Inductive Effect

E-content for B.Sc. I Students of Prof Rajendra Singh (Rajju Bhaia) University, Prayagraj

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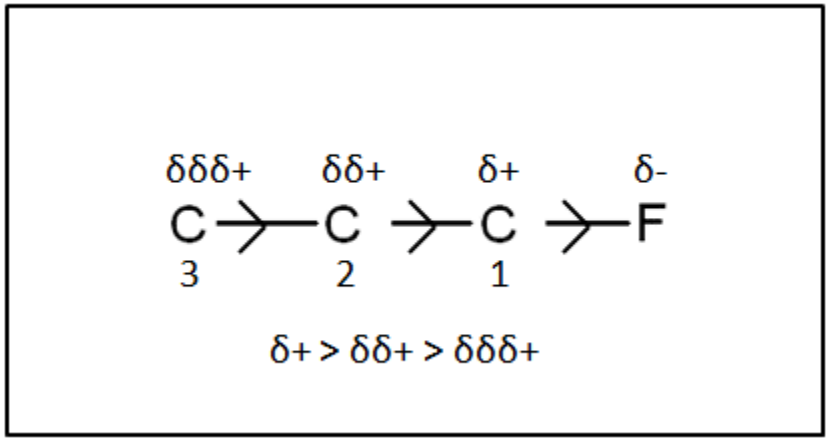
Content

- Inductive Effect –Definition
- Salient features
- Measurement
- -I Effect
- +I Effect
- Direct or Field Effect
- Applications
- Reference

Inductive Effect

- The intrinsic tendency of a substituent to release or withdraw electrons , i.e., its electronegativity, is acting either through the molecular chain or through space.
- The effect weakens steadily with increasing distance from the substituent.



- Consider a carbon chain in which one carbon atom is joined to a chlorine atom.

$$C_3 \rightarrow C_2 \rightarrow C_1 \rightarrow Cl$$

- Chlorine has a greater electronegativity than carbon, therefore the electron pair forming covalent bond between the Cl and C_1 will be displaced towards chlorine atom. This causes the Cl atom to acquire a small negative charge and C_1 a small positive charge.
- Since C_1 is positively charged, it will attract towards itself the electron pair forming the covalent bond between C_1 and C_2 . This will cause C_2 to acquire a small positive charge, but the charge will be smaller than that on C_1.
- Similarly, C_3 acquires a positive charge which will be smaller than that on C_2.
- This type of electron displacement along a chain due to the presence of a polar bond is known as **Inductive Effect.**

Salient Features

- Inductive effect is a permanent effect.
- It decreases rapidly as the distance from the source increases.
- The electron pairs although permanently displaced, remain in the same valency shell.
- This effect operates through σ bonds.

Measurement

- For measurement of relative inductive effects, hydrogen is chosen as reference standard.

- (+) or (-) sign is assigned to group having relative electron attracting or repelling character, respectively.

- This terminology is according to **Ingold** (1926)

-I Effect

- Any atom or group which attracts electrons more strongly than hydrogen is said to have negative inductive effect.

- The decreasing order of groups is as follows

  $N^{+}R^{3} > NO_2 > SO_2R > CN > SO_2Ar > COOH > F > Cl > Br > I > OAr > COOR > OR > COR > SH > SR > OH > NH_2 > Ar$

+I Effect

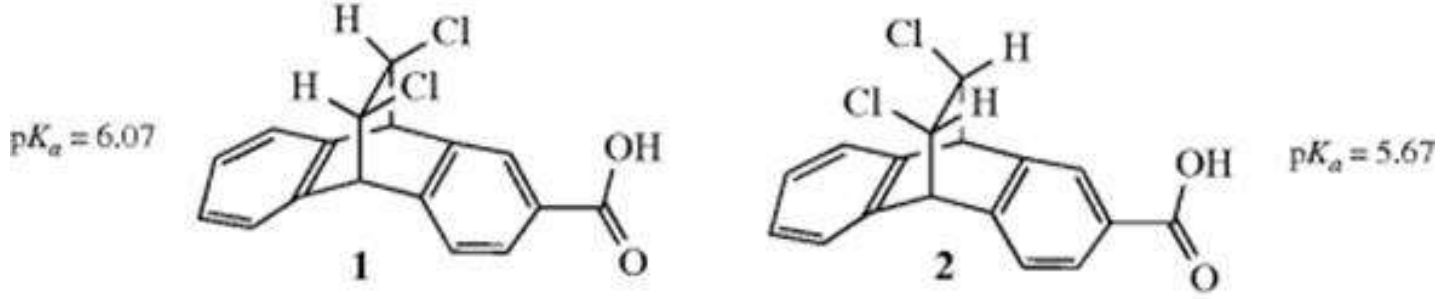
- Any atom or group which attracts electrons less strongly than hydrogen is said to have positive inductive effect.

- The decreasing order of groups is as follows

$O^- > CO^-O > CR_3 > CHR_2 > CH_2R > CH_3 > D$

Direct or Field Effect

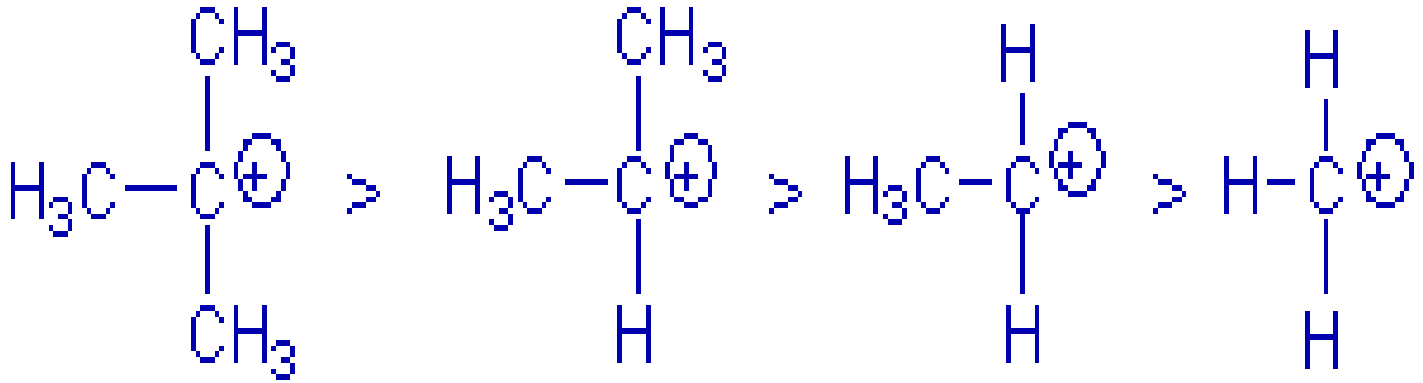
- There is also another effect possible, the **direct or field effect,** which results from the electrostatic interaction across space or through a solvent of two charged centres in the same molecule.
- The direct effect takes place independently of the electronic system in the molecule.



Applications

- Magnitude of positive charge on cations can be compared by +I or –I groups present in it.
- More is the +I power of the group, less will be magnitude of positive charge.
- More is the –I power of the group, more will be magnitude of positive charge.

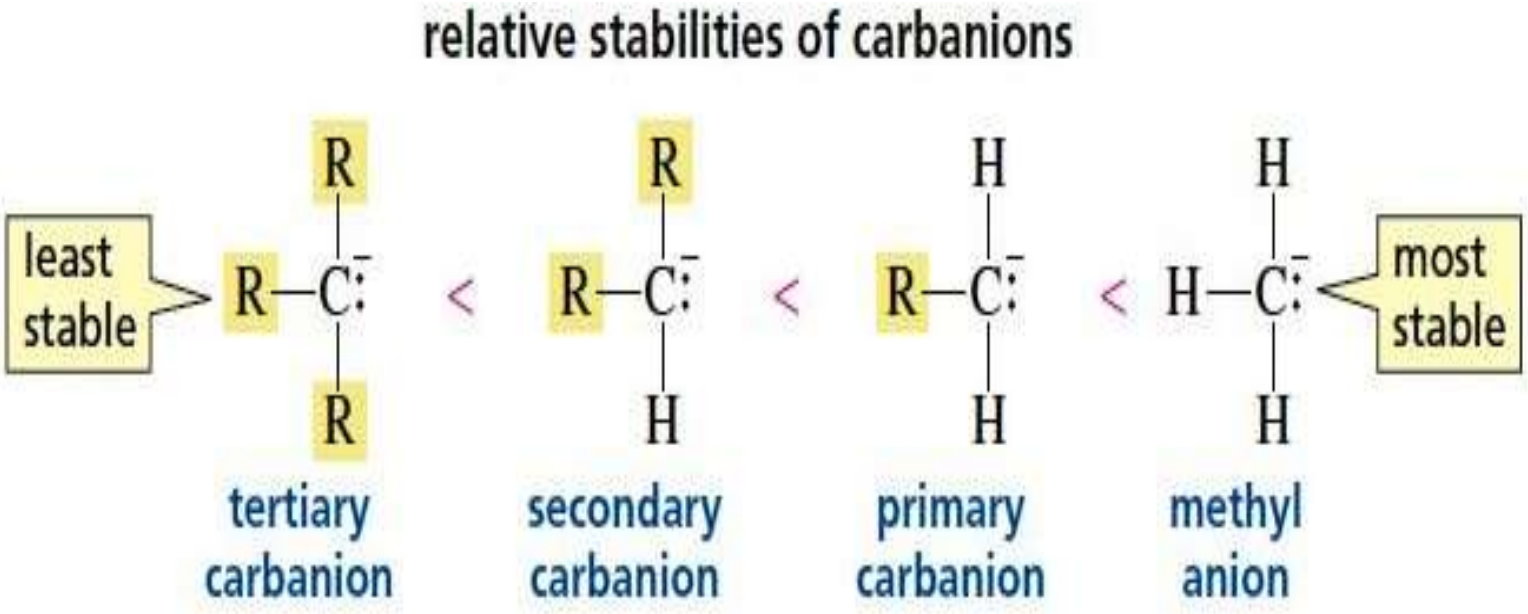
Stability of Alkyl Carbocation



3° 2° 1° methyl

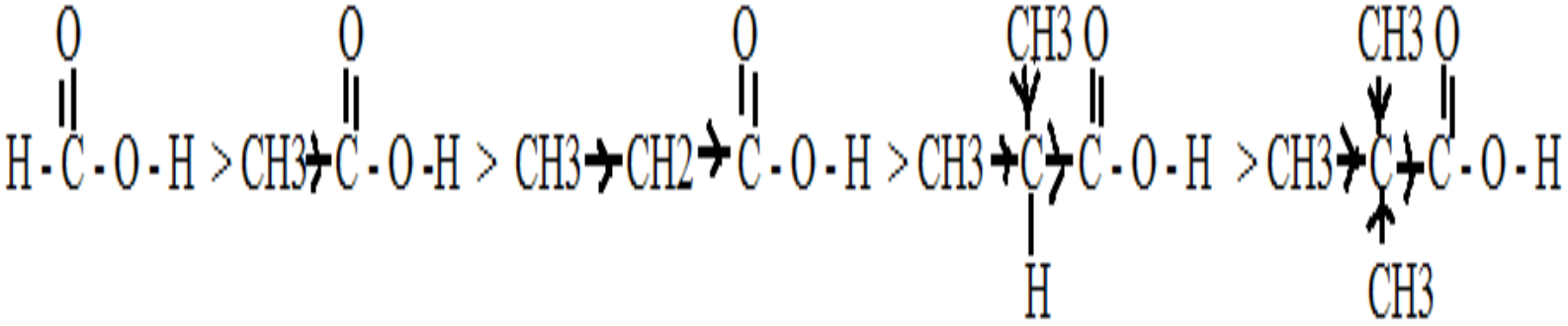
- Magnitude of negative charge on anions can also be compared by +I or –I groups present in it.
- More is the +I power of the group, more will be magnitude of negative charge.
- More is the –I power of the group, less will be magnitude of negative charge.

Stability of Alkyl Carbanion



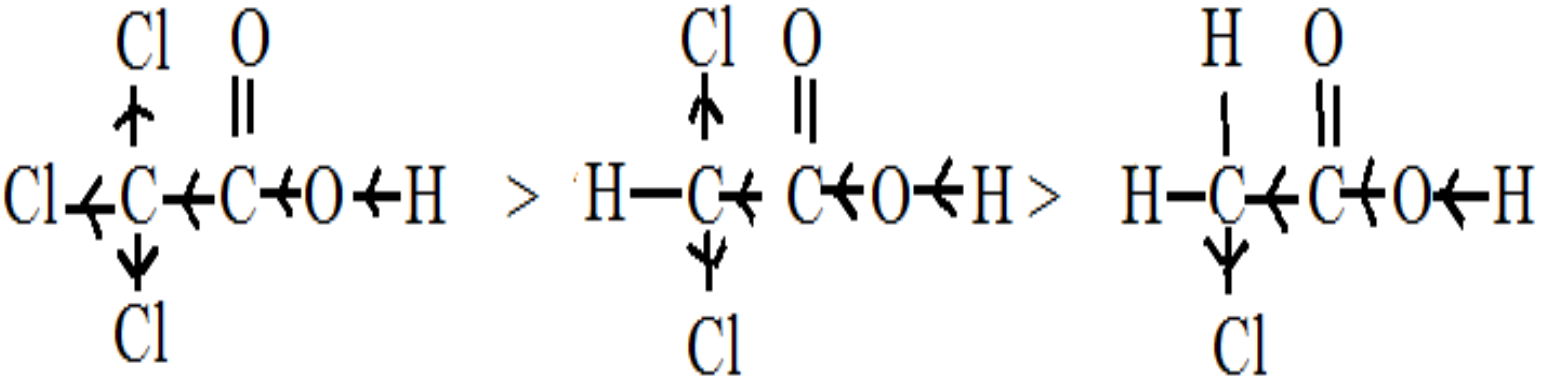
Strength of carboxylic acids

- Electron donating groups destabilise acid anion and weaken the acid
- i.e., +I group decreases strength of acid



Strength of carboxylic acids

- Electron withdrawing groups stabilise acid anion and increase strength of the acid.
- i.e., -I group increases strength of acid.



Reference

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- Bahl & Bahl, Organic Chemistry