

Inductive versus mesomeric effects:

Mesomeric effects are generally stronger than inductive effects. A +M group is likely to stabilise a cation 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.

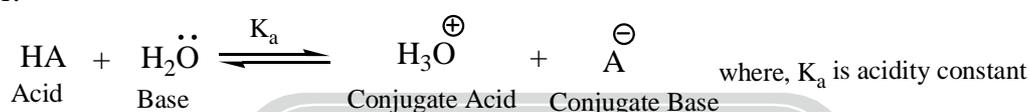
Inductive versus mesomeric effects:

Resonance : Delocalization of electrons in ground state and excited state. But mesomeric involved only ground state delocalization.

1.8. 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

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

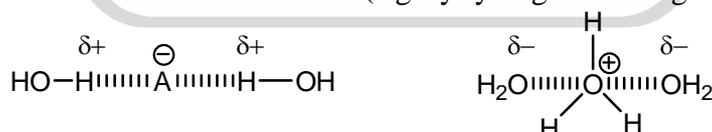
The higher the value of K_a , the lower the pK_a value and the more acidic is HA

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.

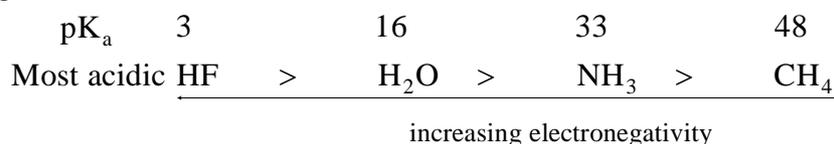
$$pH = pK_a + \log \left\{ \frac{[\text{A}^{\ominus}]}{[\text{HA}]} \right\}$$

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).



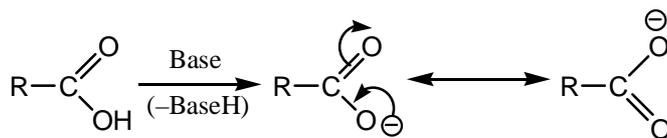
Therefore, F^{\ominus} is more stable than $\text{H}_3\text{C}^{\ominus}$.

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)

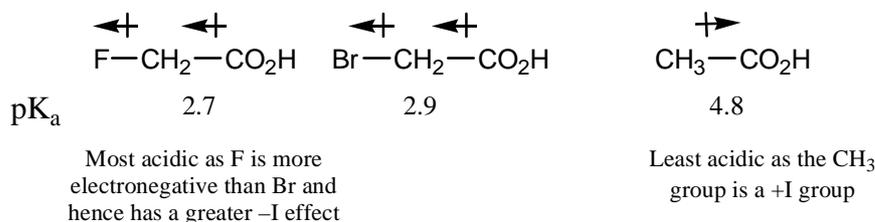
-I and -M groups therefore lower the pK_a , while
+I and +M groups raise the pK_a

(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.



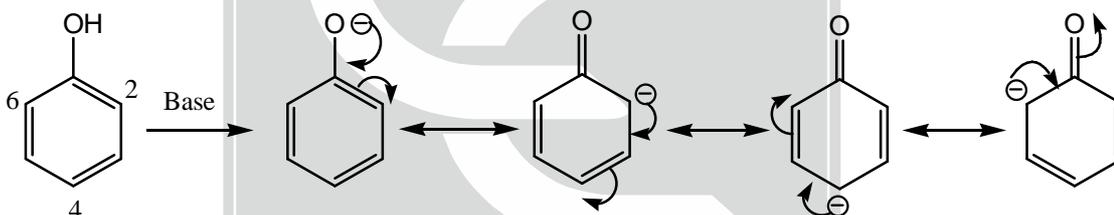
The greater the -I effect, the more stable the carboxylate anion and the more acidic is carboxylic acid.

**(b) Inductive and mesomeric effects and phenols:**

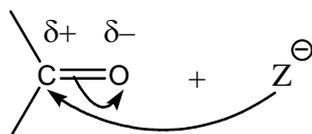
Mesomeric effects can also stabilise positive and negative charges.

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.

**Temporary Effect :****(a) Electromeric Effect :**

- Temporary effect.
- Takes place between two atoms joined by a multiple bond
- Occurs at requirement of attacking reagent.



Instantaneous shift of electron pair of carbonyl group towards oxygen.

It is of two types.

(1) + E effect : Transition of electron towards the attacking reagent.

