

AMINES AND UREA

(Lecture-2) 05-05-2020

TOPIC - BASIC STRENGTH OF AMINES

Degree-I (Hons.& Sub.)

P-II, C-4, C-4, G-'C'

BASIC STRENGTH OF AMINES

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

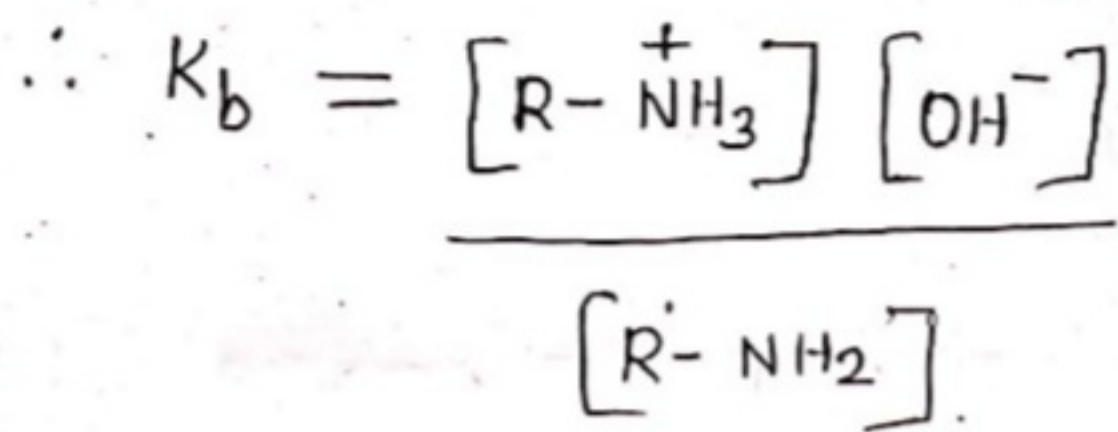


$$K_{eq} = \frac{[R-\overset{+}{N}H_3][OH^-]}{[R-NH_2][H_2O]}$$

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

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

2.



Where, K_b = Dissociation const. of base.

**
* Basic strength $\propto K_b$

As K_b increases, basic strength of amine increases.

$$\therefore pK_b = -\log K_b$$

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

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

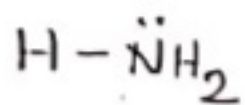
$pK_b \propto \frac{1}{K_b} \times \frac{1}{\text{Basic strength}}$

* Basic strength of amine is inversely proportional to pK_b .

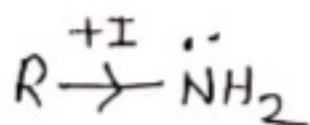
ie; Higher the pK_b value of amine, lesser will be their basic strength.

BASIC STRENGTH OF AMMONIA Vs. ALIPHATIC 3.

PRIMARY AMINE :-



Ammonia

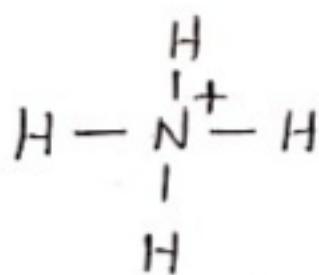


Aliphatic primary amine

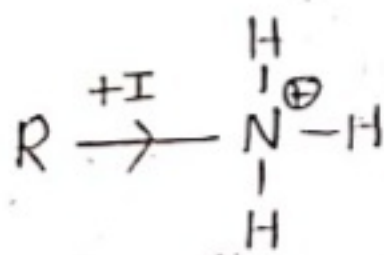
Due to +I effect of alkyl group, the electron density of N of 1° amine increases and hence, Aliphatic primary amine is stronger base than ammonia.

* The conjugate acid of NH_3 is NH_4^+ and the conjugate acid of 1° amine is $\text{R}-\text{NH}_3^+$.

* More stable the conjugate acid of a base, stronger is the base.



Ammonium ion



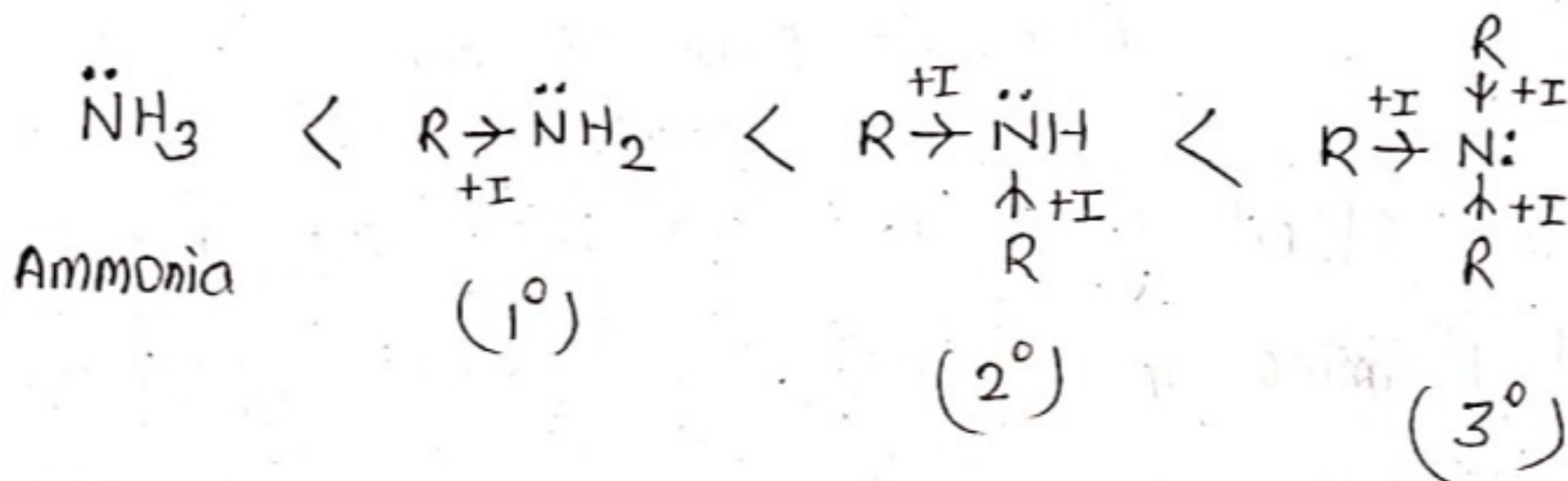
conjugate acid of 1° amine

(Conjugate acid of NH_3)

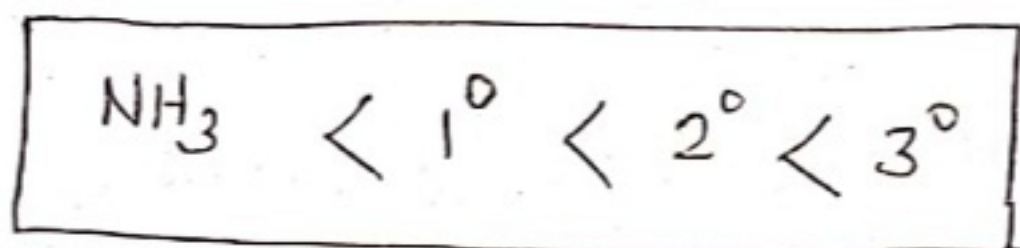
* Since the conjugate acid of 1° amine is stabilized by +I effect of alkyl group, hence more stable than the ammonium ion. Therefore, the aliphatic primary amine is stronger base than ammonia.

BASIC STRENGTH OF 1°, 2°, 3° AMINES AND AMMONIA 4.

IN GASEOUS PHASE



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

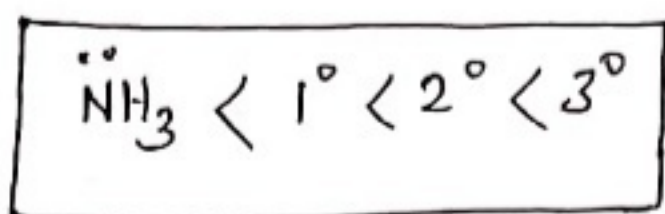


IN AQUEOUS SOLUTION

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

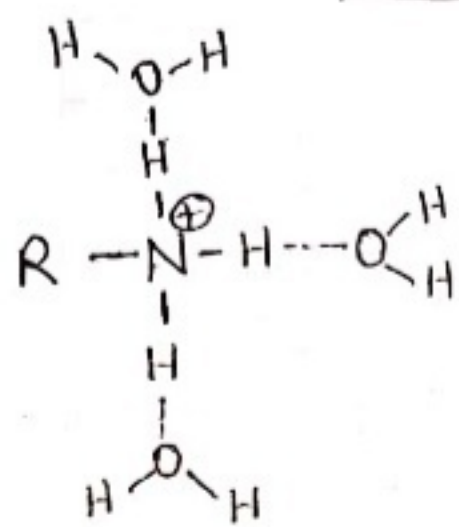
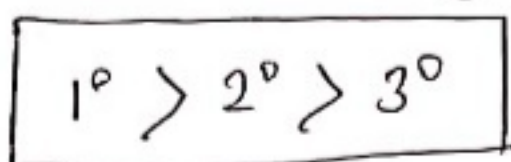
1. Inductive effect
2. Solvation effect
3. Steric effect

On the basis of inductive effect, the order should be. 5

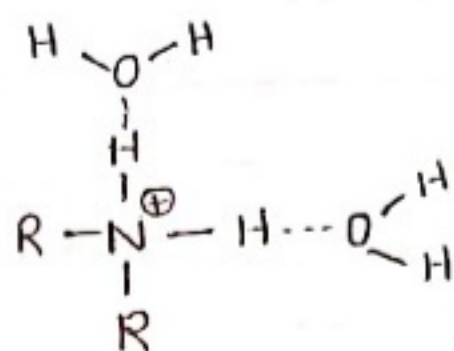


But in an aqueous solution the conjugate acid of 1° amine is more stable than that of 2° and conjugate acid of 2° amine is more stable than that of 3° due to solvation effect.

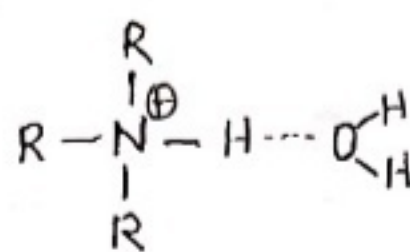
Therefore, Basic strength should be: -



Conjugate acid of
1° amine



Conjugate acid of
2° amine.

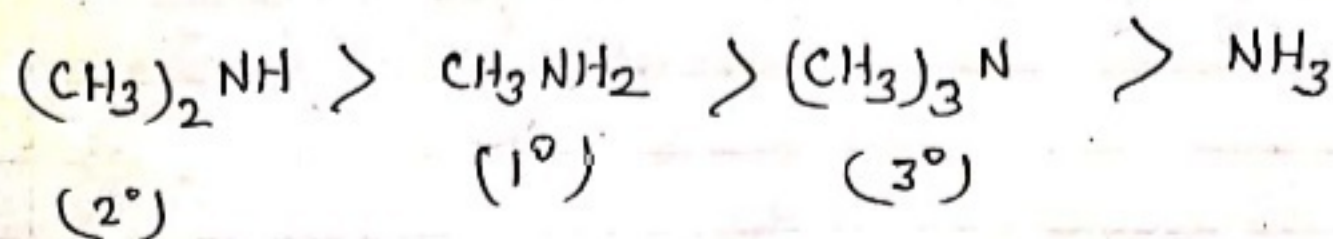
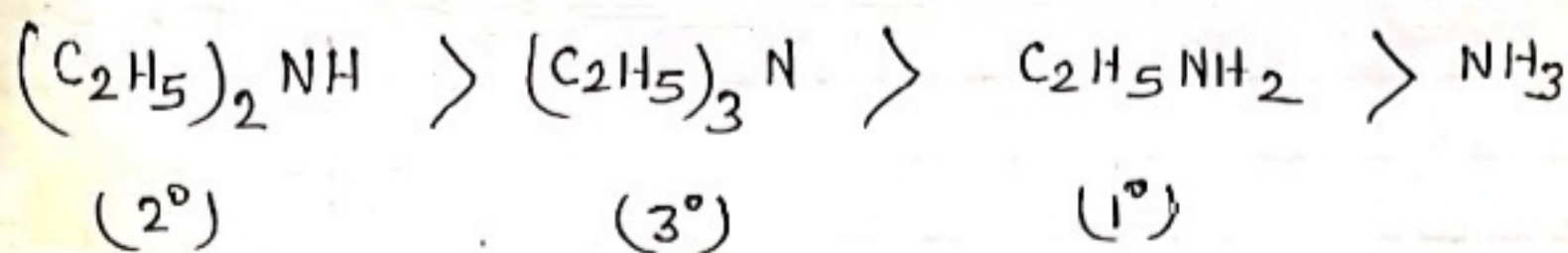


Conjugate acid
of 3° amine.

More the H₂O molecule attached, more stable will be conjugate acid.

- * Size of alkyl group decide steric effect.
- * When the alkyl group is small like -CH₃, there is no steric effects.
- * 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 and ethyl substituted amines in aqueous solution is as follows....



**Basic strength
of Amines
completed.**