

# Study material: For B.Sc. part-III

## Subject: Organic Chemistry, paper VII

### Topic: General Principles

By Dr. Archana Kumari

Asst. professor, Dept. of Chemistry, S.B College, Ara

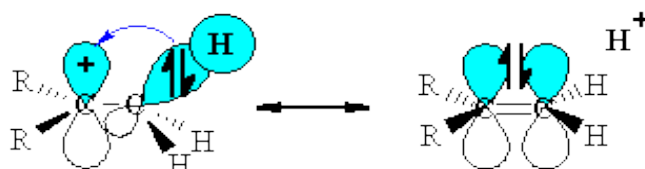
Electronic factors that influence organic reactions include the **hyperconjugation**, **inductive effect**, **mesomeric effect** and **resonance effects**. Electronic effects complicate chemical reactions, and they can stabilize a molecule, make a compound less volatile, make a molecule more likely to react in a desired fashion or affect the acidity or basicity.

**Hyperconjugation:** Hyperconjugation is the interaction of electrons in a sigma ( $\sigma$ ) bond (e.g. C–H or C–C) with an adjacent empty or partially filled p orbital, which results in an increased stability of the molecule. Hyperconjugation is known as no bond resonance.

The empty p orbital associated with the positive charge at the carbocation centre is in the same plane (*i.e.* coplanar) with one of the **C–H**  $\sigma$ -bonds (shown in blue.)



This geometry means the electrons in the  $\sigma$ -bond can be stabilised by an interaction with the empty p-orbital of the carbocation centre



**More the C-H bond, more will be the no bond resonating structure (Hyperconjugation) and the more is the stability.**

Example: The trend for stability in Tertiary ( $3^\circ$ ), secondary ( $2^\circ$ ) and primary carbocation is as follows  $\text{CH}_3)_3\text{C}^+ > (\text{CH}_3)_2\text{CH}^+ > (\text{CH}_3)\text{CH}_2^+ > \text{CH}_3^+$

$3^\circ$  carbocation is more stable than a  $2^\circ$ ,  $1^\circ$ , or methyl carbocation because the positive charge is delocalized over more than one atom.

- less electronegative atoms are more willing to share their electrons with the carbocation. Therefore, the 2-methyl butane is more stabilized through hyperconjugation than the 3-fluoro 2-methyl butane

**Inductive Effect:** Inductive effect is defined as permanent displacement of shared electron pair in a carbon chain towards more electronegative atom or group. The electron density in a sigma bond between two different atoms, is not uniform. So, the electrons are attracted towards the most electronegative atom.

## Study material: For B.Sc. part-III

### Types of Inductive effect :

1. Negative Inductive Effect : ( —I effect, Electron withdrawing effect) when an electronegative atom or group (more electro negative than hydrogen) is attached to the terminal of the carbon chain in a compound, the electrons are displaced in the direction of the attached atom or group.  $-\text{NO}_2 > -\text{CN} > -\text{COOH} > \text{F} > \text{Cl} > \text{Br} > \text{I} > \text{OH} > \text{C}_6\text{H}_5 > \text{H}$ . Electron-withdrawing groups stabilize a (–) charge.

2. Positive Inductive effect : (+I effect, Electron releasing effect) When an electro positive atom or group (more electro positive than hydrogen) is attached to the terminal of the carbon chain in a compound, the electrons are displaced away from the attached atom or group.  $(\text{CH}_3)_3\text{C}- > (\text{CH}_3)_2\text{CH}- > -\text{C}_2\text{H}_5 > -\text{CH}_3$ . Electron donor groups stabilize a (+) charge.

### Applications of Inductive effect:

Inductive effect is useful in explaining the strength of some organic acids and bases.

(a) Effect of substituent on the acid strength of aliphatic acids.



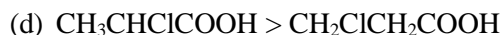
Reason : Acidic strength decreases as +I effect of the alkyl group increases.



Reason : Acidic strength decreases as -I effect of the group or halogen decreases.



Reason : Acidic strength decreases as the number of halogen atoms decreases.



Reason : Acidic strength decreases as the distance of the halogen from carboxylic group increases.

(e) Benzoic acid is stronger than acetic acid.

Reason : due to –I effect of phenyl group.

Relative basic strength of amines:

1. All aliphatic amines are more basic than ammonia. e.g. Methyl amine is more basic than ammonia. Reason : Due to +I effect of methyl group.

2. Aniline is weaker base than Ammonia. Reason : Due to +R effect and –I Effect of phenyl group.