Acidity of Carboxylic Acids

Carboxylic acids are a class of organic compounds which contain at least one carboxyl group (-COOH) as a functional group. Acids containing one, two or three carboxyl groups are known as mono ,di and tricarboxylic acids respectively. They are obtained by replacement of a hydrogen atom from an aliphatic or aromatic hydrocarbon and are represented by the general formula RCOOH or ArCOOH respectively. Whether the group is aliphatic or aromatic, saturated or unsaturated, substituted or unsubstituted the properties of the carboxyl group are essentially the same. However, the nature of R and Ar may increase or decrease the acidity of carboxylic acids.

In aqueous solution a carboxylic acid exists in equilibrium with the carboxylate anion and the hydrogen ion:

$$RCOOH + H_2O \rightleftharpoons RCOO^- + H_3O^+$$

and,

$$K_{eq} = \frac{[RCOO^-]\,[H_3O^+]}{[H_2O]\,[RCOOH]}$$

Since water is the solvent, its concentration remains constant. Therefore,

$$K_a = \frac{[RCOO^-]\,[H_3O^+]}{[RCOOH]}$$

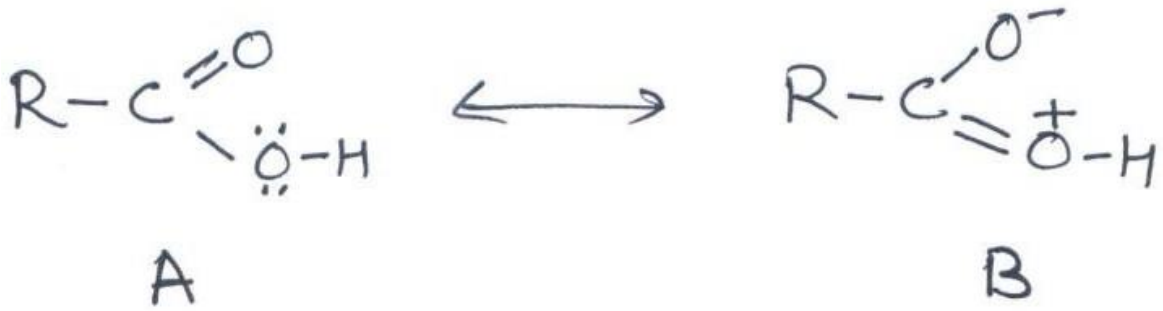
Where K_a is called **acid dissociation constant** or **acidity constant** and is equal to K_{eq} $[H_2O]$. Each carboxylic acid has its characteristic value for K_a which indicates its strength. Higher is the value for K_a stronger is the acid and vice versa. A higher value for K_a indicates better ionisation of RCOOH or K_a is proportional to concentration of hydronium ion or concentration of hydrogen ion.

The strength of an acid is represented by the negative logarithm of K_a (pK_a). pK_a is very much similar to pH or

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

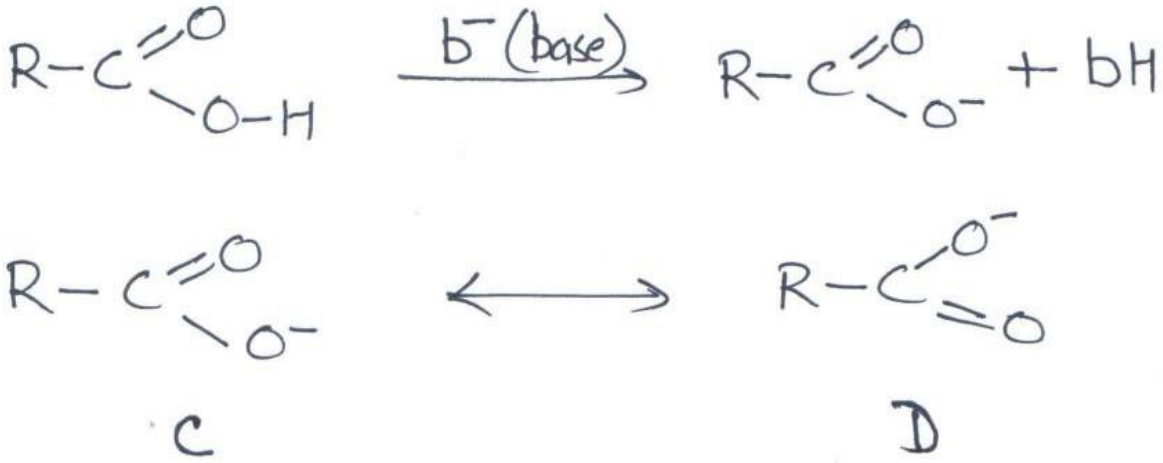
A strong acid has a low value of pK_a whereas a higher value of pK_a indicates that the acid is weak. Value of pK_a for Formic acid is 3.77, for Acetic acid it is 4.74 and for trichloroacetic acid it is 0.65.

The Bronsted-Lowry acid base theory defines acids (HA) as species that lose hydrogen ions and form a conjugate base. A strong acid loses its hydrogen ion easily and forms a stable conjugate base. In case of carboxylic acids loss of hydrogen ion is easier due to conjugation between lone pair of electron of Oxygen of --OH and pi electrons:



A B

The delocalisation of electrons creates a positive charge on Oxygen atom making it more electronegative. This weakens the hydroxyl bond and loss of hydrogen ion becomes easier. The loss of hydrogen ion generates a carboxylate anion (C&D):



C D

The anion is resonance stabilised and structure C & D contribute equally. Therefore, carboxylate anion serves as a stable conjugate base.

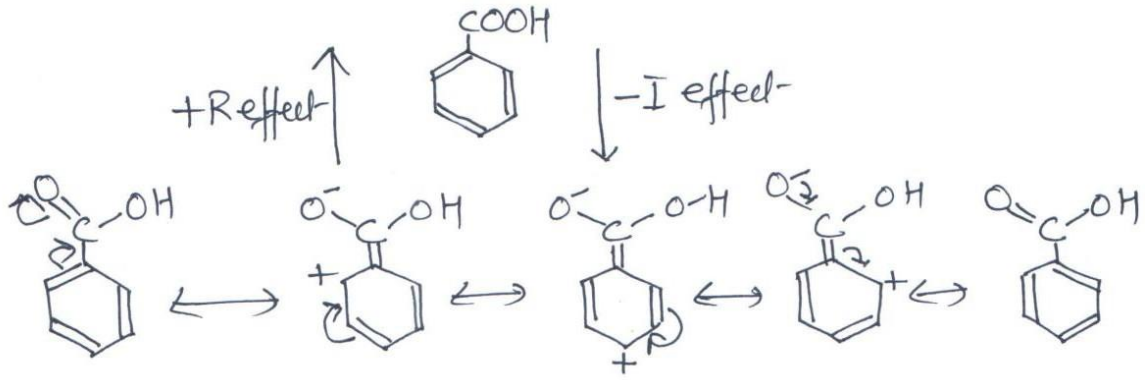
All those factors(in R/Ar) which increase the positive charge of structure B and decrease the negative charge of structure C & D will increase the

acidity and the factors which decrease the positive charge of structure B and increase the negative charge of structure C&D decrease the acidity.

Effects of substituents on acidity of carboxylic acids

Aliphatic Acids: Aliphatic acids are represented by general formula RCOOH. R may be a hydrogen atom (HCOOH, Formic acid) or an alkyl group or an alkyl group with electron donating substituents or an alkyl group with electron withdrawing substituents. HCOOH has a pK_a value of 3.77 whereas acetic acid (CH_3COOH) and chloroacetic acid ($ClCH_2COOH$) have pK_a values of 4.74 and 2.86 respectively. These values indicate that a methyl group is an electron donating group which decreases positive charge in structure B and increases the negative charge in structure C and D making **acetic acid less acidic than formic acid**. Greater is the +I effect of alkyl group, weaker is the acid. On the other hand, Cl of chloroacetic acid increases the positive charge of structure B and decreases negative charge of structure C and structure D due to its --I effect. This results in increased acidity of chloroacetic acid. This can be further confirmed by pK_a value of 0.65 for trichloroacetic acid (Cl_3CCOOH). Trichloroacetic acid has three Cl atoms which create a strong –I effect. Acidity of α-haloacids decreases in the decreasing order of electronegativity of halogens. For example, for FCH_2COOH, $ClCH_2COOH$, $BrCH_2COOH$ and ICH_2COOH, the pK_a values are 2.57, 2.86, 2.90 and 3.16 respectively. For F_3CCOOH it is 0.23.

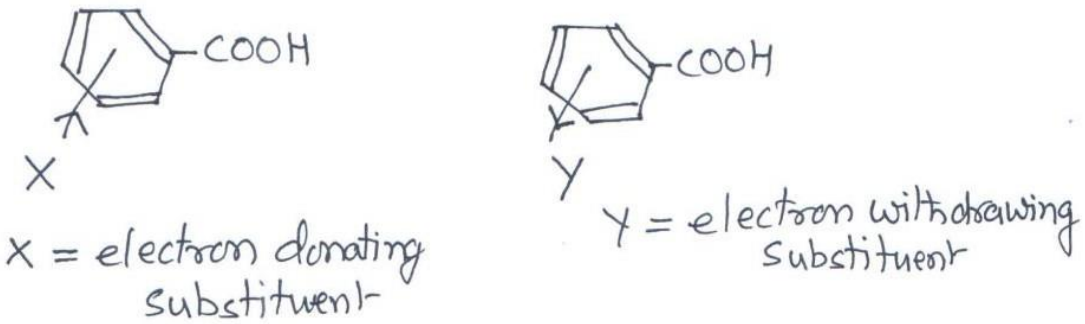
Aromatic Acids: The simplest member of this group is Benzoic acid (C_6H_5COOH). Carboxyl group is directly attached to phenyl ring. Phenyl ring has a +R effect as well as -I effect. +R effect overcomes the -I effect and net result is electron donation (+I effect) by phenyl ring to carboxyl group. This effect is acid weakening and therefore Benzoic acid is weaker (pK_a = 4.2) than formic acid (HCOOH).



Methyl group of acetic acid (pK_a = 4.74) has a greater +I effect than (+R and -I) effect of phenyl ring of Benzoic acid. Therefore, acetic acid is weaker than Benzoic acid. Phenylacetic acid ($C_6H_5CH_2COOH$) (pK_a = 4.31) is stronger than acetic acid because phenyl ring has a -I effect. +R effect of phenyl ring in phenyl acetic acid is absent as phenyl ring and carboxyl group are separated by methylene group.

Effects of substituents on acidity of substituted Benzoic acids

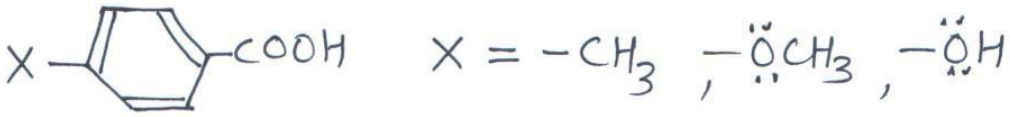
Electron donating substituents decrease the acidity where electron withdrawing substituents increase the acidity of substituted Benzoic acids. However, the acidity varies with the position of the substituents. Decrease or increase in acid strength is more pronounced when electron releasing/withdrawing substituents are at para position. Substituents at meta position affect the acidity to a lesser degree. All ortho substituted Benzoic acids are stronger than Benzoic acids irrespective of the nature of substituents. This is known as ***Ortho Effect*** and is probably due to combination of steric and electronic factors.



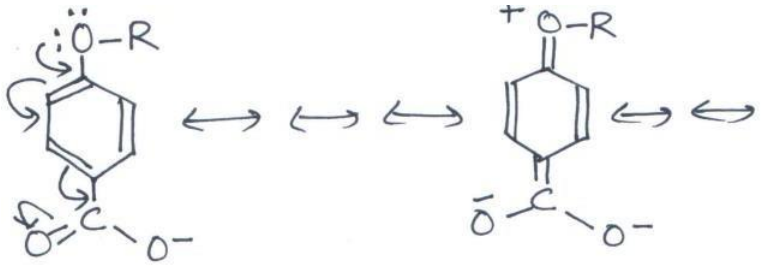
Substituents	pK_a Values		
	para	meta	ortho
$-CH_3$	4.4	4.3	3.9
$-OCH_3$	4.5	4.1	4.1
-OH	4.6	4.1	3.0
-Cl	4.0	3.8	2.9
$-NO_2$	3.5	3.4	2.2

pK_a Values of substituted Benzoic acids

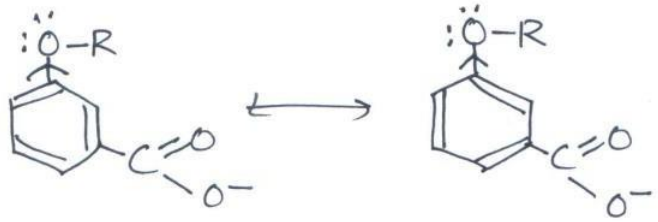
$-CH_3$, $-OCH_3$ and -OH are electron releasing substituents and therefore substituted benzoic acids with these substituents at para position are weaker than benzoic acid.



Substituted benzoic acids having hydroxy and alkoxy substituents at meta and ortho position show anomalous behaviour. They are stronger acids than Benzoic acid. $-OCH_3$ and -OH have both resonance and inductive effects. At para position resonance effect (electron releasing effect) outweighs the inductive effect (electron withdrawing effect) and so para-hydroxy and para-methoxy benzoic acids are weaker than benzoic acid. At meta position inductive effect is operating and therefore meta-hydroxy and meta-methoxy benzoic acids are stronger benzoic acids.

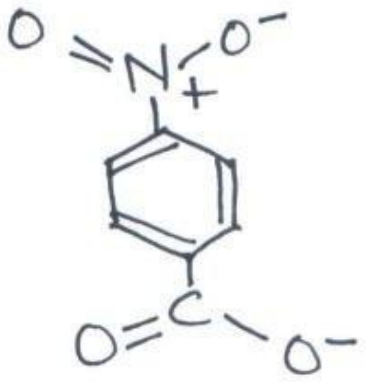


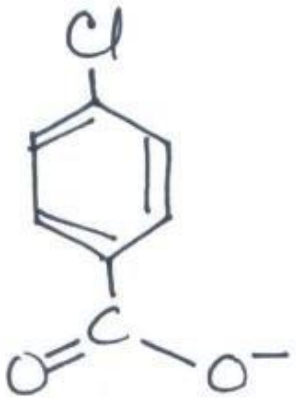
Release of electrons by substituents (acid weakening factor)



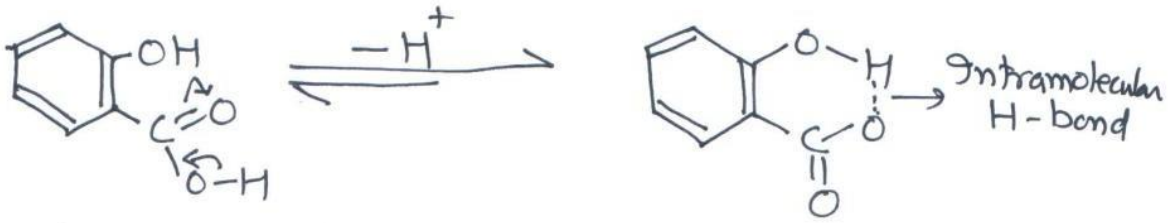
Electron withdrawl by electronegative oxygen atom (acid strengthening effect)

p-chlorobenzoic acid is stronger acid than benzoic acid but weaker than m-chlorobenzoic acid because inductive effect of Cl is more effective when it is at meta position in comparison to when Cl is at para position (Inductive effect decreases with distance). p-nitrobenzoic acid is stronger acid than p-chlorobenzoic acid. This is because in p-nitro benzoic acid, nitrogen of nitro group is positively charged and hence electron withdrawing effect of positively charged nitro group is more. Also, in p-chlorobenzoic acid non-bonding electron of -Cl increase the electron density (acid weakening) of ring.





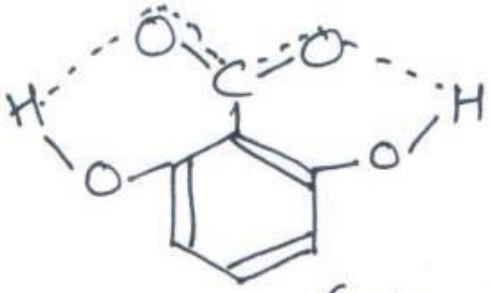
Ortho Effect: All ortho substituted benzoic acids are stronger acids than benzoic acid no matter whether the substituent is electron releasing (-CH_3, -OCH_3, -OH, -NH_2) or electron withdrawing (-Cl, -NO_2, -CN, -COOR etc.). This effect is known as Ortho effect. It is mainly due to steric effect and if inductive effect is also favourable, acidity increases to a greater extent. For example, methyl group has +I effect and therefore, p-methyl and o-methyl benzoic acids have pK_a values of 4.4 and 3.9 respectively, indicating that o-methyl benzoic acid is stronger than benzoic acid and in this case steric effect (for ortho effect) overweighs the inductive effect. The difference between pK_a values of p-chloro and ortho-chloro benzoic acid is larger than that of methyl benzoic acids. p-chloro benzoic acid has a pK_a of 4.0 and that of o-chloro benzoic acid is 2.9. In this case ortho effects involves both steric and inductive effect. If there is possibility of hydrogen bonding between carboxylate anion and ortho substituent, acidity increases to a large extent. For example, salicylic acid forms a six membered ring by intramolecular Hydrogen bond.



Salicylic acid

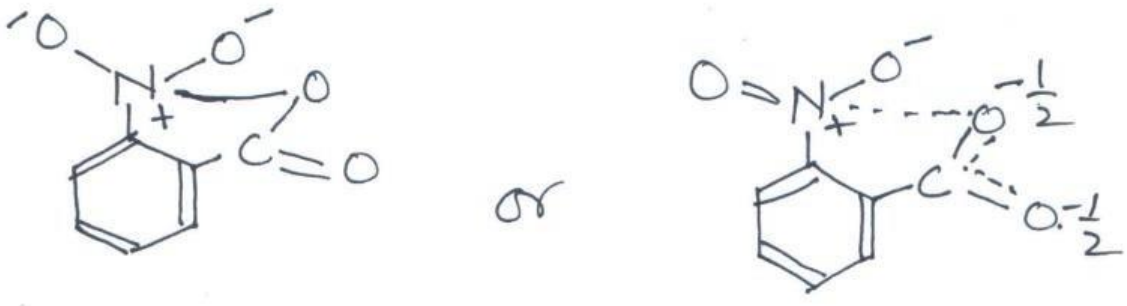
$pK_a = 3.0$

Therefore, anion of Salicylic acid is more stable than anion of p-hydroxy benzoic acid or m-hydroxy benzoic acid. If there are two hydroxy groups on both sides of carboxylate anion, stabilisation of anion further increases.



2, 6 Dihydroxy benzoic acid ($pK_a = 2.30$)

The much greater strength of o-nitrobenzoic acid (pK_a = 2.2) as compared to its meta (pK_a = 3.4) and para isomer (pK_a = 3.5) is the result of intermolecular H-bonding.



Ortho - Nitrobenzoic acid

In an ortho-substituted benzoic acid, the ortho substituents prevent the co-planarity between carboxyl group and the ring. Decrease in coplanarity diminishes resonance between ring and carboxyl group and it results in increased positive charge on oxygen of -OH group (structure B) or loss of Hydrogen becomes easier or acidity increases. If the resulting anion (structure C & D) is further stabilized by intramolecular Hydrogen bonding, acidity increases to a greater extent.

Acidity of Dicarboxylic acids

Aliphatic dicarboxylic acids like oxalic acid (HOOC-COOH), malonic acid (HOOC-CH_2-COOH), succinic acid (HOOC-CH_2-CH_2-COOH), Glutaric acid (HOOC-$(CH_2)_3$-COOH), and Adipic acid (HOOC-$(CH_2)_4$-COOH have pK_a values lower than their monocarboxylic acid analogues. It is reasonable if they are considered as substituted monocarboxylic acid in which substituent is a carboxyl group. Carboxyl group is an electron withdrawing group and therefore acidity of dioic acids will be more than monocarboxylic acids for example:

$HOOC\text{-}COOH \rightleftharpoons HOOC\text{-}COO^- + H^+$ Ionisation of 1st carboxyl group

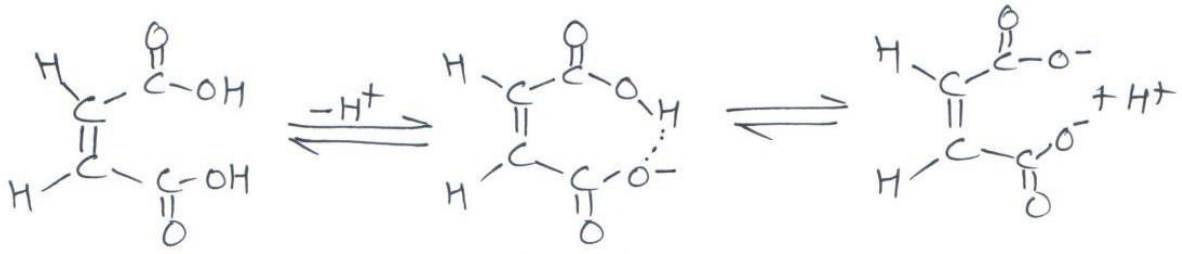
$HOOC\text{-}COO^- \rightleftharpoons {}^-OOC\text{-}COO^- + H^+$ Ionisation of 2nd carboxyl group

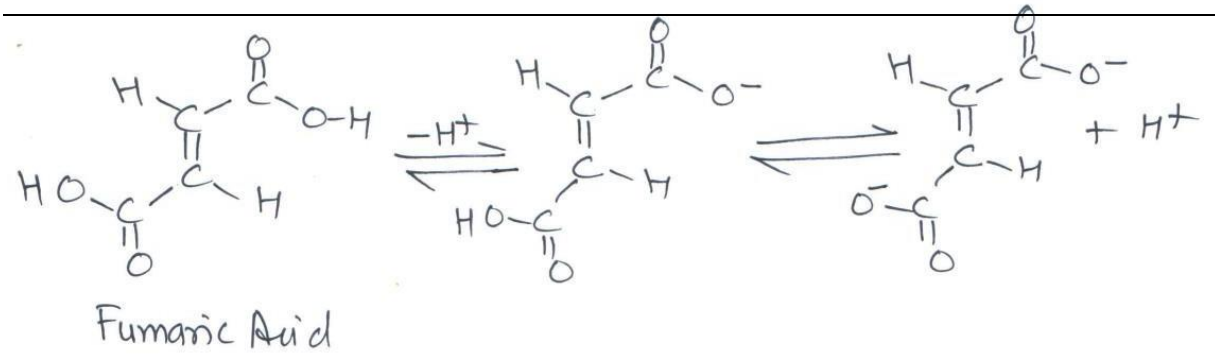
In first step loss of H^+ is easier due to -I effect of carboxyl group and therefore pK_{a1} value of oxalic acid is 1.27. But pK_{a2} value of oxalic acid is 4.28. This is because in the second step, loss of H^+ occurs from an anion so it is a slow process and requires a stronger base for removal of Hydrogen ion. As the distance between two carboxyl groups increases pK_{a1} increases or acidity decreases but value of pK_{a2} decreases showing that loss of Hydrogen ion from anion becomes easier.

Dicarboxylic acid	pK_{a1}	pK_{a2}
Malonic acid	2.80	5.82
Succinic acid	4.20	5.60
Glutaric acid	4.33	5.52
Adipic acid	4.43	5.45

Acidity of unsaturated dicarboxylic acids

Maleic acid and Fumaric acid are cis and trans forms of Butenedioic acid that is the two carboxyl groups in these acids are separated by a double bond which has an electron withdrawing effect. Therefore, they are stronger acids than their saturated analogue i.e. Succinic acid (pK_{a1} = 4.20). Maleic acid has pK_{a1} of 1.92 and Fumaric acid has pK_{a1} of 3.02. But pK_{a2} of Maleic acid is 6.23 and pK_{a2} of Fumaric acid is 4.38. This can be explained by their configuration. Maleic acid is cis form of acid and first ionisation is easier than first ionisation of Fumaric acid (trans-form). In the cis form, the maleate anion is stabilized by intramolecular hydrogen bonding. This type of stabilisation is not possible due to trans configuration of Fumarate anion. pK_{a2} of Maleic acid (6.23) is more than pK_{a2} of Fumaric acid (4.38) because stable anion of maleic acid requires a stronger base for loss of second Hydrogen ion in comparison to anion of Fumaric acid.

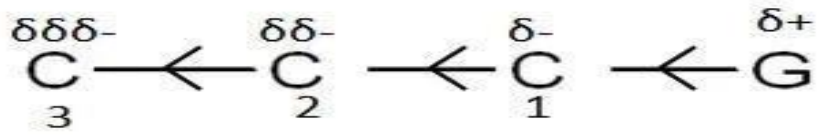




INDUCTIVE EFFECT

The **inductive effect** refers to the phenomenon wherein a permanent dipole arises in a given molecule due to the unequal sharing of the bonding electrons in the molecule. This effect can arise in sigma bonds, whereas the electromeric effect can only arise in pi bonds.

When an electron-releasing or an electron-withdrawing species is introduced to a chain of atoms (generally a carbon chain), the corresponding negative or positive charge is relayed through the carbon chain by the atoms belonging to it. This causes a permanent dipole to arise in the molecule and is referred to as the inductive effect.



δ- > δδ- > δδδ-

G = Electron Donating Group

Types of Inductive Effect

- Negative inductive effect or -I effect
- Positive inductive effect +I effect

-I Effect (Negative Inductive Effect)

When an electronegative atom, such as a halogen, is introduced to a chain of atoms (generally, carbon atoms), the resulting unequal sharing of electrons generates a positive charge which is transmitted through the chain.

This causes a permanent dipole to arise in the molecule wherein the electronegative atom holds a negative charge, and the corresponding effect is called the electron-withdrawing inductive effect or the -I effect.

+I Effect (Positive Inductive Effect)

When a chemical species with the tendency to release or donate electrons, such as an alkyl group, is introduced to a carbon chain, the charge is relayed through the chain, and this effect is called the positive inductive effect or the +I effect.

Inductive Effect on Stability of Molecules

The charge on a given atom and the charge on a group bonded to the atom plays a strong part when determining the stability of the resulting molecule as per the inductive effect.

An example of this can be observed when a group displaying the -I effect is bonded to a positively charged atom, and the positive charge on the resulting molecule is amplified, reducing its stability.

On the other hand, when a negatively charged atom is introduced to a group displaying a -I effect, the charge disparity is somewhat quenched, and the resulting molecule would be stable as per the inductive effect.

Also,

When a group displaying the -I effect is bonded to a molecule, the electron density of the resulting molecule effectively reduces, making it more likely to accept electrons and, thereby, increasing the acidity of the molecule.

When a +I group attaches itself to a molecule, there is an increase in the electron density of the molecule. This increases the basicity of the molecule since it is now more capable of donating electrons.