Important Question

30-07-2020 (From Previous Year) By-Dr.Rinky

For Degree-I (Hons.)

Question

a. Give a brief account of primary, secondary & tertiary amines.

b. Compare basic strength of 1° ,2° & 3° amines.

Answer

a. Brief account of 1° ,2° & 3° amines :-

* Amines are classified as Primary (1°), secondary(2°) or Tertiary (3°) according to the number of alkyl groups attached to the nitrogen atom.

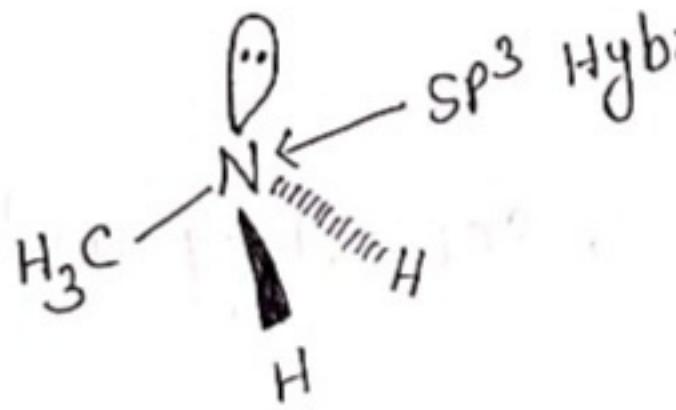
* **Primary amine :-** It has only one alkyl group directly attached to the nitrogen.

eg; $R-\underset{\underset{H}{|}}{\overset{\overset{H}{|}}{N}}-H$

* **Secondary amine :-** It has two alkyl groups directly attached to the nitrogen.

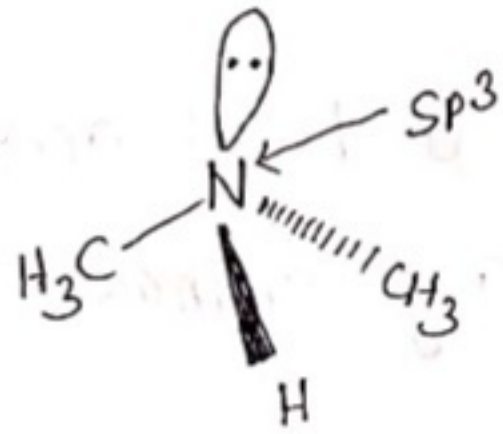
$R-\underset{\underset{R}{|}}{\overset{\overset{\cdot\cdot}{|}}{\ddot{N}}}-H$

* **Tertiary amine :-** A tertiary amine has three alkyl groups directly attached to the nitrogen.



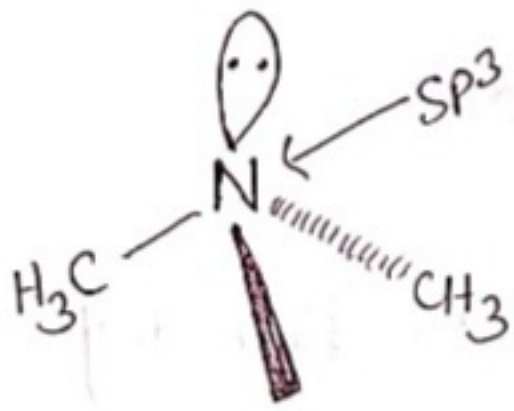
Methyl amine

(1°)



Dimethyl amine

(2°)



Trimethyl amine

(3°)

Ans.

b. BASIC STRENGTH OF AMINE

* Due to presence of lone pair of electron, Amines are Lewis base.

$$R-\ddot{N}H_2 + H_2\ddot{O}: \rightleftharpoons R-\overset{\oplus}{N}H_3 + OH^-$$

$$K_{eq} = \frac{[R-\overset{\oplus}{N}H_3][OH^-]}{[R-NH_2]\ [H_2O]}$$

$\because$ $[H_2O]$ is large excess, hence taken as const.

$$K_{eq.} \times [H_2O] = \frac{[R-\overset{+}{N}H_3][OH^-]}{[R-NH_2]}$$

$$\therefore K_b = \frac{[R-\overset{\oplus}{N}H_3][OH^-]}{[R-NH_2]}$$

Where, K_b = Dissociation const. of base.

** * Basic strength $\propto K_b$

As K_b increases, basic strength of amine increases.

$\because pK_b = -\log K_b$

$\therefore pK_b = \log \frac{1}{K_b}$

$\therefore pK_b \propto \frac{1}{K_b}$

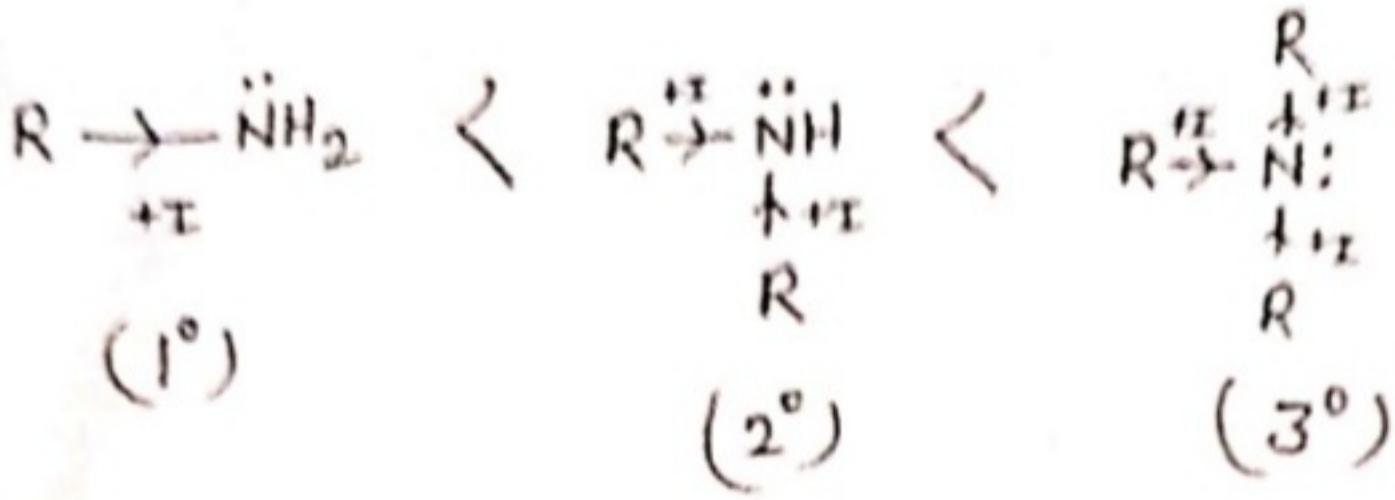
$\therefore pK_b \propto \frac{1}{K_b} \propto \frac{1}{\text{Basic strength}}$

* Basic strength of amine is inversely proportional to pK_b.

ie; Higher the pK_b value of amine, lesser will be their basic strength.

BASIC STRENGTH OF 1°,2° & 3°AMINE

In Gaseous Phase



(1°) (2°) (3°)

* With increase in no. of alkyl group attached to nitrogen, the electron density increases hence, the basic Staength is in following Oxdex.

$$1^\circ < 2^\circ < 3^\circ$$

In Aqueous Solution

The basic strength of amine is subtle interplay of the following thsee effect:-

1. Inductive effect
2. Solvation effect
3. Steric effect.

* On the basis of Inductive effect; the Order Should be

$$1^\circ < 2^\circ < 3^\circ$$

But in aqueous solution the conjugate acid of 1° amine is more stable than that of 2° and conjugate acid of

2° amine is more stable than that of 3° due to solvation effect. Therefore, Basic strength should be -

$$1^{\circ} > 2^{\circ} > 3^{\circ}$$

* Size of alkyl group decide steric effect.
* When the alkyl group is small like $-CH_3$, there is no steric effect.
* In case of bigger alkyl group there is steric hindrance due to H-bonding.

So, conclusively the order of basic Strength is subtle interplay of these effect.

* The order of basic strength in case of methyl substituted amines in aqueous solution is as follows.

$$\underset{(2^{\circ})}{(C_2H_5)_2NH} > \underset{(3^{\circ})}{(C_2H_5)_3N} > \underset{(1^{\circ})}{C_2H_5NH_2}$$

$$\underset{(1^{\circ})}{(CH_3)_2NH} > \underset{(2^{\circ})}{CH_3NH_2} > \underset{(3^{\circ})}{(CH_3)_3N}$$

Completed..