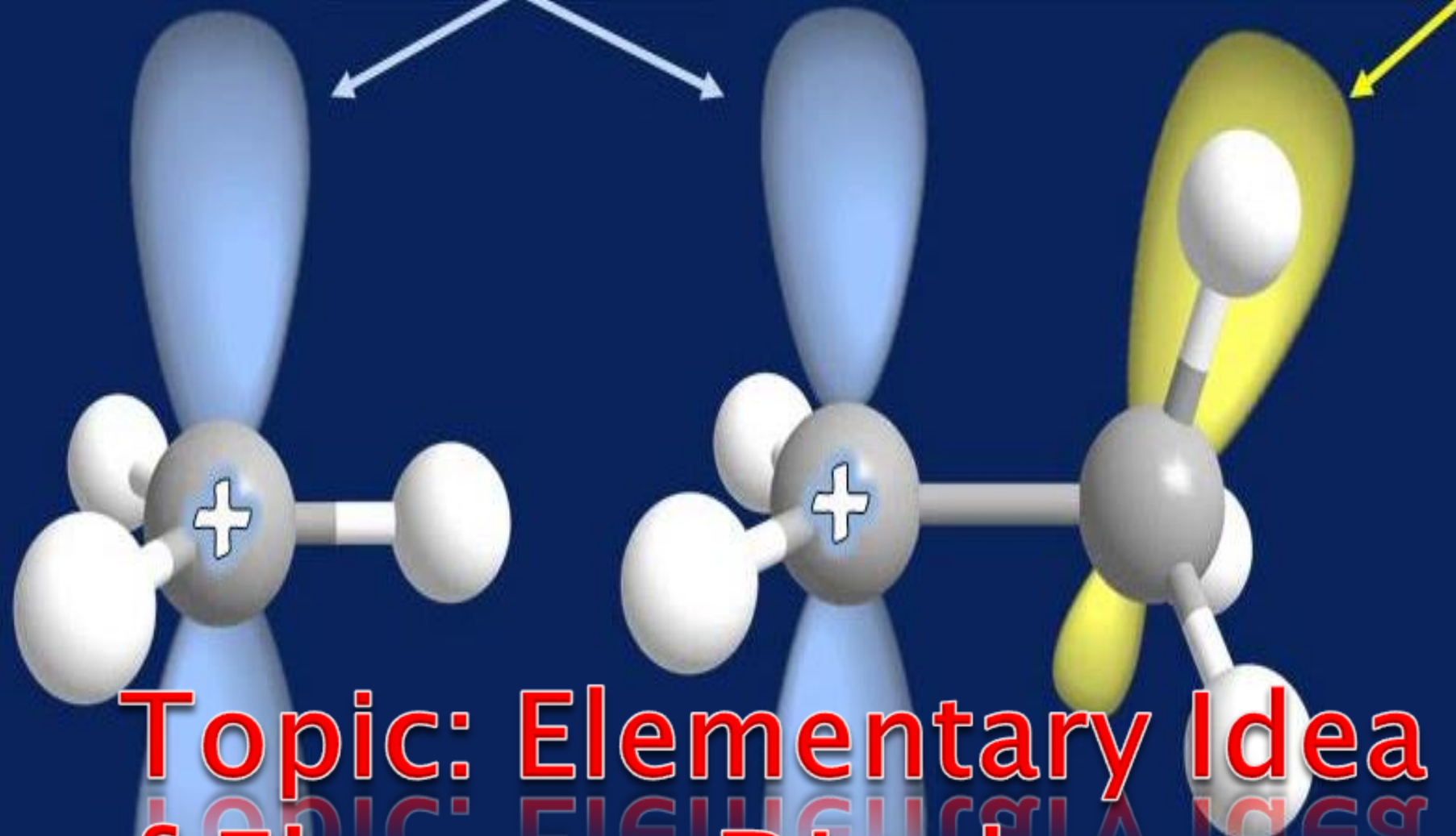


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# Topic: Elementary Idea of Electron Displacement Effects

# Electron Displacement Effect

- ▶ Displacement of electron pair in the covalent bonds can result in two types of polarizations, permanent polarization and temporary polarization.
- ▶ **Permanent Polarizations:**-Occurs in the ground state under the influence of an atom or a substituent group, e.g.; Inductive effect, Mesomeric effect and Hyperconjugation.
- ▶ **Temporary Polarization:**-occurs in presence of an attacking reagent, e.g.; Electromeric effect.

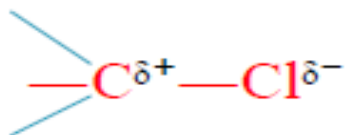
# Inductive Effect

1. it refers to the polarity produced in a molecule as a result of higher electronegativity of one atom compared to another. e.g.



1. polarization of  $\sigma$ -bond results in partial charge over adjacent atoms and is transmitted along a chain.
1. occurs in  $\sigma$ -bonds only formed between atoms of different electronegativity.
2. electron cloud is displaced towards more electronegative atom .
3. C—H bond is used as standard ,zero effect is assumed in this case.
4. It is of two types;+I effect and –I effect .

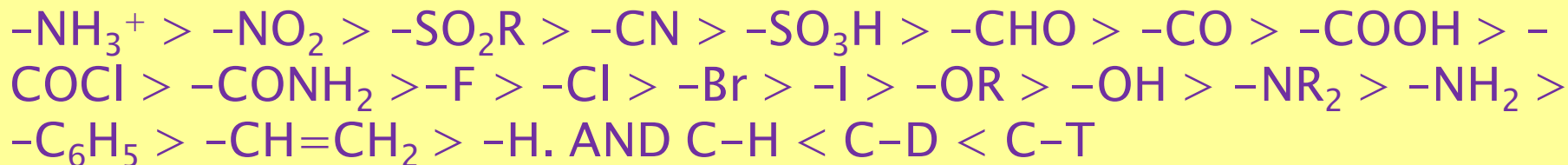
- ▶ **-I Effect:**-occurs when atoms or group of atoms having more electron attracting capacity than H-atom (e-withdrawing group) is attached to a molecule , e.g.  $\text{NO}_2$  ,  $\text{COOH}$  ,  $\text{Cl}$  ,  $\text{Br}$ , etc.



- ▶ **+I Effect:**-occurs when atoms or group of atoms having less electron attracting capacity than H-atom (e-releasing group) is attached to an organic molecule ,e.g.  $(\text{CH}_3)_3\text{C-}$  ,  $(\text{CH}_3)_2\text{CH-}$ ,  $\text{CH}_3\text{CH}_2\text{-}$  ,  $\text{CH}_3\text{-}$ .

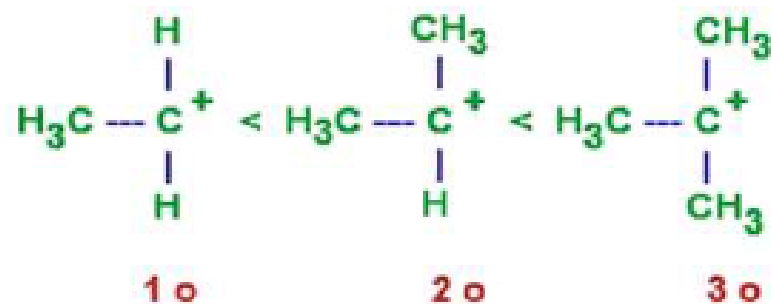


increasing order of  $-$ /effect or decreasing order of  $+$ /effect:

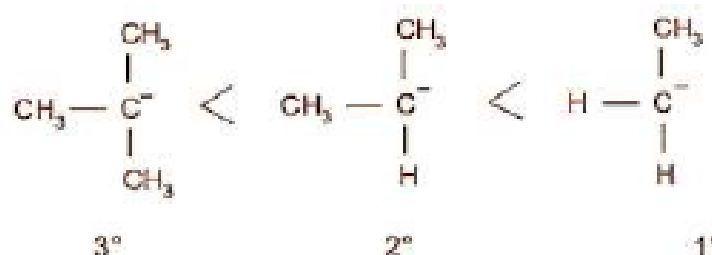


▶ **Applications of Inductive Effect**:-it explains the relative stability of

▶ **Carbocation's** ; stability increases with increase in the no of alkyl groups . E.g.



▶ **Carbanions** ; stability decreases with increase in the no of alkyl groups.eg:

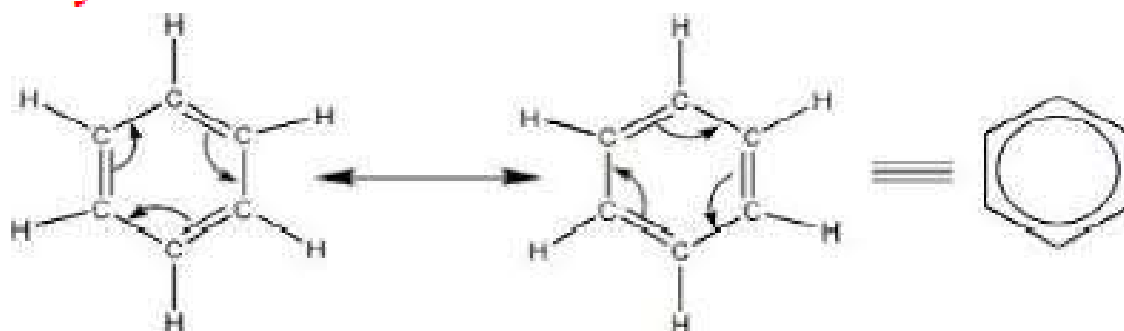


▶ **Acidic strength** ; Electron withdrawing group decreases the negative charge on the carboxylate ion by stabilizing it ,hence the acidic strength increases ,e.g.



## Mesomeric Effect

There are many molecules whose structure can not be explained by a single Lewis structure. To explain their behavior two or more structures may be proposed and the actual molecule is said to be **resonance hybrid** of these molecules.

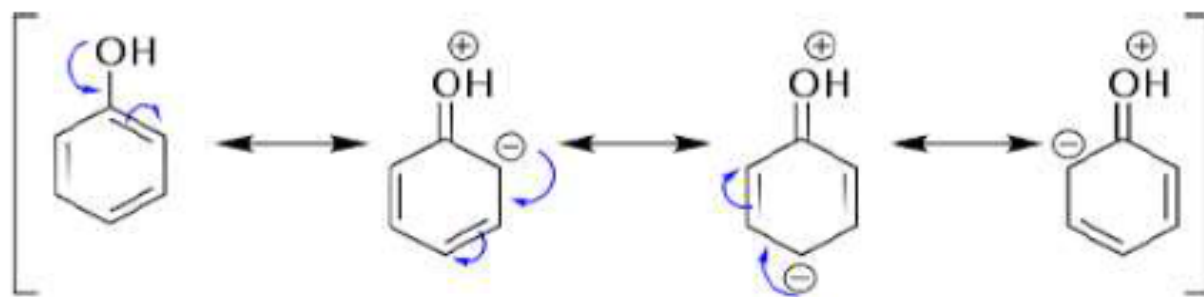


It refers to the polarity produced in a molecule as a result of interaction between two  $\pi$ -bonds or a  $\pi$ -bond and a lone pair of electrons.

- ▶ It involves  $\pi$ -electrons of double or a triple bond.
- ▶ It can be divided into two types, +M effect & -M effect.



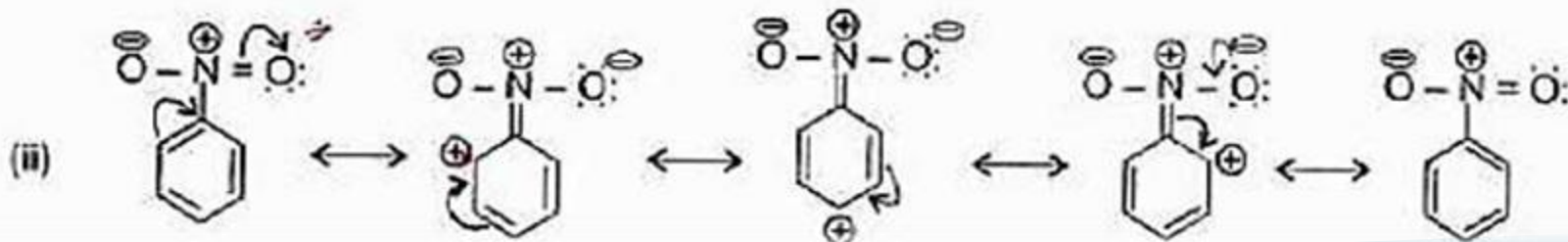
carbon atom are said to have +M effect, e.g.  $\text{NH}_2$ ,  $\text{Cl}$ ,  $\text{Br}$ ,  $\text{I}$ ,  $\text{OH}$ , etc.



### +M EFFECT ORDER :

$-\text{O}^- > -\text{NH}_2 > -\text{NHR} > -\text{OR} > -\text{NHCOR} > -\text{OCOR} > -\text{Ph} > -\text{F} > -\text{Cl} > -\text{Br} > -\text{I}$

- ▶ **-M effect:** -atoms or groups of atoms which draw electrons away from the carbon atom are said to have -M effect , e.g.  $\text{NO}_2$ ,  $\text{C}\equiv\text{N}$ ,  $\text{C}=\text{O}$ , etc.



### -M EFFECT ORDER :

$-\text{NO}_2 > -\text{CN} > -\text{S(=O)}_2-\text{OH} > -\text{CHO} > -\text{C}=\text{O} > -\text{COOCOR} > -\text{COOR} > -\text{COOH} > -\text{CONH}_2 > -\text{COO}^-$



## Rules for resonance

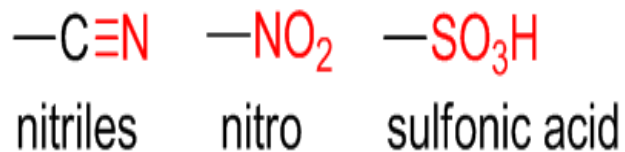
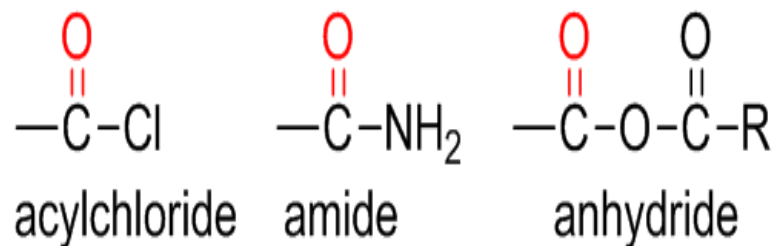
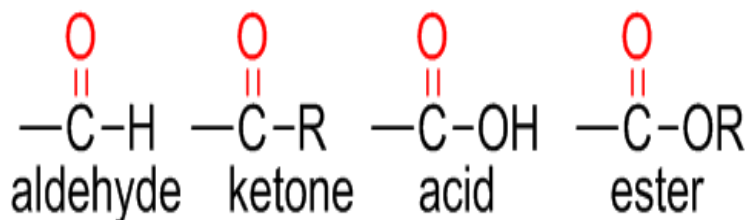
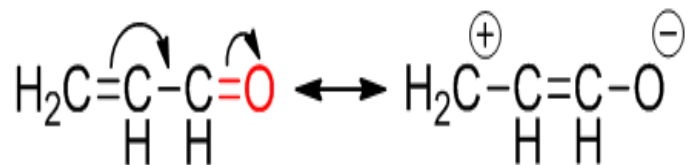
- ▶ Only pi-electrons or non bonding electrons are involved.
- ▶ Energy of resonance hybrid should be lower than contributing structures.
- ▶ Structure should be planar .
- ▶ No of paired or unpaired electrons should be same.
- ▶ Contributing structures have nearly same energy.

## Stability of resonating structures

- ▶ More the no. of covalent bonds more stable the structure is .
- ▶ Structure with complete octet are more stable.
- ▶ Negative charge should be on more electronegative atom.
- ▶ Like charges should not be on adjacent positions.

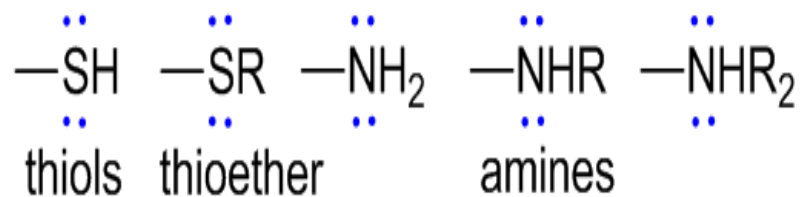
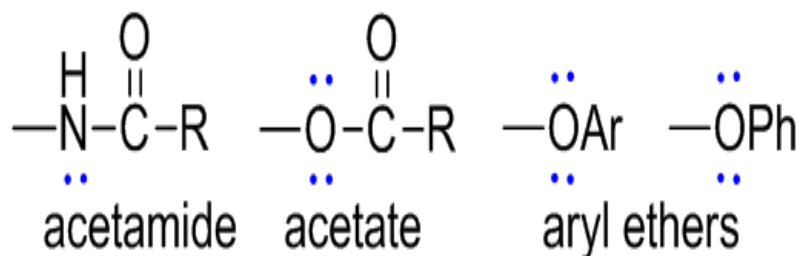
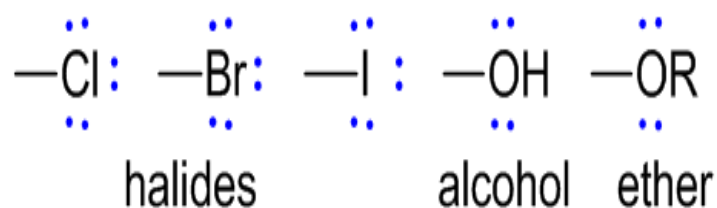
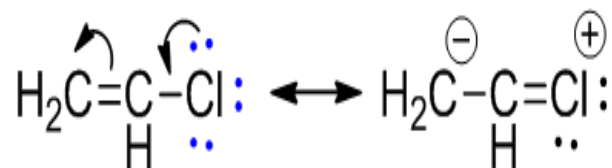
- Mesomeric Effect (-ME)

$\pi$  electrons are involved



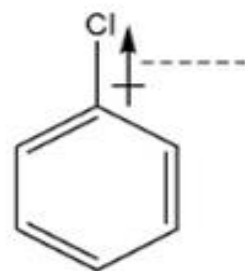
+ Mesomeric Effect (+ME)

non-bonding 'n' electrons are involved



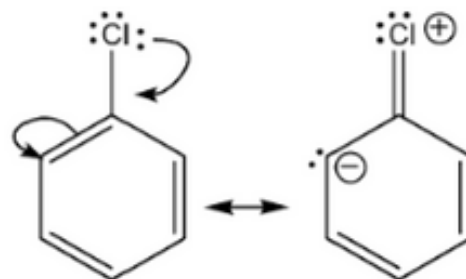
Inductive effect	Resonance effect
Based on electronegativity.	Based on Conjugation.
Electron moves via sigma bonds.	Electron moves via pi bonds or lone pairs.
It involves displacement of only $\sigma$ electrons and hence occurs only in saturated compounds.	It involves delocalization of $\pi$ (pi) or n lone pairs of electrons and hence occurs in unsaturated and conjugated systems.
During inductive effect the electron pair is only slightly displaced towards the more electronegative atom and hence only partial positive and negative charges appear.	During resonance effect, the electron pair is completely transferred and hence full positive and negative charges appear.

## Inductive Effect



Cl is more electronegative than C, so it inductively withdraws electron density from the ring.

## Resonance Effect



Resonance-donating effects place extra electron density at the *ortho* and *para* positions on the ring.

## Electromeric Effect

It refers to the polarity produced in a multiple bonded compound as it is approached by a reagent. The presence of reagent disturbs the symmetry of pi-molecular orbitals in favor of one of the carbon atoms.

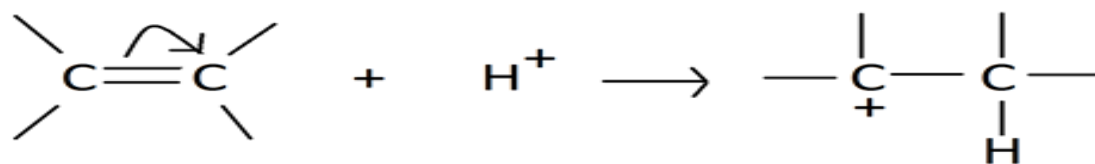
It is a temporary effect.

It is classified as, +E, and -E effect.

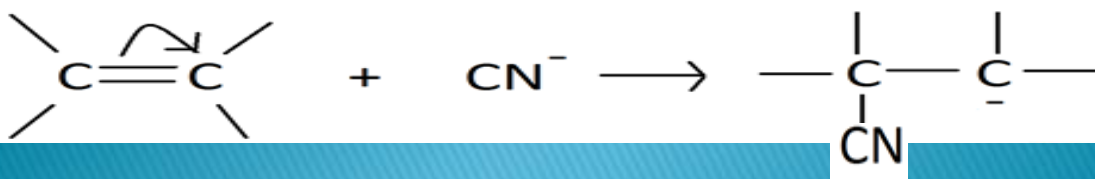
**+E effect**:-when the transfer of electrons takes place towards the attacking reagent is called +E effect. e.g.

**-E effect** :-when transfer of electron takes place away from the attacking reagent it is called -E effect, e.g.

Positive electromeric effect



Negative electromeric effect





### Inductive effect

- 1) It is a permanent effect
- 2) The presence of multiple bond is not essential
- 3) The polarity of bond is essential
- 4) Partial charge separation takes place
- 5) No ions are formed
- 6) Attacking reagent is not Required
- 7) The displaced electrons do not leave their molecular orbitals . however, distortion of electron position cloud take place
- 8) It involves mere displacement of electrons

### Electromeric effect

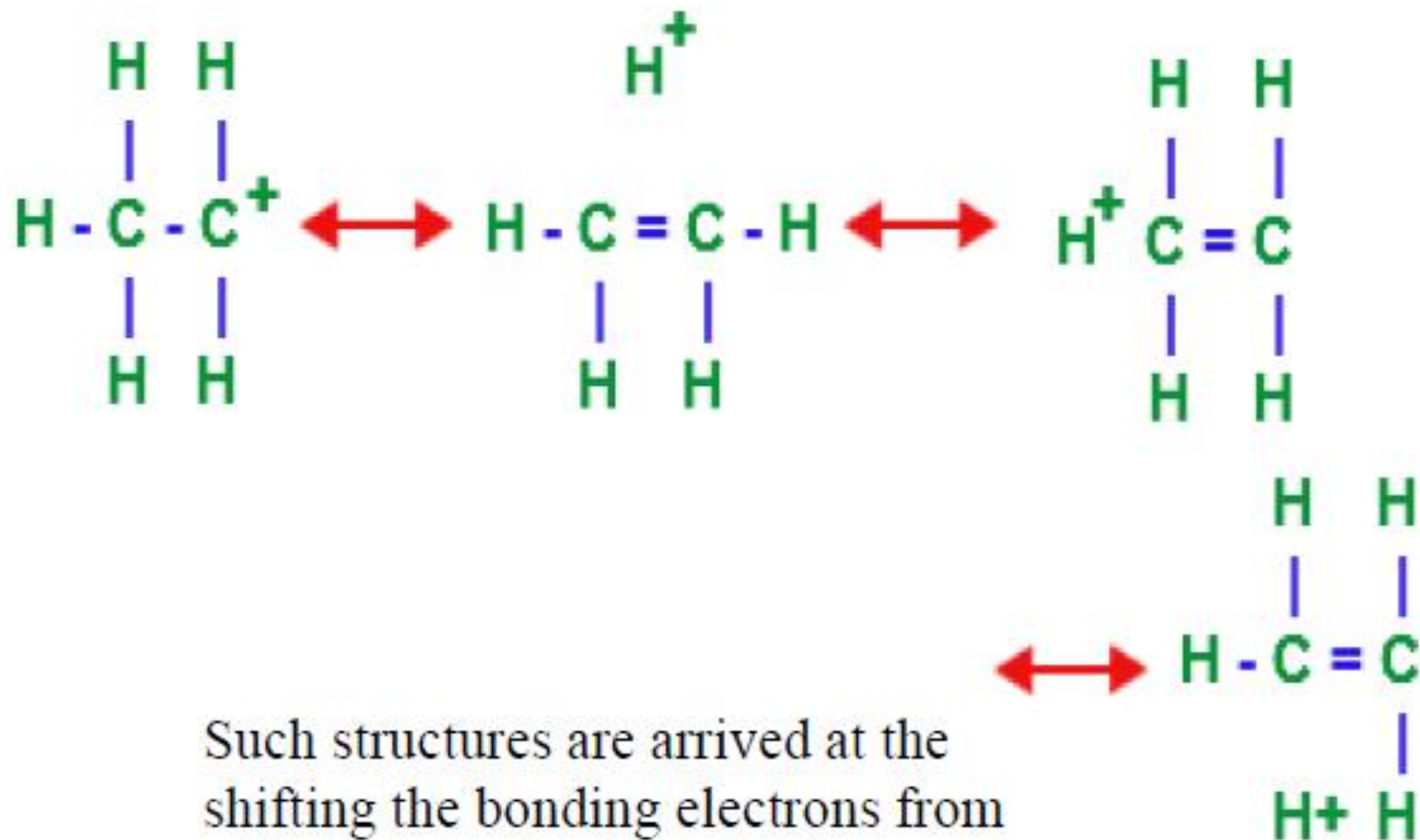
- 1) It is a temporary effect
- 2) The presence of a multiple bond is essential.
- 3) The polarity of bond is not essential.
- 4) Complete charge separation takes place
- 5) Ions are formed.
- 6) Attacking reagent is required
- 7) The displaced electrons leave their orbitals and attain a new position
- 8) It involves complete transference of  $\pi$  –electrons

## Hyperconjugation

- ▶ Refers to the displacement of electrons through delocalization of  $\sigma$ -electrons from  $\alpha$ - C-H bond with the  $\pi$ - electrons ( $\pi$ -orbitals) of the adjacent multiple bond or to an atom with p-orbital is called hyperconjugation or no bond resonance.
- ▶ The relative stability of various carbocation's can be explained by no bond resonance structures that can be written for them . Such structures are arrived at the shifting the bonding electrons from adjacent C-H bond to the electron deficient carbon. In this way the positive charge originally on carbon is dispersed to the hydrogen.
- ▶ Greater the no of alkyl groups attached to a positively charged C-atom greater is the hyperconjugation interaction & more stable the carbocation is, thus,
- ▶  $3^\circ > 2^\circ > 1^\circ > \text{CH}_3^+$

The total no of possible canonical structures is (n+1).





Such structures are arrived at the shifting the bonding electrons from adjacent C-H bond to the electron deficient carbon.

# Hyperconjugation Explained

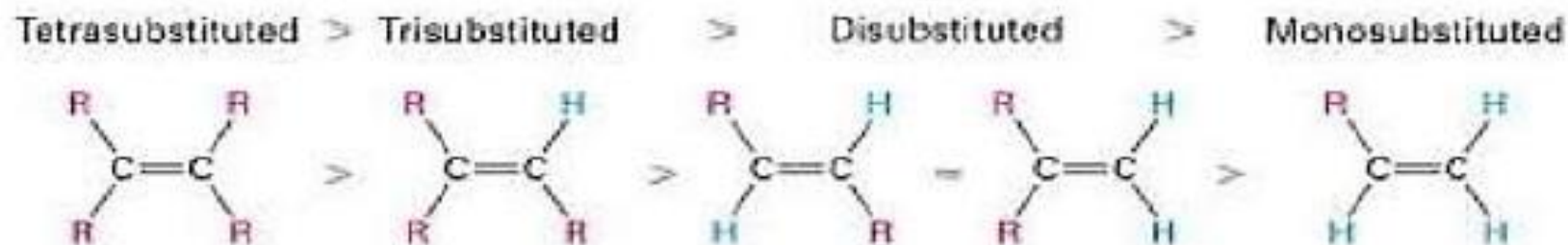
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Dept. of Chem. B. N. College BGP  
Dr. Ambika Kr.

- ▶ In carbocation's positive charge remains same in all the canonical structures including the hyperconjugative one is called **Isovalent hyperconjugation**.
- ▶ In case of alkenes more substituted alkenes are relatively more stable than unsubstituted alkenes, thus;

Alkenes become more stable with increasing substitution

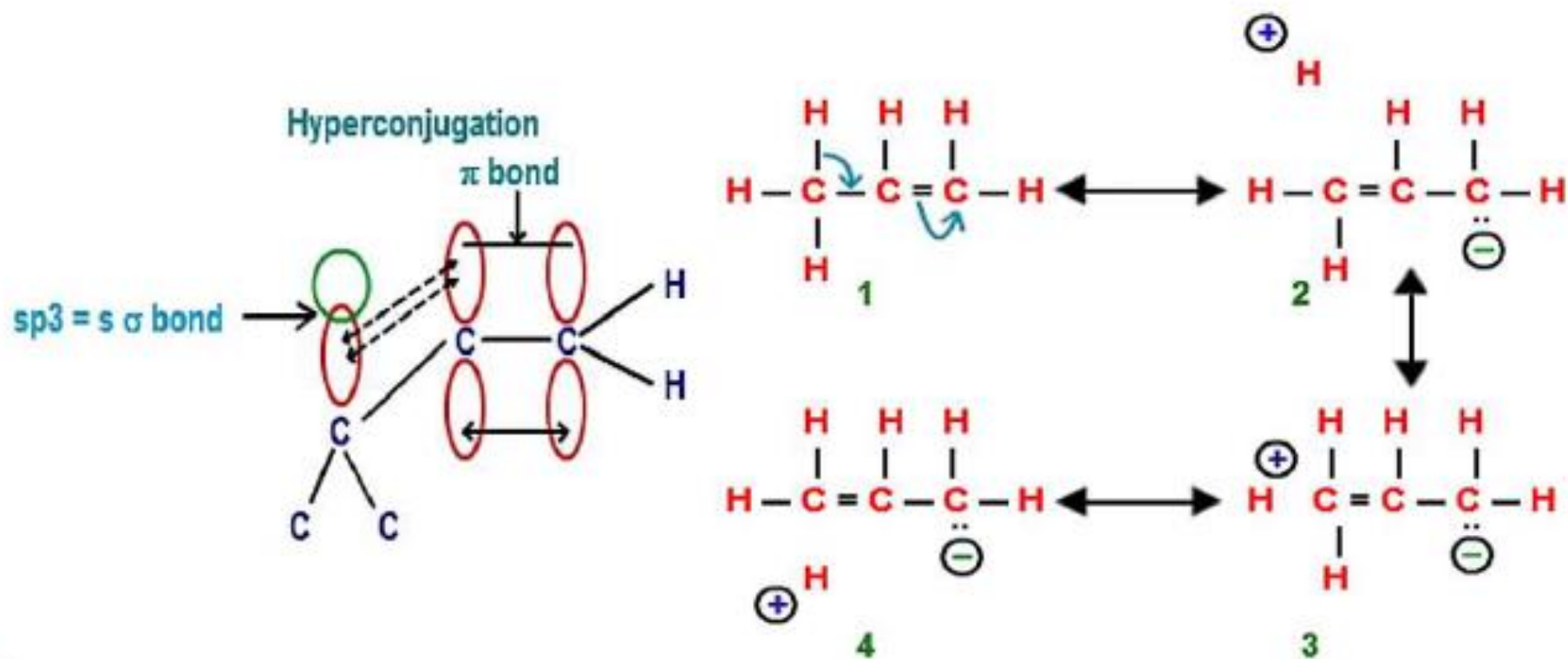


Stability order due to two factors:

- **Hyperconjugation**

- Stabilizing interaction between the C=C  $\pi$  bond and adjacent C-H  $\sigma$  bonds on substituents
- The more substituents there are the greater the stabilization of the alkene.

- Hyperconjugation in alkenes results from donation of electron density from an adjacent  $\sigma$ -bond to  $\pi$ -antibonding orbital. e.g.





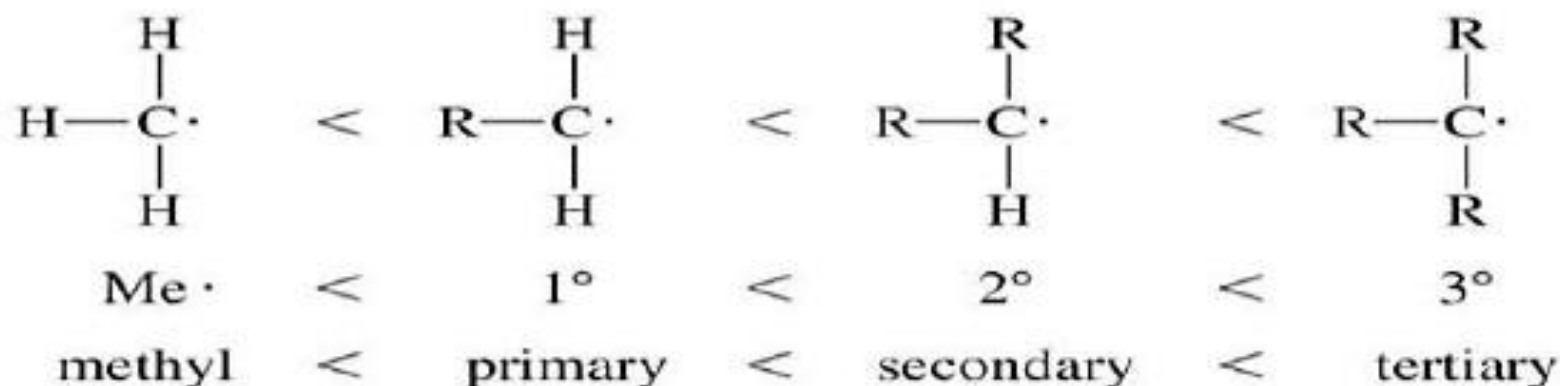
In alkenes there is one less real bond in the canonical structures than the hyperconjugative structure,

also there is no real separation of charge as  $H^+$ . This is termed as **Sacrificial Hyperconjugation**.

It results in shortening of C-C bonds adjacent to multiple bonds.

**Stability of free radicals** ; greater the no. of alkyl groups attached to a free radical more stable it is , thus;

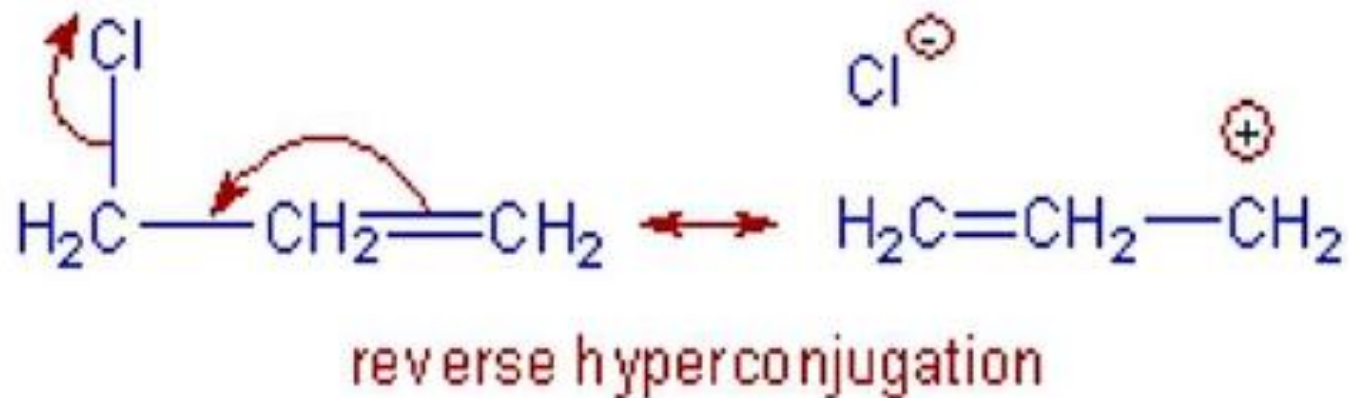
## Stability of Free Radicals



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- Free radicals are more stable if they are highly substituted.

- ▶ In case of  $\alpha$ -Halo alkenes the delocalization of electrons occurs towards the halogen group through the hyperconjugative mechanism, it is referred to as **Reverse Hyperconjugation**.





You may attempt various objective problems on the discussed topic, using this link:

<https://www.neetprep.com/question/40371?courseId=57>