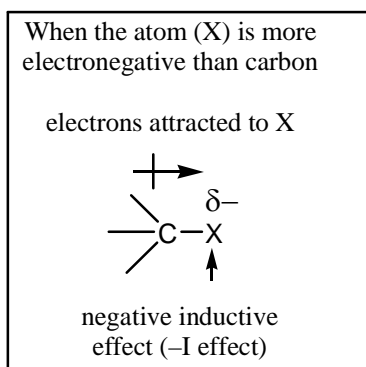


Basic Concepts of Organic Chemistry

1.1 Inductive effects, hyperconjugation and mesomeric effects:

(1) Inductive effects:

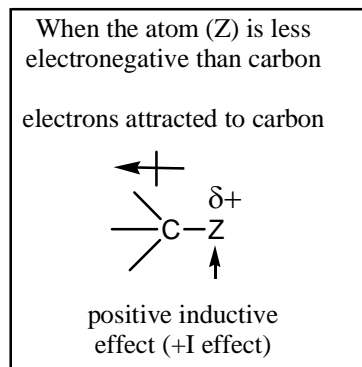
In a covalent bond between two different atoms, the electrons in the σ – bond are not shared equally. The electrons are attracted towards the most electronegative atom. An arrow drawn above the line representing the covalently bonded electrons shifts towards higher electronegative atom can show this. Electrons are pulled in the direction of the arrow.



–I groups

X=Br, Cl, NO₂, OH, OR, SH,
SR, NH₂, NHR, NR₂, CN, CO₂H,
CHO, COR

The more electronegative the atom(X),
the stronger the –I effect

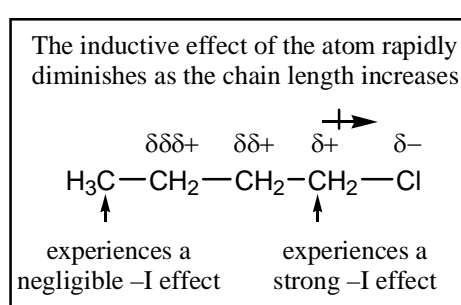


+I groups

Z=R(alkyl or aryl),
metals (e.g. Li or Mg)

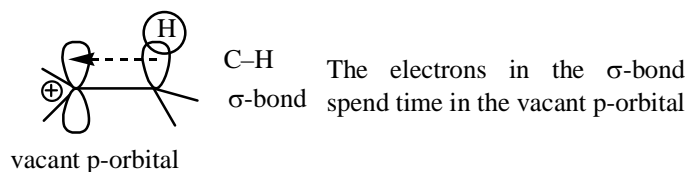
The more electropositive the atom (Z),
the stronger the +I effect.

Pauling electronegativity scale	
K = 0.8	I = 2.5
C = 2.5	Br = 2.8
N = 3.0	Cl = 3.0
O = 3.5	F = 4.0
Higher the value, more electronegative will be atom	



The overall polarity of a molecule is determined by the individual bond polarities, formal charges and lone pair contributions, and this can be measured by the dipole moment (μ). Higher the dipole moment (measured in debyes (D)), more polar will be compound.

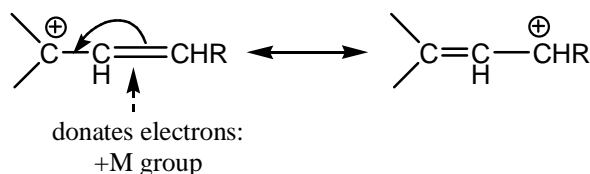
(2) Hyperconjugation: A σ – bond can stabilise a neighbouring carbocation (or positively charged carbon) by donating electrons to the vacant p-orbital. The positive charge is delocalised or ‘spread out’, and this stabilising effect is known as “*no-bond resonance*”.



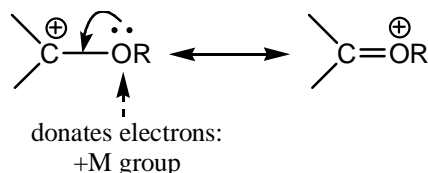
(3) Mesomeric effects: Whilst inductive effects pull electrons through the σ – bond framework, electrons can also move through the π – bond network. A π – bond can stabilise a negative charge, a positive charge, a lone pair of electrons or an adjacent bond by resonance (i.e. delocalisation or ‘spreading out’ of the electrons). Curly arrows are used to represent the movement of π or non-bonding electrons to give different resonance forms. It is only the electrons, not the nuclei, that move in the resonance forms and a double-headed arrow is used to show their relationship.

(a) Positive mesomeric effect:

- When a π -system donates electrons, the π -system has a positive mesomeric effect (+M effect).

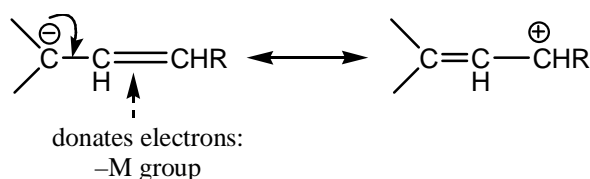


- When a lone pair of electrons is donated, the group donating the electrons has a positive mesomeric effect.



(b) Negative mesomeric effect:

- When a π – system accepts electrons, the π – system has a negative mesomeric effect (–M effect).

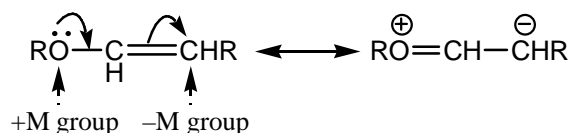


The actual structures of the cations or anions lie somewhere between the two resonance forms. All resonance forms must have the same overall charge and obey the same rules of valency.

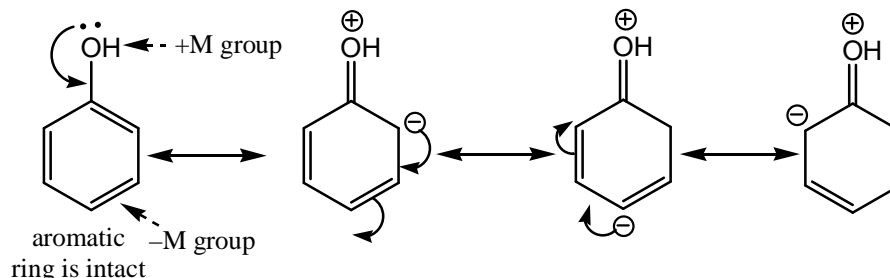
–M groups generally contain an electronegative atom(s) and/or a π -bond(s):
 CHO, C(O)R, CO₂H, CO₂Me, NO₂, aromatics groups, alkenes etc.
 +M groups generally contain at least a lone pair of electrons or a π -bond(s):
 :Cl:, :Br:, :OH:, :OR:, :SH:, NH₂, NHR, NR₂, aromatics, alkenes etc.
 Aromatic (or aryl) groups and alkenes can be both +M or –M effect.

In neutral compounds, there will always be a +M and –M groups(s):

One group donates (+M) the electrons and the other group(s) accepts the electrons(–M).



All resonance forms are not of the same energy. In phenol, for example, the resonance form which the intact aromatic benzene ring is expected to predominate.



As a rule of thumb, the more resonance structures an anion, cation or neutral π -system can have, the more stable it is.

Inductive versus mesomeric effects:

Mesomeric effects are generally stronger than inductive effects. A +M group is likely to stabilise an anion more effectively than a +I group.

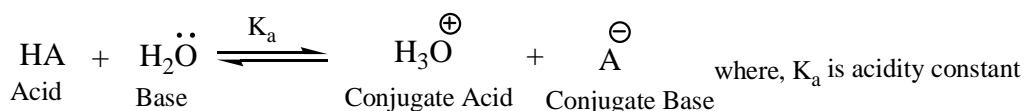
Mesomeric effects can be effective over much longer distances than inductive effects, provided that conjugation is present (i.e. alternating single and double bonds). Whereas inductive effects are determined by distance, mesomeric effects are determined by the relative positions of +M and –M groups in a molecule.

1.2 Application of inductive effect, hyperconjugation and mesomeric effect:

Acidity and basicity:

Acids: An acid is a substance that donates a proton (Bronsted-Lowry). Acidic compounds have low pK_a -values and are good proton donors, as the anions (or conjugate bases), formed on the deprotonation, are relatively stable.

In water:



The more stable the conjugate base the stronger the acid

$$K_a = \frac{[\text{H}_3\text{O}^{\oplus}][\text{A}^{\ominus}]}{[\text{HA}]}$$

As H_2O is in excess

$$pK_a = -\log_{10} K_a$$

The higher the value of K_a , the lower the pK_a value and the more acidic is HA

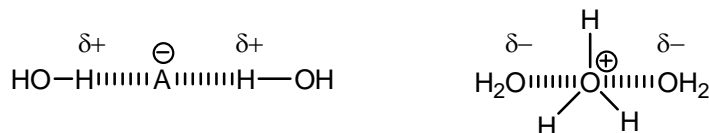
The pK_a -value equals the pH of the acid when it is half dissociated. At pH above the pK_a the acid exists predominantly as the conjugate base in water. At pH below the pK_a , it exists predominantly as HA.

pH = 0 (strongly acidic)

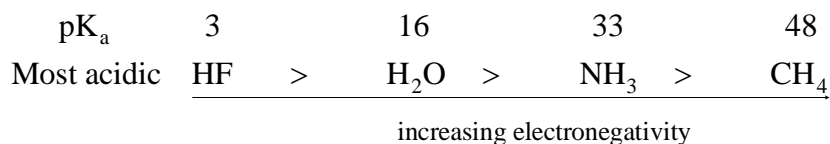
pH = 7 (neutral)

pH = 14 (strongly basic)

The pK_a -values are influenced by the solvent. Polar solvents will stabilise cations and/or anions by solvation, in which the charge is delocalised over the solvent (e.g. by hydrogen-bonding in water).



The more electronegative the atom bearing the negative charge, the more stable the conjugate base (which is negatively charged).



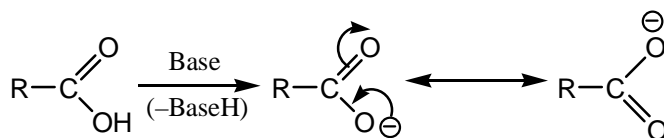
Therefore, F[⊖] is more stable than H₃C[⊖].

The conjugate base can also be stabilised by –I and –M groups which can delocalise the negative charge. (The more spread out the negative charge, the more stable it is)

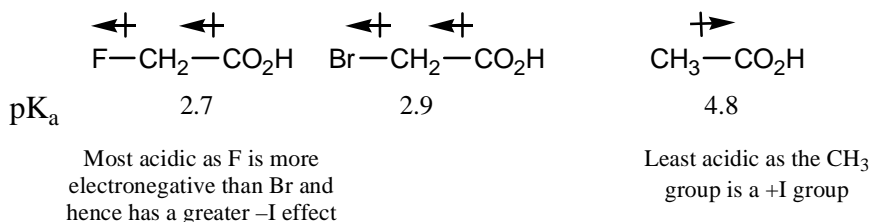
–I and –M groups therefore lower the pK_a, while
+I and +M groups raise the pK_a

(a) Inductive effects and carboxylic acids:

The carboxylate anion is formed on deprotonation of carboxylic acids. The anion is stabilised by resonance (i.e. the charge is spread over both oxygen atoms) but can also be stabilised by the R group if this has a –I effect.



The greater the –I effect, the more stable the carboxylate anion and the more acidic is carboxylic acid.

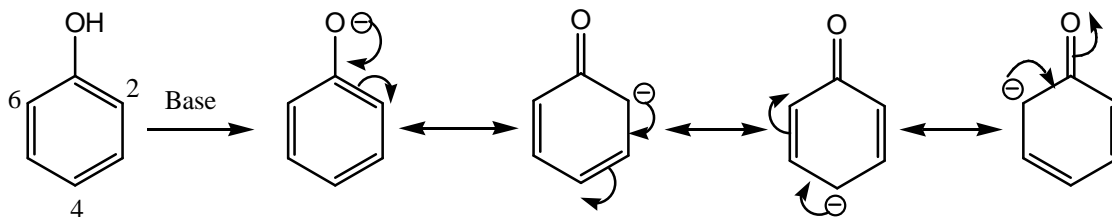


(b) Inductive and mesomeric effects and phenols:

Mesomeric effects can also stabilise positive and negative charges.

The negative charge needs to be on adjacent carbon atom for a –M group to stabilise it
The positive charge needs to be on adjacent carbon atom for a +M group to stabilise it

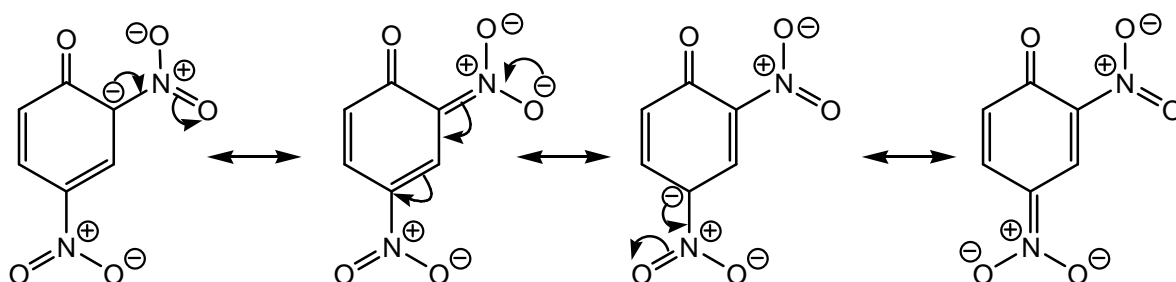
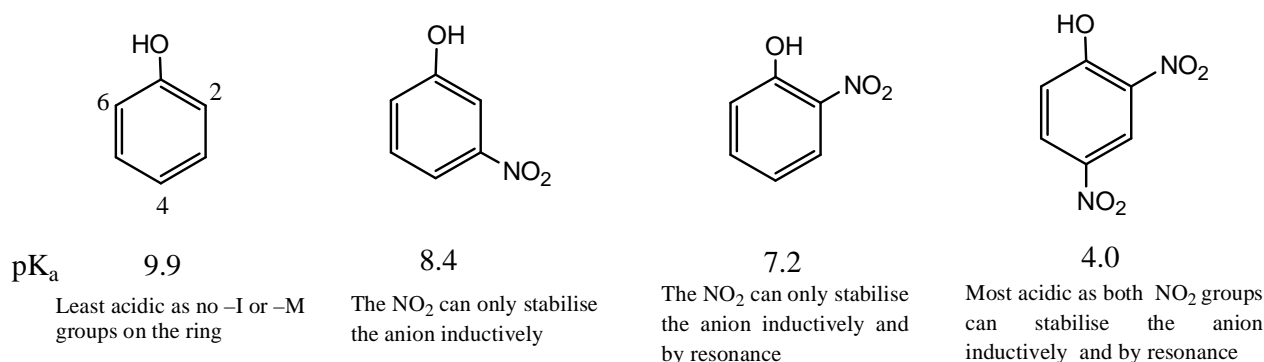
On deprotonation of phenol the phenoxide anion is formed. This is stabilised by delocalisation of the negative charge at the 2-, 4- and 6-positions of the benzene ring.



Keynotes in Organic Chemistry:

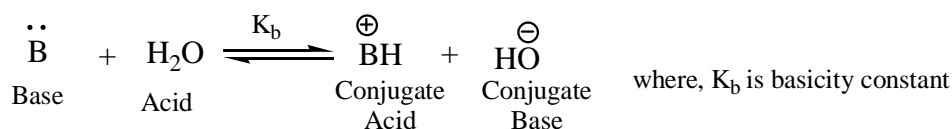
- If –M groups are introduced at 2-, 4- and/or 6-positions, the anion can be further stabilised by delocalisation through the π -system, as the negative charge can be spread onto the –M group. We can use double-headed curly arrows to show this process.
- If –M groups are introduced at the 3- and/or 5-positions, the anion can not be stabilised by delocalisation, as the negative charge cannot be spread onto the –M group. There is no way of using curly arrows to delocalise the charge onto the –M groups.
- If –I groups are introduced on the benzene ring, the effect will depend on their distance from the negative charge. The closer the –I group is to the negative charge, the greater the stabilising effect will be. The order of –I stabilisation is therefore 2-position > 3-position > 4-position.
- The –M effects are much stronger than –I effects.

Example: The NO_2 group is strongly electron-withdrawing; –I and –M.

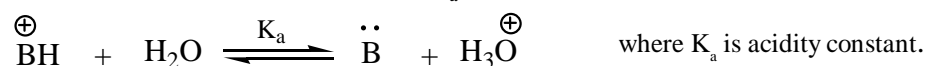


Bases: A base is a substance that accepts a proton (Bronsted-Lowry). Basic compounds have high pK_a -values and are good proton acceptors, as the cations (or conjugate acids), formed on protonation, are relatively stable.

In water:



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

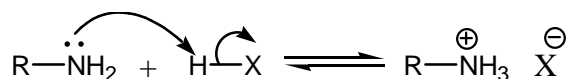


$$K_a = \frac{[\text{B}][\text{H}_3\text{O}^{\oplus}]}{[\text{BH}^{\oplus}]} \quad [\text{As } \text{H}_2\text{O} \text{ is in excess}]$$

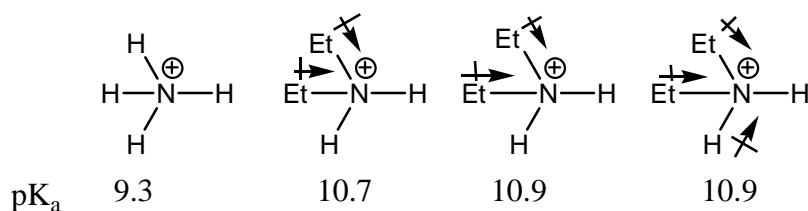
- If B is a strong base, then BH^{\oplus} will be relatively stable and not easily deprotonated. BH^{\oplus} will therefore have a high pK_a -value
- If B is a weak base, then BH^{\oplus} will be relatively unstable and easily deprotonated. BH^{\oplus} will therefore have a low pK_a -value.

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.



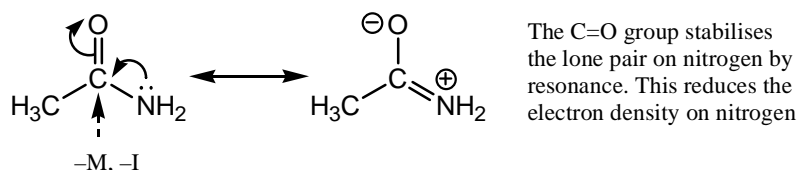
The pK_a -values should increase steadily as more +I alkyl groups are introduced on nitrogen. However, the pK_a -values are determined in water, and the more hydrogen atoms on the positively charged nitrogen, the greater the extent of hydrogen-bonding between water and the cation. This solvation leads to the stabilisation of the cations containing N–H bonds.

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



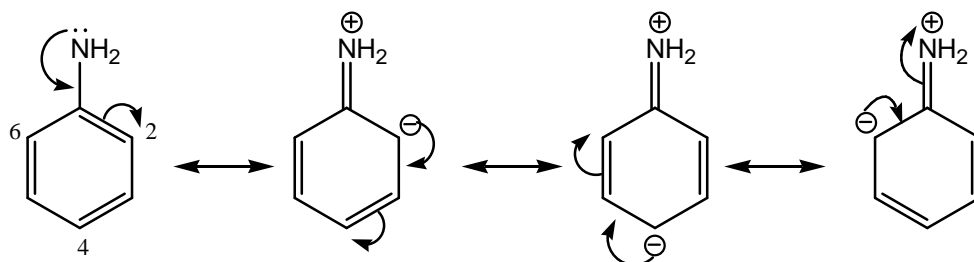
The presence of –I and/or –M groups on nitrogen reduces the basicity, and hence, for example, amides are poor bases.

Ethanamide has a pK_a of –0.5.

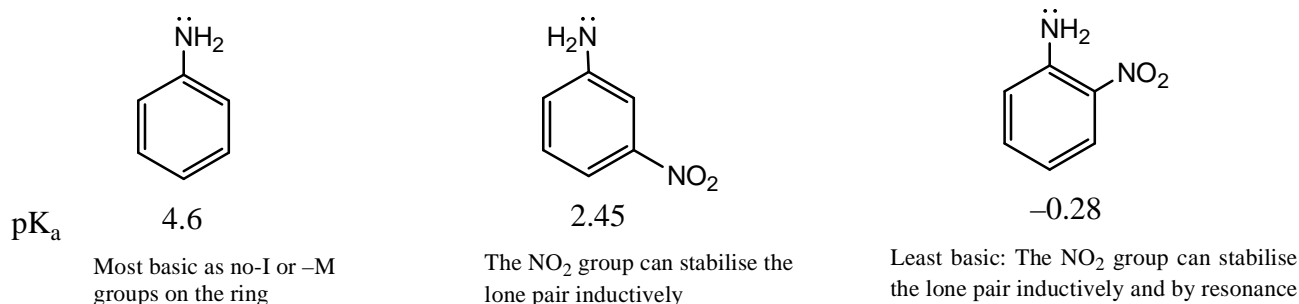


(d) Mesomeric effects and aryl (or aromatic) amines:

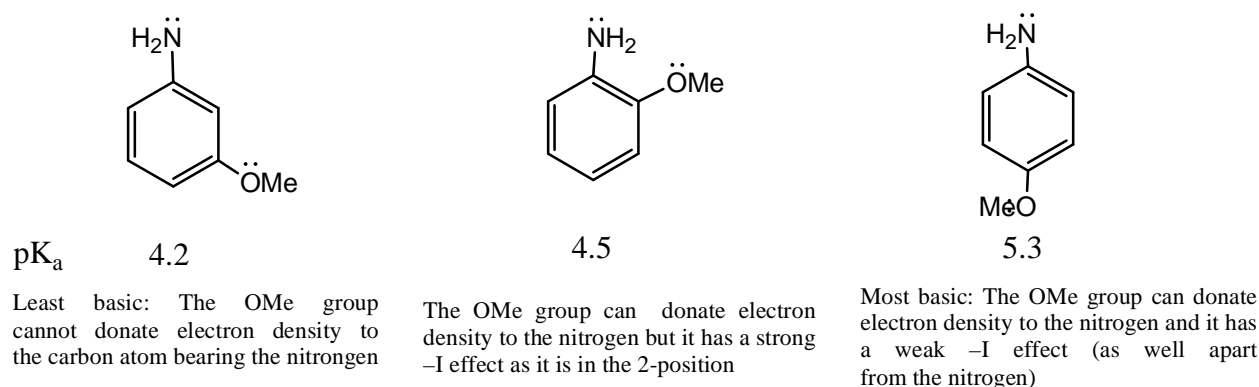
The lone pair of electrons on the nitrogen atom of aminobenzene (or aniline) can be stabilised by the delocalisation of the electrons onto the 2-, 4- and 6-positions of the benzene ring. Aromatic amines are therefore less basic than aliphatic amines.



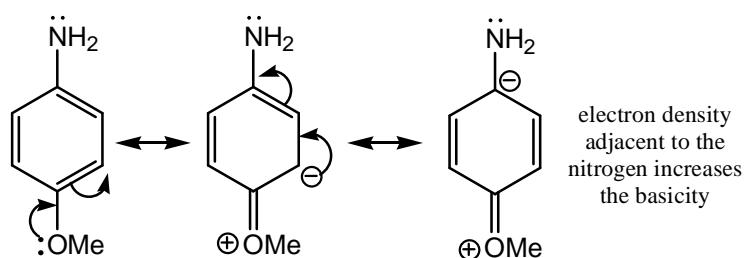
- If $-M$ groups are introduced at the 2-, 4- and/or 6-positions (but not at the 3- or 5-position), the anion can be further stabilised by delocalisation, as the negative charge can be spread onto the $-M$ group. This reduces the basicity of the amine.
- If $-I$ groups are introduced on the benzene ring,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



- 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.

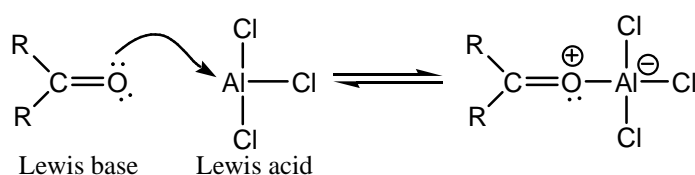


Curly arrows can be used to show the delocalisation of electrons onto the carbon atom bearing the nitrogen.



(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 pairs.
- A Lewis base is any substance that donates an electron pair in forming a coordinate bond. Examples include H_2O , ROH , $RCHO$, R_2CO , R_3N and R_2S . They all have a lone pair(s) of electrons on the hetero atom (O, N or S)



(f) Basicity and hybridisation:

The greater the 's' character of an orbital, the lower is energy the electrons and the more tightly the electrons are held to the nucleus. The electrons in an sp-orbital are therefore less available for protonation than those in an sp²- or sp³-hybrid orbital and hence the compounds are less basic.

