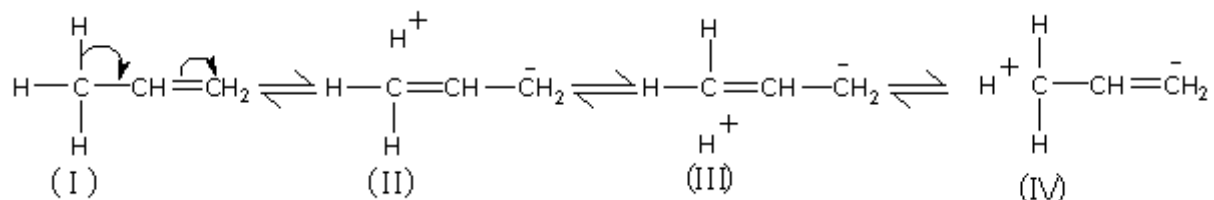


Hyperconjugation

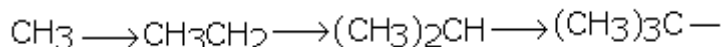
The conjugation between electrons of single (H-C) bond with multiple bonds is called hyperconjugation. This occurs when the sigma (s) electrons of the H-C bond that is attached to an unsaturated system, such as double bond or a benzene ring, enter into conjugation with the unsaturated system.

The concept of hyperconjugation was developed by Baker and Nathan and is also known as Baker and Nathan effect. According to this concept, if an alkyl group carrying at least one hydrogen atom is attached to an unsaturated carbon atom, it releases the electrons of carbon-hydrogen single bond towards the multiple bond. For example, the hyper conjugation in propene is shown below:



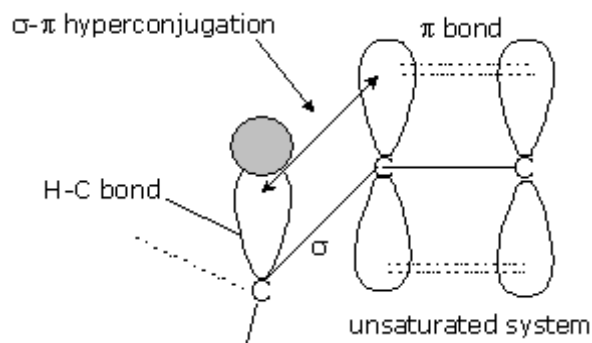
The various hyperconjugation forms of propene are called contributing structures. The hyperconjugation effect bears similarities to the resonance effect. In hyperconjugation, there is no bond between the α -carbon atom and one of the hydrogen atoms, thus it is also called no-bond resonance. Since this effect depends upon the presence of H-atoms at α -carbon atom, it is expected to be more due to CH_3 - group than due to CH_3CH_2 - group as the latter has only two H atoms attached to the α -carbon atom. Similarly, hyperconjugation effect will be less if $(\text{CH}_3)_2\text{CH}$ - group is attached to an unsaturated system and there will be no hyperconjugation effect if $(\text{CH}_3)_3\text{C}$ - group is attached to the α -carbon of the unsaturated system.

Therefore, the order of hyperconjugation is :



Orbital Concept of Hyperconjugation

The orbital concept of hyperconjugation is well illustrated with the help of propene. In this, the electron pair of C-H bond (s-bond) is involved in conjugation with the p-electron pair of the double bond. In hyperconjugation the delocalisation of s-electrons of H-C bond takes place through overlapping of p orbitals of the double bond as shown:



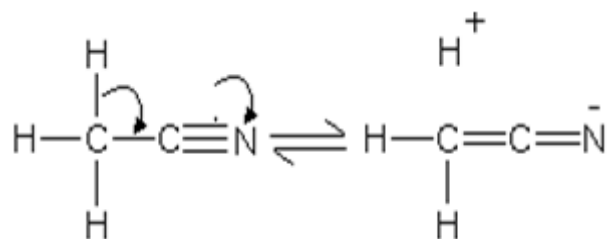
Orbital representation of s-p hyperconjugation

Applications of Hyperconjugation

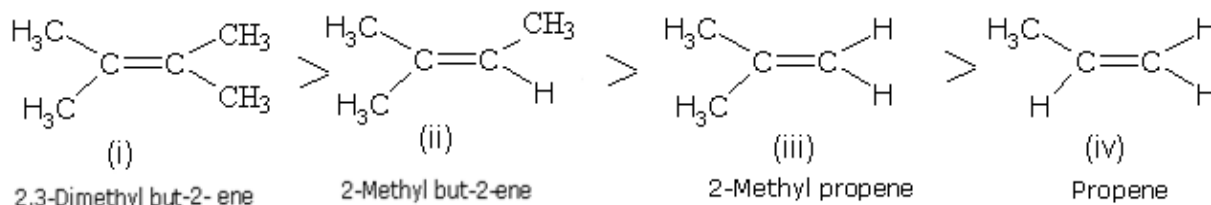
The concept of hyperconjugation is very useful in explaining stabilities of some organic molecules.

- Shortening of carbon-carbon single bonds adjacent to multiple bonds: For instance in acetonitrile the carbon-carbon bond adjacent to triple bond acquires some double bond character and hence is little shorter.

Due to hyperconjugation the C-C single bond adjacent to a triple bond is shorter than normal bond.



- Stability of methylated alkenes: When the number of methyl groups linked to carbon-carbon double bond is more, the hyperconjugative C-H bond number increases and the stability of alkene increases. Thus, the stability of alkenes is:



The above order of stability occurs because of greater number of contributing structures, which cause large delocalisation and hence stabilises the alkene. For instance, alkene-I has 12 α -hydrogens while alkene-II has nine α -hydrogen atoms. Therefore, there will be larger hyperconjugation in alkene-I and it will be more stable than alkene-II.

Hyperconjugation can also explain relative stabilities of carbocations and free radicals.

