CHEMICAL PROPERTIES

Chemical Properties of Amines

(i) The fundamental alkaline nature of amines can be attributed to the existence of a lone pair of electrons on the nitrogen atom.

(ii) The strength of their basic properties is contingent upon their electron-donating capacity. This order of basicity is applicable in both aqueous solutions and liquid phases.

$$Et_2 NH > Et_3 N > Et NH_2$$
.

Due to steric hindrance in 3° amine, it is less basic, than 2° amine.

Steric hindrance of three $-C_2H_5$ group protect the lone pair of nitrogen from the attack of H^{\oplus} .

But in gaseous phase basic order is $R_2H > RH_2 > R_3 > H_3$

Some other basic order of different amine if alkyl group would be change

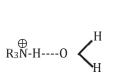
Alkyl groups (R-) Relative base strength
(i) CH_3 - $R_2NH > RNH_2 > R_3N > NH_3$ (ii) C_2H_5 - $R_2NH > RNH_2 > NH_3 > R_3N$ (iii) $(CH_3)_2CH$ - $RNH_2 > NH_3 > R_2NH > R_3N$ (iv) $(CH_3)_3C$ - $NH_3 > RNH_2 > R_2NH > R_3N$

1. Special Point

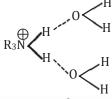
(I) Tertiary amine is less basic then secondary due to following reasons:

(i) Steric hindrance: In tertiary amines (R₃N), three alkyl groups attached to N are bulkier and as such exert steric hindrance.

(ii) Decrease in hydration: In tertiary amine in secondary amine



Protonated t-amine can form H-bonding With water molecule only at one point [less stable]



Protonated s-amine can form H-bonding With water molecules at two points [More stable]

3° amine are less stable as compare to 2° amine due to low hydration so less basic

(II) The reduced basicity of aniline in comparison to aliphatic amines can be attributed to the interaction of the lone pair of electrons on the nitrogen atom with the delocalized π -orbital of the benzene ring, making it less accessible for protonation on the nitrogen atom.

The order of basicity among aniline, pyridine, and pyrrole follows the pattern:

Pyridine > Aniline > Pyrrole.

(2) Reactions Showing Basic Nature

(A) It reacts with acids to form salts.

(B) Amines can undergo a reaction with auric acid and platinic chlorides in the presence of HCl to produce double salts. These double salts subsequently break down upon heating, yielding pure metal. This process of forming and decomposing double salts is employed as a method for determining the molecular weight of amines.

$$\begin{array}{c} 2R-NH_2+\underbrace{PtCl_4+2HCl} & \bigoplus \\ \text{ (chloro platinic acid)} & \text{Alkyl ammonium chloroplatinate} \\ RNH_2+\underbrace{AuCl_3+HCl} & \bigoplus \\ \text{ [Chloroauric acid]} & \text{Alkyl ammonium chloroaurate} \\ & \bigoplus \\ \text{ (RNH_3)} \text{ AuCl_4} & \text{Alkyl ammonium chloroaurate} \\ & \bigoplus \\ \text{ (RNH_3)}_2 \text{ PtCl}_6^{-2} & \bigoplus \\ \text{ (RNH_3)}_2 \text{ PtCl}_6^{-2} & \bigoplus \\ \text{ pt} & \bigoplus \\ \text{ (RNH_3)}_2 \text{ PtCl}_6^{-2} & \bigoplus \\ \text{ (RNH_3)}_2 \text{ PtCl}_6^{-2} & \bigoplus \\ \text{ (RNH_3)}_2 \text{ PtCl}_6^{-2} & \bigoplus \\ \text{ (RNH_3)}_2 & \text{ (RNH_3)}_2$$

(C) Reaction with H₂O: It creates alkyl ammonium hydroxide when combined with water. Ammonium hydroxides of this kind are applied in the precipitation of cations from the second and third groups during qualitative analysis.

$$RNH_2 + H_2O \qquad --- \Rightarrow \qquad \begin{pmatrix} \bigoplus & \Theta \\ (RNH_3) + OH \\ Base \end{pmatrix}$$

$$FeCl_3 + 3[RNH_3]OH \qquad --- \Rightarrow \qquad Fe (OH)_3 + 3[RNH_3]CI$$

$$Brown ppt \qquad \bigoplus & \Theta \\ AlCl_3 + 3[RNH_3]OH \qquad --- \Rightarrow \qquad Al (OH)_3 + 3[RNH_3]CI$$

$$White ppt \qquad \bigoplus & \Theta \\ CrCl_3 + 3[RNH_3]OH \qquad --- \Rightarrow \qquad Cr (OH)_3 + 3[RNH_3]CI$$

$$Green ppt \qquad \bigoplus & \Theta \\ Green ppt \qquad --- \Rightarrow \qquad Green ppt \qquad --- \Rightarrow Green ppt \qquad --$$

(3) Reaction With Alkyl Halides

Alkyl amine reacts with alkyl halides and form sec., ter. amines and quaternary ammonium salt.

$$RNH_2 + R - X \xrightarrow{\quad -HX \quad} R_2NH \xrightarrow{\quad RX \quad} R_3N \xrightarrow{\quad RX \quad} R_4NX$$

(4) Acetylation

Acetylation takes place when alkyl amine combines with acetyl chloride or acetic anhydride.

$$RNH_2 + CICOCH_3 \longrightarrow RNHCOCH_3 + HCI$$
 $(N - alkyl acetamide)$
 $RNH_2 + (CH_3CO)_2O \longrightarrow RNHCOCH_3 + CH_3COOH$
 $(N - alkyl acetamide)$

(5) Benzoylation (Schotten Baumann Reaction)

$$\begin{array}{c} \text{COCl} \\ \hline \\ \text{Denzoyl chloride} \end{array} + \text{H - NH - R} \qquad \begin{array}{c} \text{NaOH} \\ \hline \\ \text{N - alkyl benzamide} \end{array} + \text{HCl}$$

(6) Acidic Nature

Amines are very weak acids only 1° and 2° amines show acidic nature.

R-NH₂ + Na
$$\longrightarrow$$
 R-NHNa + $\frac{1}{2}$ H₂ N - alkyl sodamide

(7) Reaction With Tilden Reagent

The reaction of alkylamine with nitrosyl chloride (commonly known as the Tilden reagent) results in the production of alkyl chloride. This reaction holds significance in interconversion processes.

$$R-NH_2 + NOCl$$
 \longrightarrow $RCl + N_2 + H_2O$

(8) Reaction With Phosgene

$$R-NH_2 + COCl_2$$
 + 2HCl Alkyl isocyanate

(9) Reaction With Halogen

The hydrogen atoms of the amino group are replaced by halogen atoms in presence of alkali solution.

$$\begin{array}{c} R - NH_2 + Br_2 \xrightarrow[or KOH]{NaOH} \rightarrow R - NH - Br + HBr \\ \qquad N - bromo \ alkylamine \end{array}$$

$$R - NH - Br + Br_2 \xrightarrow{NaOH} R - NBr_2 + HBr$$

$$N, N - dibromo alkyl amine$$

(10) Reaction With Aldehydes

Alkylamine exhibits an additive reaction with aldehydes, leading to the creation of α -hydroxyl amines. These α -hydroxyl amines are subsequently transformed into Schiff bases through the removal of a water molecule.

$$R - NH_2 + O = C - R$$

$$R - NH_2 + O = C - R$$

$$R - N - C - R$$

$$OH$$

$$RCH = NR (Schiff's base)$$

(11) Mannish Reaction

$$\begin{array}{c} O \\ \parallel \\ R-CH_2NH_2+CH_2O+HCH_2-C-C_6H_5 \end{array} \xrightarrow{-H_2O} \begin{array}{c} O \\ \parallel \\ R-CH_2NHCH_2-CH_2-C-C_6H_5 \end{array}$$
 Acetophenone
$$\begin{array}{c} O \\ \parallel \\ Manniche\ base \end{array}$$

(12) Oxidation

KMnO₄/H⁺: When alkylamine undergoes oxidation in the presence of acidified potassium permanganate, it produces aldimine. Subsequent hydrolysis of this aldimine results in the formation of both an aldehyde and ammonia.

$$R - CH_2NH_2 \xrightarrow{[O]} RO_4/H^+ \rightarrow R - CH = NH \xrightarrow{H_2O} RCHO + NH_3$$

$$(Aldimine)$$

$$R_2CHNH_2 \xrightarrow{[O]} R_2CH = NH \xrightarrow{H_2O} R_2C = O + NH_3$$

$$(Ketimine) \qquad (Ketone)$$

$$\begin{array}{c} R_3CHNH_2 \xrightarrow{ \begin{array}{c} [\ O \] \\ \end{array}} R_3CNO_2 \\ & (Nitroalkane) \end{array}$$

With ${\rm H_2SO_5}$ (Caro's acid) Or ${\rm H_2O_2}$ /Fe⁺² (Fenton reagent):

RCH₂NH₂
$$\xrightarrow{[0]}$$
 R - CH₂ = NH - OH + RCHNOH + R - C - NHOH

N-alkyl hydroxylamine Aldoxime Hydroxamic acid

R₂CHNH₂ $\xrightarrow{[0]}$ R₂CH = N OH (Ketoxime)

R₃CHNH₂ $\xrightarrow{[0]}$ RCNO (Nitroso compound)

(13) Carbylamine Reaction (Iso Cyanide Test)

Upon heating alkylamines with chloroform and alcoholic KOH, alkyl isocyanide is generated, characterized by its unpleasant odor. Aniline also exhibits this same reaction during testing. This is a test for p– amines.

$$R-NH_2 + CHCl_3 + 3 KOH \rightarrow R-N \stackrel{\scriptstyle \longrightarrow}{} C + 3KCl + 3H_2O$$

Nucleophile RNH₂ attacks electrophilic intermediate [:CCl₂] dichlorocarbene.

Mechanism:

$$CHCl_3 + OH = S \xrightarrow{-H_2O} Cl - \overset{\Theta}{Cl} \overset{Cl}{\underset{Cl}{\longrightarrow}} :CCl_2$$
Dichlorocarbene

$$R-NH_2 +: CCl_2 \rightarrow R-HN-C \xrightarrow{\bigoplus} Cl \xrightarrow{-HCl} R-N = C \xrightarrow{-HCl} R-N = C \xrightarrow{-HCl} R-N = C$$

(14) Hofmann's Mustard Oil Test

Upon heating an alkylamine in the presence of carbon disulfide and mercuric chloride, alkyl isothiocyanate is generated, characterized by an odor reminiscent of mustard oil.

$$R NH_2 + C = S \longrightarrow R NH + C SH \xrightarrow{HgCI_2} R - N = C = S + HgS + 2HCI$$

$$R NH_2 + C = S \longrightarrow R NH_2 + C = S \xrightarrow{HgCI_2} No reaction$$

$$R NH_2 + C = S \longrightarrow No reaction$$

$$R NH_2 + C = S \longrightarrow No reaction$$

(15) Reaction With HNO₂ (NaNO₂ + HCl or H₂SO₄)

(A) Primary amines react with nitrous acid to produce nitrogen gas [seen as bubbles]

$$R-NH_2 + HONO \longrightarrow R-OH + N_2 + H_2O$$

$$CH_3 NH_2 + HNO_2 \longrightarrow CH_3-O-CH_3$$

$$R_2 NH + HONO \longrightarrow R_2 N-NO + H_2O$$

N-nitroso amine (Yellow oily layer)

This is called libbermann's nitroso test

(C)
$$R_3N + HONO$$
 $--\rightarrow$ Trialkyl ammonium nitrite (Soluble in water)