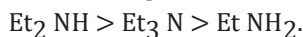


## CHEMICAL PROPERTIES

### 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.



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

Steric hindrance of three  $-\text{C}_2\text{H}_5$  group protect the lone pair of nitrogen from the attack of  $\text{H}^+$ .

But in gaseous phase basic order is  $\text{R}_2\text{H} > \text{RH}_2 > \text{R}_3 > \text{H}_3$

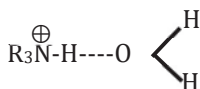
Some other basic order of different amine if alkyl group would be change

Alkyl groups (R-)	Relative base strength
(i) $\text{CH}_3 -$	$\text{R}_2\text{NH} > \text{RNH}_2 > \text{R}_3\text{N} > \text{NH}_3$
(ii) $\text{C}_2\text{H}_5 -$	$\text{R}_2\text{NH} > \text{RNH}_2 > \text{NH}_3 > \text{R}_3\text{N}$
(iii) $(\text{CH}_3)_2\text{CH} -$	$\text{RNH}_2 > \text{NH}_3 > \text{R}_2\text{NH} > \text{R}_3\text{N}$
(iv) $(\text{CH}_3)_3\text{C} -$	$\text{NH}_3 > \text{RNH}_2 > \text{R}_2\text{NH} > \text{R}_3\text{N}$

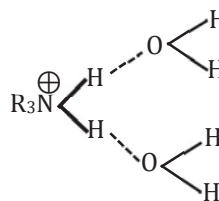
### 1. Special Point

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

- (i) Steric hindrance: In tertiary amines ( $\text{R}_3\text{N}$ ), 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

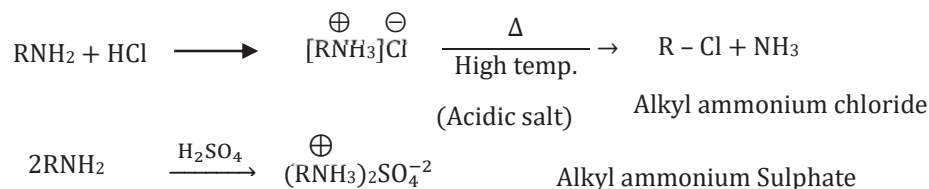
- (II) The reduced basicity of aniline in comparison to aliphatic amines can be attributed to the interaction of the lone pair of electrons on the nitrogen atom with the delocalized  $\pi$ -orbital of the benzene ring, making it less accessible for protonation on the nitrogen atom.

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

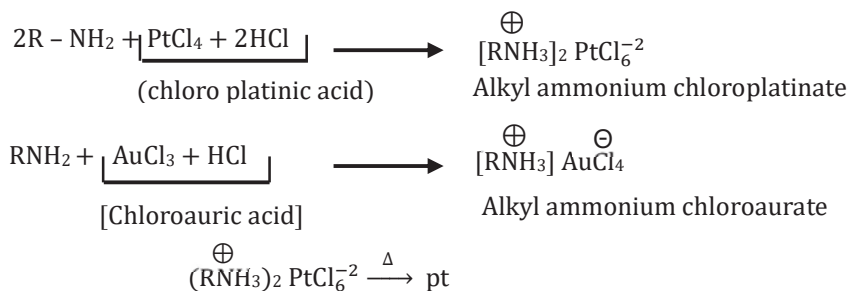


### (2) Reactions Showing Basic Nature

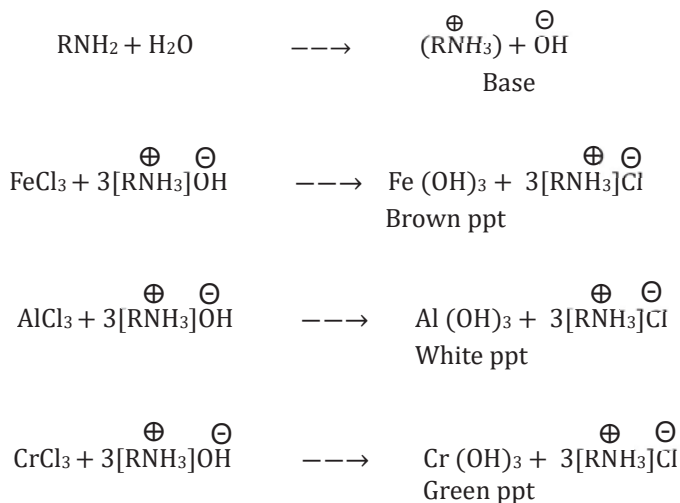
(A) It reacts with acids to form salts.



- (B) Amines can undergo a reaction with auric acid and platinum 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.

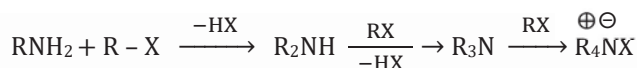


- (C) **Reaction with H<sub>2</sub>O:** It creates alkyl ammonium hydroxide when combined with water. Ammonium hydroxides of this kind are applied in the precipitation of cations from the second and third groups during qualitative analysis.



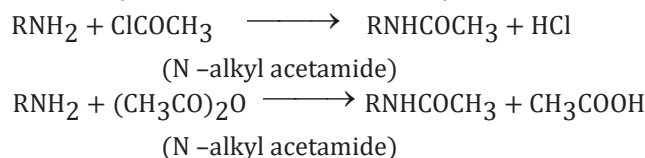
### (3) Reaction With Alkyl Halides

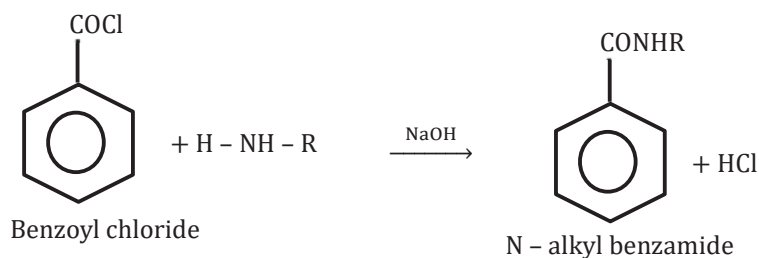
Alkyl amine reacts with alkyl halides and form sec., ter. amines and quaternary ammonium salt.



### (4) Acetylation

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

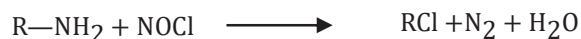


**(5) Benzoylation (Schotten Baumann Reaction)****(6) Acidic Nature**

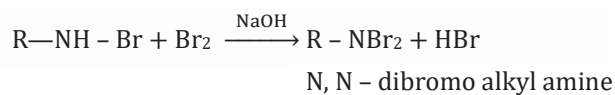
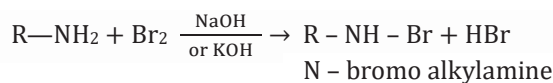
Amines are very weak acids only 1° and 2° amines show acidic nature.

**(7) Reaction With Tilden Reagent**

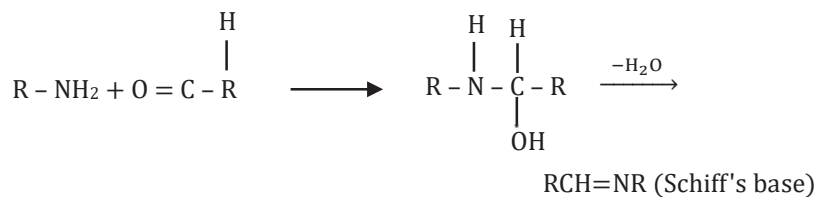
The reaction of alkylamine with nitrosyl chloride (commonly known as the Tilden reagent) results in the production of alkyl chloride. This reaction holds significance in interconversion processes.

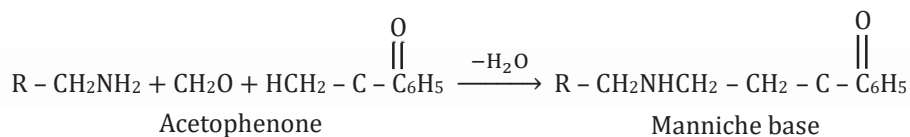
**(8) Reaction With Phosgene****(9) Reaction With Halogen**

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

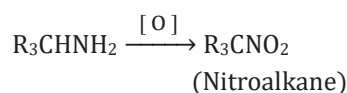
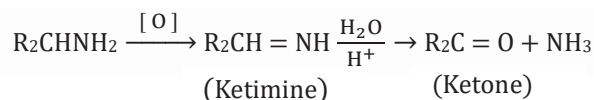
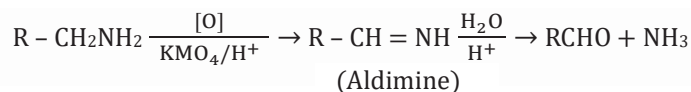
**(10) Reaction With Aldehydes**

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.

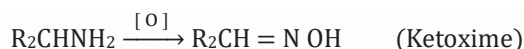
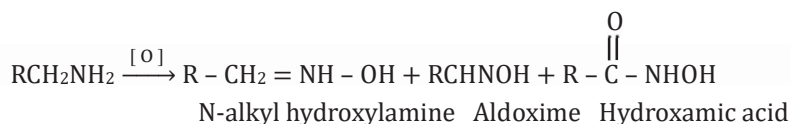


**(11) Mannish Reaction****(12) Oxidation**

**KMnO<sub>4</sub>/H<sup>+</sup>:** 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.

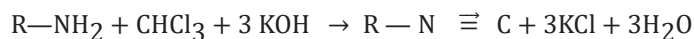


With H<sub>2</sub>SO<sub>5</sub> (Caro's acid) Or H<sub>2</sub>O<sub>2</sub> /Fe<sup>+2</sup> (Fenton reagent):

**(13) Carbylamine Reaction (Iso Cyanide Test)**

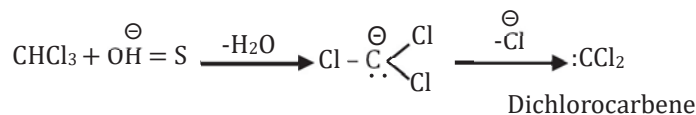
Upon heating alkylamines with chloroform and alcoholic KOH, alkyl isocyanide is generated, characterized by its unpleasant odor. Aniline also exhibits this same reaction during testing.

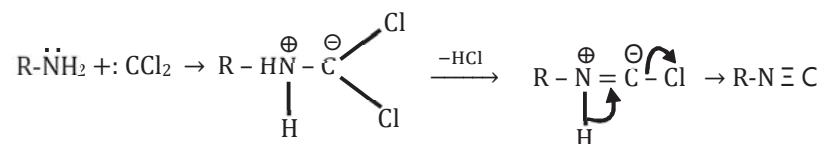
This is a test for p- amines.



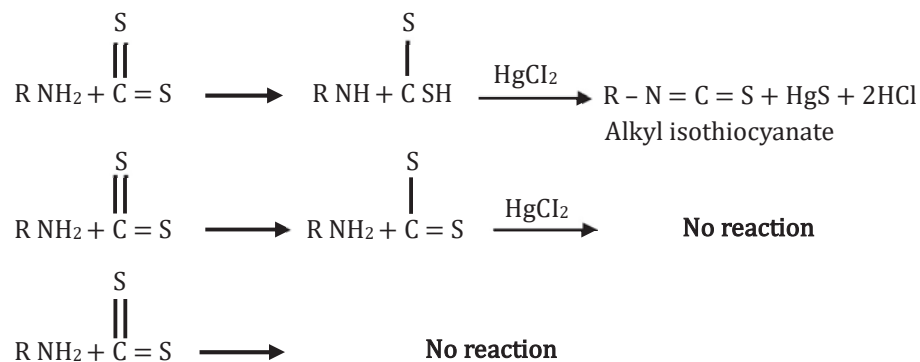
Nucleophile RNH<sub>2</sub> attacks electrophilic intermediate [ :CCl<sub>2</sub> ] dichlorocarbene.

**Mechanism:**

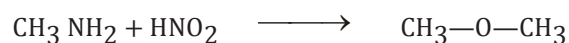


**(14) Hofmann's Mustard Oil Test**

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.

**(15) Reaction With HNO<sub>2</sub> (NaNO<sub>2</sub> + HCl or H<sub>2</sub>SO<sub>4</sub>)**

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



(B)  $\text{R}_2\text{NH} + \text{HONO} \longrightarrow \text{R}_2\text{N}-\text{NO} + \text{H}_2\text{O}$

N-nitroso amine (Yellow oily layer)

This is called libbermann's nitroso test

(C)  $\text{R}_3\text{N} + \text{HONO} \longrightarrow \text{Trialkyl ammonium nitrite}$   
(Soluble in water)