

## CHAPTER -1

Acids & Bases**1. Definitions of acid and base**

There are theories that can fully define the acids and bases.

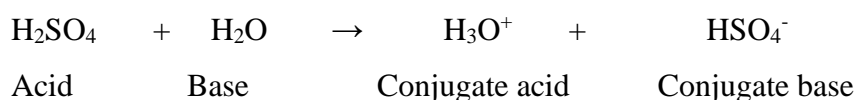
**1) Arrhenius Theory**

According to this theory any compound which can yield hydrogen ions,  $H^+$  in solution is called acid, while the compound which yield hydroxyl ion,  $OH^-$  in solution is called bases.

This definition is only restricted for the compounds that are water soluble. So for the generalized definition of acid and bases, Bronsted have given another definition.

**2) Bronsted Theory**

Any substance that can accept protons is called bases while the substances that can give protons are called acids. It means that the acids are proton donors and bases are proton acceptors. For example the ionization of sulphuric acid in aqueous solution can be represented as below:



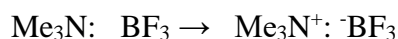
Here water accepts a proton to form hydroxonium ion so it is acting as a base. While sulphuric acid is donating a proton to act as an acid.

According to this theory any acid after proton donation is converted into a base which is called the conjugate base of that acid. While the base after proton acceptance is converted into an acid which is called as the conjugate acid of that base. Here  $H_3O^+$  is called conjugate acid of water while  $HSO_4^-$  is called conjugate base of sulphuric acid.

However the more generalized definition is provided by Lewis.

### 3) Lewis Theory

According to this theory any specie which can donate a pair of electrons for coordination is called bases while any specie which can accept a pair of electrons to make coordination is called acids. It means that the acids are electron acceptor species while electron donor species are called bases. In the given example BF<sub>3</sub> is considered as an acid because it can accept a pair of electrons from Me<sub>3</sub>N which is a base as it is an electron donor.

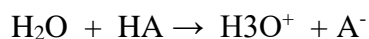


Other common examples of Lewis acids are Aluminium chloride, tin (IV) chloride, and Zinc chloride etc.

## 2. Acids

### 2.1 Strength of acids

The strength of any acid can be measured from the extent of its ionization in water. If an acid is more ionisable in water, it will be strong acid than the acid which is less ionisable in water. So more ionisable an acid in water, more strong it will be. The extent of ionization of an acid can be measured from its equilibrium constant value. Consider an example in which an acid HA is dissociated in water:



The equilibrium constant for this reaction can be given as

$$K \approx \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}][\text{H}_2\text{O}]}$$

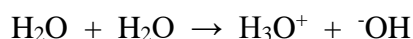
Here the concentration of water remains constant, so we can write  $K [\text{H}_2\text{O}] = K_a$  and the equation becomes,

$$K_a \approx \frac{[\text{H}_3\text{O}^+][\text{A}^-]}{[\text{HA}]}$$

Here  $K_a$  is called as the acidity constant of the acid in water. The  $K_a$  is dependent on many factors including the nature of the solvent. However it is a useful value to compare the strengths of different acids.

As we know that the value of  $K_a$  is often very small, so to replace this another term  $pK_a$  is introduced. The  $pK_a$  of an acid can be measured by taking  $-\log$  of the  $K_a$  value of an acid. For example the  $K_a$  value of ethanoic (acetic) acid in water is  $1.79 \times 10^{-5}$  at  $25^\circ\text{C}$ , however its  $pK_a$  value is 4.76. It means that the acid strength and  $pK_a$  are inversely proportional to each other. The smaller the numerical value of  $pK_a$ , stronger the acid is.

However very weak acids with  $pK_a \approx 16$  will not be detected as acids in water as  $[\text{H}_3\text{O}^+]$  produced by an acid will be less than produced by the autolysis of water itself.



So the  $pK_a$  of very weak acids cannot be measured in water. Similarly all the strong acids that fully ionized in water, e.g. HCl,  $\text{HNO}_3$ ,  $\text{H}_2\text{SO}_4$  and show same  $pK_a$  values. This is called as the **leveling effect of water**.

## 2.2 The origin of acidity in organic compounds.

The factors which influence the acidity of an organic compound HA are given below.

- The strength of H-A bond.
- The electronegativity of A.
- Factors stabilizing  $\text{A}^-$  compared with HA.
- The nature of the solvent.

Among all these factors (a) is not mostly the limiting factor.

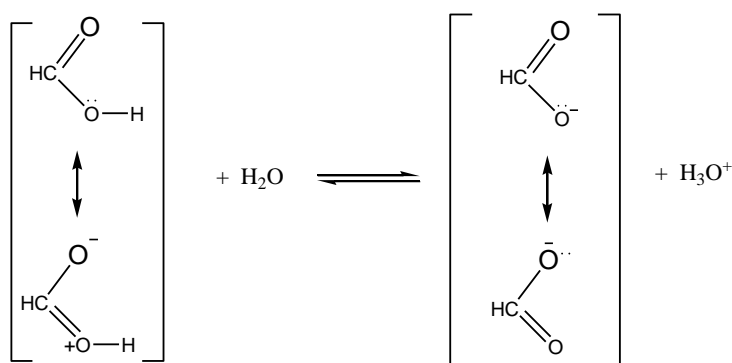
**Example:** On descending group VII (group 7), the  $pK_a$  values for HF, HCl, HBr, and HI decrease in the order 3, -7, -9, and -10. It means the acidity is increasing down the group. Instead, we were expecting a decrease in acidity on going down due to a decrease in electronegativity. However the main reason here is the weakening of bond on going down and to some extent the reason is that the charge can be spread easily on the larger anions.

The effect of (b) can be explained by the following example.

**Example:** The  $pK_a$  of methanol  $\text{CH}_3\text{O-H}$  is  $\approx 16$  while that of methane,  $\text{CH}_3\text{-H}$  is  $\approx 43$ . The reason is that after the removal of H from methane, the negative charge comes on carbon as  $\text{CH}_3^-$ , while in case of methanol negative charge comes on Oxygen after the removal of proton as  $\text{CH}_3\text{O}^-$ . As Oxygen is more electronegative so it is more stabilized, and so the methanol is strong acid than methane.

**2<sup>nd</sup> example:** The  $pK_a$  values for second row hydrides  $\text{CH}_4$ ,  $\text{NH}_3$ ,  $\text{H}_2\text{O}$ , and  $\text{HF}$  are about 48, 33, 16, and 3, respectively. As the  $pK_a$  is decreasing down the group, it means the acidity is increasing. This trend is due to an increase in the electronegativity as we move from carbon to F. So the  $\text{F}^-$  is more stable than  $\text{CH}_3^-$ .

The effect of factor (c) can be explained by the example of formic acid,  $\text{HCOO-H}$  which has  $pK_a \approx 3.77$  as compared to the  $pK_a$  of methanol  $\text{CH}_3\text{O-H} \approx 16$ . Here the most important factor is the stabilizing effect of negative charge on the oxygen of formate ion  $\text{HCOO}^-$  due to the resonance as compare to the formic acid.

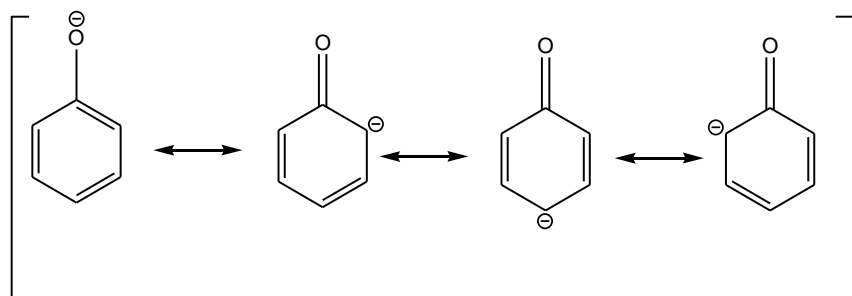


Delocalization can take place both in methanoic acid and methanoate anion; however the methanoate anion has two canonical forms of equal energy and is more stabilized, while the two forms of methanoic acid have separation of charges and thus is less stable. Due to the less stability of methanoic acid, the proton will not attach back with the methanoate anion and the equilibrium will remain in the right direction. However in alcohols there is no such factor stabilizing the alkoxide anion  $\text{RO}^-$  as compared to the alcohol. That is the reason that all the carboxylic acids are stronger than the alcohols.

**2<sup>nd</sup> example:** Phenols ( $pK_a = 9.95$ ) are less acidic than carboxylic acids but stronger than alcohols.

In phenols the delocalization takes place but there is a charge separation in canonical forms which makes them less stable. However after the removal of proton, the Phenoxide anion is formed. In this case the canonical forms have equal energy and are more stabilized due to resonance. This makes phenoxide ion more stabilized than alkoxide ion of alcohol.

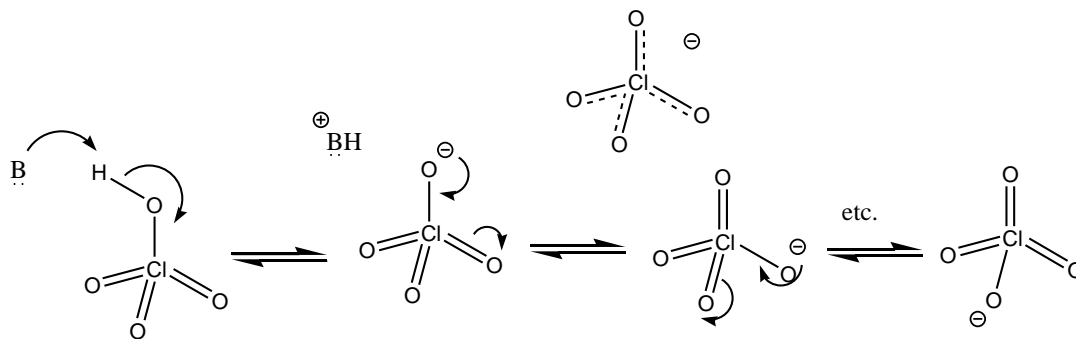
However in carboxylate anion, both canonical forms have negative charge on oxygen which makes it more stabilized while in case of phenoxide anion, only one canonical form have negative charge on more electronegative oxygen but all others have negative charge on carbon atom which is less electronegative. Due to this reason carboxylate anion is more stabilized hence carboxylic acids are stronger than the phenols.



### 3rd example:

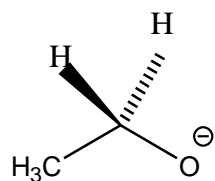
The acids  $\text{HClO}$ ,  $\text{HClO}_2$ ,  $\text{HClO}_3$ , and  $\text{HClO}_4$  have  $\text{p}K_a$  values 7.5, 2,  $-1$ , and about  $-10$ , respectively.

It means that perchloric acid,  $\text{HClO}_4$ , is stronger in acidity than hypochlorous acid,  $\text{HClO}$ . The reason is that once the proton is removed, we end up with a negative charge on oxygen. In hypochlorous acid, this is localized on the one oxygen. In chlorous acid it is spread in two, in chloric acid it is spread on three and finally in perchloric acid the charge is spread on four oxygen atoms and is more stabilized.

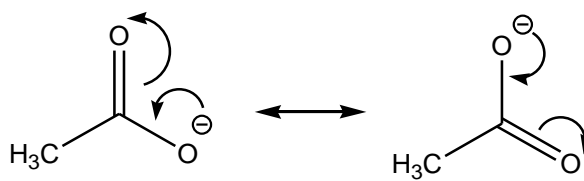


**Perchlorate anion**

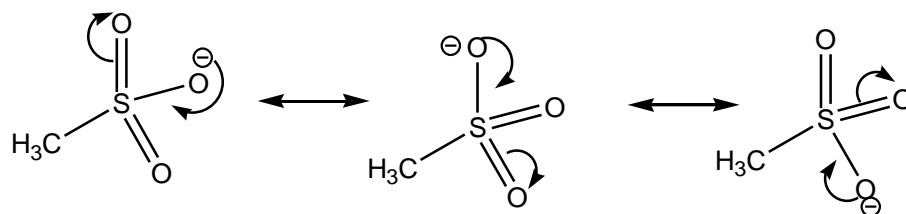
Similar arguments explain the  $pK_a$ s for other oxygen acids, for example, ethanol ( $pK_a$ , 15.9), acetic acid (4.8), and methane sulfonic acid ( $-1.9$ ). In ethoxide, the negative charge is localized on one oxygen atom, while in acetate the charge is delocalized over two oxygens and in methane sulfonate it is spread over three oxygens.



Charge localized on one oxygen



Charge delocalized over two oxygens



Charge delocalized over three oxygens

(d) The last one effect, the solvent effect is the most important one in deciding the strength of the acids. Water is a solvent in which many organic compounds are not soluble; still the water is an efficient solvent due to the following two reasons:

- It is of high dielectric constant ( $\epsilon = 80$ )
- Secondly it has high solvation ability.

Due to high dielectric constant the ion pairs are formed readily and remain stabilized.

The solvating ability of water is very high because the water is readily polarized and is relatively small in size. So it can stabilize both cations and anions. However the effect is more pronounced for anions due to powerful hydrogen bonding type solvation which cannot in general occur with cations; however in special case of acids  $H^+$  can also solvate through hydrogen bonding with the solvent water molecules.

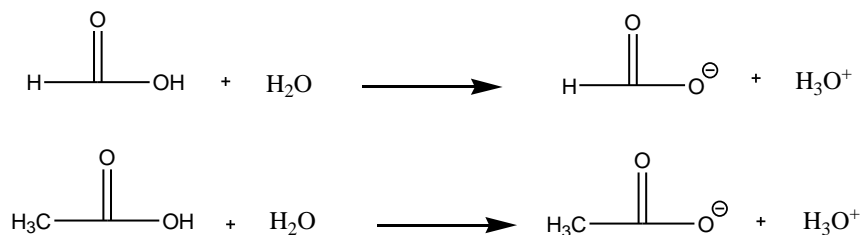
Some of the alcohols which are not too bulky have similar properties of water e.g. HCl is a strong acid in methanol too.

However the most important requirement for a solvent is that it should be capable of functioning as a base. The weaker the base is smaller the dissociation of acid and vice versa. For example in toluene, HCl almost remain completely undissociated.

## 2.3 Acidity of some organic compounds

### 2.3.1 Some aliphatic acids

When the non hydroxyl hydrogen atom of the aliphatic carboxylic acids is replaced with an alkyl group, it decreases the acidity of the acid. The reason is that the alkyl group is electron donating inductive effect, so it increases the availability of negative charge on the oxygen atom of carboxylate anion after electron donation, which increases the protonation and the reaction moves to the left direction. It is true for all electron donating groups and decrease the acidity when are attached with an acid.



#### Example 1:

$pK_a$  of ethanoic acid is 4.76 compared with 3.77 of methanoic acid. When the hydrogen of formic acid is replaced with methyl group, the negative charge density on oxygen atom of ethoxide anion increases due to electron donating ability of the methyl group, so the ethoxide anion become destabilized and combine again with proton to move the equilibrium to left, which make it less acidic as compared to formic acid in which equilibrium moves to right direction. The difference of  $pK_a$  between the two is very large, so there is also some sort of solvation effect which is playing a part.

Addition of a second alkyl group in ethanoic acid must decrease the acidity to a further extent. However the effect is not so regular and steric and other influences also play their part. The  $pK_a$  values are observed as:



		4.86		5.05
CH <sub>3</sub> COOH	MeCH <sub>2</sub> CO <sub>2</sub> H			
4.76	4.88			
		Me(CH <sub>2</sub> ) <sub>2</sub> CO <sub>2</sub> H		Me(CH <sub>2</sub> ) <sub>3</sub> CO <sub>2</sub> H
		4.82		4.86

### Example 2:

If there is a doubly bonded carbon atom adjacent to a carboxylic carbon, the acidity is increased. Thus propenoic acid has  $pK_a = 4.25$  while the saturated analogue propanoic acid has  $pK_a = 4.88$ .

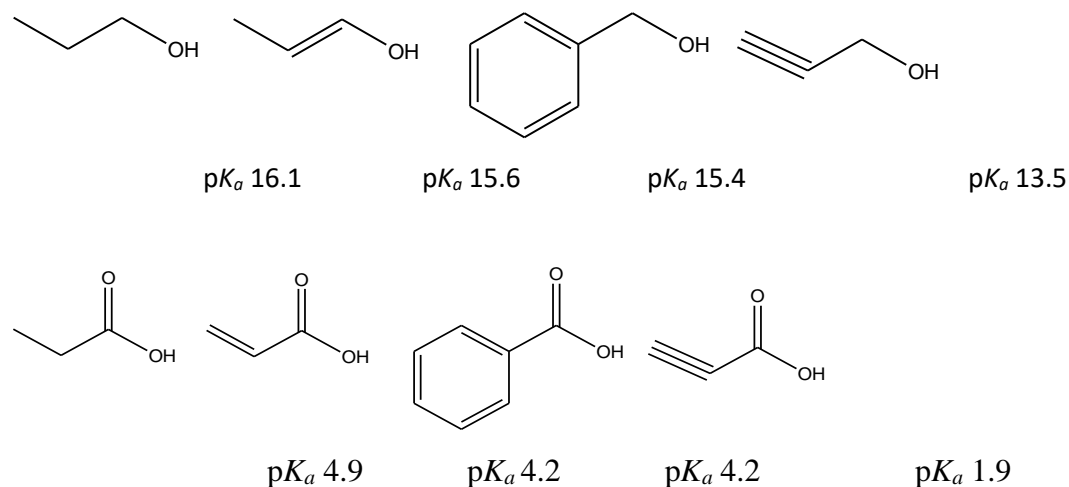


The reason is that in propenoic acid, the carbon which is attached to carboxylic carbon ( $\alpha$ -carbon) is  $sp^2$  hybridized as compared to the  $\alpha$ -carbon of propanoic acid. The hybridization of the orbital from which the proton is removed affects the  $pK_a$ . As  $sp^2$  hybridization has more s character as compared to  $sp^3$  hybridized carbon which means that the electrons are drawn more closely to nucleus of carbon than in  $sp^3$  carbon. Due to this reason, the  $sp^2$  hybridized  $\alpha$ -carbon in propenoic acid is donating less electron density and as a result more acidic than the saturated propanoic acid.

This effect is much more marked with  $sp^1$ -hybridized carbon atom of triple bond, thus  $pK_a$  of propynoic acid (propiolic acid)  $\text{HC}\equiv\text{CCO}_2\text{H}$  is 1.77.

Due to similar reason the H- atom of ethyne is more acidic than of ethene and ethane, and can be replaced readily with many metals.

### Some More Examples:



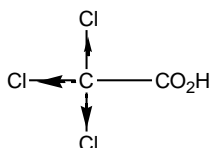
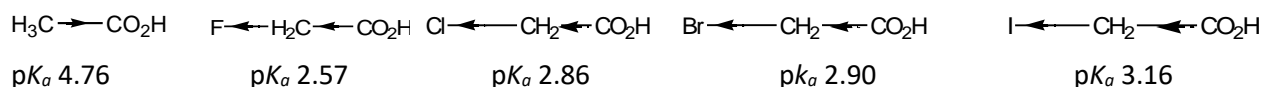


### 2.3.2 Substituted aliphatic acids

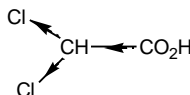
The effect of electron withdrawing groups is more pronounced and opposite to that of electron donating groups. So they increase the acidity when become attached with a carboxylic acid.

#### Examples:

Consider the  $pK_a$  values of following compounds:



$pK_a$  0.65

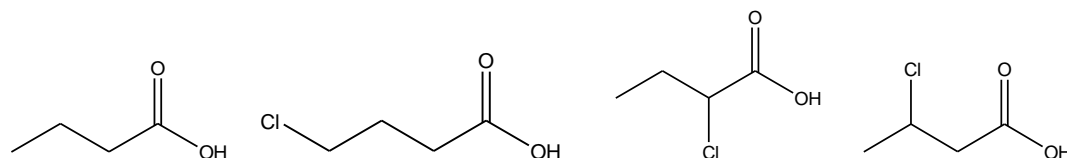


$pK_a$  1.25

The halogen with withdrawing inductive effect is going to increase the acidity as shown by  $pK_a$  values. As the electronegativity and electron withdrawing effect is decreasing down the group so the fluorine substituted acid is stronger than chlorine substituted one. This trend can be extended to further down the group.

Also the substitution of second chlorine withdraws the electron density to a further extent and this ultimately increases the acidity. Trichloro substituted acid will certainly be the strongest acid among the list.

However substitution of the halogen atom further away from the  $\alpha$ -carbon of an acid has a little influence. As we know the conductive effect decrease with distance, so the electron withdrawing inductive effect of the halogens dies away quickly down a saturated chain. As a result the negative charge will remain concentrated on the carboxylate anion, and the acidic strength will remain almost same as of the original aliphatic acid.



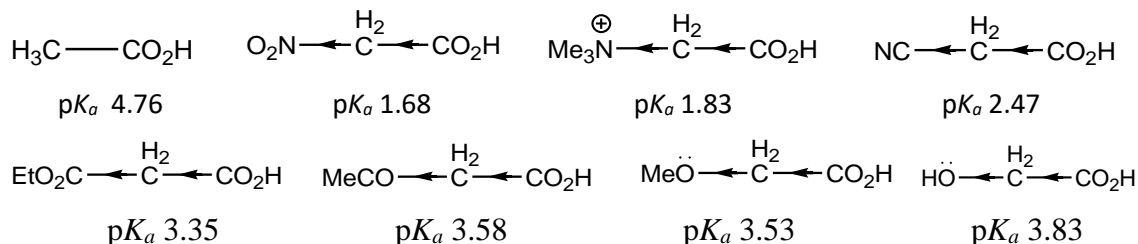
$pK_a$  4.82

$pK_a$  4.52

$pK_a$  2.84

$pK_a$  4.06

Other electron withdrawing groups increase the acidity of simple aliphatic acids in the same sequence.



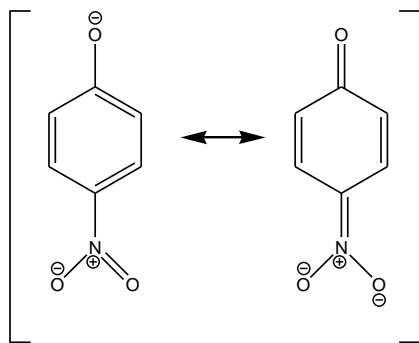
Here in last two cases, the unshared electro pair on the oxygen atom of hydroxyl and methoxyl groups is not able to exert an electron donating mesmeric effect due to the intervening saturated carbon atoms.

### 2.3.3 Phenols

The results, here are similar to that of aliphatic acids. Electron withdrawing groups increase the acidity and electron donating groups decrease the acidity.

Nitro group is an electron withdrawing group, so it increase the acidity of phenol when is attached with phenol. However its inductive effect falls off with distance on going from *o*- to *m*- to *p*- nitrophenol. However nitro group also has electron withdrawing mesomeric effect when is present at *o*- or *p*- position but not at *m*- position. So we expect *o*-nitrophenol and *p*-nitrophenol to be more acidic than *m*-nitrophenol, which is in fact, found to be the case. Introduction of further nitro groups further increase the acidity, so the dinitro is more acidic than nitro phenol, and 2,4,6-trinitrophenol (picric acid) is found to be very strong acid.

	$pK_a$		$pK_a$
$\text{C}_6\text{H}_5\text{OH}$	9.95	<i>o</i> - $\text{O}_2\text{NC}_6\text{H}_4\text{OH}$	7.23
<i>m</i> - $\text{O}_2\text{NC}_6\text{H}_4\text{OH}$	8.35	<i>p</i> - $\text{O}_2\text{NC}_6\text{H}_4\text{OH}$	7.14
2,4-( $\text{O}_2\text{N}$ ) $_2\text{C}_6\text{HOH}$	4.01	2,4,6-( $\text{O}_2\text{N}$ ) $_3\text{C}_6\text{HOH}$	1.02



However the Introduction of electron donating alkyl group into phenol rings is not so effective and the resulting substituted phenol rings are very slightly weaker acids.

	$pK_a$		$pK_a$
$C_6H_5OH$	9.95	<i>o</i> -MeC <sub>6</sub> H <sub>4</sub> OH	10.28
<i>m</i> -MeC <sub>6</sub> H <sub>4</sub> OH	10.08	<i>p</i> -MeC <sub>6</sub> H <sub>4</sub> OH	10.19

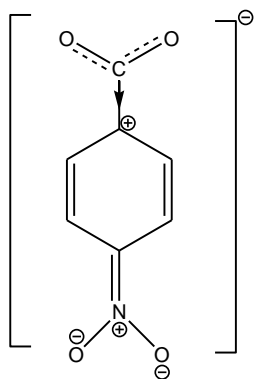
### 2.3.4 Aromatic carboxylic acids

**Benzoic acid is stronger acid ( $pK_a = 4.20$ ) than cyclohexane carboxylic acid ( $pK_a = 4.87$ ).** The reason is that the carboxylic acid group in benzoic acid is attached with  $sp^2$  hybridized carbon which is less electron donating group as compared to  $sp^3$  hybridized carbon to which the carboxylic acid group is attached in cyclohexene carboxylic acid.

However the strength of benzoic acid is less effective by introducing methyl group into the benzene ring.

	$pK_a$		$pK_a$
$C_6H_5CO_2H$	4.20	<i>m</i> -Me C <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> H	4.24
<i>p</i> -Me C <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> H	4.34		

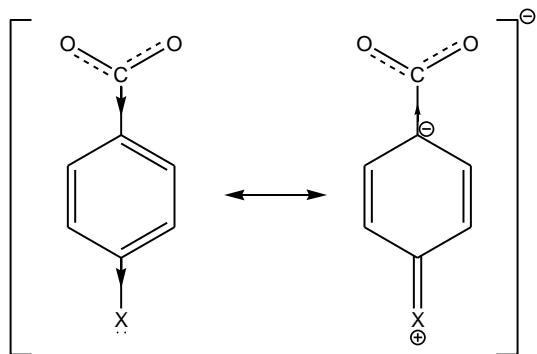
However the introduction of electron withdrawing groups in the benzene ring of benzoic acid increases the acidic strength. For example the  $pK_a$  values of nitro substituted benzoic acids are given below:



	$pK_a$		$pK_a$
$C_6H_5CO_2H$	4.20	<i>o</i> - $O_2NC_6H_4CO_2H$	2.17
<i>m</i> - $O_2NC_6H_4CO_2H$	3.45	<i>p</i> - $O_2NC_6H_4CO_2H$	3.43
3,5-( $O_2N$ ) $_2C_6H_3CO_2H$	2.83		

When the nitro group is at ortho position of benzoic acid, both electron withdrawing inductive and mesomeric effects are working but at para position inductive effect is less due to increased distance and only mesomeric effect is fully working. However for *m*- $NO_2$  benzoic acid there is no mesomeric effect and only the inductive effect is working. Although the marked effect at ortho position is due to the reason that powerful inductive effect is working at a short distances but still it is believed that there may be some interaction between nitro and carboxylic group.

However there are many groups e.g. hydroxyl, methoxyl, halogens etc, which have electron withdrawing inductive effect but electron donating resonance effect (mesomeric effect). As the both effects are working in opposite directions, introduction of these groups into the benzene ring of benzoic acid will affect the acidic strength differently. Their  $pK_a$  values are given below:

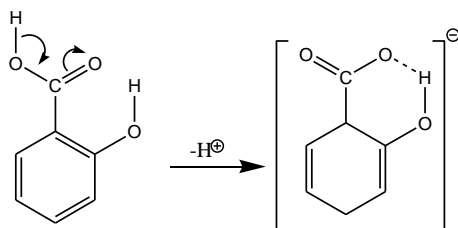


### $pK_a$ of $\text{XC}_6\text{H}_4\text{CO}_2\text{H}$

	<b>H</b>	<b>Cl</b>	<b>Br</b>	<b>OMe</b>	<b>OH</b>
<i>o</i> -	4.20	2.94	2.85	4.09	2.98
<i>m</i> -	4.20	3.83	3.81	4.09	4.08
<i>p</i> -	4.20	3.99	4.00	4.47	4.58

As the both positive resonance and negative inductive effects are working (in opposite directions) at ortho and para positions but at meta position only negative inductive effect is working, this makes para substituted ones weaker acids than the meta ones. Even in some cases para acids are weaker than the unsubstituted acids, e.g. *p*-hydroxy benzoic acids.

The behavior of *o*-hydroxy benzoic acids is very strange and their  $pK_a$  is very low from expectations. It means that they are stronger acids than our expectations. The reason is due to the direct interaction between the adjacent groups. The hydroxyl group can make intramolecular hydrogen bonding in the dissociated form of carboxylic acid, which is very less effective in undissociated form.



So the intramolecular hydrogen bonding stabilizes the negative charge on the oxygen. The case is not with para and meta substituted benzoic acids. So *o*-hydroxy benzoic acid is stronger than our expectations.

The effect is more marked when the groups are present on both *o*-positions. The negative charge on oxygen is more stabilized by intramolecular hydrogen bonding on both sides which will increase the acidity to a further extent, hence 2,6-dihydroxybenzoic acid have  $pK_a = 1.30$ .

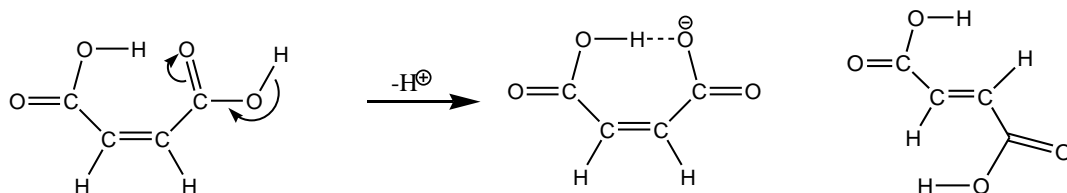
### 2.3.5 Dicarboxylic acids

As the carboxylic group has an electron withdrawing inductive effect, so the introduction of another carboxylic group might increase the acidity as shown by  $pK_a$  values.

HCO <sub>2</sub> H 3.77	CH <sub>3</sub> CO <sub>2</sub> H 4.76	CH <sub>3</sub> CH <sub>2</sub> HCO <sub>2</sub> H 4.88	C <sub>6</sub> H <sub>5</sub> CO <sub>2</sub> H 4.17
HO <sub>2</sub> CCO <sub>2</sub> H 1.23	HO <sub>2</sub> CCH <sub>2</sub> CO <sub>2</sub> H 2.83	HO <sub>2</sub> CCH <sub>2</sub> CH <sub>2</sub> HCO <sub>2</sub> H 4.19	HO <sub>2</sub> CC <sub>6</sub> H <sub>4</sub> CO <sub>2</sub> H <i>o</i> -2.98, <i>m</i> -3.46, <i>p</i> -3.51

The effect is very strong but falls off as the distance is increased from more than one carbon.

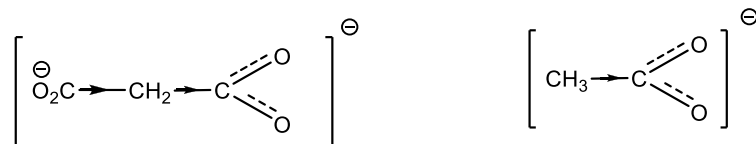
**Maleic acid (*cis*-butenedioic acid) (pK<sub>a</sub>= 1.92) is stronger than fumaric acid (*trans*-butenedioic acid) (pK<sub>a</sub> = 3.02).** The reason here is intramolecular hydrogen bonding which is present in *cis* form but is absent in *trans* form. Due to which maleate mono anion is more stabilized than the fumarate mono-anion.



However the second dissociation of *trans* acid ) (pK<sub>a</sub><sup>2</sup> = 4.38) occurs more readily than the *cis* acid ) (pK<sub>a</sub><sup>2</sup> = 6.23). The reason is that in *trans* form acid group is present in free form so it is easy to remove proton, while in *cis* form the carboxylic group is involved in hydrogen bonding which makes it very difficult to remove proton.

**Ethanedioic (oxalic), propane-1,3-dioic (malonic) and butane-1,4-dioic (succinic) acids are each weaker in their second dissociations than methanoic, propanoic and butanoic acid respectively.**

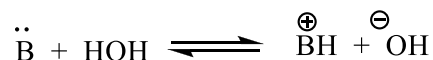
The reason here is that for second dissociation we need to remove proton from a negatively charged specie with an electron donating CO<sub>2</sub><sup>-</sup> substituent which destabilize the anion as compared to the undissociated acid and so very difficult. This is not the case with first dissociation.



### 3. Bases

#### 3.1 $pK_b$

The strength of a base in water may be calculated from the following equilibrium equation:



The equilibrium constant in water,  $K_b$ , is given as:

$$K_b \approx \frac{[\text{BH}^+][\text{OH}^-]}{[\text{B:}]}$$

The term  $[\text{H}_2\text{O}]$  is incorporated in  $K_b$  because water is in excess and its concentration remains constant.

However, now it becomes usual to express the strengths of bases and acids both in terms of  $K_a$  and  $pK_a$ .

#### 3.2 $K_a$ and $pK_a$

To calculate the  $K_a$  and  $pK_a$  of a base, we will check the acidic strength of the conjugate acid of the base by considering the following equation:



So the  $K_a$  value for this equation can be:

$$K_a \approx \frac{[\text{B:}][\text{H}_3\text{O}^+]}{[\text{BH}^+]}$$

Here  $K_a$  and  $pK_a$  is the measure of the acid strength of the conjugate acid  $\text{BH}^+$  of the base  $\text{B:}$ . As we know that the strength of the conjugate acid is inversely proportional to the strength of the base, stronger the conjugate acid weaker will be the base and vice versa. It means that larger the  $pK_a$  value of conjugate acid, weaker will be the conjugate acid, and stronger will be the base. So here the  $pK_a$  value of a base is directly proportional to the strength of the base. Larger the  $pK_a$  value of a base, stronger it is and vice versa. For example the  $pK_a$  value of  $\text{NH}_4^+$  is 9.25. It means that the base  $\text{NH}_3$  is a stronger base.

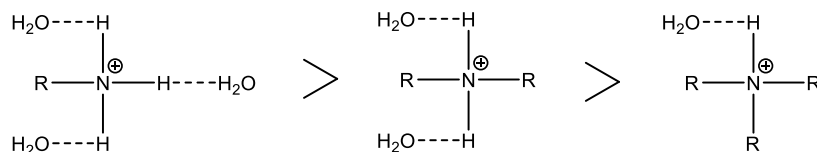


### 3.3 Aliphatic bases

The basic strength of a base depends upon the readiness with which it can donate a proton and /or accept electron. So an increased electron density on the base increases the basic strength. This is the reason that a base substituted with an electron donating groups is stronger base than an unsubstituted one. Basic strength increases on going :  $\text{NH}_3 \rightarrow \text{RNH}_2 \rightarrow \text{R}_2\text{NH} \rightarrow \text{R}_3\text{N}$  due to the increasing inductive effect of successive alkyl groups making the nitrogen more negative. Due to the same reason following series have been obtained:

$\text{NH}_3$	$\text{Me-NH}_2$	$\text{Me}_2\text{NH}$	$\text{Me}_3\text{N}$	$\text{EtNH}_2$	$\text{Et}_2\text{NH}$	$\text{Et}_3\text{N}$
9.25	10.64	10.77	9.80	10.67	10.93	10.88

The introduction of alkyl group increases the basicity, introduction of a second group further increases the basicity but to a smaller extent. Surprisingly the introduction of third alkyl group actually decreases the basicity so that trialkyl amine is weaker base than the dialkyl and alkyl amine. No doubt the addition of alkyl group increases the electron density on the nitrogen of amine, but here the basic strength is determined not only by the availability of electrons on nitrogen but also by the extent to which the cation formed by the uptake of protons is stabilized by solvation in water. As the more protons are attached with the nitrogen in the cation, greater will the possibility of the powerful solvation via hydrogen bonding between this and water.

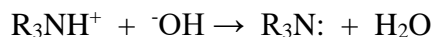


Thus on going along the series,  $\text{NH}_3 \rightarrow \text{RNH}_2 \rightarrow \text{R}_2\text{NH} \rightarrow \text{R}_3\text{N}$ , inductive effect will tend to increase the basicity but the less stabilization of the cation by hydrogen bonding will tend to decrease the basicity. So the net result will be a mixed one on the actual series will be the following due to the mixed effect of both factors.  $\text{NH}_3 \rightarrow \text{R}_3\text{N} \rightarrow \text{RNH}_2 \rightarrow \text{R}_2\text{NH}$ .

If this is the explanation, then the series will be different one in a solvent in which no hydrogen bonding can take place. So it is found that the order of basicity of butyl amine in chlorobenzene is  $\text{BuNH}_2 < \text{Bu}_2\text{NH} < \text{Bu}_3\text{N}$ .

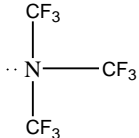


Tetraalkyl ammonium salts  $R_4N^+ I^-$  on treatment with moist silver oxide  $AgOH$ , yield  $R_4N^+ OH^-$  which is highly basic with basicity comparable to the mineral alkalis. The reason is that it is completely ionized and there is no possibility of making unionized form as with tertiary amines.

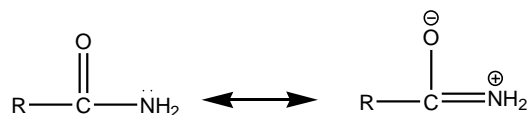


### Effect of electron withdrawing group

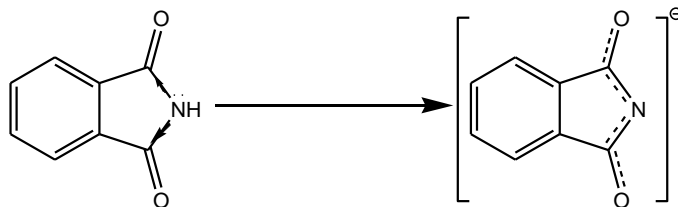
When an electron withdrawing group is attached with the basic center, it withdraws the electron

density and make a base weaker, thus the amine  will be very less even non basic due to the attachment of three strong  $-CF_3$  electron withdrawing groups.

Amides are very less basic in water as compared to the amines.  $pK_a$  for ethanamide (acetamide) in water is 0.5. There are two reasons for the weak basicity of the amides. First the nitrogen is attached with  $sp^2$  hybridized  $C=O$  group which is electron withdrawing in nature. Secondly there is also electron withdrawing resonance effect which is responsible for further decrease in basicity.



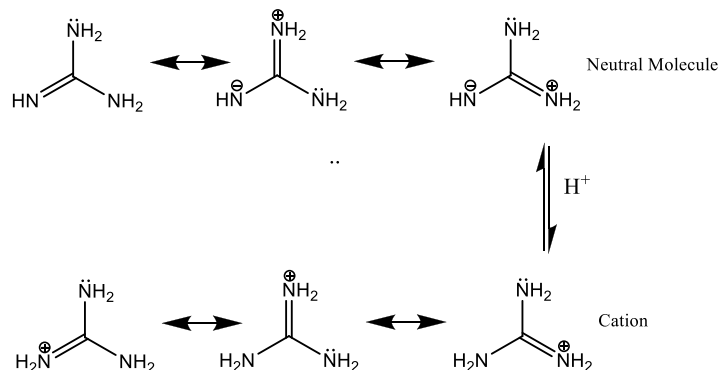
Two  $C=O$  groups further decreases the basicity due to the above mentioned reasons. So the imides with two  $C=O$  groups attached with nitrogen are not basic but sufficiently acidic to make alkali metal salts e.g. benzene-1,2-dicarboximide ( Phthalimide).



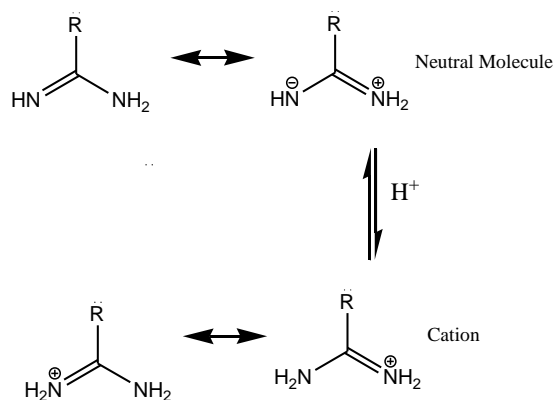
**Guanidine  $HN=C(NH_2)_2$  is among the strongest organic nitrogenous bases with  $pK_a \approx 13.6$ .**

The resonance is present in the neutral molecule but after the protonation cation is formed which is more stabilized. The reason is that all the contributing structures of the cation are of equal energy so making the cation more stable than the original structure. The original structure is also

stabilized by resonance but to a little extent because the two of the contributing structures involve separation of charges.



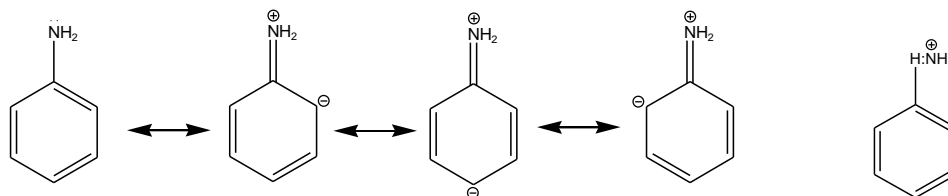
Due to a similar situation, amidines,  $\text{RC}(=\text{NH})\text{NH}_2$  are stronger bases. However the stabilization due to the delocalization in the cation is not to the effect as with guanidine cation. Ethyl amidines  $\text{CH}_3\text{C}(=\text{NH})\text{NH}_2$  ( $\text{p}K_a \approx 12.4$ ) are stronger base than ethyl amines  $\text{CH}_3\text{CH}_2\text{NH}_2$  ( $\text{p}K_a \approx 10.67$ ).



### 3.4 Aromatic Bases

**Aniline ( $pK_a=4.62$ ) is a very weak base as compared to ammonia ( $pK_a=9.25$ ) or cyclohexyl amine ( $pK_a=10.68$ ).**

In aniline the case is reverse as with alkyl amidines. In aniline  $-NH_2$  group is attached with an  $sp^2$  hybridized carbon but still the lone pair can interact with delocalized  $\pi$  orbital of the phenyl group.



However when the amino group is protonated, the stability of the anilinium cation is decreased as compared to aniline, due to unavailability of lone pair of electrons on the nitrogen. This makes aniline less basic because it cannot accept proton.

Introduction of another phenyl group to aniline further decreases the basicity. So the diphenyl amine is very weak base and triphenyl amine is actually not a base.

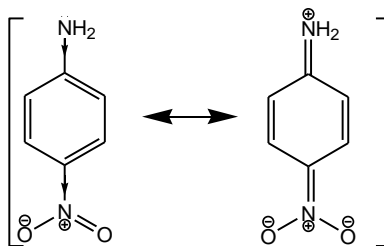
Introduction of methyl groups on the nitrogen of the aniline increases the basicity to a little extent. This trend is against the aliphatic amines. It shows that solvation due to hydrogen bonding in aromatic amines is not working as in aliphatic amine. So the factor that determines the basicity in aromatic amines remains only the resonance of lone pair of electrons of nitrogen on the benzene ring in aniline as compared to cation. This born out due to the irregular behavior of *o*-, *m*- and *p*- substituted methyl aniline.

$C_6H_5NH_2$	$C_6H_5NHMe$	$C_6H_5NMe_2$	$MeC_6H_4NH_2$
4.62	4.84	5.15	<i>o</i> - 4.38
			<i>m</i> - 4.67
			<i>p</i> - 5.10

#### Introduction of an electron withdrawing group

An electron withdrawing group withdraws the electron density when it is attached at the ortho, meta and para positions of the aromatic amine. For example a nitro group at ortho, meta and para positions of the aniline decreases its basicity. At ortho and para position, nitro group reduces the basicity to a large extent, because at these positions the lone pair of electrons on nitrogen can interact with the  $\pi$  orbital of benzene.  $pK_a$  of nitro anilines are given below:

PhNH <sub>2</sub>	NO <sub>2</sub> C <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>
4.62	<i>o</i> - -0.28
	<i>m</i> - 2.45
	<i>p</i> - 0.98



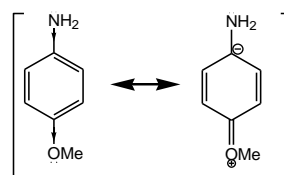
Very low basicity at ortho position is due to the electron withdrawing effect working at a very short distance as well as due to the hydrogen bonding between the nitro group at ortho position and the amino group. *o*-Nitroaniline is such a weak base that its salts are largely hydrolyzed in aqueous solution, while 2,4-dinitroaniline is insoluble in aqueous acid. 2,4,6-trinitroaniline resembles an amide and called as picramide which readily undergoes hydrolysis in water to form picric acid (2,4,6-trinitrophenol).

#### Groups with electron donating inductive but electron withdrawing resonance effect:

When –OH or –OMe groups that have unshared electron pair are attached at the ortho and para positions, they exert resonance as well as inductive effect in opposite directions, but at meta position they only have electron donating inductive effect. Due to the two effects working in opposite directions, para substituted amines are more basic than the meta one, because at para position, resonance effect is more than the inductive effect due to the distance. The *m*-compound is weaker base than aniline itself due to only inductive effect. The effect of *o*-substituent remains abnormal due to the direct interaction with the amino group and due to polar and steric effects.

The values of substituted anilines are given below:

PhNH <sub>2</sub>	HOC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>	MeOC <sub>6</sub> H <sub>4</sub> NH <sub>2</sub>
4.62	<i>o</i> - -4.72	<i>o</i> - -4.49
	<i>m</i> - 4.17	<i>m</i> - 4.20
	<i>p</i> - 5.30	<i>p</i> - 5.29



**2,4,6-trinitro-N,N-dimethylaniline is 40,000 times stronger base than 2,4,6-trinitroaniline and aniline itself.**

The reason is that in former, two methyl groups attached with the amino group of aniline. Two bulky nitro groups are also present at the ortho positions, which create a steric hindrance. To decrease this hindrance, the nitrogen and carbon bond twists a little bit. As a result the hindrance is decreased but the p orbitals of the nitrogen atom no longer remain parallel to the p orbitals of the carbon. Due to which the resonance effect cannot work and the lone pair of electrons of amino group remains on the nitrogen and are available for the donation, which ultimately increases the basicity.

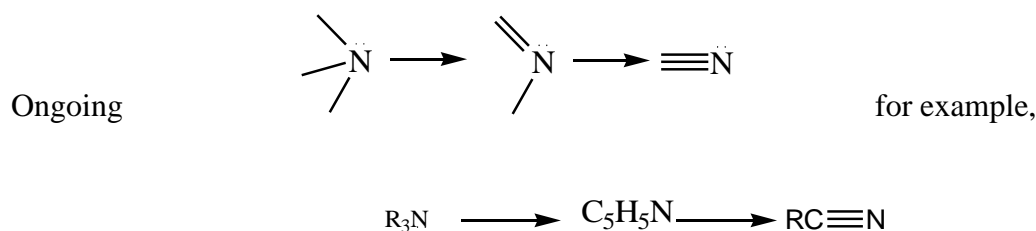
On the other hand the lone pair of electrons of amino group of 2,4,6-trinitroaniline is delocalized on the benzene ring and is not available for donation. So it is a weak base than the 2,4,6-trinitro-N,N-dimethylaniline.

### 3.5 Heterocyclic bases

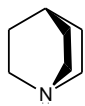
Pyridine is an aromatic compound. Its nitrogen is  $sp^2$  hybridized. Two of its hybridized  $sp^2$  orbitals are involved in bonding with two carbons. One of its electrons is in unhybridized p orbital which is involved in resonance. While the unshared pair of its electrons is in third hybridized  $sp^2$  orbital. As its unshared pair is not involved in resonance, it can donate it easily, due to which it is a stronger base  $pK_a = 5.21$ .

**Pyridine is a very much weaker base than an aliphatic tertiary amine  $pK_a = 10.75$ .**

The reason is that the nitrogen in pyridine is  $sp^2$  hybridized which has a more s character, so the electrons remain closer to nucleus and will be unavailable for donation. In aliphatic tertiary amine, nitrogen is  $sp^3$  hybridized. It has less s character and electrons are available for donation.

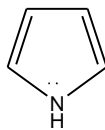


The unshared pairs are in  $sp^3$ ,  $sp^2$  and  $sp$  orbitals respectively and decreased basicity is reflected from their  $pK_a$  values. The  $pK_a$  values of the cyanides are very low ( $MeCN$ ,  $pK_a = -4.3$ ).

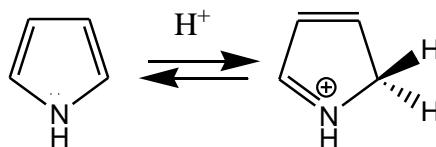


In quinoclidine, the unshared pair is in  $sp^3$  orbital, so it is strongly basic with  $pK_a = 10.95$  comparable to the  $pK_a$  of triethyl amine  $pK_a = 10.75$ .

**Pyrrole is a weak base ( $pK_a = -0.27$ ) as compared to pyridine:**



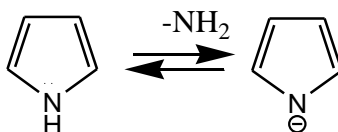
Pyrrole is an aromatic compound. To complete six electron ( $4n + 2$ ,  $n=1$ ) for aromaticity, the two electrons of the nitrogen are also involved in the resonance. Nitrogen in pyrrole is  $sp^2$  hybridized. All three  $sp^2$  hybridized orbitals have one electron each, while the unhybridized p orbital have two electrons, which are involved in the resonance. Due to this reason, the electrons on the nitrogen are not available, so it cannot be donated which makes pyrrole a very weak base as compared to pyridine and aniline.



However in Pyridine, the lone pair of electrons is in  $sp^2$  hybridized orbital and are not involved in resonance. So they are free to donate which makes pyridine a strong base than pyrrole.

If pyrrole is forced for protonation, then it takes place at  $\alpha$  carbon rather than on nitrogen. Reason is that the unshared pair of electrons of nitrogen is involved in resonance. If nitrogen gives this pair for protonation, then aromatic character is lost, which leads to instability.

Pyrrole is a very weak base; even it can function as a weak acid. Hydrogen atom of  $-NH_2$  Group can be removed with a strong base, resulting anion is then retains the aromatic character which is not possible in cation.



No such condition is applied on pyrrolidine which is a fully reduced pyrrole. In this case the electrons are present on nitrogen which can be donated which makes pyrrolidine a stronger base with  $pK_a = 11.27$ , comparable to that of ethylamine.

