Shia P. G. College, Lucknow

Online course content for the student of B.Sc IV sem

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Unit IV: Amines

- *Introduction*
- *Classification*
- *Nomenclature*
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- *Stereochemistry*
- *Physical Properties*
- *Separation*
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- *Factor effecting strength of basic nature of amines*
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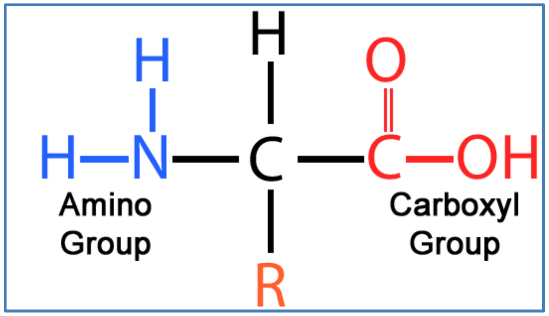
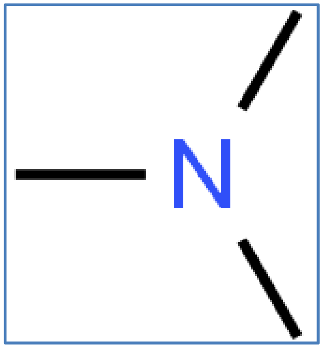
Amines

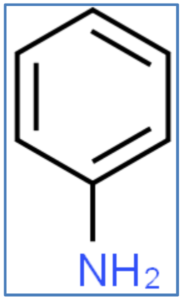
- Amines are compounds having amino group that contain a nitrogen atom with a lone pair.
- Amines are identify as derivatives of ammonia. In which one or more alkyl or aryl groups attached to the nitrogen atom (these may respectively be called alkylamines and arylamines; amines in which alkyl & aryl both groups are attached to one nitrogen atom may be called alkylarylamines).
- Important amines are amino acids, trimethylamine, and aniline; The substituent -NH2 is called an amino group.



Amino acids



Trimethylamine



Aniline

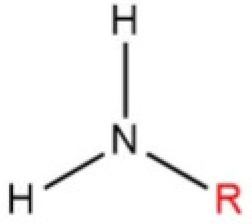
Classification of Amines

➢Classification of Amines are based on the nature and number of substituents present on nitrogen.

➢In aliphatic amines alkyl group directly attached to the amino group, where as in Aromatic amines have the nitrogen atom connected to an aromatic ring.

Alkyl and Aryl Amines are classified into three subcategories according to the number of alkyl or aryl groups adjacent to the nitrogen atom:

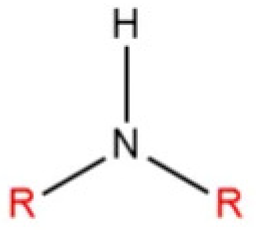
•**Primary (1°) amines**—Primary amines in which one of three hydrogen atoms in ammonia is substituted by an alkyl or aromatic group. Most common alkyl or aryl amines include, methylamine, amino acids, and aniline.



Primary (1°)

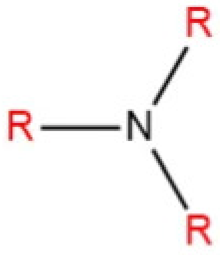
Classification of Amines

- **Secondary (2°) amines**—Secondary amines have two alkyl or aryl or both substituents attached to the nitrogen with one hydrogen. Mostly includes dimethylamine, diphenylamine.



Secondary (2°)

- **Tertiary (3°) amines**—In which three hydrogen of amonia substituted by alkyl or aryl groups are called as **Tertiary (3°) amines**, Examples trimethylamine, EDTA etc.

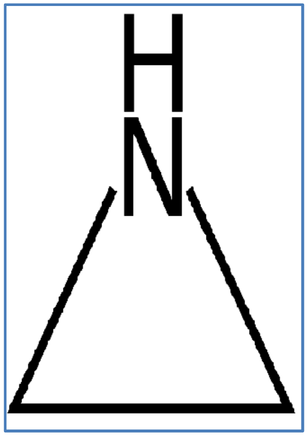


Tertiary (3°)

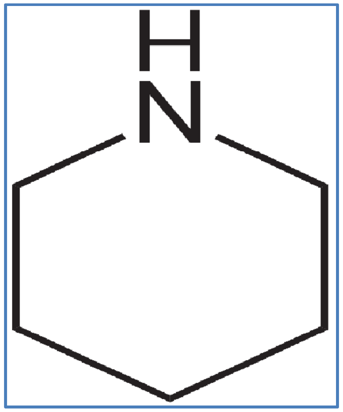
Classification of Amines

- **Cyclic amines**—Cyclic amines are categories as secondary or tertiary amines. Examples secondary cyclic amine includes 3-membered ring aziridine, the six-membered ring piperidine and tetrtiary amines includes *N*-methylpiperidine and *N*-phenylpiperidine.

There is another category of amine compounds in which nitrogen attached to the four organic substituents and known as quaternary ammonium cations exist with many kinds of anions.



Aziridine



Piperidine

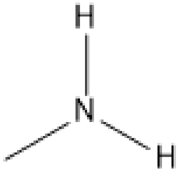
Nomenclature of Amines

- Amines are named in various ways. Most commonly, the compound is given with a prefix "amino-" or the suffix: "-amine".
- The prefix "N-" shows substitution on the nitrogen atom.
- An organic compound with several amino groups is called a diamine, triamine, tetraamine and so on…

Systematic naming for some common aliphatic amines

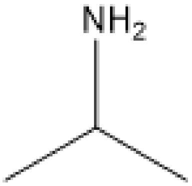
Common name system:

- Amines are named with the suffix *-amine e.g.*



Methylamine

n-propyl amine



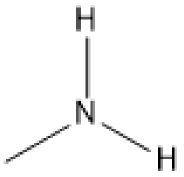
iso-propyl amine

Methyl n-ethyl amine

Nomenclature of Amines

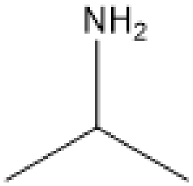
IUPAC System:

➢ Primary Amines are named as amino *derivatives of corresponding alkanes. Secondary and tertiary amines are regarded as a N-alkyl substituted derivatives of amines e.g.*



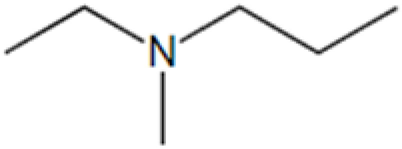
Methylamine

Propan-1-amine



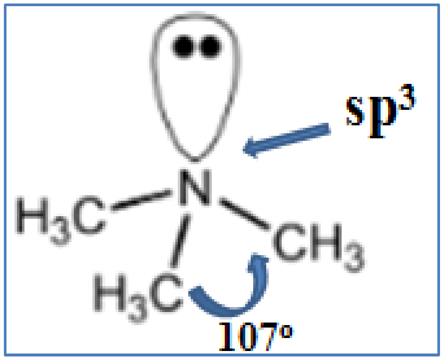
Propan-2-amine

N-methylethanamine



N-ethyl-N-methylpropan-1-amine

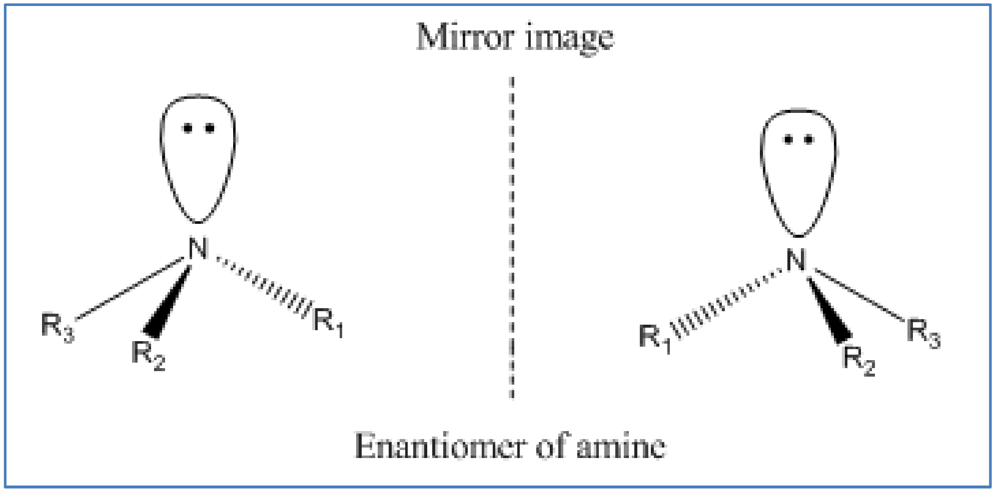
Structure of Amines



Nitrogen has 5 valence electrons and the electron configuration of nitrogen is $1s^2\ 2s^2\ 2p_x^{\ 1}\ 2p_y^{\ 1}\ 2p_z^{\ 1}$. In amine nitrogen and carbon both are sp^3 hybridized. Three sp^3 hydrid orbitals of nitrogen are half filled and one of them are filled with electron which can not take part in bond formation. So according to VSEPR theory the amines are trigonal pyramidal shape where the nitrogen atom is at the apex and the lone pair of electrons stay just above it. Each C-C σ bond is formed by overlapping the two sp^3 hybrid orbitals of two atoms. To form N-H bond the sp^3 hybrid orbital of nitrogen is overlapped with the s orbital of hydrogen atom.

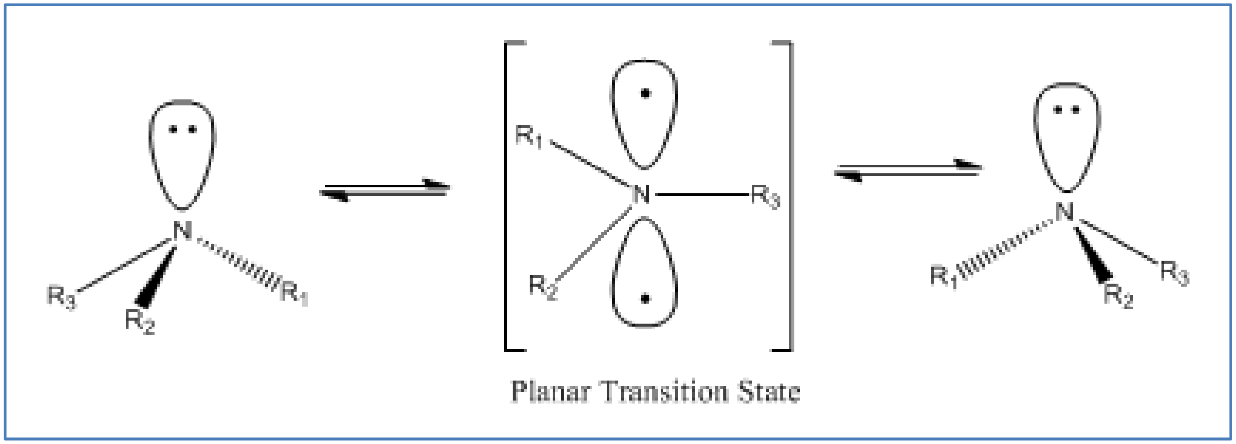
Stereochemistry of Amines

A consequence of the pyramidal configuration at nitrogen is that, when the attached groups R_1R_2 and R_3 are nonidentical, the nitrogen becomes a chiral atom. Under these circumstances, we would expect two enantiomeric configurations:



Stereochemistry of Amines

The separation or resolution of an acyclic chiral amine into its enantiomers still not achieved, and it comes under observation that the enantiomers are very rapidly interconvertable to each other via planar transition state.



If we take an example of ammonia, the rate of inversion is about 4×10^{10} times per second at room temperature, this indicated that the planar state being less stable than the pyramidal state by about 6kcal mol^{-1}. whereas aliphatic tertiary amines, the rateof inversion is about10^3 to 10^5 times per second. The rates of inversion in case of aliphatic tertiary amines are much high and not allow resolution of an amine into its enantiomers by presently available techniques.

Physical Properties of Amines

- The lower aliphatic amines are gaseous in nature. They have a fishy smell.
- Primary amines with three or four carbon atoms are liquids at room temperature whereas higher ones are solids.
- Aniline and other arylamines are generally colourless. However, they get coloured when we store them in open due to atmospheric oxidation.
- Lower aliphatic amines can form hydrogen bonds with water molecules. Therefore, such amines are soluble in water.
- With the Increase in the size of hydrophobic alkyl part the solubility of amine in water decreases.
- Higher amines are insoluble in water. Organic solvents like alcohol, benzene and ether readily dissolve amines.
- Alcohols have higher polarity as compared to amines and hence, they form stronger intermolecular hydrogen bonds.
- The intermolecular hydrogen association is more prominent in case of primary amines as compared to secondary due to the availability of two hydrogen atoms. In tertiary amines, there is no intermolecular association due to the absence of free hydrogen atom for bonding.

The order of boiling point of amines is as follows: Primary > Secondary > Tertiary.

Separation of Amines

➢ Mixture of primary , secondary and tertiary amines can be separated by following methods.

(i) Fractional distillation
(ii) Hinsberg method
(iii) Hofman method

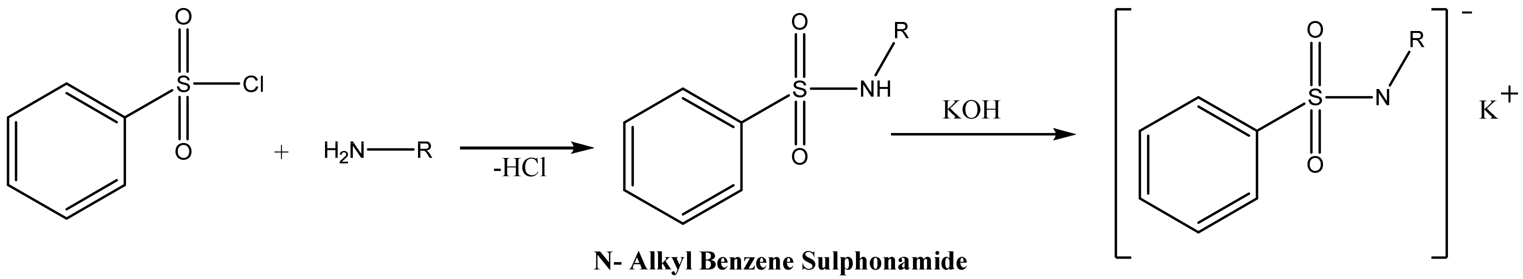
Fractional Distillation:

The mixture of amines may be fractional distillation because their boiling points are quite different. It is used in industry.

Separation of Amines

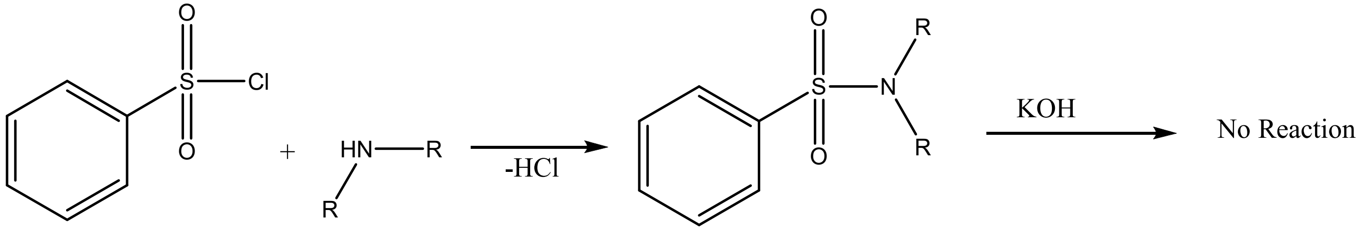
Hinsberg method: In this method mixture of amines is separated by using benzenesulphonyl chloride (Hinsberg's reagent).

a) The reaction of the benzene sulfonyl chloride with primary amines gives a sulfonamide product that is soluble in alkali.



N- Alkyl Benzene Sulphonamide
soluble in KOH

b) The reaction of the benzene sulfonyl chloride with secondary amines gives a sulfonamide product that is not soluble in alkali.

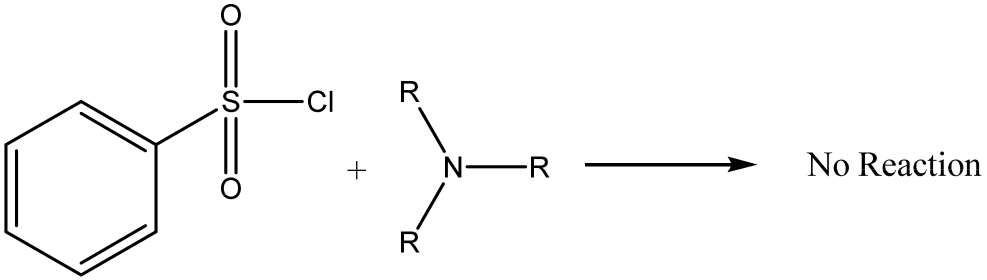


N,N- Dialkyl Benzene Sulphonamide
Insoluble in KOH

Separation of Amines

<u>Hinsberg method continued………</u>

c) Tertiary amine does not react with benzene sulphonyl chloride.



Sulphonamide from secondary and unreacted tertiary amines dissolve in ether and forms the upper layer.

The two layer are seperated.

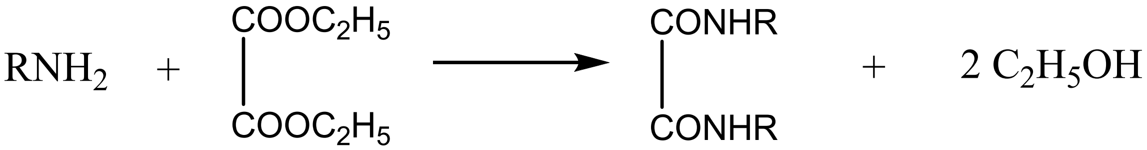
i) The aqueous layer is acidified with dil. HCl and then hydrolysed with conc. HCl. It is thendistilled over naoh gives pri. Amine

ii) The ether layer is also collected. It is put to frictional distillation when tertiary amine distils over. The remaining sulphonamide of sec. amine is treated with conc. HCl dialkylamine hydrochloride obtained then treated with naoh gives sec. amine.

Separation of Amines

Hofmann's method : *In this method mixture of amines is separated by using ethyl oxalate*

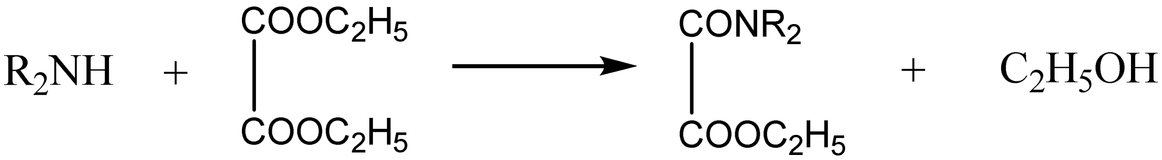
a) The primary amine forms a solid oxamide.



$$RNH_2 + \begin{array}{l} COOC_2H_5 \\ | \\ COOC_2H_5 \end{array} \longrightarrow \begin{array}{l} CONHR \\ | \\ CONHR \end{array} + 2\,C_2H_5OH$$

Pri. amines Diethyloxalate Oxamide (solid)

b) The secondary amine gives a liquid oxamic ester



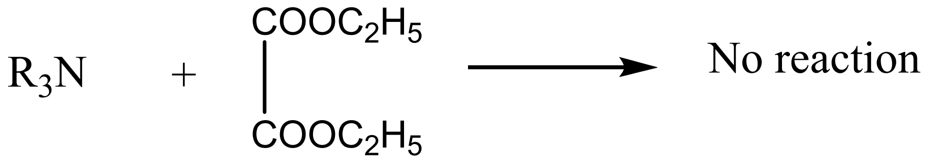
$$R_2NH + \begin{array}{l} COOC_2H_5 \\ | \\ COOC_2H_5 \end{array} \longrightarrow \begin{array}{l} CONR_2 \\ | \\ COOC_2H_5 \end{array} + C_2H_5OH$$

Sec. amines Diethyloxalate Oxamic ester (liquid)

Separation of Amines

Hofmann's method continued…….

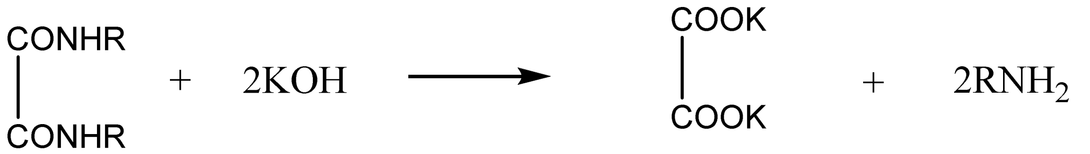
c) The tertiary amine does not react.



$$R_3N + \begin{array}{l} COOC_2H_5 \\ | \\ COOC_2H_5 \end{array} \longrightarrow \text{No reaction}$$

Ter. amines Diethyloxalate

Primary amine is recovered when solid oxamide is heated with caustic potash solution and collected as distillate on distilling the reaction mixture.



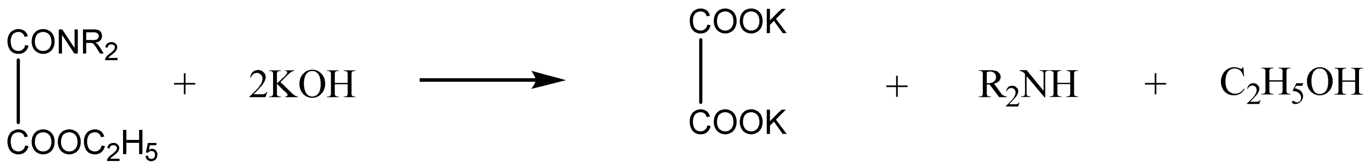
$$\begin{array}{l} CONHR \\ | \\ CONHR \end{array} + 2KOH \longrightarrow \begin{array}{l} COOK \\ | \\ COOK \end{array} + 2RNH_2$$

Oxamide (solid) Pot. Oxalate Pri. amine

Separation of Amines

Hofmann's method continued…….

The liquid (mixture of oxamic ester+ tertiary amine) is subjected to fractional distillation when tertiary amine distils over. The remaining liquid is distilled with *KOH* to recover secondary amine.



$$\begin{array}{l} \mathrm{CONR_2} \\ | \\ \mathrm{COOC_2H_5} \end{array} + 2\mathrm{KOH} \longrightarrow \begin{array}{l} \mathrm{COOK} \\ | \\ \mathrm{COOK} \end{array} + \mathrm{R_2NH} + \mathrm{C_2H_5OH}$$

Oxamic ester (liquid)

Pot. Oxalate

Sec. amine

These methods can also used to distinguished between primary, secondary & tertiary amine

Basicity of Amines

Basic Nature of Amine: *Amine are basic in nature as ammonia due the a pair of unshared electrons, which they can share with other atoms. These unshared electrons create an electron density around the nitrogen atom. The greater the electron density, the more basic the molecule. Groups that donate or supply electrons will increase the basicity of amines while groups that decrease the electron density around the nitrogen decrease the basicity of the molecule.*

$$RNH_2 + H_2O \rightleftharpoons RNH_4^+ + OH^-$$

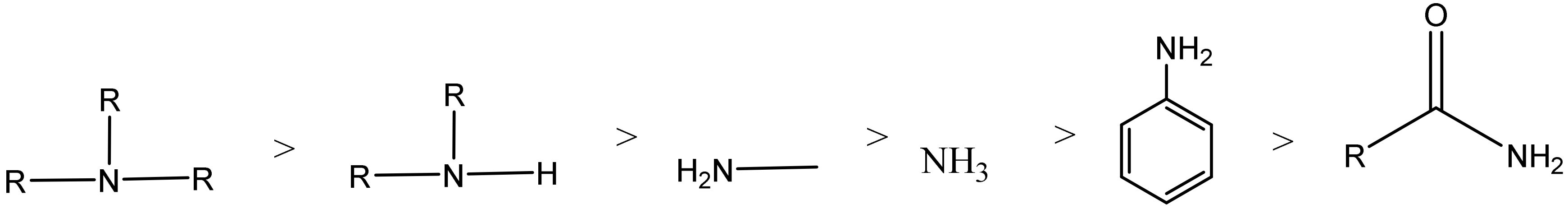
In this reaction due to the formation of Hydroxy ion, aqueous solution of amines are basic in nature. The strength of a base can be known from the value of its dissociation constant, k_b, for this reaction

$$K_b = \frac{[RNH_4^+]\ [OH^-]}{[RNH_2]} \qquad pK_b = -\log K_b$$

Higher is the value of Kb; greater is the strength of base.
Lower the value of pKa value; greater is the strength of base

Comparison of basicity of Amines

Nitrogen Compounds can act as Lewis bases as there is a lone pair of electrons available on nitrogen for donation. How basic the nitrogen compound is depends on the availability of that lone pair.
Let's look at the organic compounds that contain nitrogen and their difference in basicity:



Notice that amines are the strongest bases, followed by ammonia, then phenylamine, and finally amides.
Let's take a closer look to understand why.

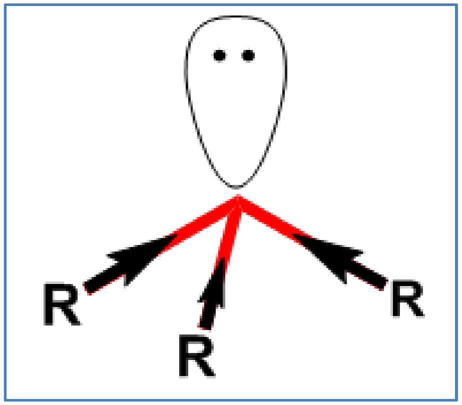
Comparison and factors of basicity of Amines

1. Amines and ammonia (Inductive Effect)

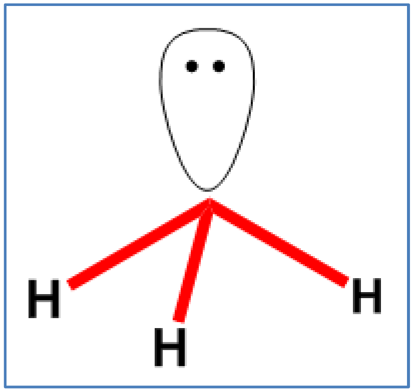
In general the basicity trend for amines and ammonia is as follows:

tertiary amines > secondary amines > primary amines > ammonia

This is due to the electron donating effect of alkyl groups which increase the electron density on nitrogen. Tertiary amines have more electron donating R groups and increase the electron density on nitrogen to a greater extent.



This makes the lone pair on nitrogen more available for donation, and tertiary amines are the strongest bases. Hence the more R groups the amine has, the more basic it is.

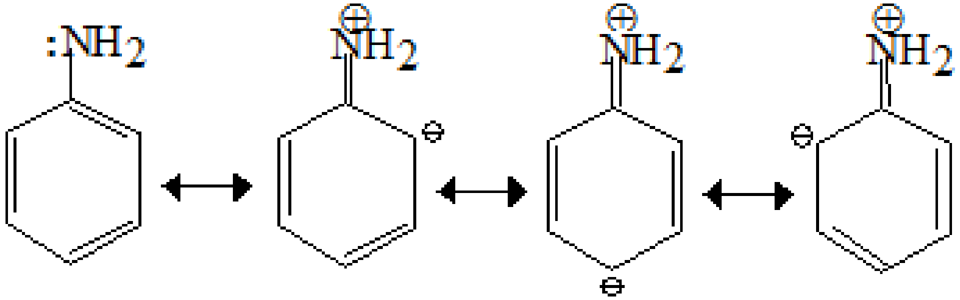


Conversely, ammonia has no electron donating R group. So lone pair on nitrogen is less available for donation and ammonia is less basic than amines.

Comparison of basicity of Amines

2. Phenylamine (Resonance Effect)

The lone pair of nitrogen is delocalised into the pi electron system of benzene.



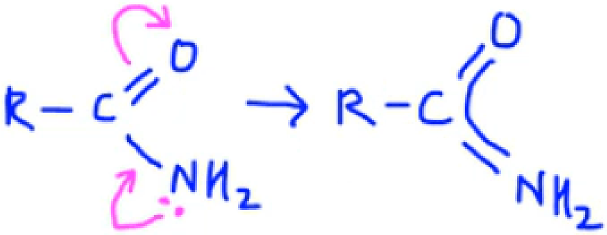
(a) (b) (c) (d)

This makes the lone pair less available for donation and hence phenylamine is less basic than ammonia.

3. Amides

The lone pair on nitrogen is delocalised extensively into the acid group, between both electronegative atoms oxygen and nitrogen.

This makes the lone pair unavailable for donation. Hence amides are neutral and do not use the lone pair for donation at all.

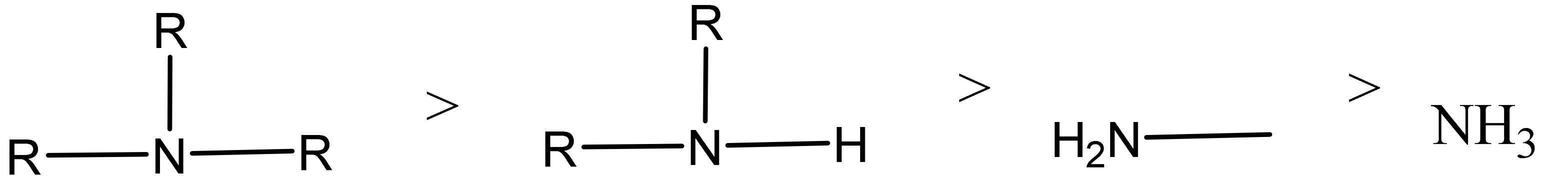


Factors effecting the basicity of Amines

1. Steric Effect:

Steric effect refers to the crowding of alkyl groups around N atom which hinders the attack of proton on the **amine** molecule and this decreases its basic strength. Since crowding of alkyl groups around N atom increases from 1^o to 3^o **amines**, the basic strength of **amine** should decrease in the order 1^o > 2^o> 3^o

b) Inductive effect: Amines are basic because they having a pair of unshared electrons, which they can share with other atoms. These unshared electrons create an electron density around the nitrogen atom. The greater the electron density, the more basic the molecule. The electron donating groups will increase the basicity of amines while electron withdrawing groups decrease the basicity of the molecule. For alkyl halides in the gas phase, the order of base strength is given below:

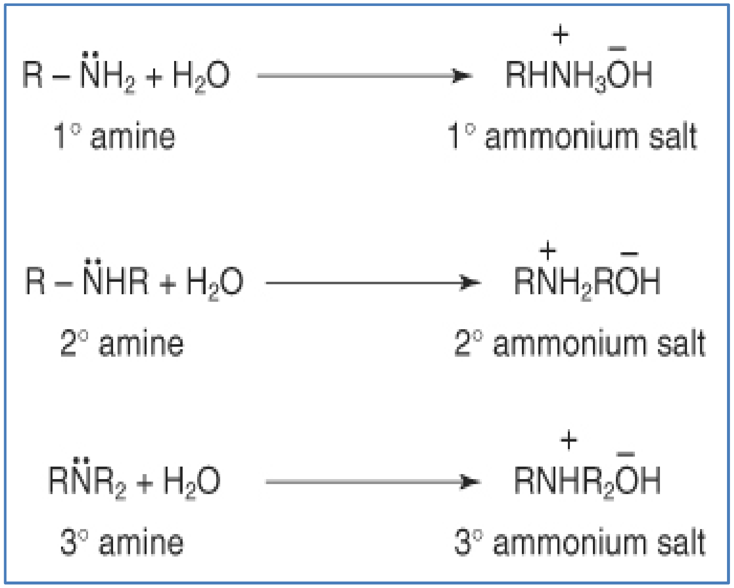


Factors effecting the basicity of Amines

b) ***Solvation of ions :*** it is refers to the stabilization of the protonated amine by water molecules. The water molecules from H - bonds with the protonated amine and release energy called hydration energy.

Greater the extent of H - bonding in protonated amine more will be its stabilization and consequently greater will be the basic strength of the corresponding amine. Hydration due to hydrogen-bonding is maximum in monoalkyl ammonium ion (protonated cation of 1°amine), it is less in dialkyl ammonia ion and much less in trialkyl ammonium ion. Thus basic strength in aqueous solutions changes and the order of basicity becomes .

$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$



In 3° amine, hydration is least, steric hinderance is maximum so least basic inspite of maximum inductive effect. In 1° amine, steric hinderance is least, hydration is maximum and inductive effect is minimum. So its basic strength is more than 3° amine.

The resultant of all factors cause 2° amine to be still more basic than 1°amine. So overall basic strength varies as 2° > 1° > 3°.

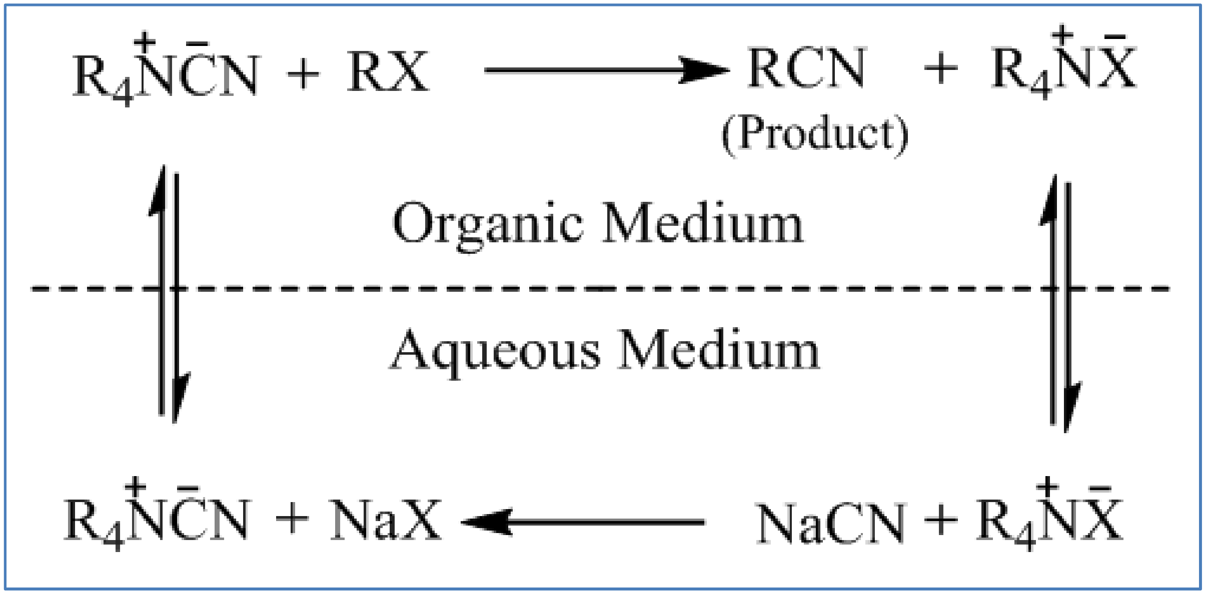
Amine Salts as Phase Transferred catalyst

due to insoluble nature of reactants in one solvent many nuclephilic substitution reactions cannot be carried out. Conventionally a solvent is selected which can dissolve all the reactants in to it but use of such solvents are highly expensive in nature. To solve this problem, reactants are allowed to dissolve in their respective aqueous and organic solvents and then catalyst is added to transfer the reactant from the aqueous or solid phase into the organic phase, where reaction occurs. The phenomenon is called as phase transfer catalysis (PTC) and catalyst used is called as phase transfer (PT) catalyst.

In phase transferred catalyst, a catalyst is used to carry the nuceophile from the aqueous phase into the organic phase. As an example, simple heating or stirring a two phase mixture of 1-cholorooctane for several days with aqueous NaCN give essentially no yield of 1-cyanooctane. But if small amount of appropriate quaternary ammonium salts is added, the product is quantitatively formed in few hours. The use of quaternary ammonium salts brings, the anion into organic phase and allow it to react with reactant to give final products.

Amine Salts as Phase Transferred catalyst

Mechanism



References

i) Organic Chemistry By Y. R. Sharma
ii) Organic Chemistry By S. N. Dhawan
iii) Organic Chemistry By S. M. Mukherjee