Basicity of Amines

All amines possess a lone pair of electron on the nitrogen atom. The basic character of these compounds depends upon how readily this lone pair of electron is available for coordination with a proton. Greater the tendency to donate the lone pair of electron, stronger the base. The basicity of amine is usually expressed by the following basicity constant K_b also known as the base dissociation constant.

$$K_b = \frac{[RNH_3^+][OH^-]}{[RNH_2]}$$

Larger the K_b value, stronger the base. For convenience the strength of base is usually indicated by its pK_b value.

$$pK_b = -\log K_b$$

Smaller the pK_b value, stronger will be the base.

In reaction (1) any structural feature that stabilizes the ammonium ion (relative to the free base), the amine would be a stronger base, whereas any structural feature that stabilizes the free amine (relative to ammonium ion), the amine would be a weaker base. Thus basicity of amines is largely dependent on the following factors

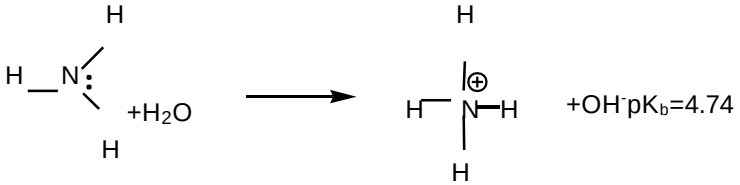
(i) + I and–I effect of alkyl groups

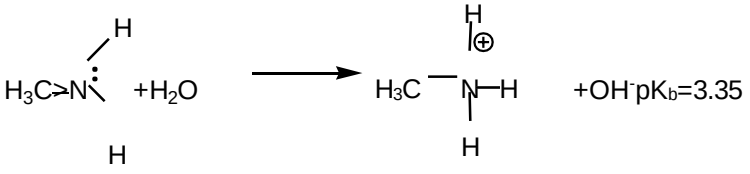
(ii) Hybridization

(iii) Steric effects

(iv) Resonance

Basicity of aliphatic amines: **(+I effect of alkyl groups**): In case of methylamine, the methyl group because of its +Ieffect helps to stabilize the positive charge on nitrogen (makes the lone pair of electron easily available for protonation). The positive charged ammonium ion is dispersed better because it has a methyl group instead of hydrogen. This stabilization lowers the potential energy of methyl ammonium cation, thus making it a strong base than ammonia.





Thus more the alkyl groups are attached to positively charged nitrogen, the more

stable the alkyl ammonium cation becomes and more basic the amine would be. As a result in gaseous phase tertiary amines are stronger bases in comparison to secondary amines which in turn would be stronger bases than primary amine.

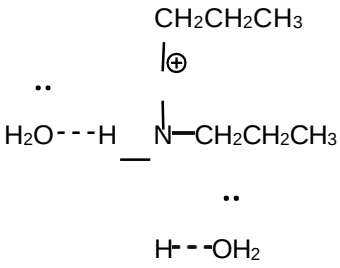
Basicityingaseous phase:$(CH_3)_3N>(CH_3)_2NH$ $>CH_3NH_2>NH_3$

Effect of hydrogen bonding and steric effect:

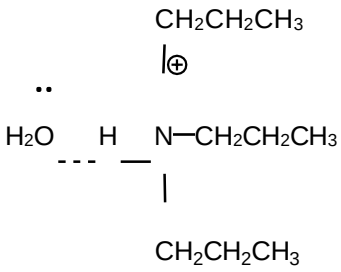
Thus it can be said that the basicity of amine in gaseous phase depeneds largely on the +I effect of the alkyl group. But this basicity order of amines does not hold true in aqueous solution. In aqueous phase tertiary amines are weaker bases even in comparison to primary amines. This altered order of amine basicity in solution is due to solvation effect.

Basicity in aqueous phase: $(CH_3CH_2)_2NH>CH_3CH_2NH_2>(CH_3CH_2)_3N>NH_3$

Alkyl substitution increases the ability of ammonium cation to disperse its positive charge but it decreases its ability to form hydrogen bond with water molecules. In case of secondary amines the dialkylammonium cation formed still has two hydrogens to undergo hydrogen bonding, whereas in case of tertiary amines, the trialkylammonium cation has only one hydrogen available for hydrogen bonding. As a result trialkylammonium cation is less stabilized in comparison to dialkylammonium cation. Besides this, the steric hinderance of the three-alkyl groups on t-amine also prevents the lone pair of electron to be attacked by H^+ ions. Hence secondary amines are stronger bases than tertiary amines.



Dipropylammonium cation (two hydrogen available for bonding)



Tripropylammonium cation (only one hydrogen available for bonding