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**CHEMISTRY**
**PAPER No. 1: ORGANIC CHEMISTRY- I (Nature of Bonding and Stereochemistry)**
**Module No. 3: Hyper-Conjugation**

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**CHEMISTRY**

**PAPER No. 1: ORGANIC CHEMISTRY- I (Nature of Bonding and Stereochemistry)**

**Module No. 3: Hyper-Conjugation**

## 1. Learning Outcomes

After studying this module you shall be able to:

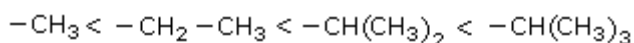
- Understand the concept of hyperconjugation.
- Know about the structural requirements in a molecule to show hyperconjugation.
- Learn about the important consequences and applications of hyperconjugation.
- Comprehend the concept of reverse hyperconjugation.

## 2. Introduction

In conjugation, we have studied that the electrons move from one p orbital to other which are aligned in parallel planes. Is it possible for electron to jump from p orbital to  $sp^3$  orbital that are not parallelly aligned with one another? The answer is yes. This type of conjugation is not normal, it is extra-ordinary. Hence, the name hyper-conjugation. It is also know as no-bond resonance. Let us study more about it.

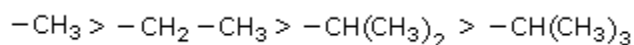
## 3. Hyperconjugation

The normal electron releasing inductive effect (+I effect) of alkyl groups is in the following order:



But it was observed by Baker and Nathan that in conjugated system, the attachment of alkyl groups reverse their capability of electron releasing. They suggested that alkyl groups are capable of releasing electrons by some process other than inductive.

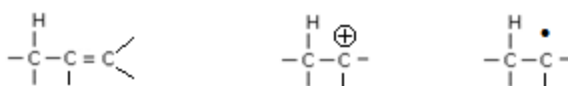
When a C - H sigma bond is in conjugation, the sigma electrons of this bond enter into conjugation. This is an extension of normal conjugation and was termed **hyperconjugation**. Unlike the normal conjugation wherein, the  $\pi$  electrons get delocalized in p orbitals, here  $\sigma$  electrons move to p orbitals. It involves the delocalisation of C - H sigma electrons. It essentially means that hyper conjugation depends on the presence of alpha-hydrogen atoms. With the increase in number of such hydrogens, the electron releasing effect of alkyl group also increases e.g.,



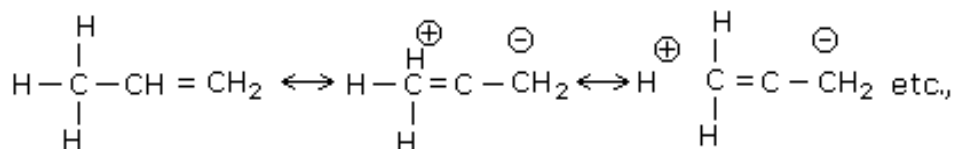
The contributing structures involving sigma electrons of C - H bond do not show any covalent bond between C and H. Hyperconjugation, therefore, is also called **no bond resonance**.

It is important to note that hydrogen does not actually separate from the molecule because if that happens, the necessary condition for resonance to occur will be violated.

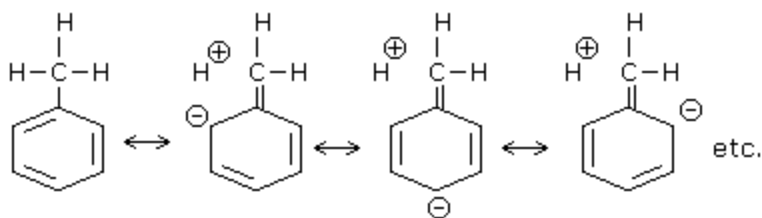
Hyperconjugation exists in the molecules having the following framework, i.e either alkenes or carbocations or free radicals having at least one  $\alpha$ -H atom, but not in carbanions.



Examples:



**Hyperconjugation in propene**



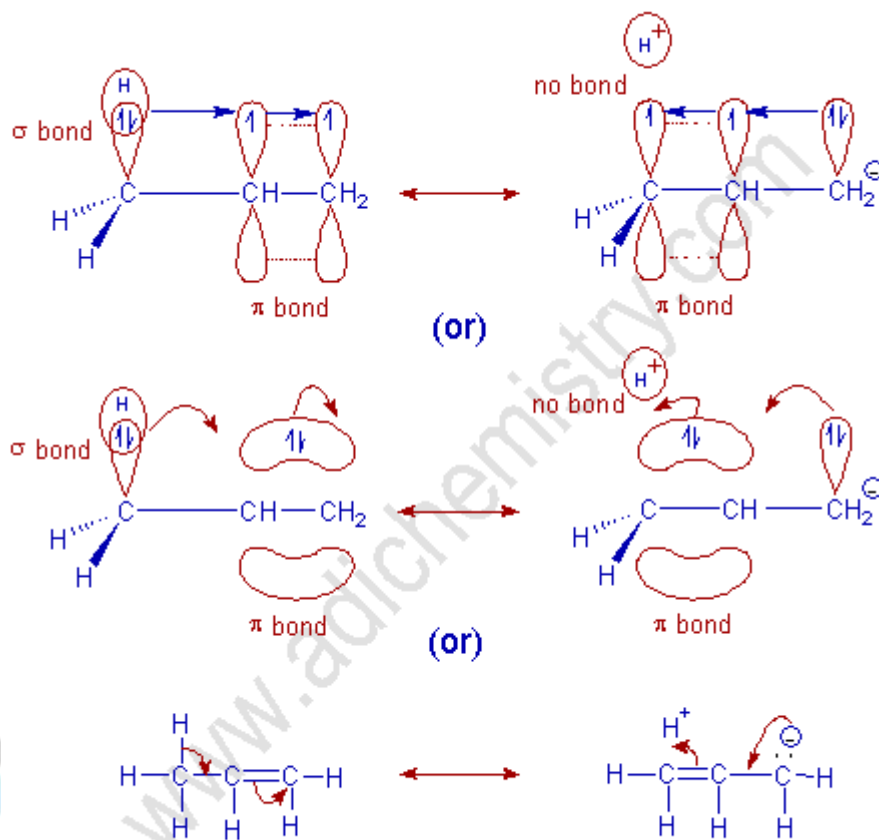
### Hyperconjugation in toluene

The  $-\text{CH}_3$  group can be denoted as having +H effect as it donates or gives electrons to the conjugated system.

#### 4. Requirements for Hyperconjugation

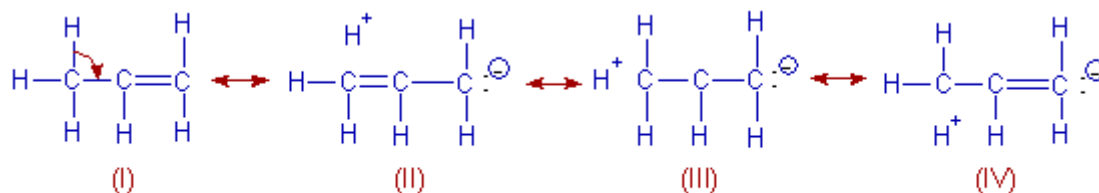
There must be an  $\alpha$ -C-H group or a lone pair on atom adjacent to  $\text{sp}^2$  hybrid carbon or other atoms like nitrogen, oxygen etc. E.g., Alkenes, alkyl carbocations, alkyl free radicals, nitro compounds with  $\alpha$ -hydrogen. Due to the presence of hydrogen on the  $\alpha$ -carbon (which is next to the multiple bond) displacement of s-electrons towards the multiple bond takes place which causes the polarization of the multiple bond.

E.g In propene, the delocalization of  $\sigma$ -electrons of C-H bond of methyl group occurs into the p-orbital of doubly bonded carbon which is shown below.



Hyperconjugation in propene

Likewise, remaining hydrogens on the methyl group also contribute in the hyperconjugation. It is possible because of free rotation of C-C bond so that the other C-H bonds can also contribute in the hyperconjugation. Therefore, propene molecule can illustrate the below resonance structures, which suggests its stability.



No bond resonance structures shown by propene due to hyperconjugation.

Notice that in the above hyperconjugative structures: (II), (III) & (IV) of propene, the bond between an  $\alpha$ -carbon and one of the hydrogen atom is absent. Thus, the hyperconjugation is also called as "no bond resonance".

These equivalent contributing structures i.e., (II), (III) & (IV) are also polar in nature and hence are responsible for the dipole moment of propene (0.36 D). The bond length of C-C in propene is equal to 1.48. The range is 1.54 (of C-C) -1.34 (of C=C). Thus, due to hyperconjugation, the approximate bond order of C-C is 1.5. This kind of hyperconjugation is also known as sacrificial hyperconjugation as one bond is missing.

Hyperconjugation is also exhibited by carbocations attached to  $\alpha$ -carbon having hydrogen atom and also by free radicals attached to  $\alpha$ -carbon having hydrogen atom. *Carbanions, however, do not exhibit hyperconjugation.*

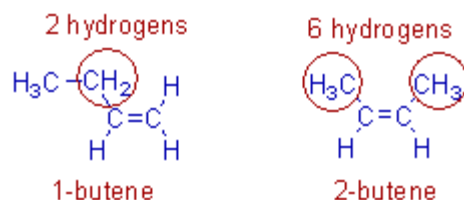
## 5. Consequences and Applications of Hyperconjugation

### 1) Stability of alkenes:

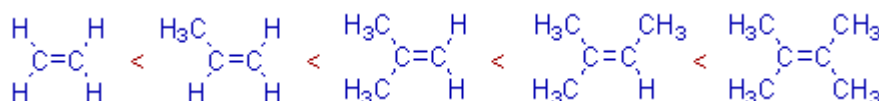
As a general rule, greater the number of alkyl groups (containing hydrogens) attached on the double bond greater is the stability of alkene. This is because of increase in number of contributing no bond resonance structures. Therefore, 2-butene is more stable than 1-butene.

For example, 2-butene is more stable than 1-butene.

This is because in 2-butene, there are six hydrogens involved in hyperconjugation whereas there are only two hydrogens involved in case of 1-butene. Hence the contributing structures in 2-butene are more and is more stable than 1-butene.



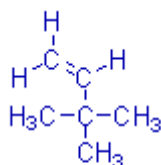
With the increase in the number of methyl groups on the double bonds, the stability of alkenes increases as shown below



The above order has been justified on the basis of heat of hydrogenation data of the given alkenes. With rise in the stability of alkene, the value of heat of hydrogenation decreases. For more substituted alkenes, heat of formation is higher than expected.

It must be kept in mind that the important condition for hyperconjugation to take place in alkenes is that the alkyl group attached to the double bond must have minimum one hydrogen atom.

For example, in case of the following alkene containing a tert-butyl group on doubly bonded carbon, the hyperconjugation is not possible.



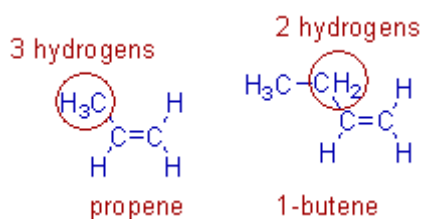
No H atoms on  $\alpha$  carbon.  
Hence no hyperconjugation.

*The effect of hyperconjugation is stronger than the inductive effect. It is because, in inductive effect there is partial delocalization of charges, but in hyperconjugation there is total transfer/delocalization of charge.*



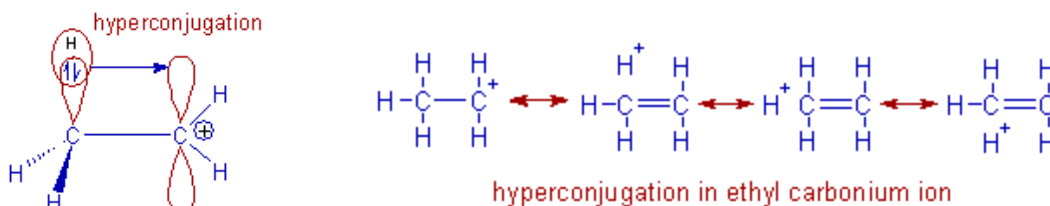
For example, considering inductive effect one may conclude that 1-butene is more stable than propene as the positive inductive effect of ethyl group is stronger than that of methyl group. But this is not correct; propene is more stable than 1-butene.

This is due to the fact that there are three hydrogens on  $\alpha$ -methyl group involved in hyperconjugation. However, in 1-butene only two hydrogen atoms are there on  $-\text{CH}_2$  group that can take part in hyperconjugation.



## 2) Stability of carbocations (carbonium ions):

The ethyl carbocation,  $\text{CH}_3\text{-CH}_2^+$  is more stable than the methyl carbocation,  $\text{CH}_3^+$ . This is because, the  $\sigma$ -electrons of the  $\alpha$ -C-H bond in ethyl group are delocalized into the empty p-orbital of the positive carbon center and thus by giving rise to 'no bond resonance structures' as shown below. But, hyperconjugation is not possible in methyl carbocation and hence is less stable.

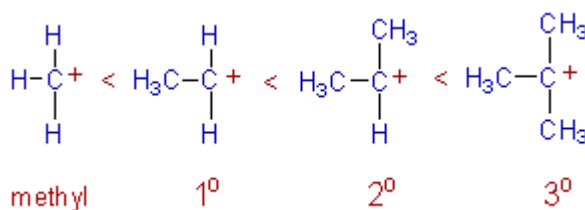


In general, As the number of alkyl groups (containing hydrogen) attached to the positively charged carbon increases, the stability of carbonium ions increases because of increase in the number of contributing structures to hyperconjugation. Note: This kind of

hyperconjugation can also be known as isovalent hyperconjugation. As there is no decrease in the number bonds in the no bond resonance forms.

Note: This type of hyperconjugation can also referred to as *isovalent hyperconjugation* since there is no decrease in the number bonds in the no bond resonance forms.

Thus the increasing order of stability of carbocations can be given as: methyl < primary < secondary < tertiary as depicted below:



### 3) Stability of free radicals:

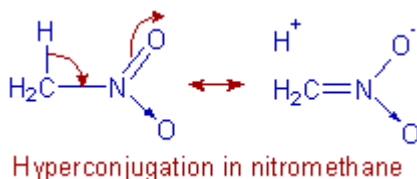
The stability of free radicals is influenced by hyperconjugation just as in case of carbonium ions. One of the two  $\sigma$ -electrons of the  $\alpha$ -C-H bond can be delocalized into the p-orbital of carbon containing an odd electron.

Due to hyperconjugation, the stability of free radicals also follow the same order as that of carbonium ions i.e., methyl < primary < secondary < tertiary.

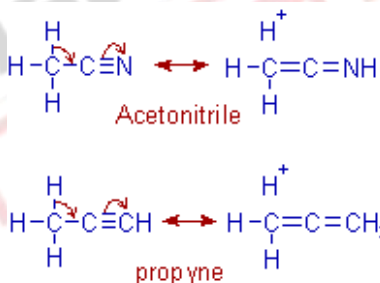
### 4) Dipole moment & bond length:

The dipole moment of the molecules is greatly affected due to hyperconjugation since the contributing structures show considerable polarity. The bond lengths are also altered due to change in the bond order during hyperconjugation. The single bond might develop partial double bond character and vice versa.

E.g. The experimental dipole moment of nitro methane is higher than the calculated value because of hyperconjugation. The experimental C–N bond length is also less than the expected value because of same reason.



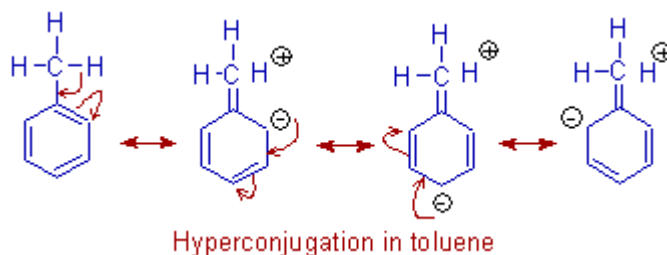
The same explanation can be given to decreasing of C-C bond adjacent to  $-C\equiv N$  in acetonitrile and also the C-C bond adjacent to the  $-C\equiv C$  in propyne. Here also, the observed dipole moments are different from their expected values due to hyperconjugation.



### 5) Reactivity & orientation of electrophilic substitution on benzene ring :

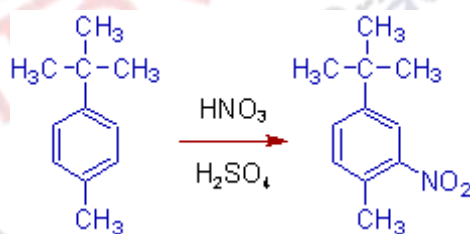
In case of Toluene, the reactivity of the ring towards electrophilic substitution increases and the substitution is directed at ortho and para positions to the methyl group. This can be explained mainly by hyperconjugative effect. The methyl group releases electrons towards the benzene ring partly due to inductive effect and mainly due to hyperconjugation.

The no bond resonance forms of toluene due to hyperconjugation are shown below.



From hyperconjugative structures, it can be seen clearly that the electron density on benzene ring is increased at ortho and para positions. These positions thus attract the electrophiles more than meta position. The inductive effect is comparatively weaker effect and hyperconjugation overpowers it.

As a proof, consider the substitution (e.g. nitration) on the following disubstituted benzene occurs ortho to the methyl group and not ortho to the tert-butyl group. This is because, although tert-butyl group has greater inductive effect than methyl, the tert-butyl group cannot exhibit hyperconjugation.

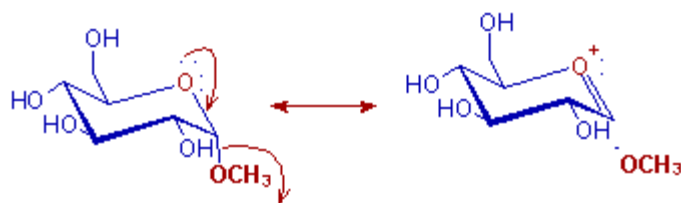


Also note that the tert-butyl group is bulky and hinders the approach of electrophile.

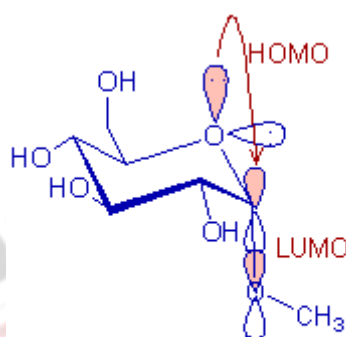
#### 6) Anomeric effect:

The overall tendency of anomeric substituents to favour an axial position is called Anomeric effect. For example, the  $\alpha$ -methyl glucoside is more stable than the  $\beta$ -methyl glucoside due to hyperconjugation.

The non-bonding HOMO with a pair of electrons on the ring of  $\alpha$ -methyl glucoside oxygen is antiperiplanar to the antibonding LUMO of C-O bond in methoxy group. This arrangement of orbitals allows hyperconjugation between them and thus stabilizing the  $\alpha$ -form.



Hyperconjugation in  $\alpha$ -D-methylglucoside

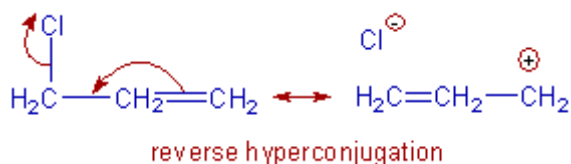


Anti periplanar arrangement is only possible in  $\alpha$  form

Whereas, in  $\beta$ -methyl glucoside the methoxy group is at equatorial position and cannot be involved in hyperconjugation since it is not antiperiplanar to the lone pair on ring oxygen. Therefore,  $\beta$ -methyl glucoside is less stable than the  $\alpha$ -methyl glucoside.

## 6. Reverse Hyperconjugation

For  $\alpha$ -halo alkenes, the delocalization of electrons takes place towards the halogen group through hyperconjugative mechanism because of electron withdrawing nature of halogen. It is known as reverse hyperconjugation. The dipole moments of  $\alpha$ -halo alkenes are remarkably increased because of this phenomenon.



## 7. Summary

- The delocalization of  $\sigma$ -electrons or lone pair of electrons into adjacent  $\pi$ -orbital or p-orbital is called hyperconjugation.
- It takes place because of overlapping of  $\sigma$ -bonding orbital or the orbital containing a lone pair with an adjacent unfilled p-orbital. It is also called as "no bond resonance" or "Baker-Nathan effect".
- It explains stability of alkenes, carbocations and free radicals.
- The dipole moment of the molecules and bond length is greatly affected due to hyperconjugation since the contributing structures show considerable polarity and change in bond order.
- Hyperconjugation also explains the reactivity & orientation of electrophilic substitution on alkyl substituted benzene ring.
- The overall tendency of anomeric substituents to favour an axial position is called Anomeric effect. For example, the  $\alpha$ -methyl glucoside is more stable than the  $\beta$ -methyl glucoside due to hyperconjugation.
- For  $\alpha$ -halo alkenes, the delocalization of electrons takes place towards the halogen group through hyperconjugative mechanism because of electron withdrawing nature of halogen. It is known as reverse hyperconjugation.