Study material: For B.Sc. part-III

Subject: Organic Chemistry, paper III(C)

Topic: General Principles

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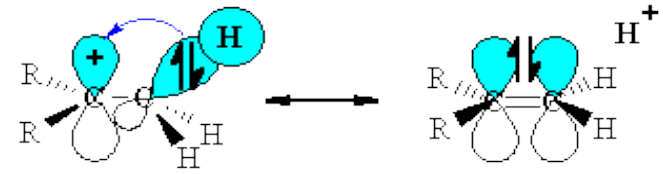
Electronic factors that influence organic reactions include the **hyperconjugation, inductive effect**, **mesomeric effect** and **resonance effects**. Electronic effects complicate chemical reactions, and they can stabilize a molecule, make a compound less volatile, make a molecule more likely to react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

Hyperconjugation: Hyperconjugation is the interaction of electrons in a sigma (σ) 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** σ-bonds (shown in blue.)

This geometry means the electrons in the σ-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°), secondary (2°) and primary carbocation is as follows $CH_3)_3C^+ > (CH_3)_2CH^+ > (CH_3)CH_2^+ > CH_3^+$
3° carbocation is more stable than a 2°, 1°, 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 hyper-conjugation 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 uniformed. So, the electrons are attracted towards the most electronegative atom.

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. $-NO_2$ > -CN > -COOH > F > Cl > Br > I > OH > C_6H_5 > 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. $(CH_3)_3C-$ > $(CH_3)_2CH-$ > $-C_2H_5$ > - 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.

$HCOOH > CH\ COOH > (CH_3)_2CHCOOH$

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

(b) $O_2NCH_2COOH > FCH_2COOH > ClCH_2COOH > BrCH_2COOH > ICH_2COOH > CH_3COOH$

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

(c) $Cl_3CCOOH > Cl_2CHCOOH > ClCH_2COOH > CH_3COOH$

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

(d) $CH_3CHClCOOH > CH_2ClCH_2COOH$

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.