

Basic Strength of Amines, DR. S. K. JHA.

Lec - 4

The basic strength of NH_3 is low than primary amine because lone pair on nitrogen atom is present on (NH_3) ammonia also and $-\text{in } \text{R}-\text{NH}_2$ (1° amine) ~~group~~ ^{also} but in primary amine one alkyl group is bonded with Nitrogen atom where alkyl group is electron donating group so it increases electron density on nitrogen atom or it increases +I effect on N, we know as +I effect increases basic strength increases, so 1° amine ($\text{R}-\text{NH}_2$) is stronger than NH_3 (ammonia).

Comparison of basic strength of amine among all three degree of amine depends on three factors mainly

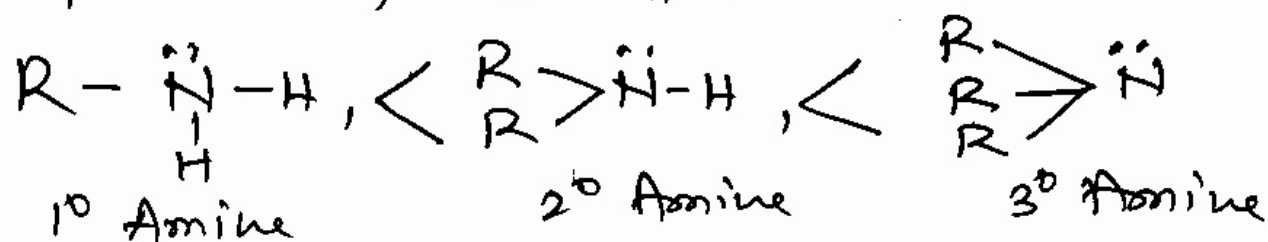
- i) +I effect
- ii) solvation or hydration effect
- iii) steric hindrance or steric effect.

Comparison of 1° Amine, 2° Amine & 3° Amines basic strength in Gaseous state -
When all three degree degree of amines i.e. 1° or primary amine ($\text{R}-\text{NH}_2$), 2° or Secondary amine (R_2NH) & 3° or tertiary amine (R_3N) are in Gaseous state then basic strength depends on only one factor i.e. +I effect.

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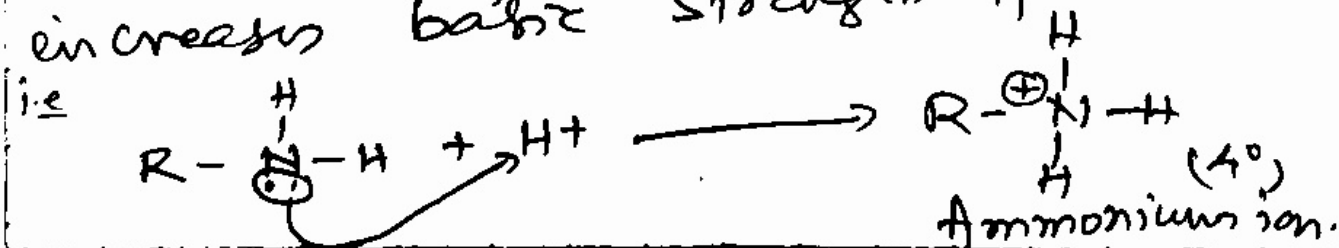
As +I effect increases in Gaseous State of amine their basic strength also increases.

Comparison of +I effect :-



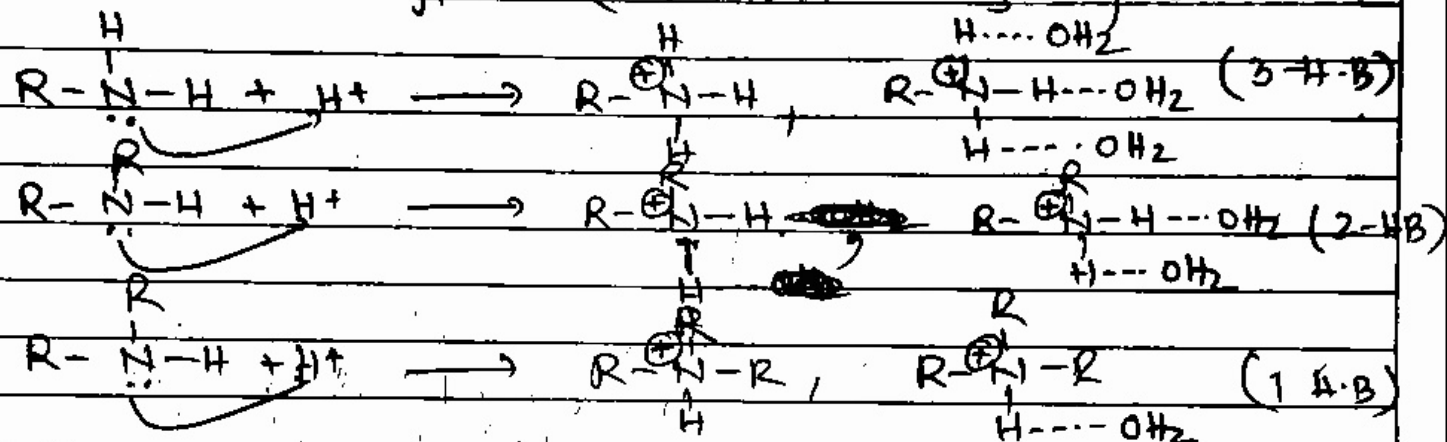
Due to presence of three alkyl group on 3° Amine its +I effect is maximum, due to two alkyl group in 2° amine its +I effect is lower than 3° Amine and in 1° amine due to presence of only one alkyl group its +I effect is lesser than 2° Amines & 3° Amines. So basic strength also are : $3^\circ \text{ Amine} > 2^\circ \text{ Amine} > 1^\circ \text{ Amine}$

Comparison in aqueous medium or in water: $\rightarrow$ In aqueous medium solvation and steric factor becomes dominant to explain basic strength of amines. Solvation means H-bonding of H & H_2O . As solvation increases basic strength of amine increases



4° Amine can be formed by 1° Amine, 2° amine & 3° amine, and in all cases the no. of hydrogen atoms bonded with positively charged Nitrogen atom are different. The no. of hydrogen atom bonded with positively charged Nitrogen atom is responsible for making hydrogen bond with water molecule (solvation or hydration).

Solvation effect $\propto$ Basic Strength of amines.



Solvation effect predicts :-

1° amines > 2° Amines > 3° Amines (for basic strength)

• If the alkyl group used in amine is methyl (CH_3) it's steric hindrance is minimum due to its small size. As the size of alkyl group increases steric hindrance also increases and it prevents the solvation or the no. of hydrogen bond in amine. means steric hindrance $\propto$ Basic strength

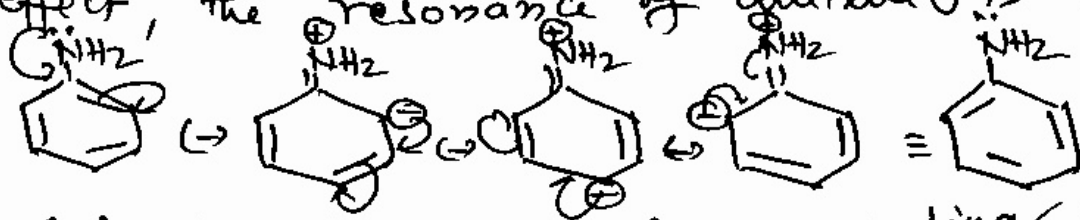
By experimental process it is observed that pK_b value of 2° Amine is smaller than 1° & 3° amine.
 For methyl group: 2° amine > 1° amine > 3° Amine
 For ethyl group: 2° amine > 3° Amine > 1° Amine

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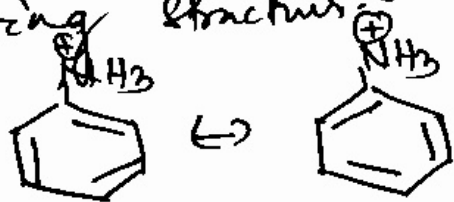
for basic strength

Basic strength of Aromatic amines: →

It has been found experimentally that pK_b value of aniline is very high, means it is very weak base. In aryl amine like aniline or benzamine NH_2 group is directly linked with benzene ring, so the lone pair of electron present on nitrogen atom participate in resonance (as activating group), so this lone pair of electron is available easily for protonation. In resonance NH_2 group is activating group for benzene ring and shows +R effect, the resonance of aniline is as follows:-



Actually there are four resonating str. But when one proton is accepted by aniline it forms anilinium ion (which is deactivating group & it becomes meta directing group), and it has only two resonating structures.



(There are only two resonating str.)

We know, no. of resonating str. & Basic strength & stability. So aniline is more stable than anilinium ion. In aniline availability of lone pair of e is less than ammonia to donate, so aniline is weaker base than ammonia. When in between benzene ring and NH_2 group there is other carbon then basic strength increases slightly.

