



# General Organic Chemistry-II

## Section (A) : Basic strength

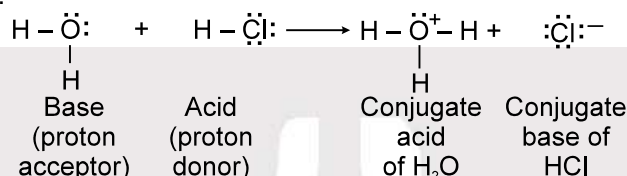
### Th1. Bases

D1: (a) **Arrhenius base:** Base is a substance that can donate (or loose)  $\text{OH}^-$  ions in  $\text{H}_2\text{O}$ .

D2: (b) **The Bronsted Lowry definition of acids and bases:**

An acid is a substance that can donate (or loose) a proton, and a base is a substance that can accept a proton.

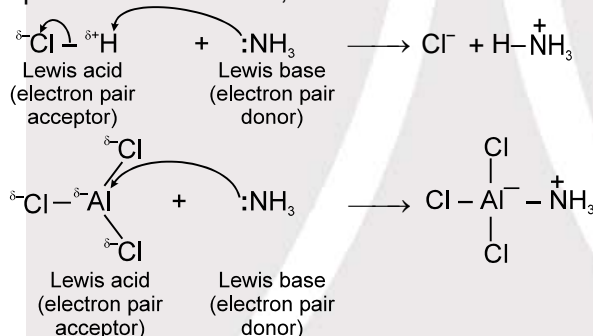
Let us consider, an example of this concept, the reaction that occurs when gaseous hydrogen chloride dissolves in water :



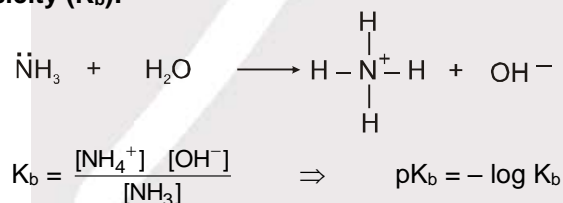
D3: (c) **The Lewis definition of acids and bases:**

Lewis proposed that acids are electron pair acceptors and bases are electron pair donors.

For example aluminiumchloride, reacts with ammonia in the same way that a proton donor does.



(d) **Basicity ( $K_b$ ):**



**Basicity order in periodic table:**

(1) Basic strength decreases down the group,

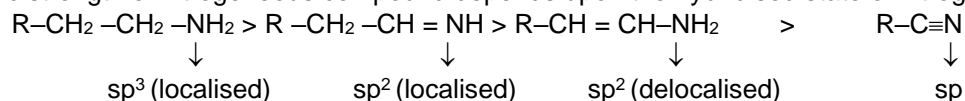
(2) Basic strength decreases along the period because electron neagativity increases, so electron donor tendency decreases.

### 1.1 Aliphatic bases:

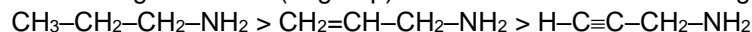
(1) On the basis of +I effect basic strength of amines should be  $3^\circ > 2^\circ > 1^\circ > \text{NH}_3$

But this order is applicable only when the amines are in gaseous state or in case of non-polar aprotic solvent.

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

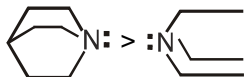


(3) More electronegative atom (-I group) will decrease the basic strength

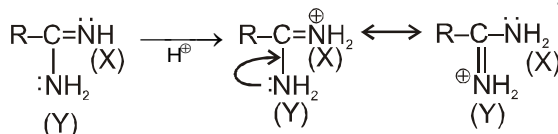




(4) Cyclic amines are more basic than acyclic amines of same nature



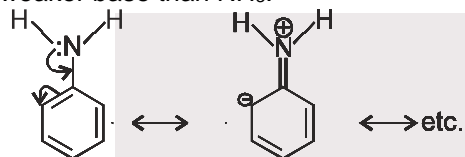
(5) Amidines are more basic in nature because their conjugate acid are more stable due to resonance.



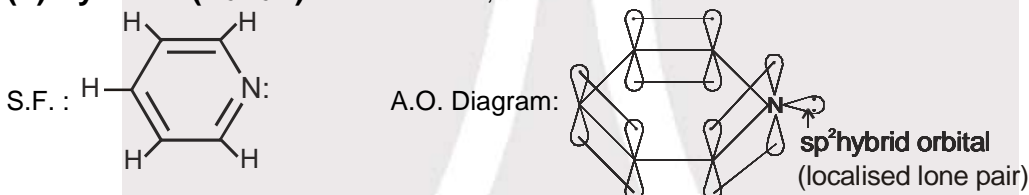
Nitrogen (X) is more basic than nitrogen (Y).

## Th2. 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  $\text{NH}_3$ .

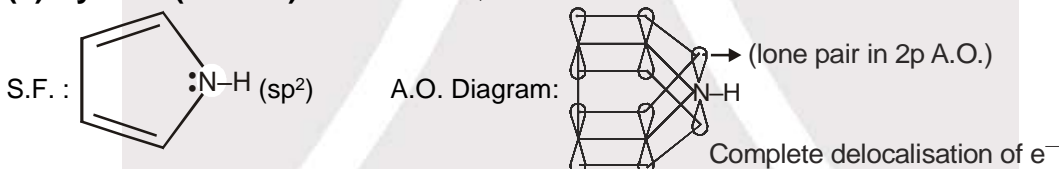


**(b) Pyridine ( $\text{C}_5\text{H}_5\text{N}$ ):** 6- $\pi$  electrons, aromatic

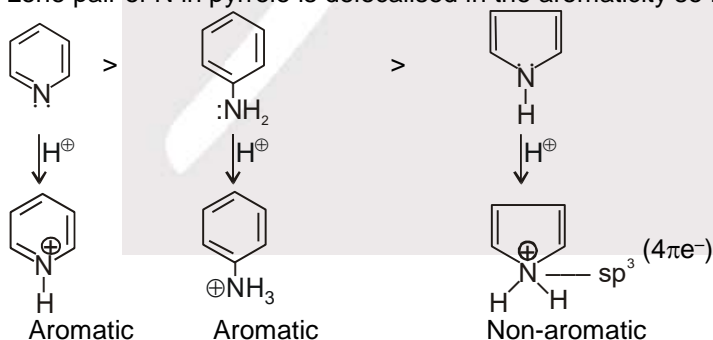


Lone pair of N in pyridine is localised so it is more basic than aniline.

**(c) Pyrrole ( $\text{C}_4\text{H}_5\text{N}$ ):** 6- $\pi$  electrons, aromatic



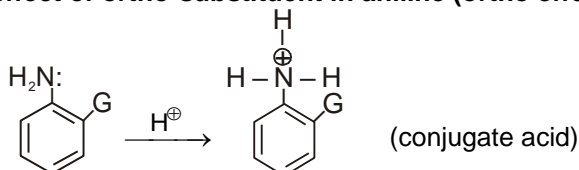
Lone pair of N in pyrrole is delocalised in the aromaticity so it is very less basic than aniline.



**(d) Ortho substituted anilines :**

Electron releasing groups (ERG) +M, HC, +I increases the  $K_b$  and  
Electron withdrawing groups (EWG) -m, -I decreases the  $K_b$

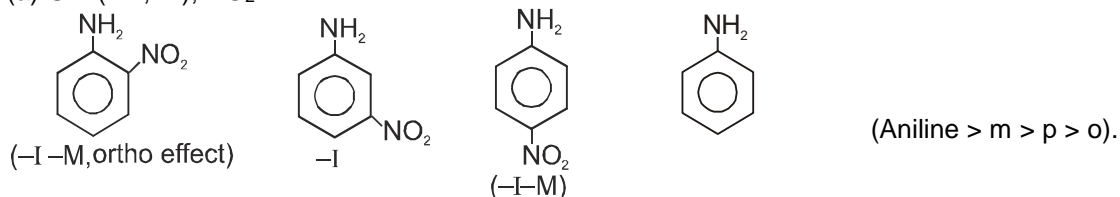
**Steric effect of ortho-substituent in aniline (ortho effect) :**



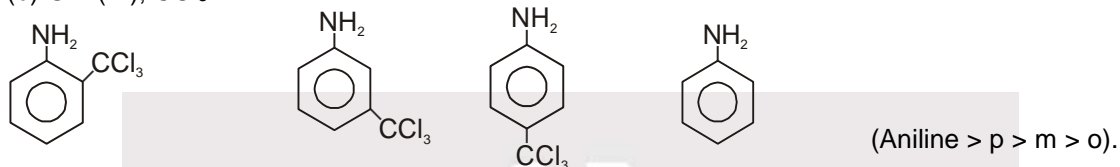


- (i) Ortho-substituted anilines are mostly weaker bases than aniline itself.  
 (ii) Ortho-substituent causes steric hinderance to solvation in the product (conjugate acid i.e. cation).  
 (iii) The small groups like  $-NH_2$  or  $-OH$  do not experience (SIR) due to small size.

Ex. (a)  $G = (-M, -I)$ ;  $NO_2$

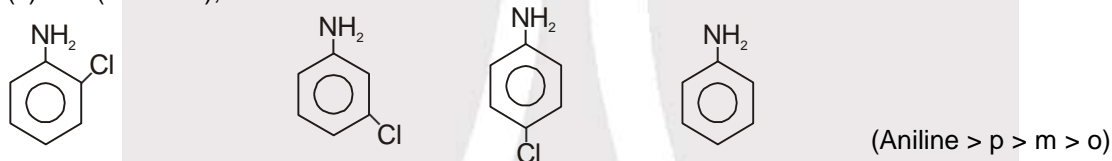


(b)  $G = (-I)$ ;  $CCl_3$



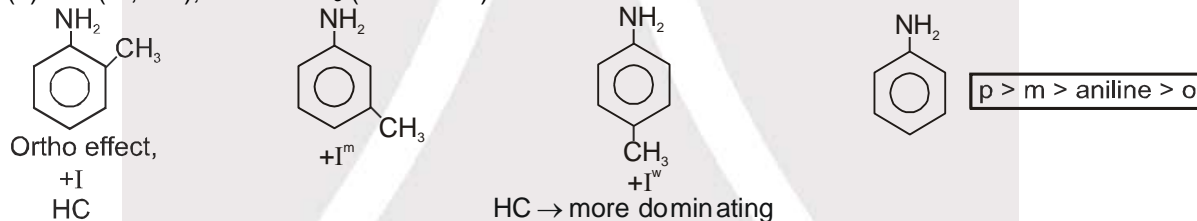
Only  $(-I)$  decides the order.

(c)  $G = (-I > +m)$ ;  $Cl$

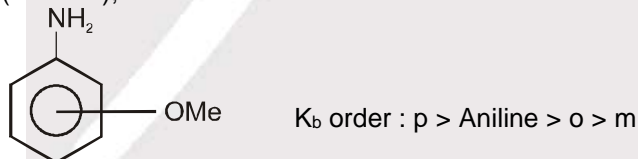


Only  $(-I)$  decides the order.

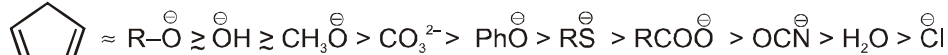
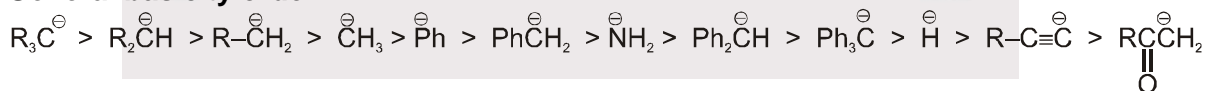
(d)  $G = (+I, HC)$ ; If  $R = -CH_3$  (Toluidines)



(e)  $G = (+M > -I)$ ;



**General basicity order :**



### Th3. Solvent effect in bases :

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

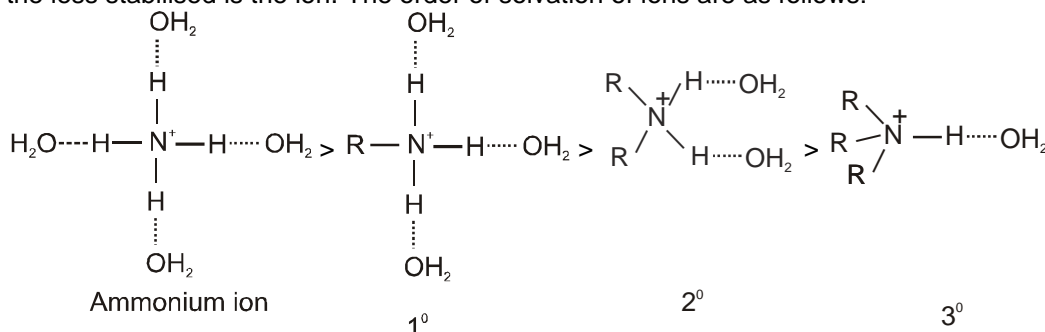
Name of amine	$pK_b$	Name of amine	$pK_b$
Methanamine	3.38	N,N-Diethylethanamine	3.25
N-Methylemethanamine	3.27	Phenylmethanamine	4.70
N, N-Dimethylmethanamine	4.22	Aniline	9.38
Ethanamine	3.29	N-Methylaniline	9.30
N-Ethylethanamine	3.00	N,N-Dimethylaniline	8.92

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



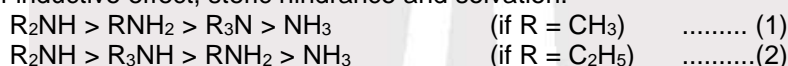


In the aqueous phase, the substituted ammonium cations get stabilised not only by electron releasing effect of the alkyl group (+I) but also by solvation with water molecules. The greater the size of the ion (Alkyl groups are hydrophobic and inhibits H bonding and solvation.), lesser will be the solvation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



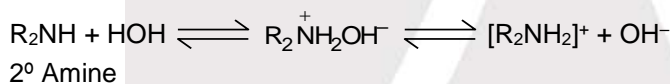
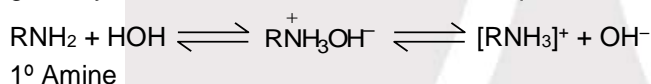
Greater is the stability of the substituted ammonium cation, stronger should be the corresponding amine as a base.

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.

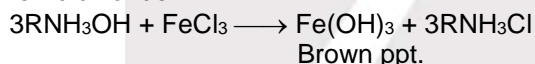


#### Th4. Reactions of bases :

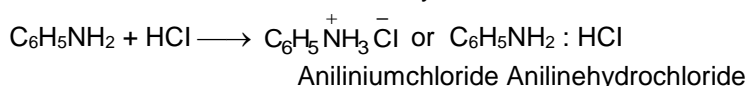
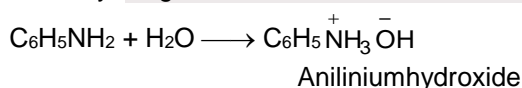
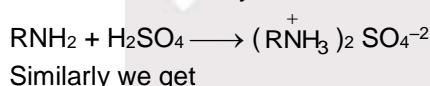
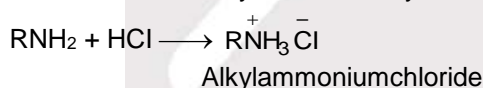
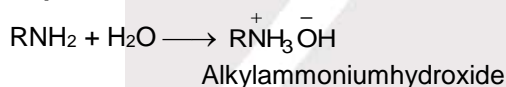
(i) **Nature of aqueous solution:** Amines combine with water to form alkyl ammonium hydroxides. This gives hydroxide ions in solution, thus the aqueous solution of amines is basic in nature.



The aqueous solution of amines behave like  $\text{NH}_4\text{OH}$  and gives the precipitate of ferric hydroxide with ferric chloride.



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



Salts of amines are ionic compounds and hence water soluble.

### Section (E) : Acidic strength

#### Th5. Acids

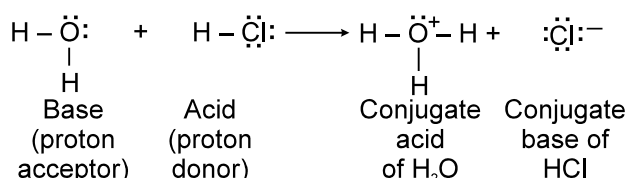
D4: (a) **Arrhenius acid:** An acid is a substance that can donate (or loose) a proton in  $\text{H}_2\text{O}$ .

D5: (b) **The Bronsted Lowry definition of acids and bases:**

An acid is a substance that can donate (or loose) a proton, and a base is a substance that can accept a proton.



Let us consider, an example of this concept, the reaction that occurs when gaseous hydrogen chloride dissolves in water :

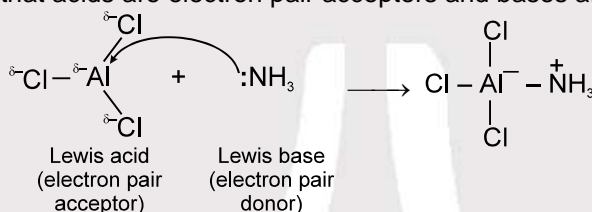


Hydrogen chloride, a very strong acid, transfers its proton to water. Water acts as a base and accepts the proton. The products that result from this reaction are a hydronium ion ( $\text{H}_3\text{O}^+$ ) and a chloride ion ( $\text{Cl}^-$ ).

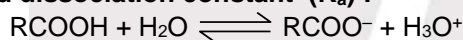
The molecule or ion that forms when an acid loses its proton is called the conjugate base of that acid. (The chloride ion is the conjugate base of HCl). The molecule or ion that is formed when a base accepts a proton is called the conjugate acid of that base.

### D6: (c) The Lewis definition of acids and bases

Lewis proposed that acids are electron pair acceptors and bases are electron pair donors.



### (d) Acid dissociation constant ( $K_a$ ) :



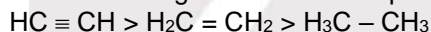
$$K_{\text{eq}} = \frac{[\text{RCOO}^-][\text{H}_3\text{O}^+]}{[\text{RCOOH}][\text{H}_2\text{O}]}$$

$$K_a = \frac{[\text{RCOO}^-][\text{H}_3\text{O}^+]}{[\text{RCOOH}]}$$

$$\text{p}K_a = -\log K_a$$

## 5.1 Relative acidity of hydrocarbons :

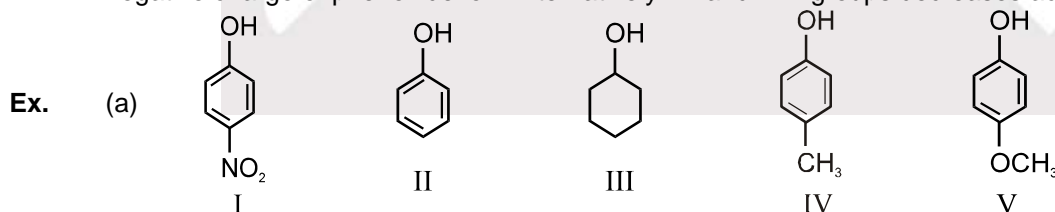
Being most electronegative the  $\text{sp}$  hybridised carbon atom of ethyne polarizes its C–H bond to the greatest extent causing its H to be most positive therefore ethyne is most acidic hydrocarbon.



## 5.2 Acidity of phenols :

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

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

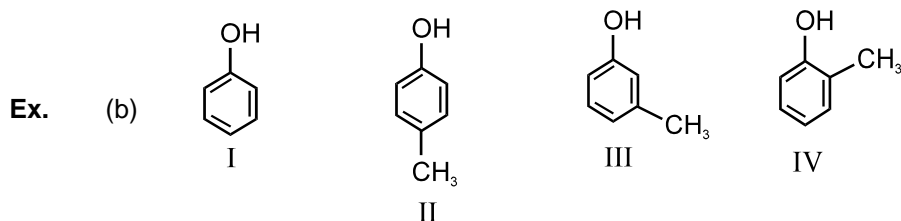


Ans. Acid strength order :  $\text{I} > \text{II} > \text{IV} > \text{V} > \text{III}$

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

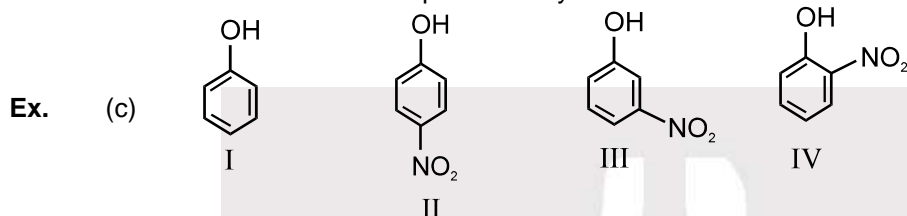
Step-2. Since  $-I$ ,  $-m$  group will increase acid strength, Nitrophenol will be most acidic followed by phenol,

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



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

Sol. Step-1: Notice that CH<sub>3</sub> have +I effect so all methylphenols (cresols) are less acidic than phenol (I).  
Step-2: Now amongst cresols p- and o-CH<sub>3</sub> are increasing the e<sup>-</sup> 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 as least e<sup>-</sup> density amongst the cresol.



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

Sol. Step-1 : In nitrophenols -I effect of NO<sub>2</sub> will help to increase acidic strength hence phenol is least acidic amongst all nitrophenols

Step-2 : Only -I effect is applicable in meta nitrophenol it will be number three. Now -o, -p have both -I and -m effect of NO<sub>2</sub> group over OH and in this particular case para isomer is more acidic than ortho since

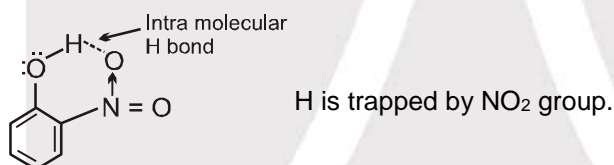


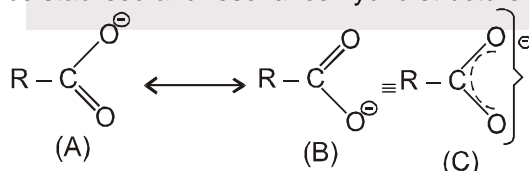
Table : pK<sub>a</sub> values of some phenols and Ethanol. (Ref. NCERT)

Compound	Formula	pK <sub>a</sub>	Compound	Formula	pK <sub>a</sub>
o-Nitrophenol	o-O <sub>2</sub> N-C <sub>6</sub> H <sub>4</sub> -OH	7.2	o-Cresol	o-CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> -OH	10.2
m-Nitrophenol	m-O <sub>2</sub> N-C <sub>6</sub> H <sub>4</sub> -OH	8.3	m-Cresol	m-CH <sub>3</sub> C <sub>6</sub> H <sub>4</sub> -OH	10.1
p-Nitrophenol	p-O <sub>2</sub> N-C <sub>6</sub> H <sub>4</sub> -OH	7.1	p-Cresol	p-CH <sub>3</sub> -C <sub>6</sub> H <sub>4</sub> -OH	10.2
Phenol	C <sub>6</sub> H <sub>5</sub> -OH	10	Ethanol	C <sub>2</sub> H <sub>5</sub> OH	15.9

From the above data, you will note that phenol is million times more acidic than ethanol.

### 5.3 Acidity of carboxylic acids :

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



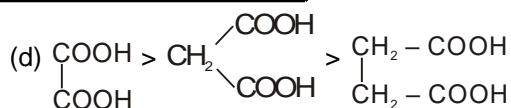
Electron withdrawing group (-M, -I effect) increases acidic nature.

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

Ex. (a) F-CH<sub>2</sub>-COOH > Cl-CH<sub>2</sub>COOH > Br-CH<sub>2</sub>COOH > I-CH<sub>2</sub>COOH

(b)  $\text{Cl}-\overset{\text{Cl}}{\underset{\text{Cl}}{\text{C}}}-\text{COOH} > \text{Cl}-\overset{\text{Cl}}{\text{CH}}-\text{COOH} > \text{Cl}-\text{CH}_2\text{COOH} > \text{CH}_3\text{COOH}$

(c) HCOOH > CH<sub>3</sub>COOH > CH<sub>3</sub>-CH<sub>2</sub>-COOH

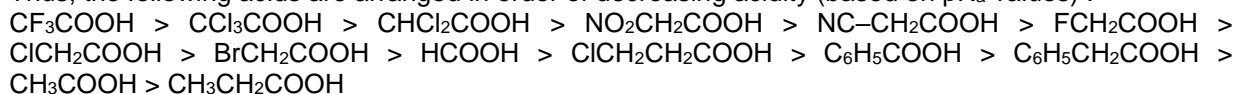


The effect of the following groups in increasing acidity order is

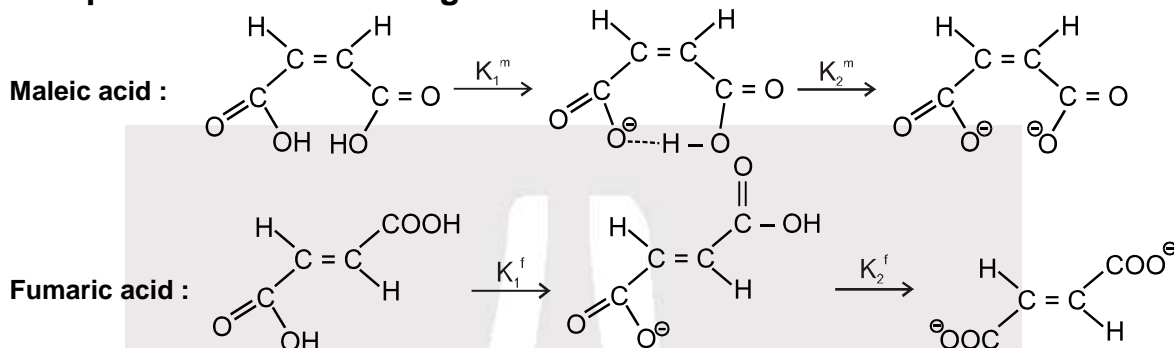


[Ref. NCERT]

Thus, the following acids are arranged in order of decreasing acidity (based on  $\text{pK}_a$  values) :



### 5.4 Comparison between two geometrical isomers :



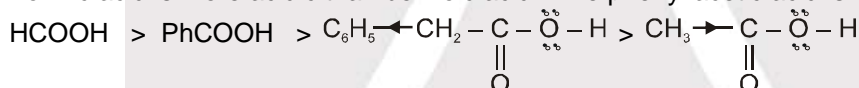
Now  $K_1^m > K_1^f$

Since the conjugate base is stabilised by intramolecular H bonding.

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

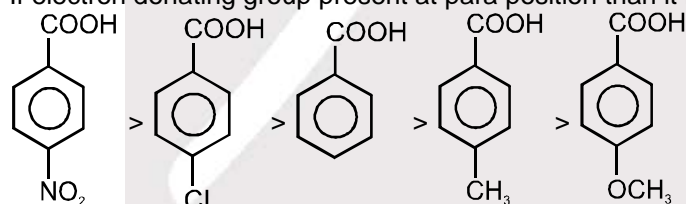
### 5.5 Acidic strength of substituted benzoic acids :

Formic acid is more acidic than benzoic acid while phenyl acetic acid is more acidic than acetic acid.

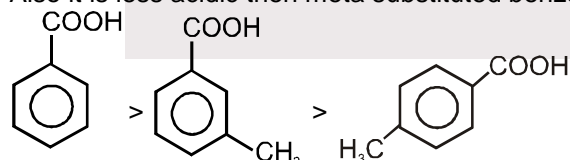


Electron withdrawing group attached to benzene ring will increase the acidic strength while electron releasing group decreases acidic strength.

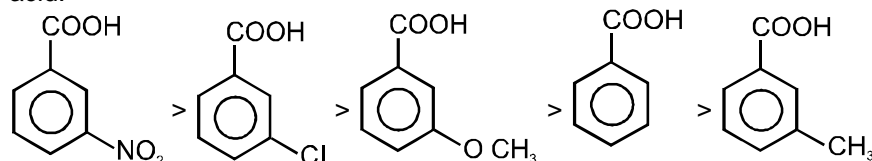
If electron donating group present at para position then it is always less acidic than benzoic acid.



Also it is less acidic than meta substituted benzoic acid.



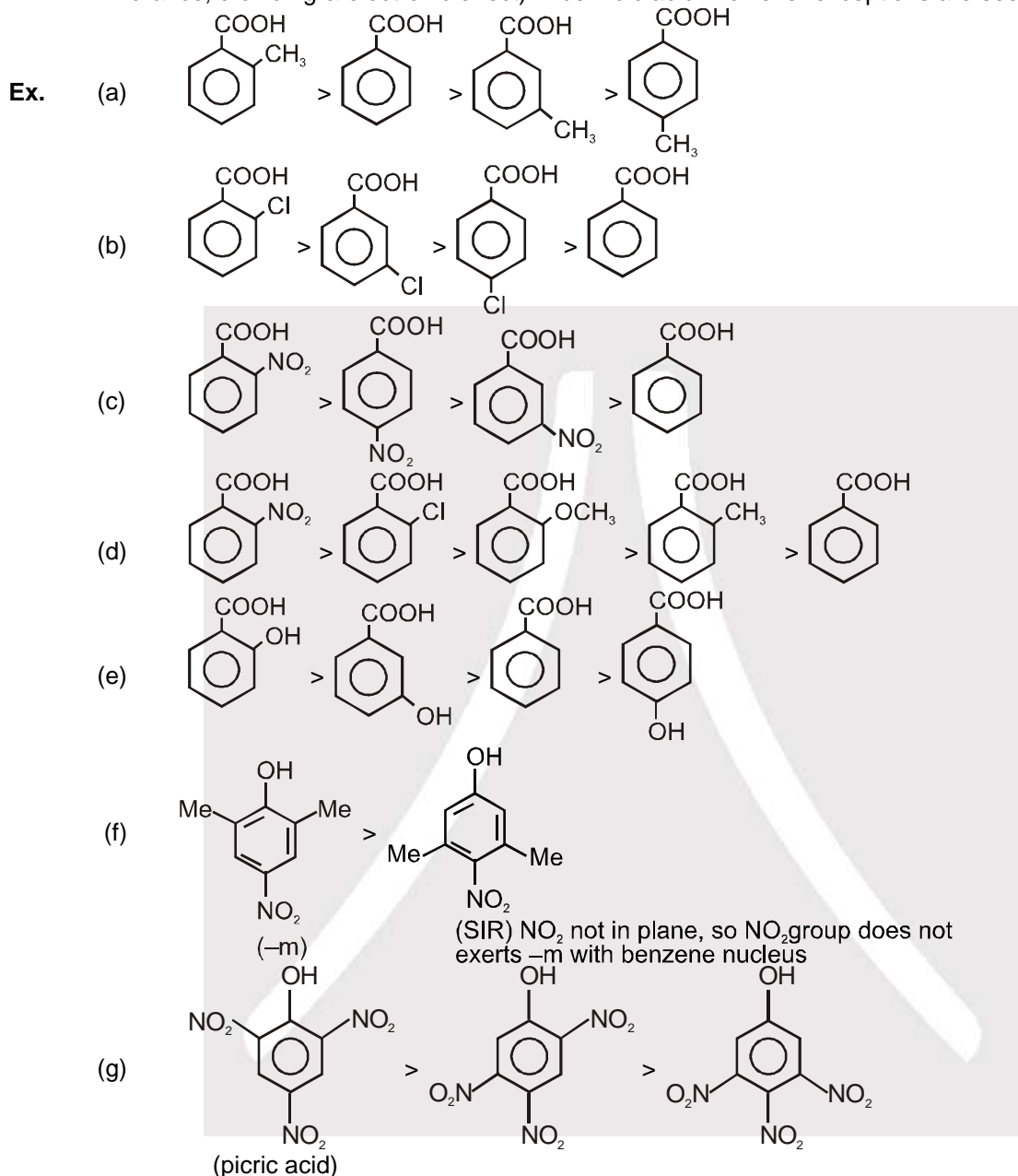
On the other hand if  $e^-$  withdrawing group is present at meta position then it is more acidic than benzoic acid.





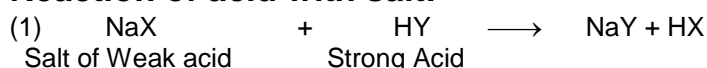
### Th6. Ortho effect :

**D6.** 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 benzoic acid. However exceptions are seen.



## Section (F) : Feasible reactions of acids and bases

### Th7. Reaction of acid with salt:



**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 precipitates out as a solid. The weaker acid cannot displace the stronger acid from the salt.

- $2 \text{NaCl} + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + 2\text{HCl}$
- $\text{Na}_2\text{SO}_4 + 2\text{HCl} \longrightarrow \text{No reaction}$
- $\text{CH}_3\text{COONa} + \text{CH}_3\text{SO}_3\text{H} \longrightarrow \text{CH}_3\text{COOH} + \text{CH}_3\text{SO}_3\text{Na}$  (feasible)
- $\text{CH}_3\text{COONa} + \text{PhOH} \longrightarrow \text{PhONa} + \text{CH}_3\text{COOH}$  (not feasible)





## Section (G) : Tautomerism

### Th8. Tautomerism

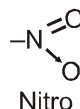
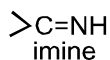
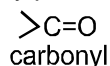
#### D7: Definition :

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.

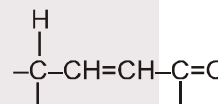
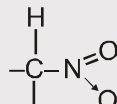
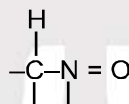
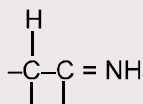
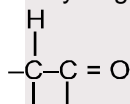
These two isomers remain in dynamic equilibrium and can be isolated also give different lab test.

#### Conditions :

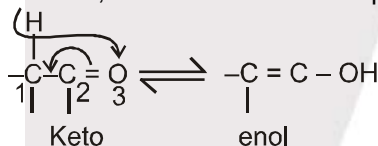
1. Usually present in the following functional groups



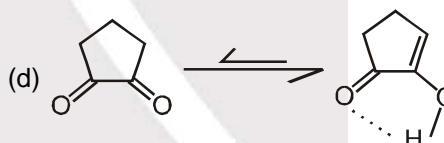
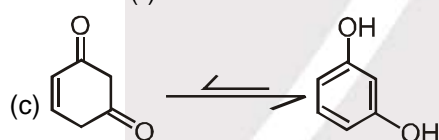
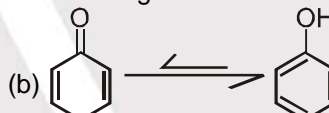
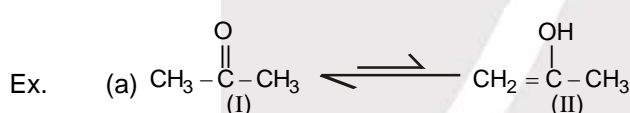
2. Basic need for its existence is attachment of these groups with the  $sp^3$  hybridised C-atom having atleast one hydrogen atom as –



To get tautomer of above structures  $\alpha$ -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:

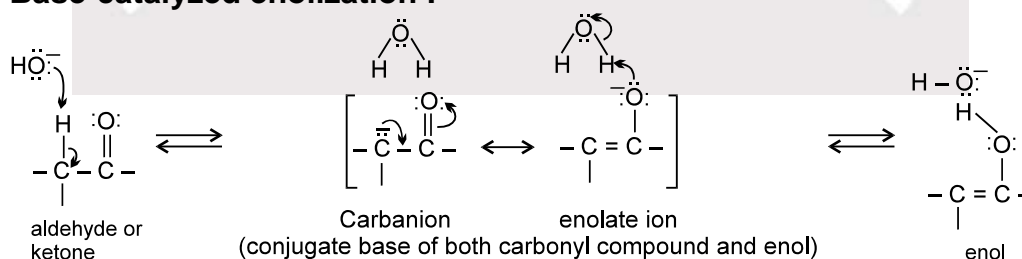


These two forms (remain in equilibrium) are called tautomers of each other. The interconvertibility of tautomers is a chemical reaction which involves making and breaking of bonds.



### Th9. Keto-enol tautomerisation :

#### 9.1 (A) Base-catalyzed enolization :

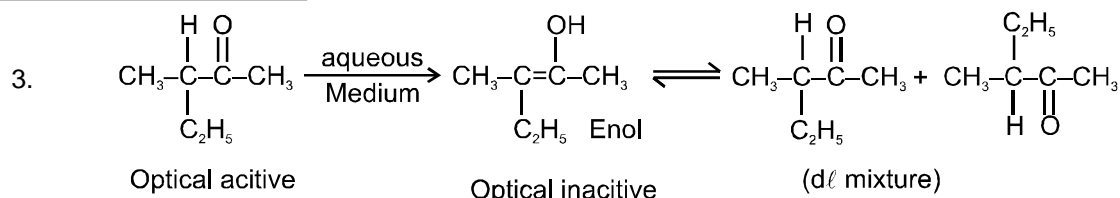


Protonation of the carbanion by water on the  $\alpha$ -carbon gives back the carbonyl compound. Protonation on oxygen gives the enol. Notice that the enolate ion is the conjugate base of both the carbonyl compound and the enol.

#### (B) Acid-catalyzed enolization :

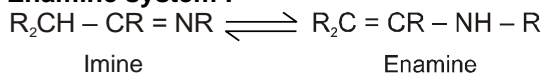
Involves the conjugate acid of the carbonyl compound. Recall that this ion has carbocation characteristics. Loss of the proton from oxygen gives back the starting carbonyl compound; loss of the proton from the  $\alpha$ -carbon gives the enol. Notice that an enol and its carbonyl isomer have the same conjugate acid.





### Th10. Other examples of tautomers (not to be done in class only for the reference of students)

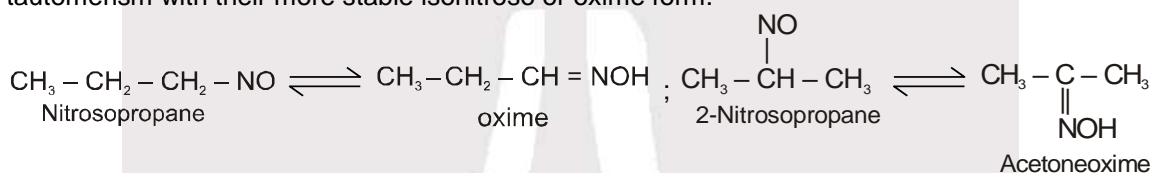
#### (a) Imine-Enamine system :



Among these two tautomers, enamines are stable only when there is no hydrogen on the nitrogen, otherwise the imine form predominates.

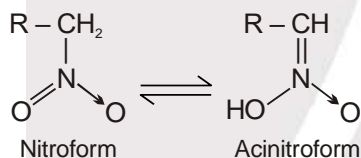
#### (b) Nitroso-oxime system:

Like primary and secondary nitro compounds, primary and secondary nitroso compounds also exhibit tautomerism with their more stable isonitroso or oxime form.

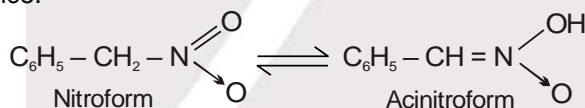


#### (c) Nitro-Acinitro system:

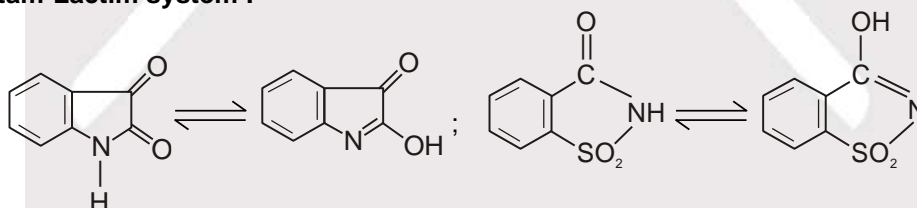
The acidic nature of the nitro compounds gives rise to the belief that the nitro compounds exist in two forms, a more stable or normal nitro form and the less stable acinitro form.



The stability of the nitro form is more as compared to the acinitro form because it is stabilised by resonance.



#### (d) Lactam-Lactim system :



## CHECK LIST

### Definitions (D)

D1 : Arrhenius base	<input type="checkbox"/>
D2 : Bronsted base	<input type="checkbox"/>
D3 : Lewis definition of acids and bases	<input type="checkbox"/>
D4 : Arrhenius acid	<input type="checkbox"/>
D5 : Bronsted acid	<input type="checkbox"/>
D6 : Lewis definition of acids and bases	<input type="checkbox"/>
D7 : Ortho effect	<input type="checkbox"/>
D8 : Tautomerism	<input type="checkbox"/>

### Theories (Th)

Th1 : Bases	<input type="checkbox"/>
Th2 : Basic strength of aromatic amines and substituted anilines	<input type="checkbox"/>
Th3 : Solvent effect in bases	<input type="checkbox"/>
Th4 : Reactions of bases	<input type="checkbox"/>
Th5 : Acids	<input type="checkbox"/>
Th6 : Ortho effect	<input type="checkbox"/>
Th7 : Reactions of acids with salts	<input type="checkbox"/>
Th8 : Tautomerism	<input type="checkbox"/>
Th9 : Keto-enol tautomerisation	<input type="checkbox"/>
Th10 : Racemisation and D-exchange	<input type="checkbox"/>
Th11 : Other examples of tautomers	<input type="checkbox"/>