

(c) Pyrrole (C_4H_5N:) : 6-π electrons, aromatic

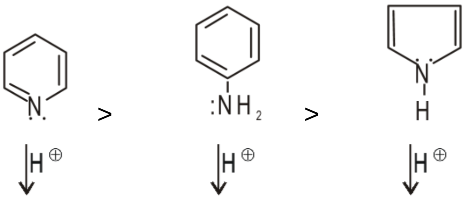
S.F.:-



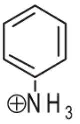
(sp^2) **A.O. Diagram:-**



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



Aromatic



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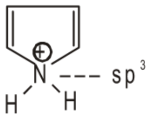


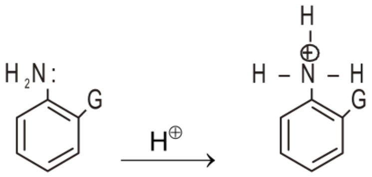
Non-aromatic

(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) :



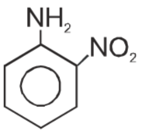
(conjugate acid)

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

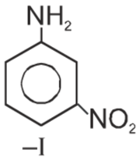
(ii) Ortho-substituent causes steric hinderance to solvation in the product (conjugate acid i.e. cation).

(iii) The small groups like $-NH_2$ or –OH do not experience (SIR) due to small size.

Ex. (a) G = (–M, –I); NO_2

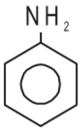


(–I –M, ortho effect)



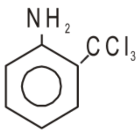
–I

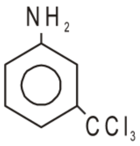
(–I–M)

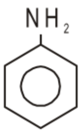


(K_b : Aniline > m > p > o).

(b) G = (–I); CCl_3



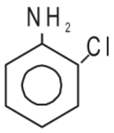


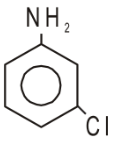


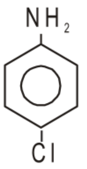
(K_b : Aniline > p > m > o).

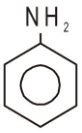
Only (–I) decides the order.

(c) G = (–I > + m); Cl





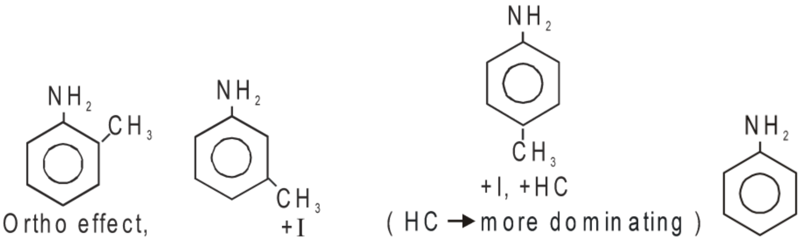




(K_b : Aniline > p > m > o)

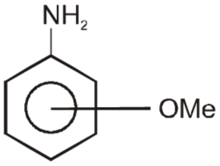
Only (–I) decides the order.

(d) G = (+I, HC); If R = $-CH_3$ (Toluidines)



(K_b : p > m > Aniline > o)

(e) G = (+m > –I);



(K_b : p > Aniline > o > m)

Solvent effect in bases :

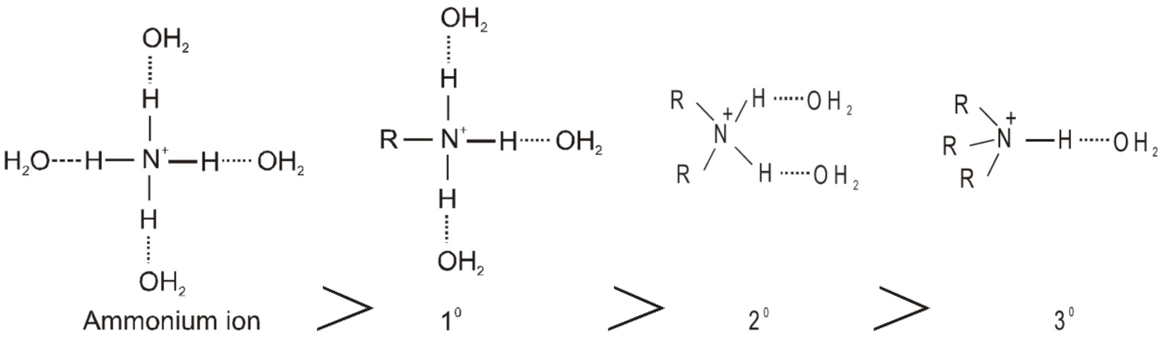
The trend is not regular in the aqueous state as evident by their pK_b values given in Table.

Name of amine	pK_b	Name of amine	pK_b
Methanamine	3.38	N,N-Diethylethanamine	3.25
N-Metheylmethanamine	3.27	Aniline	9.38
N, N-Dimethylmethanamine	4.22	Phenylmethanamine	4.70
Ethanamine	3..29	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 :

$R_2NH > RNH_2 > R_3N > NH_3$ (if $R = CH_3$) .... (1)

$R_2NH > R_3NH > RNH_2 > NH_3$ (if $R = C_2H_5$) ....(2)

Reaction of bases :

(i) 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) $$\underset{1^o \text{ Amine}}{RNH_2} + HOH \rightleftharpoons R\overset{+}{N}H_3OH^- \rightleftharpoons [RNH_3]^+ + OH^-$$

(b) $$\underset{2^o \text{ Amine}}{R_2NH} + HOH \rightleftharpoons R_2\overset{+}{N}H_2OH^- \rightleftharpoons R_2NH_2]^+ + OH^-$$

The aqueous solution of amines behave like NH_4OH and gives the precipitate of ferric hydroxide with ferric chloride.

(c) $$3RNH_3OH + FeCl_3 \longrightarrow \underset{\text{Brown ppt.}}{Fe(OH)_3} + 3RNH_3Cl$$

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

(a) $$RNH_2 + H_2O \longrightarrow \underset{\text{Alkylammoniumhydroxide}}{R\overset{+}{N}H_3\overset{-}{O}H}$$

(b) $$RNH_2 + HCl \longrightarrow \underset{\text{Alkylammoniumchloride}}{R\overset{+}{N}H_3\overset{-}{C}l}$$

(c) $$RNH_2 + H_2SO_4 \longrightarrow (R\overset{+}{N}H_3)_2\, SO_4^{-2}$$

(d) $$C_6H_5NH_2 + HCl \longrightarrow C_6H_5\overset{+}{N}H_3\overset{-}{C}l \text{ or } C_6H_5NH_2{:}HCl$$

Aniliniumchloride or Anilinehydrochloride

Salts of amines are ionic compounds and hence water soluble.

The amine salts react with base to give free amine –

$$\underset{\text{(Soluble in water)}}{R\overset{+}{N}H_3Cl^-} + OH^- \longrightarrow RNH_2 + H_2O + Cl^-$$