

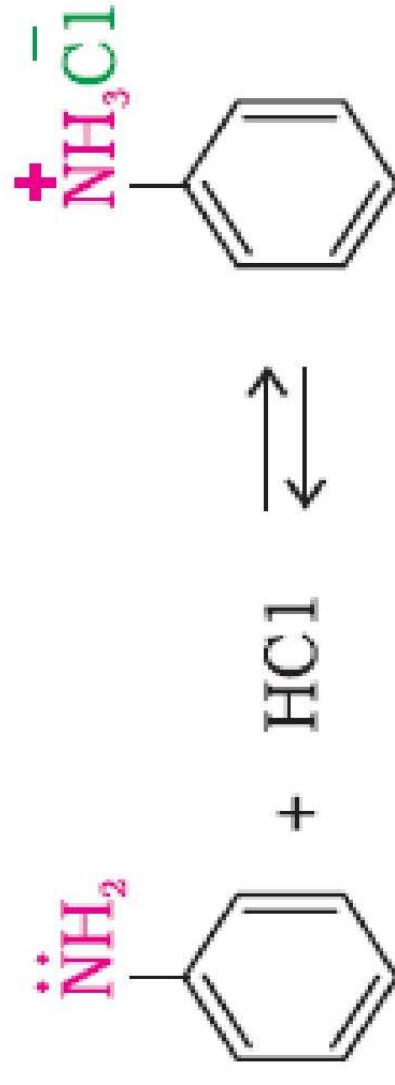
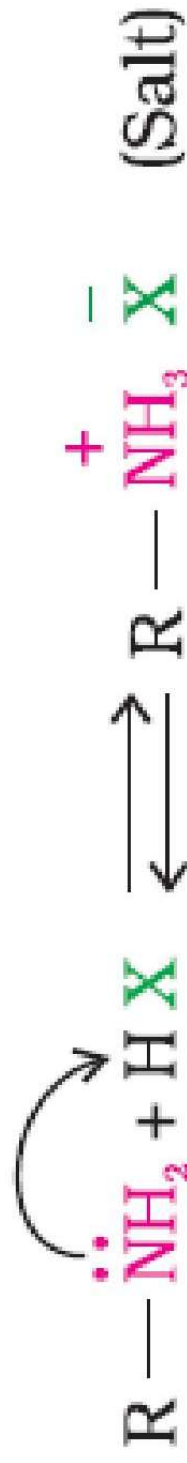
Basic Nature of Amines

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Basic character of amines

Amines, being basic in nature, react with acids to form salts



Aniline

Anilinium chloride

Why Amines are basic?

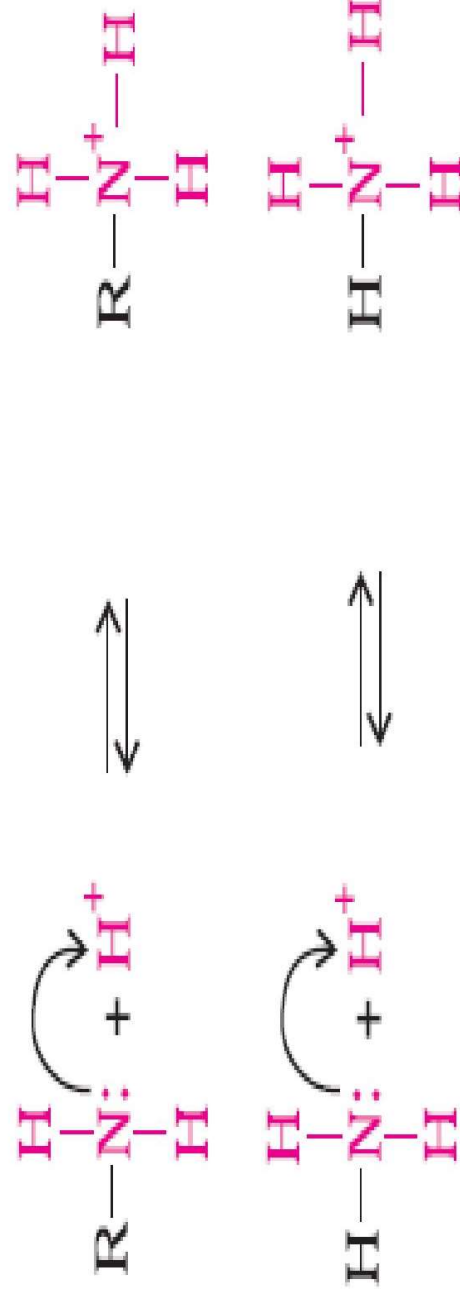
The reaction of amines with mineral acids to form ammonium salts shows that these are basic in nature. Amines have an unshared pair of electrons on nitrogen atom due to which they behave as Lewis base.

Structure-basicity relationship of amines

Basicity of amines is related to their structure. Basic character of an amine depends upon the ease of formation of the cation by accepting a proton from the acid. The more stable the cation is relative to the amine, more basic is the amine.

Alkanamines versus ammonia

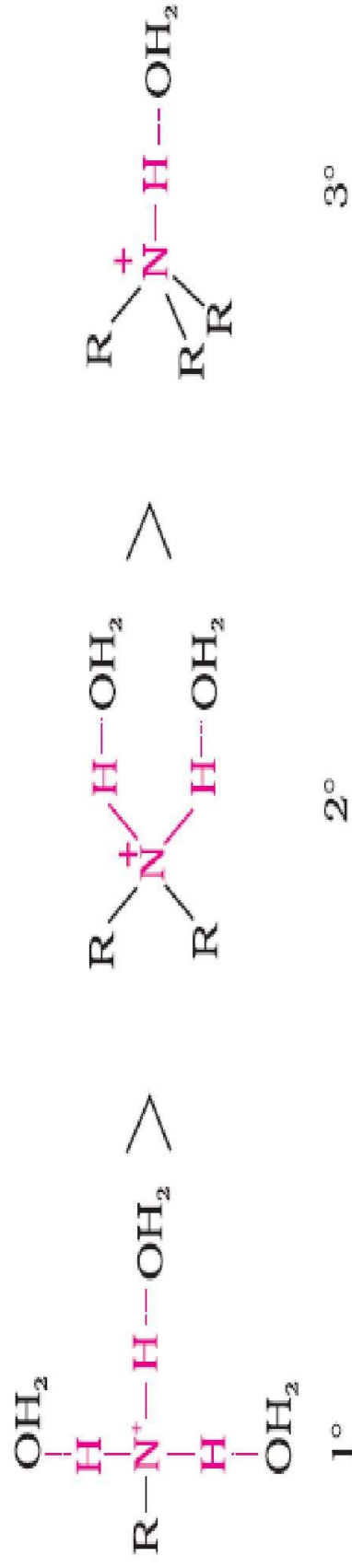
Consider the reaction of an alkanamine and ammonia with a proton to compare their basicity.



Due to the electron releasing nature of alkyl group, it (R) pushes electrons towards nitrogen and thus makes the unshared electron pair more available for sharing with the proton of the acid. Moreover, the substituted ammonium ion formed from the amine gets stabilized due to dispersal of the positive charge by the +I effect of the alkyl group. Hence, alkylamines are stronger bases than ammonia.

Thus, the basic nature of aliphatic amines should increase with increase in the number of alkyl groups. This trend is followed in the gaseous phase. The order of basicity of amines in the gaseous phase follows the expected order: tertiary amine > secondary amine > primary amine > NH₃.

In the aqueous phase, the substituted ammonium cations get stabilized not only by electron releasing effect of the alkyl group (+I) but also by solvation with water molecules. The greater the size of the ion, lesser will be the solvation and the less stabilised is the ion. The order of stability of ions are as follows:

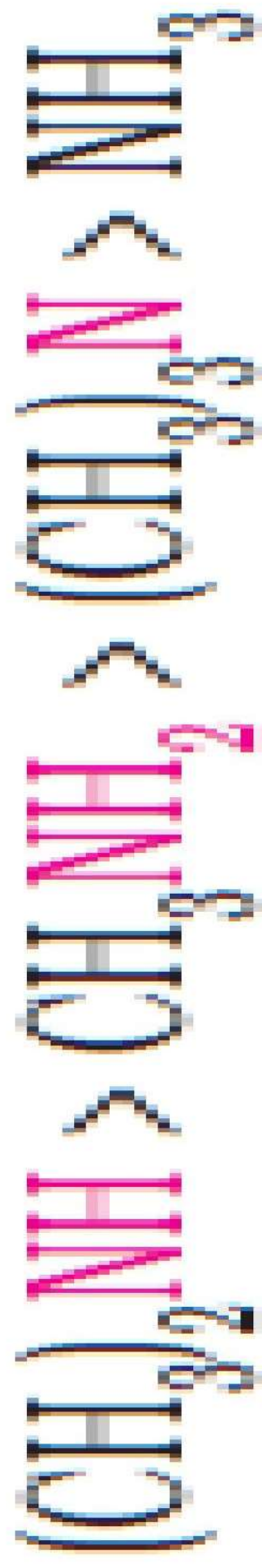


Greater is the stability of the substituted ammonium cation, stronger should be the corresponding amine as a base. Thus, the order of basicity of aliphatic amines should be:

primary > secondary > tertiary

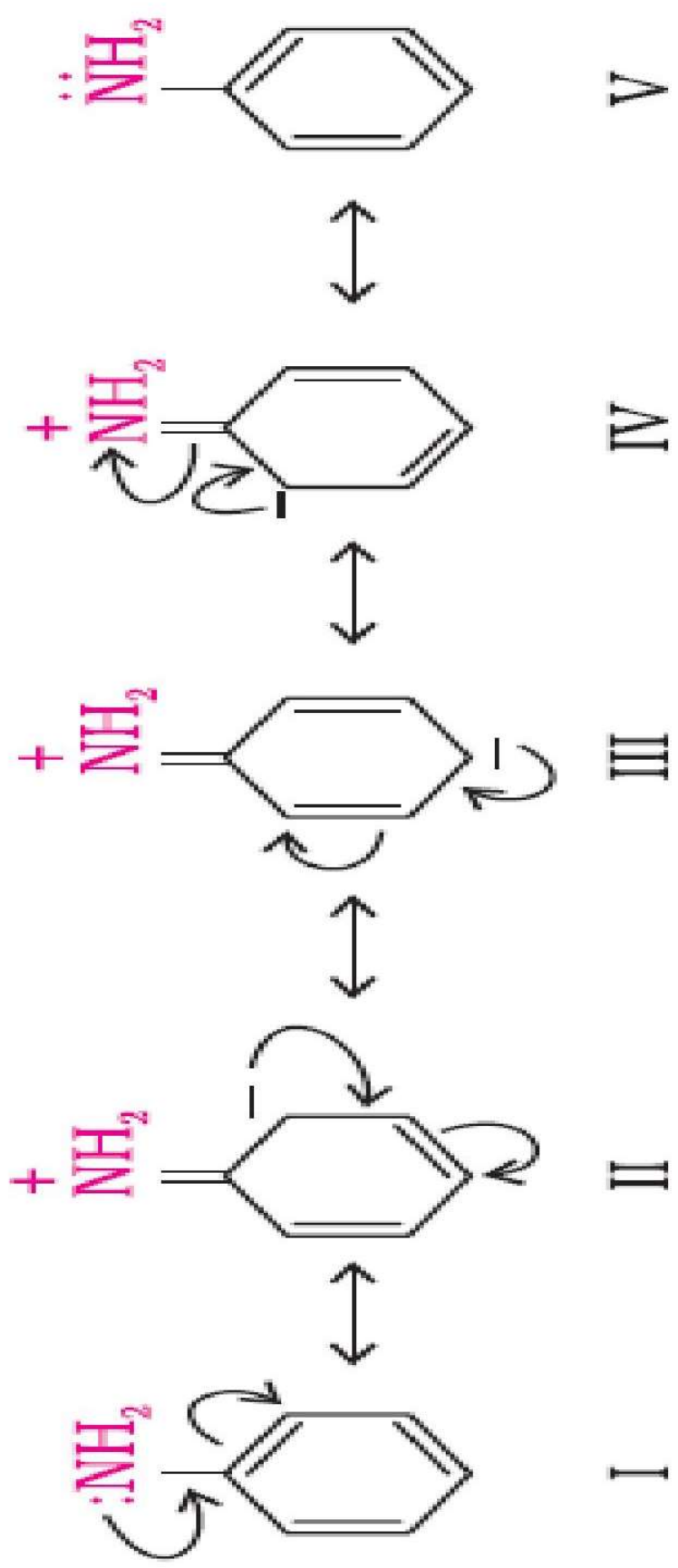
Which is opposite to the inductive effect based order.

Thus, there is a subtle interplay of the inductive effect, solvation effect and steric hinderance of the alkyl group which decides the basic strength of alkyl amines in the aqueous state. The order of basic strength in case of methyl substituted amines and ethyl substituted amines in aqueous solution is as follows:



Arylamines versus ammonia

pK_b value of aniline is quite high. Why is it so? It is because in aniline or other arylamines, the $-NH_2$ group is attached directly to the benzene ring. It results in the unshared electron pair on nitrogen atom to be in conjugation with the benzene ring and thus making it less available for protonation. If you write different resonating structures of aniline, you will find that aniline is a resonance hybrid of the following five structures.



Qus. Arrange the following in decreasing order of their basic strength:



The decreasing order of basic strength of the above amines and ammonia follows the following

order:



Thank You