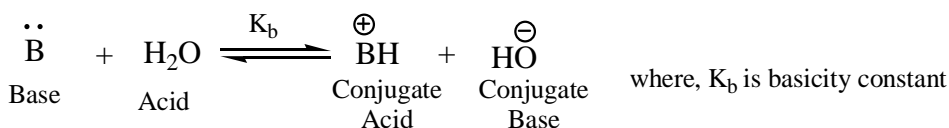
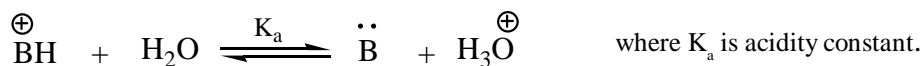


Bases: A base is a substance that accepts a proton (Bronsted-Lowry). Basic compounds have high pK_a -values and are good proton acceptors, as the cations (or conjugate acids), formed on protonation, are relatively stable.

In water:



The strength of bases are usually described by the K_a - and pK_a -values of the conjugate acid.

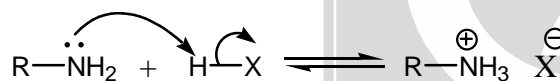


$$K_a = \frac{[\text{B}][\text{H}_3\text{O}^\oplus]}{[\text{BH}^\oplus]} \quad [\text{As H}_2\text{O is in excess}]$$

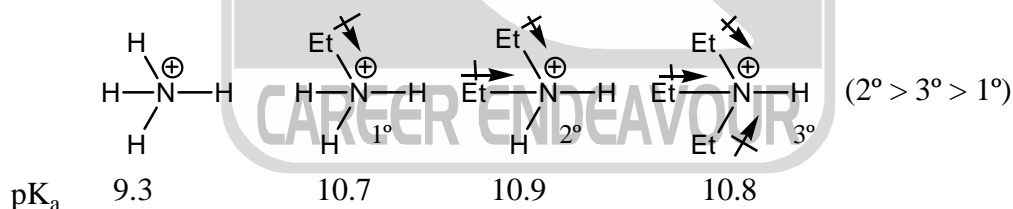
- If B is a strong base, then BH^\oplus will be relatively stable and not easily deprotonated. BH^\oplus will therefore have a high pK_a -value
- If B is a weak base, then BH^\oplus will be relatively unstable and easily deprotonated. BH^\oplus will therefore have a low pK_a -value.

The cation can be stabilised by +I and +M groups, which can delocalise the positive charge. (The more 'spread out' the positive charge, the more stable it is).

(c) Inductive effects and aliphatic (or alkyl) amines: On protonation of amines, ammonium salts are formed.

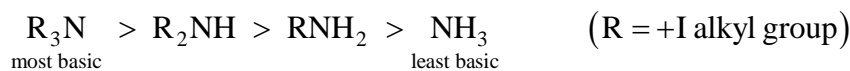


The greater the +I effect of the R group, the greater the electron density at nitrogen and the more basic the amine. The greater the +I effect, the more stable the ammonium cation and the more basic the amine.



The pK_a -values should increase steadily as more +I alkyl groups are introduced on nitrogen.

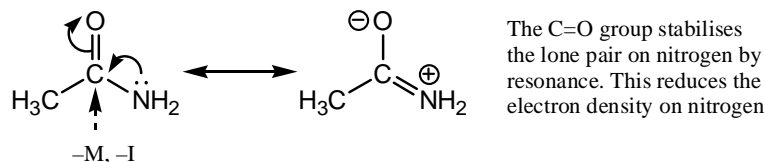
In organic solvents (which can not solvate the cation) or in gas phase, the order of pK_a s is expected to be as follows:



However, the pK_a -values are determined in water, and the more hydrogen atoms on the positively charged nitrogen, the greater the extent of hydrogen-bonding between water and the cation. This solvation leads to the stabilisation of the cations containing N–H bonds.

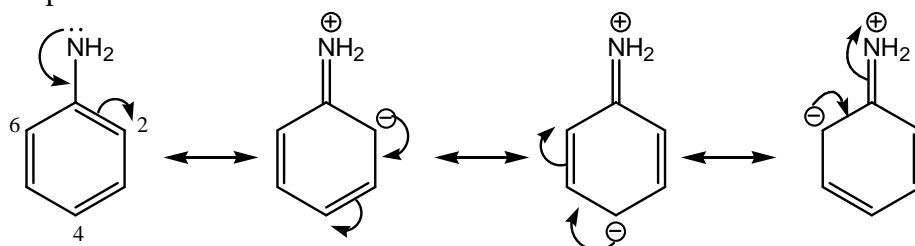
The presence of –I and/or –M groups on nitrogen reduces the basicity, and hence, for example, amides are poor bases.

Ethanamide has a pK_a of –0.5.

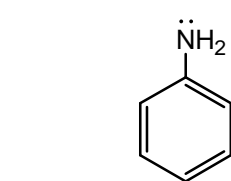


(d) Mesomeric effects and aryl (or aromatic) amines:

The lone pair of electrons on the nitrogen atom of aminobenzene (or aniline) can be stabilised by the delocalisation of the electrons onto the 2-, 4- and 6-positions of the benzene ring. Aromatic amines are therefore less basic than aliphatic amines.



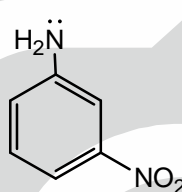
- If $-M$ groups are introduced at the 2-, 4- and/or 6-positions (but not at the 3- or 5-position), the anion can be further stabilised by delocalisation, as the negative charge can be spread onto the $-M$ group. This reduces the basicity of the amine.
- If $-I$ groups are introduced on the benzene ring, the order of $-I$ stabilisation is 2-position $>$ 3-position $>$ 4-position. This reduces the basicity of the amine.



pK_a

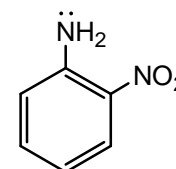
4.6

Most basic as no- I or $-M$ groups on the ring



2.45

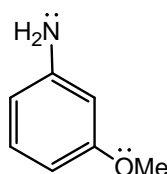
The NO_2 group can stabilise the lone pair inductively



-0.28

Least basic: The NO_2 group can stabilise the lone pair inductively and by resonance

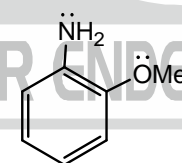
- If $+M$ group (e.g. OMe) are introduced at the 2-, 4- or 6-position of aminobenzene, then the basicity is increased. This is because the $+M$ group donates electron density to the carbon atom bearing the amine group.



pK_a

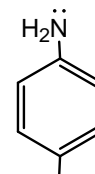
4.2

Least basic: The OMe group cannot donate electron density to the carbon atom bearing the nitrogen



4.5

The OMe group can donate electron density to the nitrogen but it has a strong $-I$ effect as it is in the 2-position

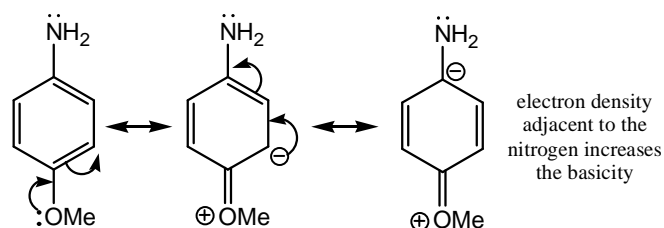


MeO

5.3

Most basic: The OMe group can donate electron density to the nitrogen and it has a weak $-I$ effect (as well apart from the nitrogen)

Curly arrows can be used to show the delocalisation of electrons onto the carbon atom bearing the nitrogen.



(e) Lewis acids and base:

- A Lewis acid is any substance that accepts an electron pair in forming a coordinate bond. Examples include H^+ , BF_3 , $AlCl_3$, $TiCl_4$, $ZnCl_2$ and $SnCl_4$. They have unfilled valence shells and hence can accept electron