Amines

Chemical Reactions

1. **Basic character of amines**: Amines react with acids to form salts.

This reaction shows that they are basic in nature.

$R\text{-}NH_2 + HX \rightleftharpoons R\text{-}NH_3^+X^-$

$C_6H_5\text{-}NH_2 + HCl \rightleftharpoons C_6H_5NH_3^+Cl^-$

Aniline Anilinium chloride

In amine, there is an unshared pair of electrons on nitrogen atom and hence it can donate this electron pair. So it acts as a Lewis base. Basic character of amines can be expressed in terms of K_b and pK_b. ($pK_b = - \log K_b$)

Greater the value of K_b, smaller will be the pK_b value and stronger will be the base.

Aliphatic amines are stronger bases than ammonia. This is due to the +I effect of alkyl groups leading to greater electron density on the nitrogen atom. But aromatic amines are weaker bases than ammonia. This is due to the electron withdrawing nature of the aryl group.

Besides inductive effect, there are some other effects like solvation effect, steric hindrance etc. affect the basic strength of amines.

Structure-basicity relationship of amines

Basicity of amines is related to their structure. Basic character of an amine depends upon the ease of formation of the cation by accepting a proton from the acid. As the stability of the cation increases, the basicity also increases.

a) Comparison of basicity of alkyl amines (alkanamines) and ammonia

Due to the electron releasing nature of alkyl group (R) in alkyl amines, it (the alkyl group) pushes electrons towards nitrogen and thus makes the unshared electron pair more available for sharing with the proton of the acid.

Also the substituted ammonium ion formed from the amine gets stabilized charge by the +I effect of the alkyl group. Hence, *alkyl amines are stronger bases than ammonia.*

The basic nature of aliphatic amines should increase with increase in the number of alkyl groups. But this trend is followed only in gas phase. The order of basicity of amines in the gaseous phase is:

Tertiary amine > Secondary amine > Primary amine > NH_3

In the aqueous solution, in addition to inductive effect, there are some other effects like solvation effect and steric hindrance determine the basicity. The greater the size of the ion, lesser will be the solvation and the less stabilised is the ion. So the basicity also decreases. Thus, the order of basicity of aliphatic amines should be: primary > secondary > tertiary, which is opposite to the inductive effect based order.

When the alkyl group is small, there is no steric hindrance to H-bonding. In case the alkyl group is bigger than CH_3 group, there will be steric hindrance to H-bonding. Therefore, the size of the alkyl group also determines the order of basic strength. Thus inductive effect, solvation effect and steric hindrance of the alkyl group decide the basic strength of alkyl amines in the aqueous state.

The order of basic strength in case of methyl substituted amines and ethyl substituted amines in aqueous solution is as follows:

$(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$

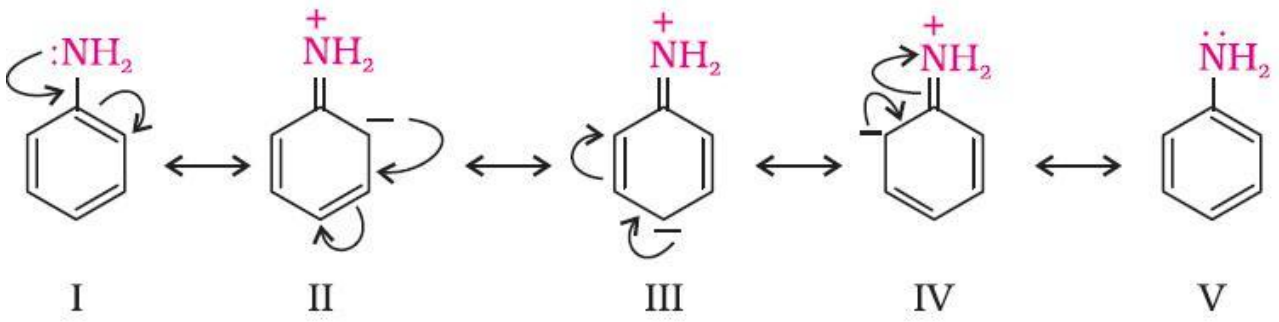
2^0 3^0 1^0

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

2^0 1^0 3^0

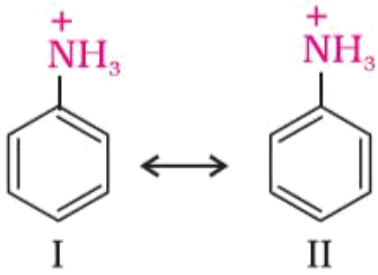
b) ***Comparison of basicity aryl amines and ammonia***

Aryl amines are less basic than ammonia. This is because in aryl amines, the -NH_2 group is attached directly to the benzene ring. So the lone pair electrons present in the nitrogen atom enter into the benzene ring and the following resonating structures are formed.



So the electron pairs are less available for protonation and hence aryl amines are less basic.

Also the anilinium ion formed by accepting a proton can have only two resonating structures as follows:



So it is less stable and hence aniline does not easily accept proton. So it is less basic. In the case of substituted aniline, the electron releasing groups like $–OCH_3$, $–CH_3$ increase basic strength while electron withdrawing groups like $–NO_2$, $–SO_3$, –COOH, –X etc. decrease the basic strength.

2. Alkylation:

Amines react with alkyl halides undergo nucleophilic substitution reaction to form a mixture of secondary and tertiary amines and quaternary ammonium salt. (Hofmann's Ammonolysis)

$$R\text{-}X + R\text{-}NH_2\ (alc.) \longrightarrow R_2NH + R_3N + R_4N^+X^-$$

3. *Acylation*:

Aliphatic and aromatic primary and secondary amines react with acid chlorides, anhydrides and esters in presence of base like pyridine to form substituted amides. This reaction is known as ***acylation***.

$$CH_3\text{-}NH_2 + CH_3\text{-}CO\text{-}Cl \xrightarrow{\text{base}} CH_3\text{-}NH\text{-}CO\text{-}CH_3 + HCl$$

Methanamine N-methyl ethanamide / (N-methyl acetamide)

$(C_2H_5)_2NH + CH_3\text{-}CO\text{-}Cl \xrightarrow{\text{base}} (C_2H_5)_2N\text{-}CO\text{-}CH_3 + HCl$

N- Ethylethanamine N, N- Diethylethanamide

$C_6H_5\text{-}NH_2 + CH_3\text{-}CO\text{-}O\text{-}CO\text{-}CH_3 \longrightarrow C_6H_5\text{-}NH\text{-}CO\text{-}CH_3 + CH_3\text{-}COOH$

Aniline Ethanoic anhydride N- Phenylethanamide (Acetanilide)

Amines react with benzoyl chloride (C_6H_5COCl) to form N-alkyl benzamide. This reaction is known as ***benzoylation***.

$CH_3\text{-}NH_2 + C_6H_5\text{-}CO\text{-}Cl \longrightarrow CH_3\text{-}NH\text{-}CO\text{-}C_6H_5 + HCl$

Methanamine Benzoyl chloride N- Methylbenzamide (Benzanilide)

4. Carbylamines reaction (isocyanide test):

Aliphatic and aromatic primary amines on heating with chloroform and alcoholic potassium hydroxide form foul smelling isocyanides or carbylamines. This reaction is known as **carbylamines reaction or isocyanide test** and is used as ***a test for primary amines***. Secondary and tertiary amines do not give this reaction.

$R\text{-}NH_2 + CHCl_3 + 3\ KOH \xrightarrow{\text{heat}} R\text{-}NC + 3\ KCl + 3\ H_2O$

$CH_3\text{-}NH_2 + CHCl_3 + 3\ KOH \xrightarrow{\text{heat}} CH_3\text{-}NC + 3\ KCl + 3\ H_2O$

Methanamine Methyl carbylamine

$CH_3\text{-}NH_2 + CHCl_3 + 3\ KOH \xrightarrow{\text{heat}} CH_3\text{-}NC + 3\ KCl + 3\ H_2O$

Methanamine Methyl carbylamine

$C_6H_5\text{-}NH2 + CHCl3 + 3\ KOH \xrightarrow{\text{heat}} C_6H_5\text{-}NC + 3\ KCl + 3\ H2O$

Aniline Phenyl carbylamine

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