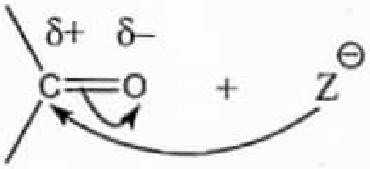
Temporary Effect :

(a) Electromeric Effect :

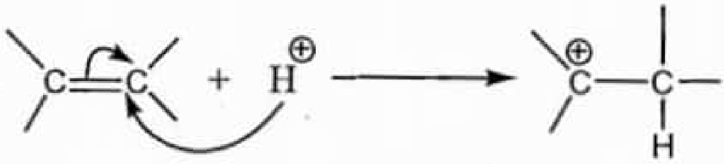
- Temporary effect.
- Takes place between two atoms joined by a multiple bond
- Occurs at requirement of attacking reagent.



Instantaneous shift of electron pair of carbonyl group towards oxygen.

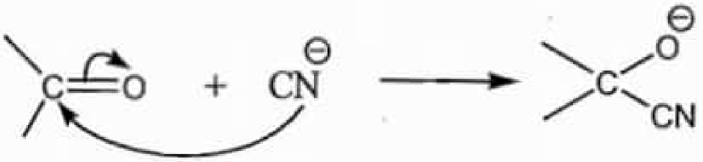
It is of two types.

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



(2) –E effect :

Transition of electron away from attacking reagent.



(b) Inductomeric Effect ;

- Temporary effect.
- Takes place in sigma bonded system
- In presence of attacking reagent, transition of a electron cloud takes place more readily.

Example :

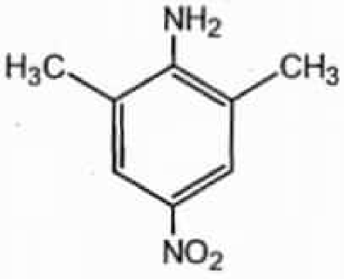
$$R—O \leftarrow H \quad + \quad B^{\ominus} \longrightarrow$$

In presence of base B, movement of sigma electron takes place faster.

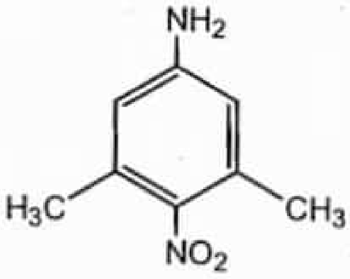
(3) Other Effect :

(a) Effect of inertia/steric inhibition of resonance:

Resonance ability of an atom is lost if it looses planarity with the other part of the system due to steric crowding by bulky group in adjacent positions.



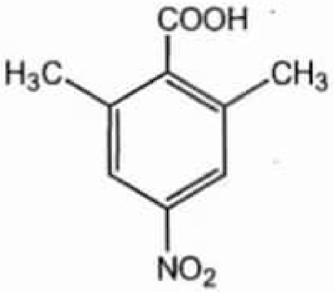
(A)



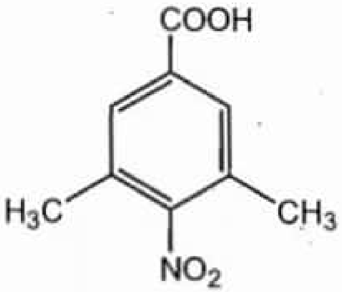
(B)

The above two compounds A and B have everything identical except position of the two methyl group. It is expected that A should be stronger base than B due to closeness of two electron donating methyl group to $-NH_2$. The fact is opposite to this. In compound B $-NO_2$ is surrounded by two bulky methyl group and they sterically repel the $-NO_2$ group. In order to minimize the steric repulsion by the two adjacent methyl group, the nitro group loses planarity with the benzene ring. So, now $-NO_2$ due to lack of planarity weigh ring, not able to resonate. This is known as steric inhibition of resonance. Thus in B , $-NO_2$ is not decreasing basic strength by resonance. In A $-NO_2$ lies in the plane of the ring, it is in resonance with the ring, decreases basic strength of $-NH_2$ by resonance, hence weaker base.

Similarly we can explain the acidic strength of C and D



(C)

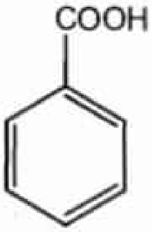


(D)

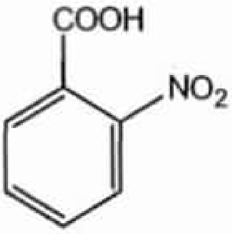
C is stronger acid inspite of closeness of two electron donating methyl group to $-COOH$.

(b) Ortho effect: If any group present on ortho position of the benzoic acid. It always increases acidic nature of acid because this group decreases outer resonance of the ring toward acidic nature. Similarly if any group present on ortho position of aniline, it decreases basic nature. This effect is known as ortho effect.

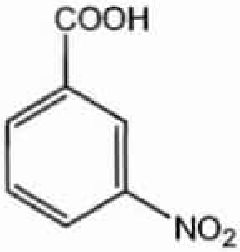
Problem : The correct order of acidity among the following compound I-IV is



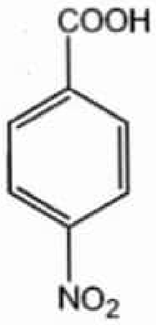
(I)



(II)



(III)



(IV)

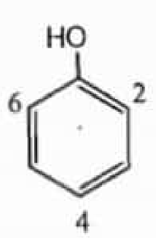
(a) II > III > IV > I (b) IV > II > III > I (c) II > IV > III > I (d) IV > III > II > I

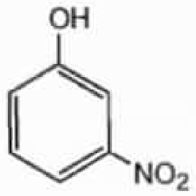
Because of ortho effect o-nitro benzoic acid is most acidic followed by para and meta.

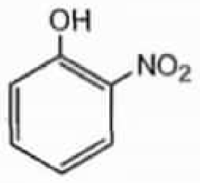
Thus order will be II > IV > III > I.

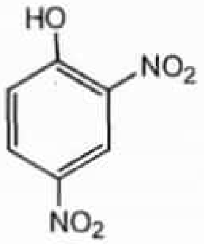
Hence, option (c) is correct.

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

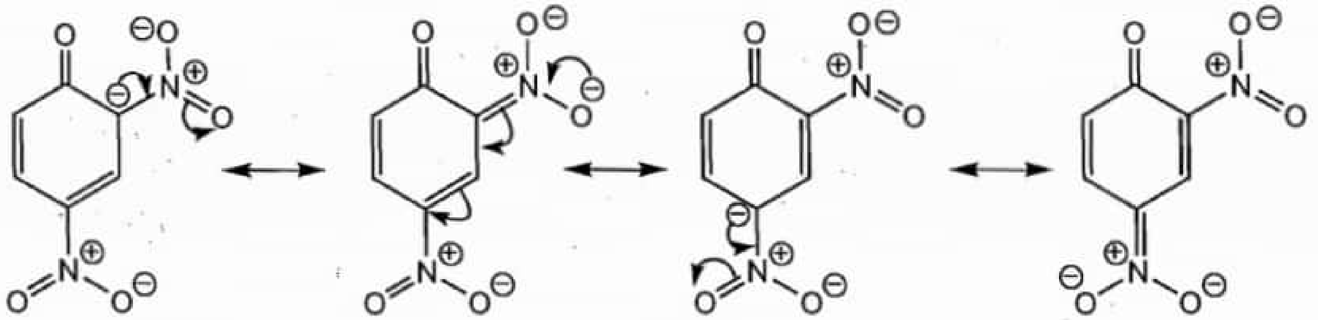








pK_a	9.9	8.4	7.2	4.0
	Least acidic as no –I or –M groups on the ring	The NO_2 can only stabilise the anion inductively	The NO_2 can only stabilise the anion inductively and by resonance	Most acidic as both NO_2 groups can stabilise the anion inductively and by resonance



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*:**

$$\underset{\text{Base}}{\overset{\bullet\bullet}{B}} + \underset{\text{Acid}}{H_2O} \xrightleftharpoons{K_b} \underset{\substack{\text{Conjugate}\\ \text{Acid}}}{\overset{\oplus}{BH}} + \underset{\substack{\text{Conjugate}\\ \text{Base}}}{\overset{\ominus}{HO}}$$

where, K_b is basicity constant

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

$$\overset{\oplus}{BH} + H_2O \xrightleftharpoons{K_a} \overset{\bullet\bullet}{B} + \overset{\oplus}{H_3O}$$

where K_a is acidity constant.

$$K_a = \frac{[B][H_3O^+]}{[^+BH]}$$

[As H_2O is in excess]

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