


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.
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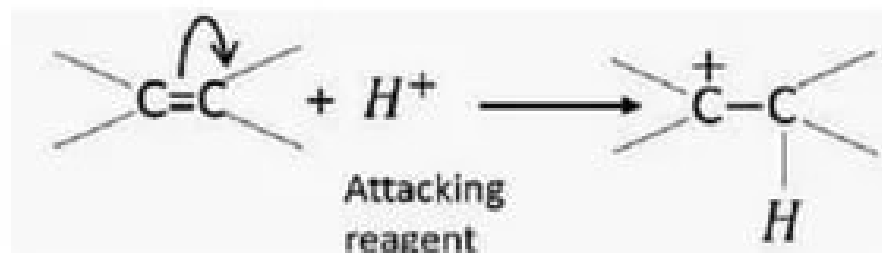
Electromeric Effect

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.

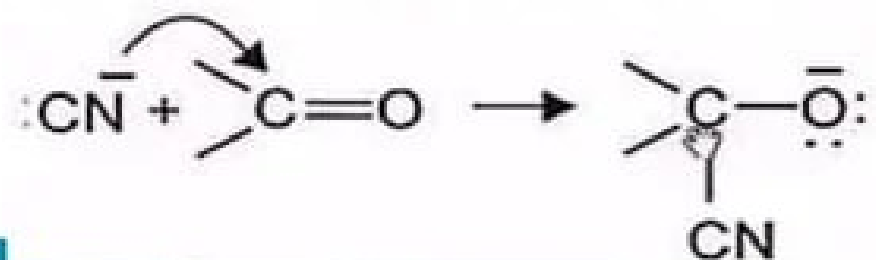
It is a temporary effect.

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.



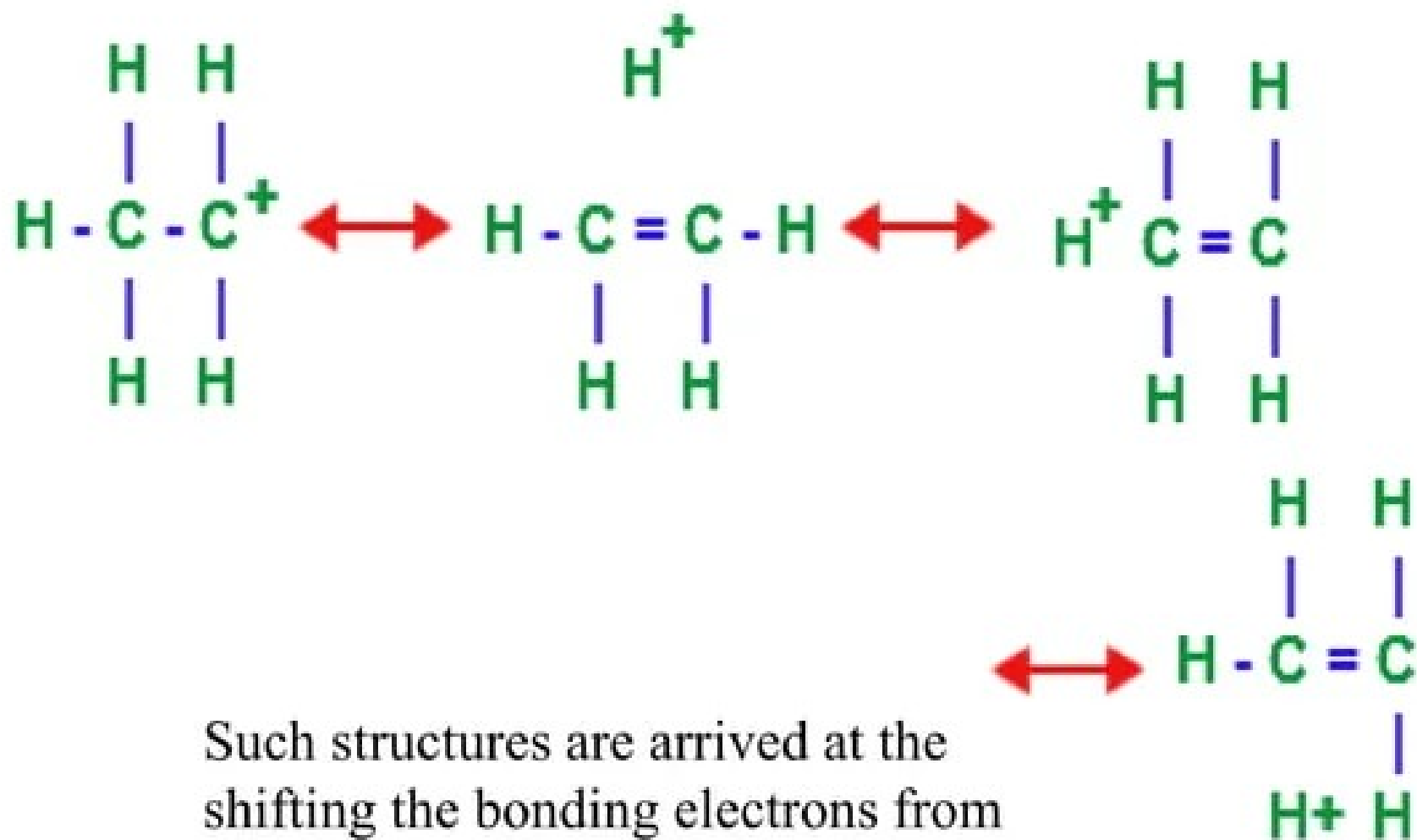
-E effect :-when transfer of electron takes place away from the attacking reagent it is called -E effect, e.g.



Hyperconjugation

- ▶ Refers to the displacement of electrons through delocalization of σ -electrons from α - C-H bond with the π - electrons (π -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,
- ▶ $3^\circ > 2^\circ > 1^\circ > \text{CH}_3^+$

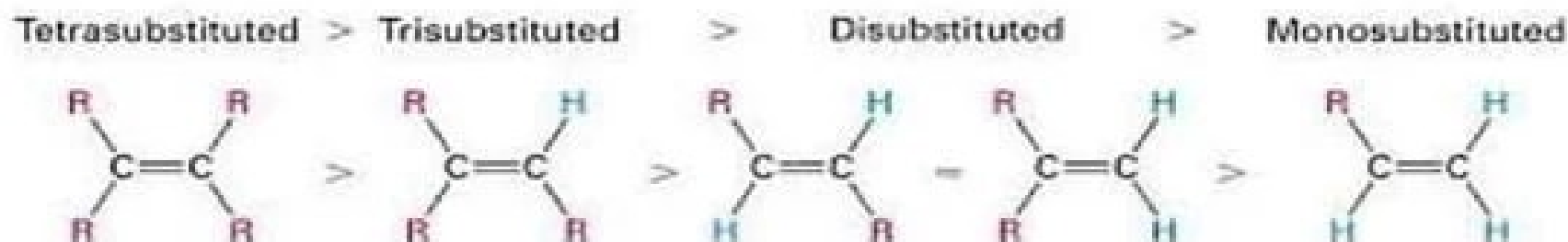
The total no of possible canonical structures is (n+1).



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

- ▶ 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;

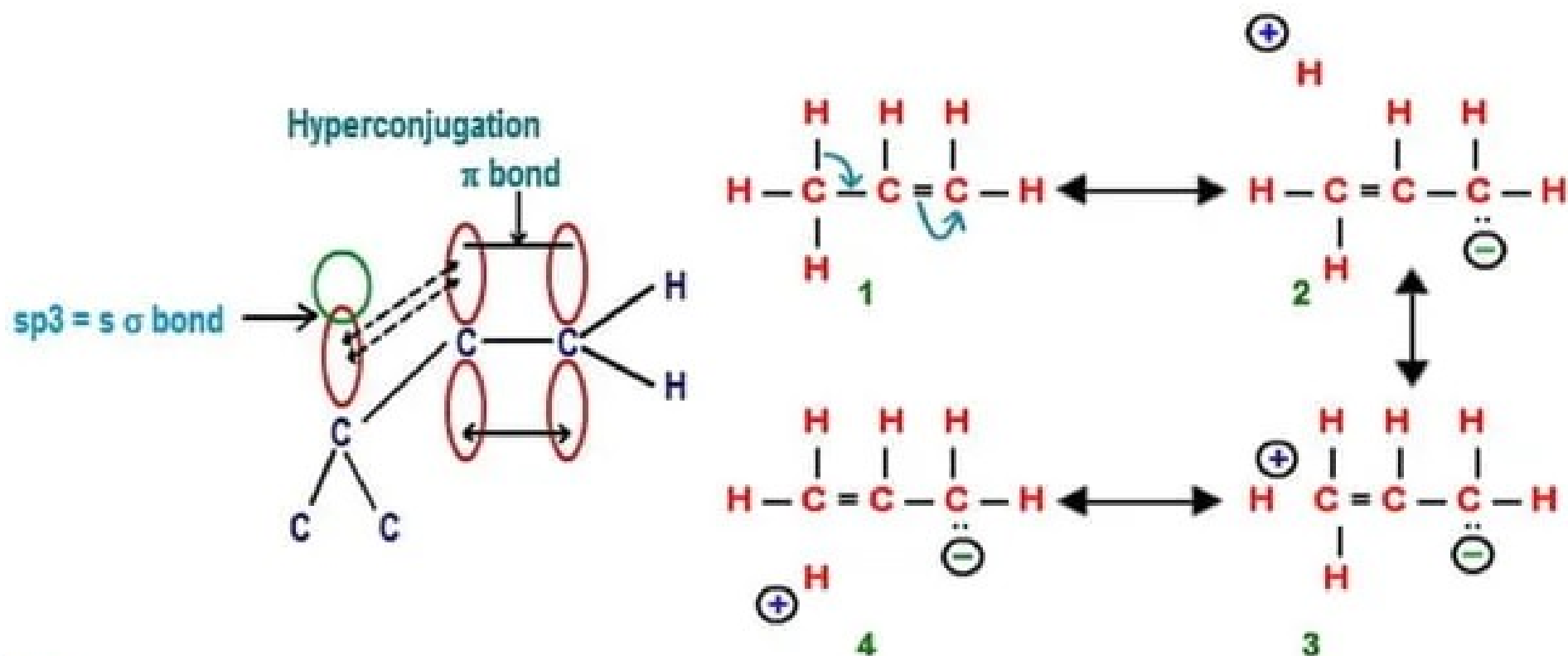
Alkenes become more stable with increasing substitution



Stability order due to two factors:

- **Hyperconjugation**
 - Stabilizing interaction between the C=C π bond and adjacent C-H σ 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 σ -bond to π -antibonding orbital. e.g.



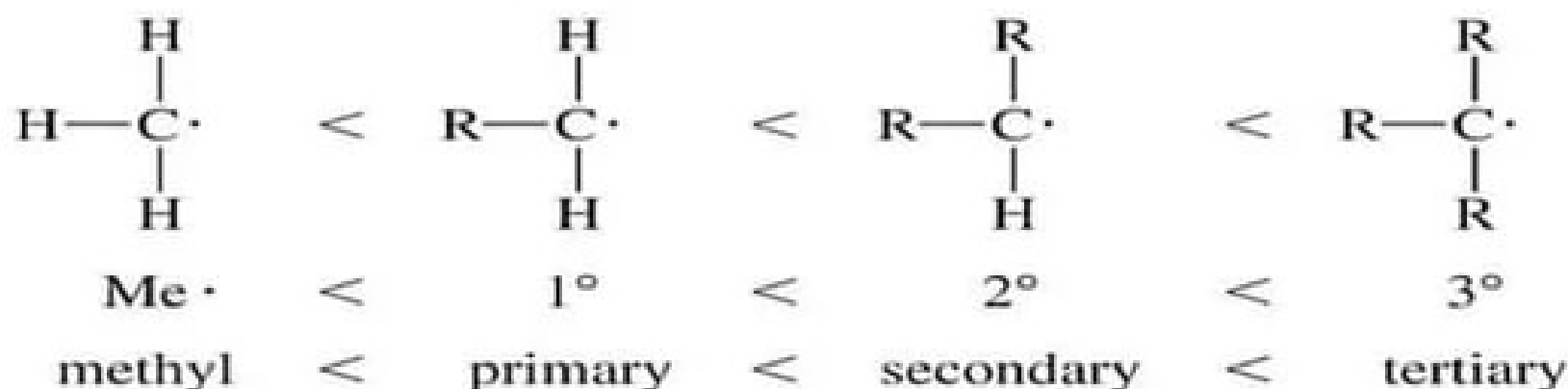
In alkenes there is one less real bond in the canonical structures than the hyperconjugative structure,

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;

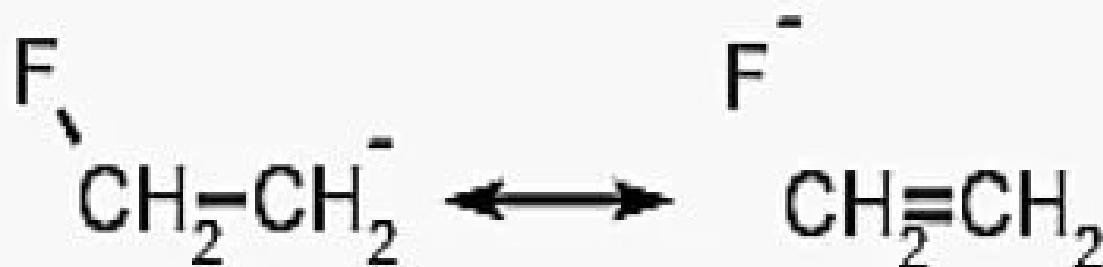
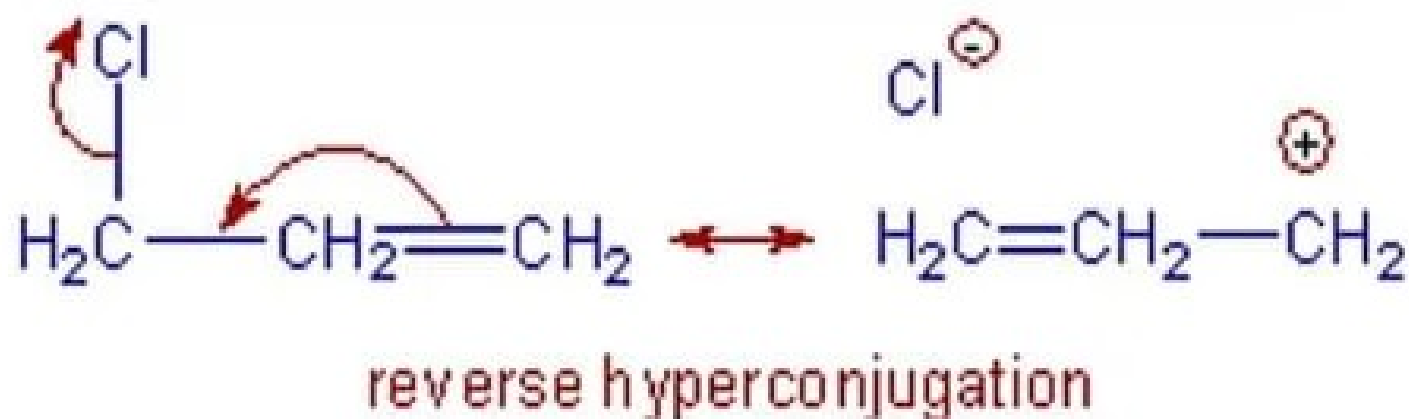
Stability of Free Radicals



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

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



Thanks To All OF You

