Chemistry Study Materials for Class 11 (NCERT Based Notes of Chapter- 12) Ganesh Kumar Date: -11/01/2021

SOME BASIC PRINCIPLES AND TECHNIQUES

Electron displacement effects in covalent bonds

In an organic molecule, the electron displacement may take place either under the influence of an atom or in the presence of an attacking reagent. The important types of electron displacement effects are inductive effect, electromeric effect, resonance effect and hyper conjugation.

1. Inductive effect (I - effect):

It is a permanent effect arising due to the shifting of sigma electrons through a carbon chain in presence of an atom or group of atom (having different electronegativity) attached to a carbon chain. This effect propagates only through $C-C\sigma$ bonds. This effect decreases rapidly as the number of C atoms increases.

E.g. 1-chlorobutane $CH_3 - CH_2 - CH_2 - CH_2 - CI$

Here CI is more electronegative than C. So the electron pair in the C–CI bond is shifted towards CI and it gets a slight –ve charge (δ^-) and C gets a slight +ve charge (δ^+). This carbon attracts the electron density from the second carbon and so the 2nd carbon gets a relatively smaller positive charge ($\delta\delta^+$).

Here CI atom attracts electron towards it. So we can say that CI atom has electron withdrawing effect or -I effect (negative inductive effect). So groups which have the ability to attract electron pairs towards it are called -I effect.

Example for such groups are –X (F, Cl, Br, I), nitro (-NO₂), Cyano (CN⁻), Carboxy (-COOH), ester (-COOR), aryloxy (-OAr) etc.

Groups which donate electron pairs towards the carbon chain are said to have +I effect or electron donating (releasing) groups. Example for such groups are alkyl groups like methyl (- CH_3), ethyl (- CH_2 - CH_3) etc.

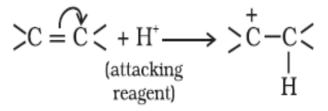
2. Electromeric effect (E effect):

It is defined as the complete transfer of a shared pair of π -electrons to one of the atoms joined by a multiple bond in presence of an attacking reagent. It is a temporary effect. It is possible only in compounds containing multiple bonds (alkene or alkyne). This effect cancels when the attacking reagent is removed from the

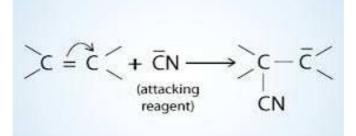
reaction site. The shifting of the electrons is shown by a curved arrow

There are two types of E effects:

a) **Positive Electromeric effect (+E effect):** Here the pi electrons are transferred to that atom to which the attacking reagent gets attached.



b) Negative Electromeric effect (-E effect): Here the pi electrons of the multiple bonds are transferred to that atom to which the attacking reagent does not get attached.



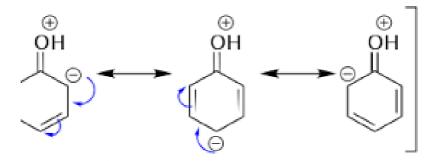
When inductive and electromeric effects operate in opposite directions, the electromeric effect predominates.

3. Resonance Effect (Reffect):

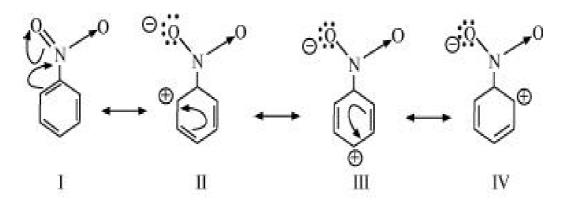
It is defined as 'the polarity (charge) produced in the molecule by the interaction of two π -bonds or between a π -bond and lone pair of electrons present on an adjacent atom'. The effect is transmitted through the chain.

There are two types of resonance or mesomeric effect (R or M effect):

a) **Positive Resonance effect (+R effect):** Here the transfer of electrons is away from an atom or substituent group attached to the conjugated system. E.g. + R effect in phenol:



b) Negative Resonance Effect (- R effect): Here the transfer of electrons is towards the atom or substituent group attached to the conjugated system. E.g. – R effect in nitrobenzene:



The presence of alternate single and double bonds in an open chain or cyclic system is termed as a conjugated system.

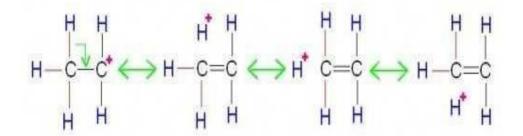
E.g. for +R effect groups: – halogen, –OH, –OR, –OCOR, –NH₂, –NHR, –NR₂, –NHCOR etc.

E.g. for – R effect groups: – COOH, –CHO, >C=O, – CN, –NO₂ etc.

4. Hyper conjugation:

It is a permanent effect. In this effect the σ electrons of C—H bond of the alkyl group enter into partial conjugation with the unsaturated system or with the unshared p orbital. i.e. the σ electrons of C –H bonds get delocalised.

e.g. ethyl cation (ĈH₃-CH ⁺)



Hyper conjugation stabilizes the carbocation because electron density from the adjacent σ bond helps in dispersing the positive charge. In general, the greater the number of alkyl groups attached to a positively charged carbon atom, the greater is the hyper conjugation interaction and stabilization of the cation.

Thus the relative stability of carbocations is in the order:

$$(CH_3)_3C^+ > (CH_3)_2CH^+ > CH_3-CH_2^+ > CH_3^+$$

Here tertiary carbocation has 9, isopropyl has 6, ethyl carbocation has 3 and methyl carbocation has zero hyper conjugative structures.

Hyper conjugation is also called no-bond resonance and it is also possible in alkenes and alkyl arenes.
