

Acidity & Basicity of Organic Compounds

ACIDITY

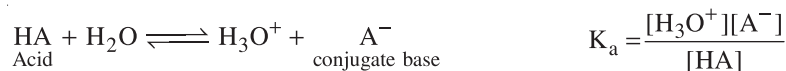
Section - 1

According to the definition of Arrhenius, acids are compounds that yield hydrogen ions, H^+ , in solution while bases yield hydroxide ions, OH^- .

Bronsted defined acids as substances that would give up protons, i.e. proton donors, while bases were proton acceptors.

Lewis defined acids as molecules or ions capable of coordinating with unshared electron pair (lone pair), and bases as molecules or ions which have such unshared electron pairs available for coordination.

Organic Compounds as Acid : The strength of an acid, HA, in water. i.e. the extent to which it is dissociated may be determined by considering the equilibrium.



The equilibrium constant, K_a , is called acidity constant or dissociated constant of acid.

The value of K_a serve as a useful guide to comparative acid strength.

Acidic strength of acid $\propto K_a$

$$\propto \frac{1}{pK_a}$$

The smaller the numerical value of pK_a of an acid, the stronger will be the corresponding acid.

Strong acids generally have pK_a values around 0, and weak acids, such as most organic acids, have pK_a values that are greater than 4. Weaker acids have larger values of pK_a .

Note : Very weak acids, those with pK_a greater than ≈ 16 will not be detectable as acids at all in water, as the concentration of H_3O^+ ions : $[H_3O^+]$, they will produce therein will be less than that produced by the autolysis of water itself. Their relative acidities thus cannot be measured in water at all. When acids are sufficiently strong, they will all be essentially fully ionised in water, and will thus all appear to be of the same strength, e.g. HCl, HNO_3 , $HClO_4$. This is known as the **Levelling Effect** of water.

The following factors may influence the acidity of an organic compound, HA.

1. The strength of the H-A bond
2. The electronegativity of A
3. Factors stabilizing A^- compared with HA

Note :

- The stronger an acid, the weaker its conjugate base.
- The weaker an acid, the stronger its conjugate base.
- An acid will donate a proton to the conjugate base of any weaker acid.
- An acid-base reaction favour the weaker acid.
- The stability of the conjugate base is a good guide to acidity. More stable anions tend to be weaker bases, and their conjugate acids tend to be stronger acids.

Acidic strength of acid (HA)

$$\propto \frac{1}{\text{Basic strength of conjugate base (A}^-)}.$$

Basic strength of conjugate base

$$\propto \text{Negative charge density of conjugate base}$$

Negative charge density of conjugate base

$$\propto \frac{1}{\text{Size of atom bearing negative charge}}$$

$$\propto \frac{1}{\text{Electronegativity of atom bearing negative charge}}$$

$$\propto \text{Strength of Electron Releasing Group (ERG)}$$

$$\propto \text{Number of ERG}$$

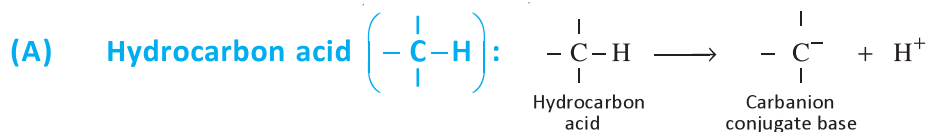
$$\propto \frac{1}{\text{Strength of Electron Withdrawing Group (EWG)}}$$

$$\propto \frac{1}{\text{No. of EWG}}$$

$$\propto \frac{1}{\text{Extent of delocalization of negative charge through resonance}}$$

➤ Intramolecular H-bond in acid decrease acidic strength while intramolecular H-bond in conjugate base increase acidic strength.

➤ Presence of ERG (+I, +R) decrease acidic strength while presence of EWG (−I, −R) increase acidic strength of organic acid.



Relative acidic strength of hydrocarbon acid depends upon stability of conjugate base carbanion.

Acidic strength of hydrocarbon $\propto$ Stability of carbanion formed

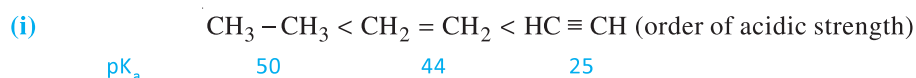
Stability of carbanion $\propto$ Electronegativity of carbon atom

$\propto$ Extent of delocalization of negative charge

$\propto$ Number and strength of EWGs

$$\propto \frac{1}{\text{No. and strength of ERGs}}$$

For Examples :

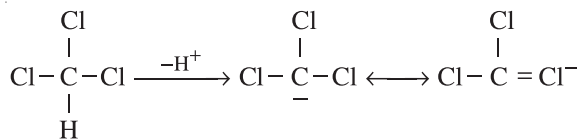


Because carbanion of $\text{HC}\equiv\text{CH}$ is more stable due to high electronegativity of triply bonded carbon atom (*sp* hybridized).

- (ii)
- $\text{F}_3\text{C}-\text{H} < \text{Cl}_3\text{C}-\text{H}$
- (order of acidic strength)

$$pK_a \quad 28 \quad 15.5$$

Conjugate base of chloroform is more stable because of greater delocalization of negative charge via **back bonding** ($p\pi-d\pi$) which is not possible in conjugate base of fluoroform due to absence of vacant d-orbitals in F-atom.

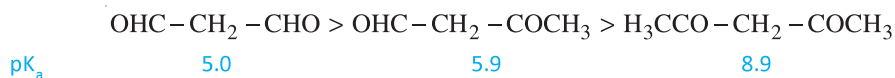


- (iii) Hydrogen atom of active methylene group and methyne group are more acidic H atoms.



EWG = $-\text{CHO}$, $-\text{CO}-$, $-\text{COOR}$, $-\text{NO}_2$, $-\text{CN}$ etc.

Order of acidic strength



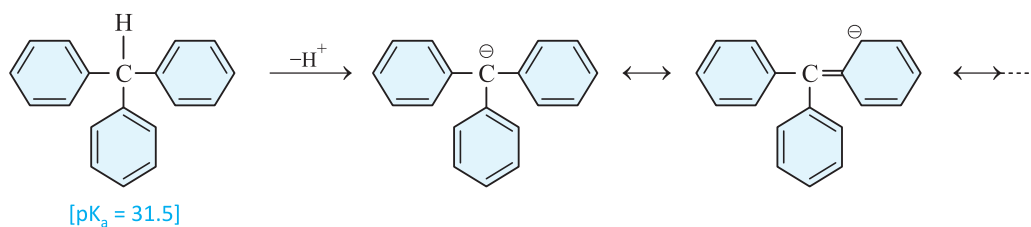
$-\text{CHO}$ is stronger EWG than $-\text{COCH}_3$ hence greater stabilization of conjugate base.

- (iv) Order of acidic strength :
- $\text{CH}_4 < \text{HCF}_3 < \text{HC}(\text{CF}_3)_3$

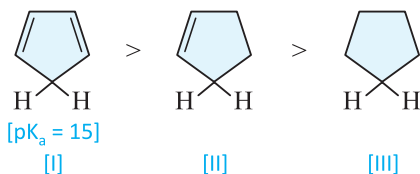


It is due to the powerful electron-withdrawing inductive effect of the fluorine atoms making the H atom more acidic, and also stabilizing the resultant carbanions, CF_3^- and $\text{C}(\text{CF}_3)_3^-$ by electron-withdrawal.

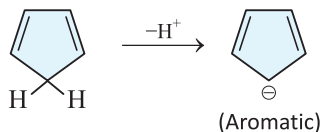
- (v)
- $\text{Ph}_3\text{C}-\text{H} (pK_a = 31.5)$
- is very much stronger acid than
- $\text{CH}_4 (pK_a = 43)$
- . Because higher stability of conjugate base of triphenyl methane due to delocalization of negative charge in benzene through resonance.



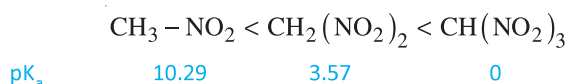
- (vi) Order of acidic strength



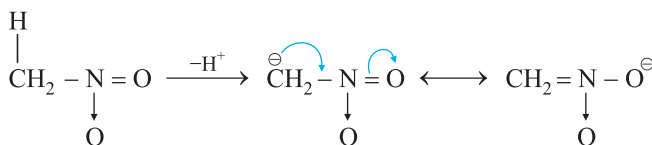
Because conjugate base of cyclopentadiene [I] is **aromatic** hence more stable thus [I] is most acidic. Conjugate base of [II] is stabilized by resonance while such resonance stabilization is not possible in conjugate base of [III].



(v) Order of acidic strength



Conjugate base of nitromethane is stabilized by delocalization of negative charge by resonance.

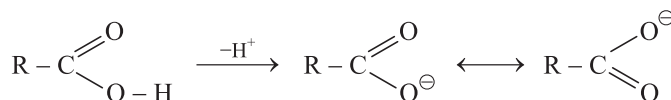


This delocalization of negative charge increase with increase in number of nitro groups on α -carbon atom.

Thus order of acidic strength is $\text{CH}_3\text{NO}_2 < \text{CH}_2(\text{NO}_2)_2 < \text{CH}(\text{NO}_2)_3$

(B) Carboxylic Acid :

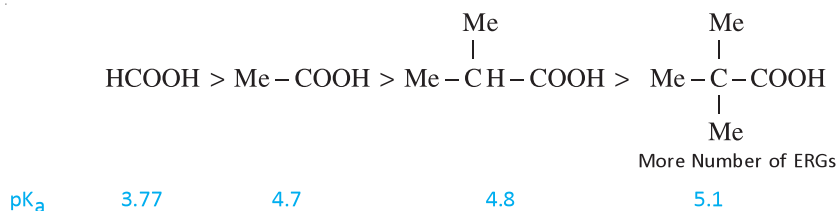
I. Simple Aliphatic Carboxylic Acid (R-COOH) :



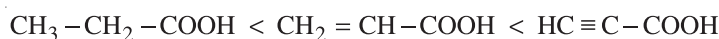
Carboxylate ion (conjugate base) is stabilized by resonance. In this case resonance stabilization is more because of formation of equivalent canonical structures.

Presence of **ERG** (e.g. alkyl groups) increase the negative charge density of conjugate base and it results in decrease in its stability and basic strength.

Order of acidic strength of aliphatic carboxylic acid is as given.



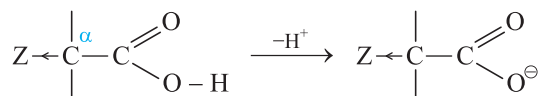
If there is a **doubly** or **triply** bonded carbon atom adjacent to the carboxylic group carbon then acidic strength is increased.



This is due to the fact that the unsaturated α -carbon atom is sp^2 or sp hybridized, which means that sp^2 or sp hybridized carbon atoms are less electron-donating due to their more electronegativity compared to sp^3 hybridized carbon atom.

II. Substituted Aliphatic Carboxylic Acids :

Presence of **EWG** increase the acidic strength of carboxylic acid because it decrease the negative charge density of conjugate base by electron withdrawing inductive effect of substituent. **EWG** stabilises the carboxylate anion and increase strength of the acid.



[Z is an electron withdrawing group (**EWG**)]

The introduction of **EWG** further away from the carboxyl group than the adjacent α -position, has much less influence. Its inductive effect quickly dies away with increase in distance from carboxylic group.

The effect of the following groups in increasing acidic order is



Acidic strength of carboxylic acid $\propto$ Stability of conjugate base

$$\propto \text{Strength of EWG}$$

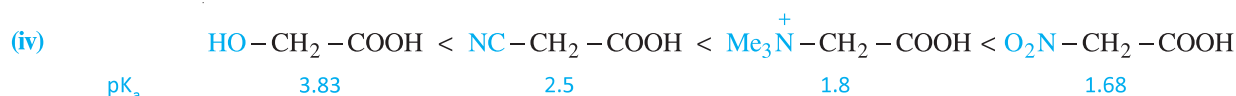
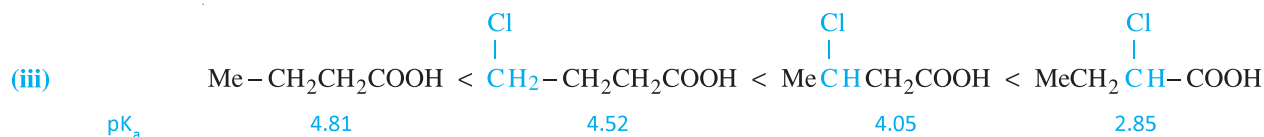
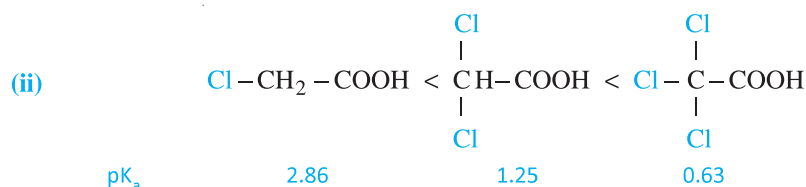
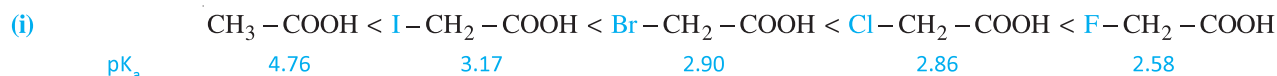
$$\propto \text{Number of EWGs}$$

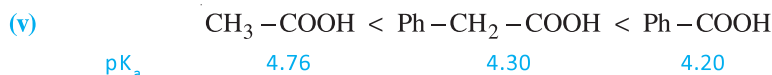
$$\propto \frac{1}{\text{Strength of ERG}}$$

$$\propto \frac{1}{\text{No. of ERGs}}$$

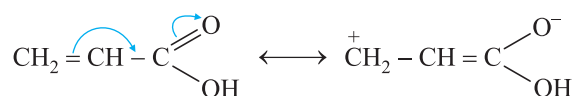
$$\propto \frac{1}{\text{Distance of EWG from } -\text{COOH group}}$$

For Examples : Increasing order of acidic strength.

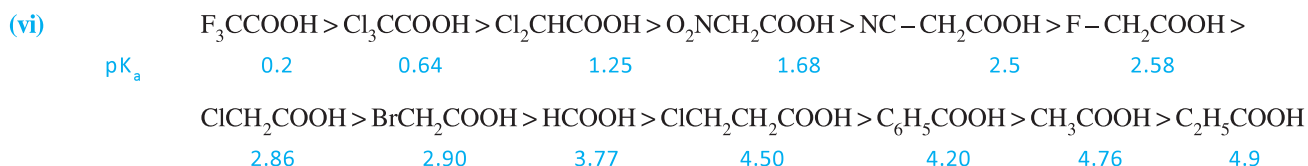
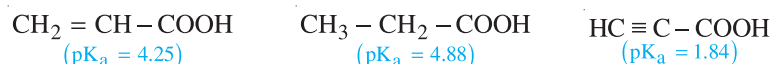




Note : Direct attachment of groups such as **phenyl** or **vinyl** to the carboxylic acid, increases the acidity of corresponding carboxylic acid, contrary to the decrease expected due to resonance effect shown below.

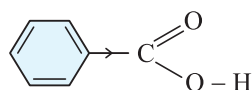


This is because of greater **electronegativity** of sp^2 hybridised carbon to which carboxylic carbon is attached.

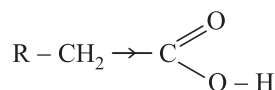
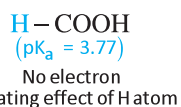
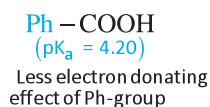


III. Aromatic Carboxylic Acids :

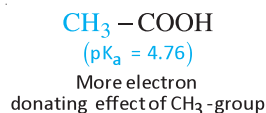
Aromatic carboxylic acids are generally more acidic than saturated aliphatic carboxylic acid because phenyl group is less electron donating compared with alkyl group.



Less Electron Donating Effect of Phenyl group, more acidic strength



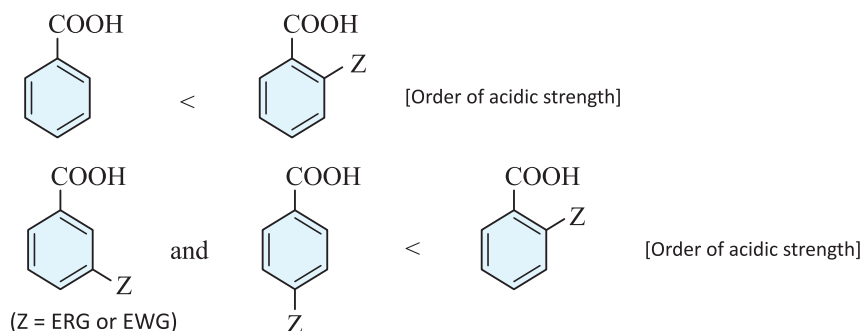
More Electron Donating Effect of Alkyl group, less acidic strength



Substituted Benzoic Acid :

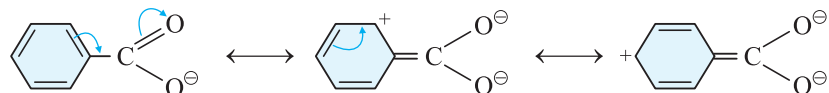
➤ For comparison of relative acidic strength of substituted benzoic acid use “**ORTHO EFFECT**”.

Ortho effect : It is common observation that generally **ortho substituted benzoic acid is more acidic** than its isomeric meta and para substituted benzoic acid even more acidic than benzoic acid itself. This effect is **irrespective** of the **polar nature** (EWG or ERG) of the **ortho-substituent**.

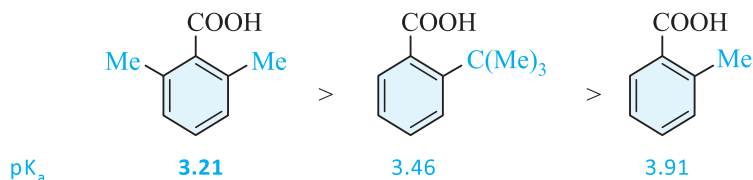


Ortho effect is a cumulative effect of various acidic strength enhancing factors such as steric inhibition of resonance, strong inductive effect from nearest position, intramolecular hydrogen bonding in conjugate base etc.

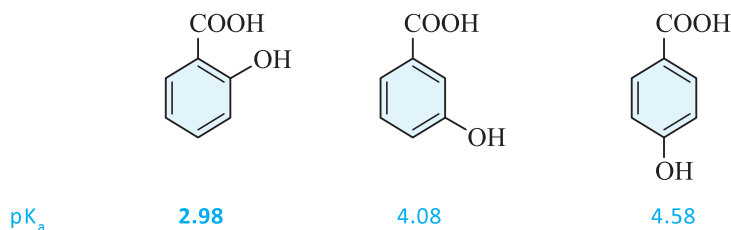
We know that carboxyl group is coplanar with the ring thus there is +R effect of Ph-group.



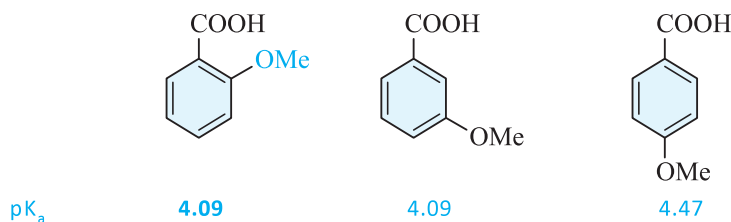
An ortho-substituent tends to prevent this **coplanarity** because of **steric hinderance**. Thus, resonance is prevented and there is no +R effect of Ph-group. This result in more stability of conjugate base due to less negative charge density and hence greater acidic strength. It can be said that greater the **steric inhibition of resonance**, the stronger is the acid. For example order of acidic strength of ortho substituted benzoic acids is as given.



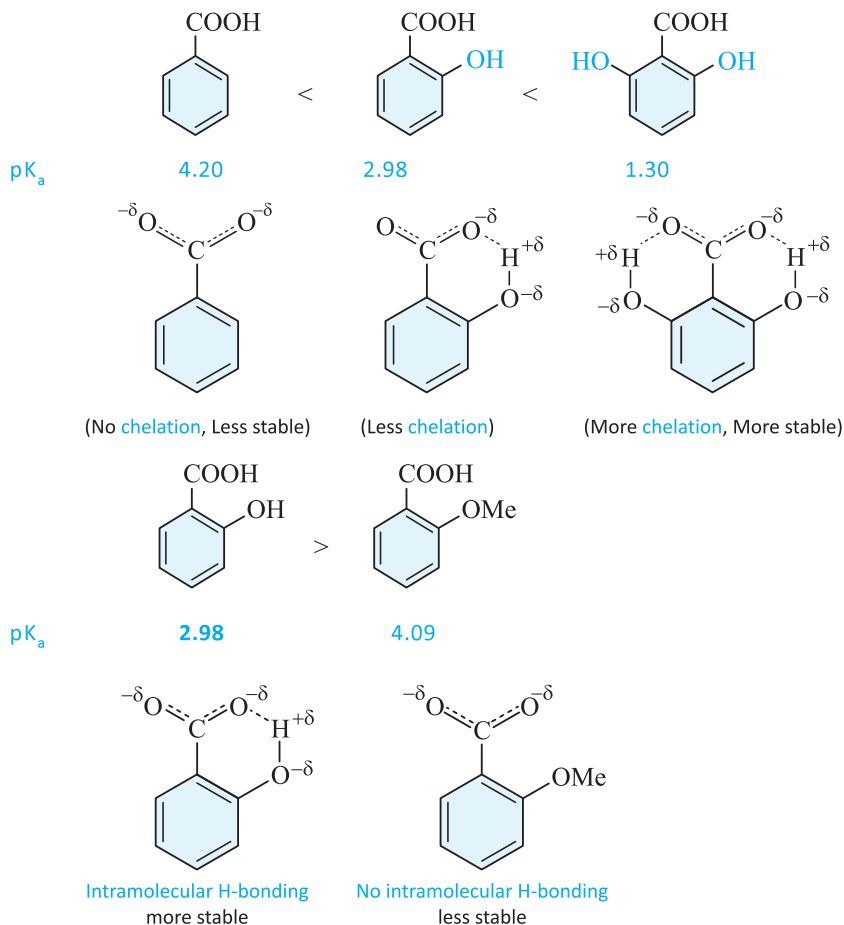
o-Hydroxy benzoic acid (salicylic acid) is far stronger than the corresponding meta and para isomer.



Steric inhibition of resonance can not explain this very large increase, since the corresponding methoxy benzoic acids all have almost similar strengths.

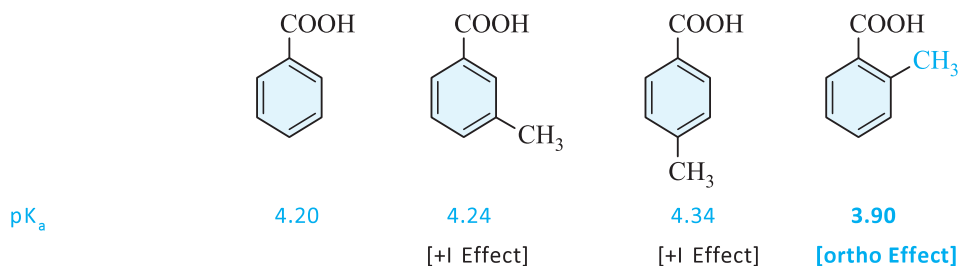


Very large increase in acidic strength of *o*-hydroxy benzoic acid is explained by considering **intramolecular H-bonding** (chelation) in conjugate base carboxylate ion of *o*-hydroxy benzoic acid. Conjugate base is stabilized by **intramolecular hydrogen bonding** while such hydrogen bonding is not feasible in *o*-methoxy benzoic acid and it is further supported by the following order of acidic strength.

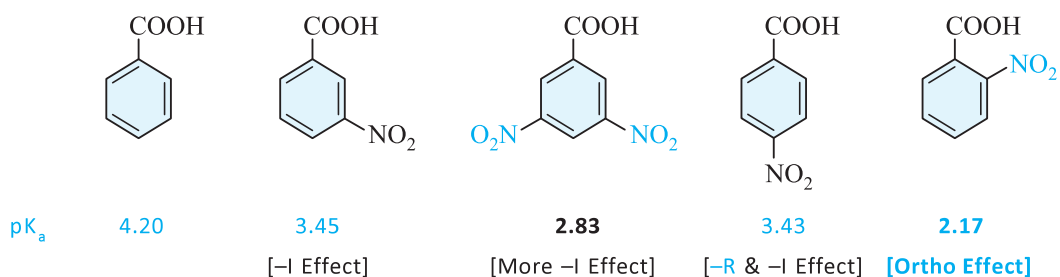


► **Comparison of Acidic Strength of *m*- and *p*-isomers :**

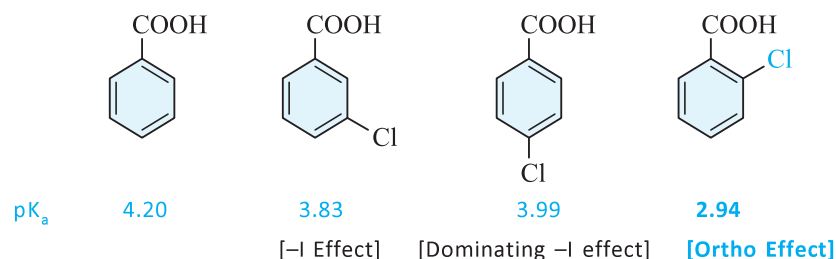
- (i) The introduction of alkyl groups into the benzene nucleus has very little effect on the strength of benzoic acid.



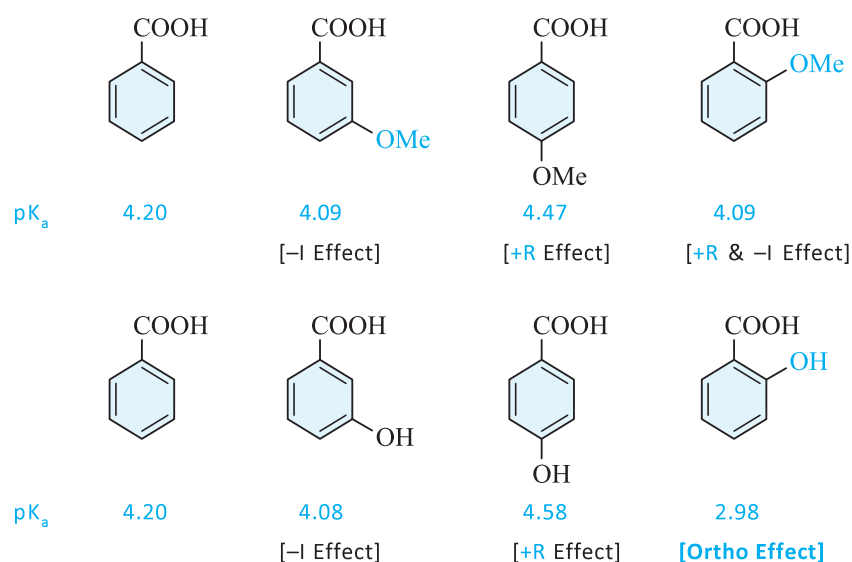
- (ii) The introduction of electron withdrawing groups (–R effect) increase the strength of benzoic acid, more increase in acidic strength when they are in the *o*- and *p*-positions.



- (iii) The presence of group such as OH, OMe, halogen having an **electron-withdrawing inductive effect**, but an **electron-donating mesomeric** when in the *o*- and *p*-positions, may cause *p*-substituted acids to be weaker than the unsubstituted acid itself. e.g. *p*-hydroxy benzoic acid.

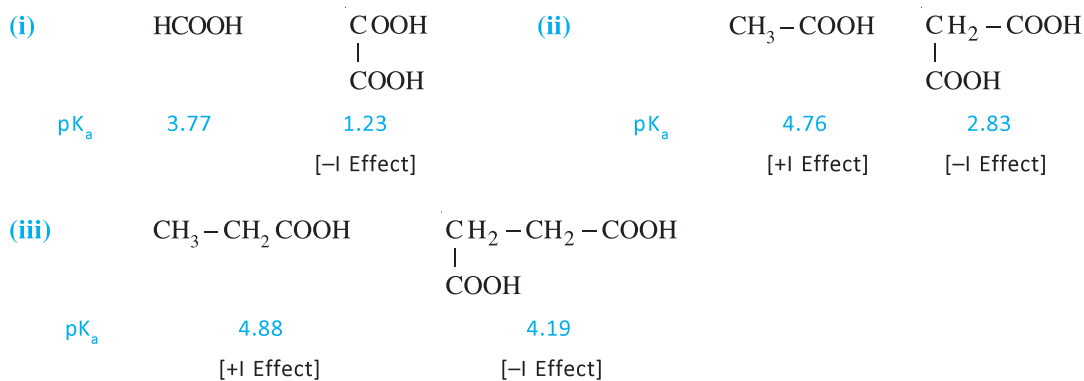


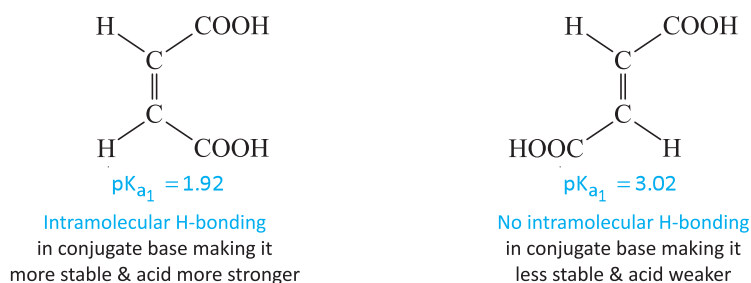
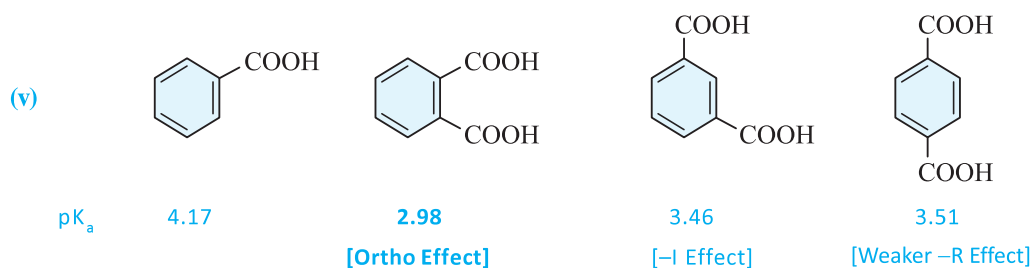
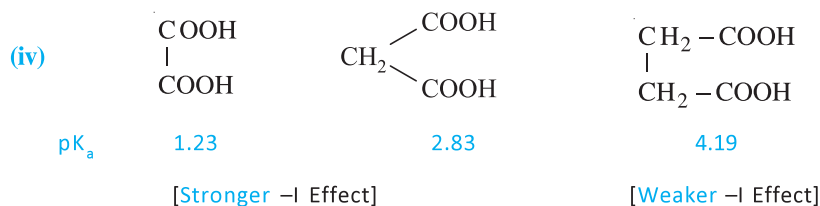
Note : −I effect of halogen dominate over their +R effect.



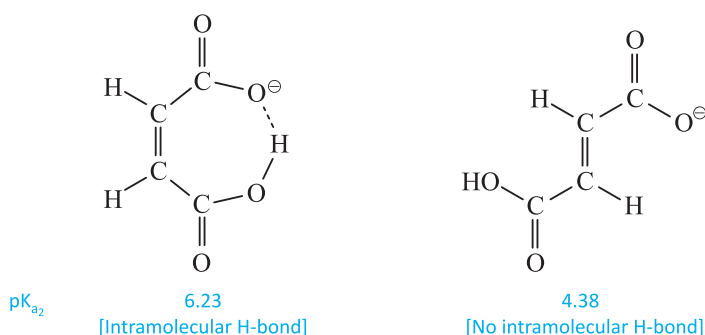
IV. Dicarboxylic acid :

As the carboxyl group itself has an electron withdrawing inductive effect, the presence of a second such group in an acid might make it stronger, as shown by following examples

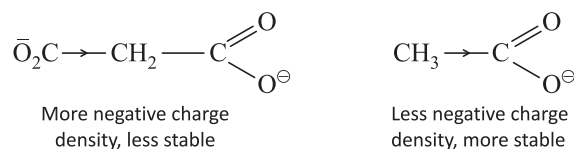




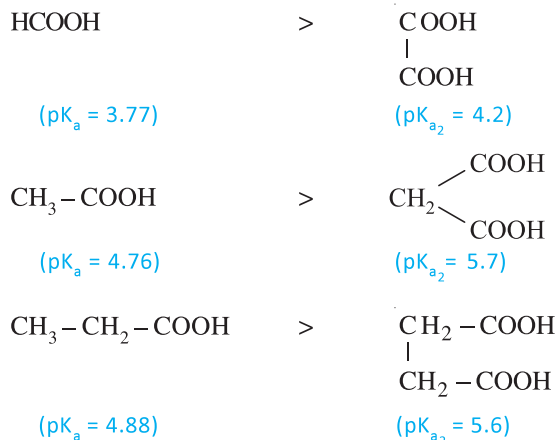
Note : The second dissociation of trans-butenedioic acid ($pK_{a2} = 4.38$) occurs more readily than that of the cis-acid ($pK_{a2} = 6.23$), because of the greater difficulty in removing a proton (H-bonded) from the negatively charged cyclic system derived from cis-butenedioic acid.



Second dissociation constant of saturated dicarboxylic acid is weaker than their corresponding saturated monocarboxylic acid. This is because the second proton has to be removed from a negatively charged species containing an electron-donating substituent i.e. CO_2^- which destabilize conjugate base more.

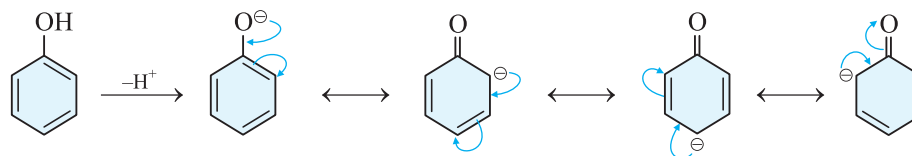


Order of second dissociation constant.

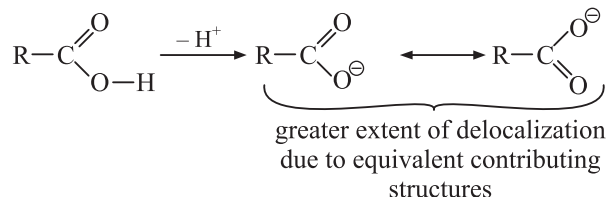


(C) Phenols :

Phenol is weaker acid because its conjugate base is stabilized by delocalization of negative charge but extent of delocalization is less due to **non-equivalent** less stable contributing structure.



Phenol is weaker acid than carboxylic acid because in carboxylic acid, conjugate base is more stabilized due to formation of **equivalent** contributing structure during delocalization of charge.

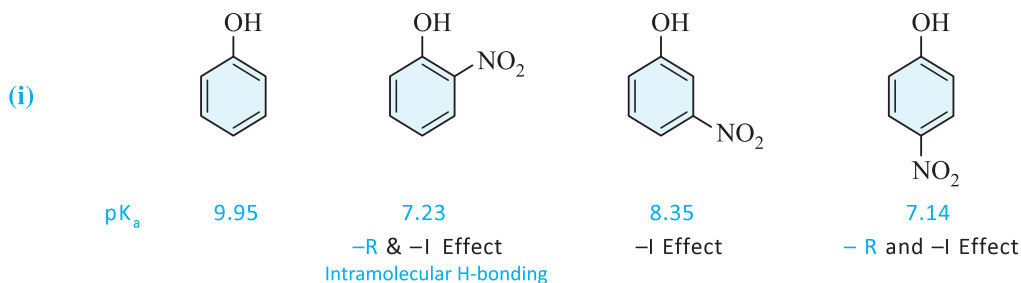


$\text{CH}_3 - \text{COOH}$	$\text{Ph} - \text{OH}$	$\text{Ph} - \text{COOH}$
pK_a 4.76	9.95	4.20

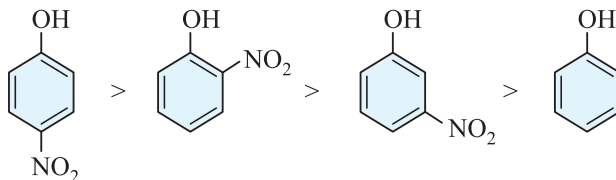
Substituted Phenols :

Presence of **EWG** increase acidic strength of phenol while presence of **ERG** decrease acidic strength of phenols.

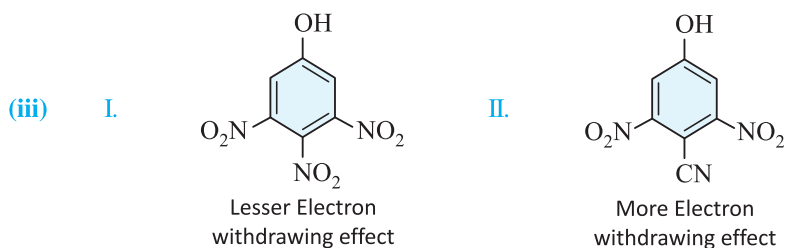
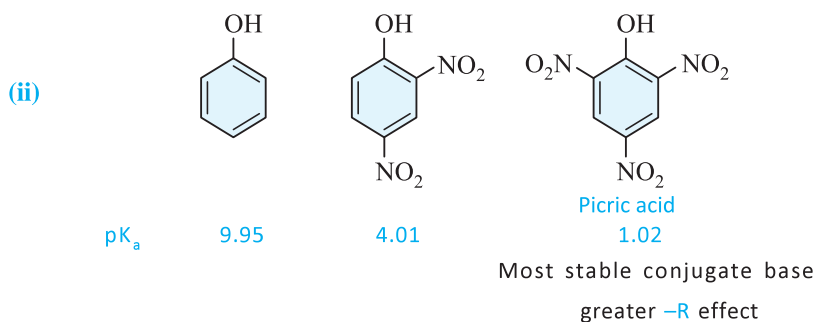
In the case of a nitro substituent, the **inductive effect** would be expected to decrease with distance on going $o - \rightarrow m - \rightarrow p$ -nitrophenol but there would also be an electron withdrawing **mesomeric effect** when the nitro group is in the o - or p -, but not in the m -position, and this would increase acidic strength of nitrophenols because of more resonance stabilisation of their conjugate base.



Order of acidic strength :

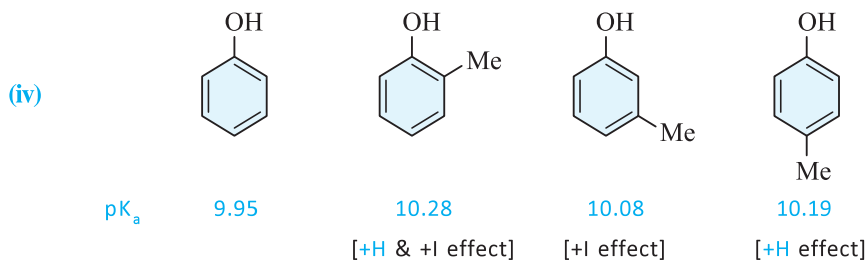


Note : Introduction of further NO_2 groups promotes acidity markedly.



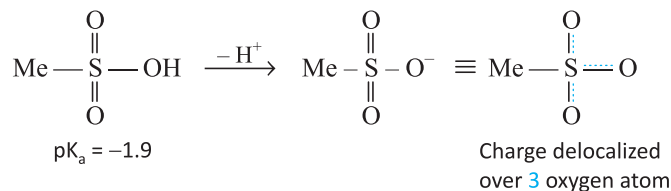
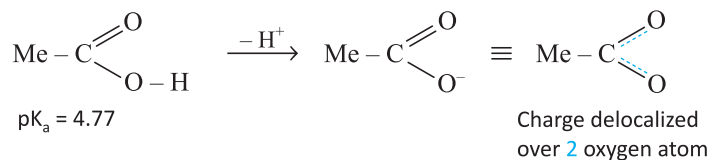
Order of acidic strength II > I

In (I) -R effect of NO_2 - group at para position is not possible because of steric inhibition of resonance while in (II) -R effect of CN group increases acidic strength. [steric inhibition of resonance is absent in this case because -CN is a linear group]

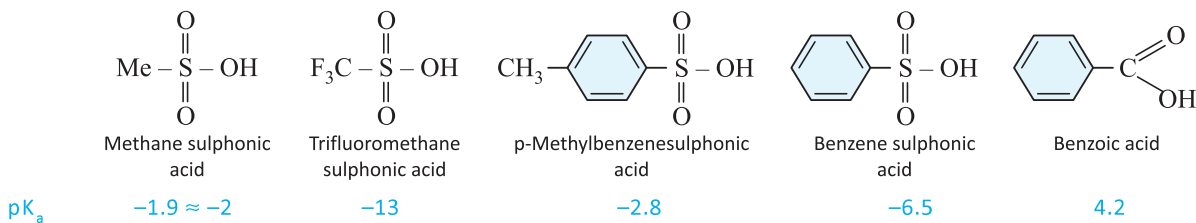


(E) Sulphonic Acid :

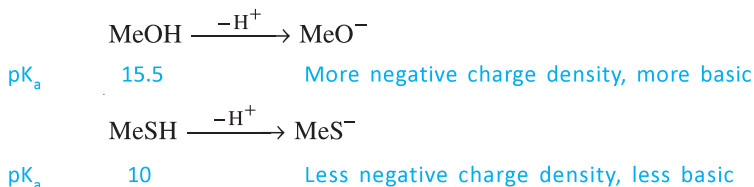
Alkane sulphonic acids ($R-SO_2OH$) are stronger acids than carboxylic acids because of greater stabilization of conjugate base of alkane sulphonic acid due to dispersion of negative charge over three oxygen atoms.



Presence of **ERGs** decrease acidic strength of alkane sulphonic acids while presence of **EWGs** increase acidic strength of alkane sulphonic acid.

**(F) Mercaptan (Thioalcohol) :**

Thioalcohols are fairly acidic with a pK_a around 10 - 11. This is because negative charge is spread over larger size sulphur atom.



Note : The solubility properties of acids and their salts may be used to remove non acidic impurities. A carboxylic acid is more soluble in the organic phase, but its salt is more soluble in the aqueous phase. Acid-base extraction can move the acid from the organic phase into the aqueous phase and back into the organic phase, leaving impurities behind.

