

HYPERCONJUGATION

E-content for B.Sc. I Students of Prof Rajendra Singh (Rajju Bhaia)
University, Prayagraj

Developed by

Dr. Poonam Shukla

Assistant Professor

Department of Chemistry

Email ID : poonampathakshukla@gmail.com

Forwarded by

Dr. Sunanda Chaturvedi

Principal

H.N.B. Government P.G. College, Naini, Prayagraj

Email ID : hnbnaini@gmail.com

Self - Declaration

- ▶ “The content is exclusively meant for academic purposes and for enhancing teaching and learning. Any other use for economic/ commercial purpose is strictly prohibited. The users of the content shall not distribute, disseminate or share it with anyone else and its use is restricted to advancement of individual knowledge. The information provided in this e-content is authentic and best as per my knowledge.”

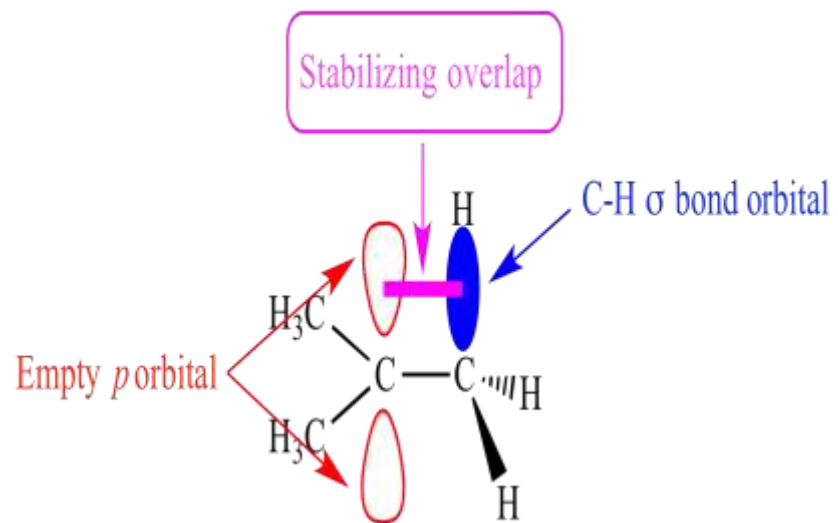
Contents

- ▶ What is hyperconjugation?
- ▶ Silent features of hyperconjugation
- ▶ Stability of carbocations, free-radicals and alkenes
- ▶ Important postulates of hyperconjugation
- ▶ Classifications of hyperconjugation
- ▶ Significances and applications of hyperconjugation
- ▶ References

HYPERCONJUGATION

- Hyperconjugation is considered as special case of resonance.
- ▶ Hyperconjugation is permanent effect.
- It is also known as NO-BOND resonance and Baker Nathan effect.
- In hyperconjugation delocalization of σ electrons of C-H bond of an alkyl group directly attached to an atom of the unsaturated system or to an atom with an unshared p orbital takes place.
- It explains the stability of carbocations, free radicals and alkenes.
- Only electrons in bonds that are β to the positively charged carbon or olefinic bond or carbon having free electron can take part in hyperconjugation.
- hyperconjugation involves the interaction of the electrons in a sigma (σ) orbital (e.g. C-H or C-C) with an adjacent unpopulated non-bonding p or antibonding σ^* or π^* orbitals to give a pair of extended molecular orbital.
- Increased electron delocalization associated with hyperconjugation increases the stability of the system.
- In particular, the new orbital with bonding character is stabilized, resulting in an overall stabilization of the molecule
- The new orbitals has increased bonding character, therefore overall stabilization of molecule takes place

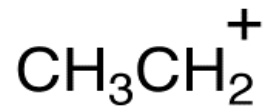
Schematic representation of hyperconjugation.



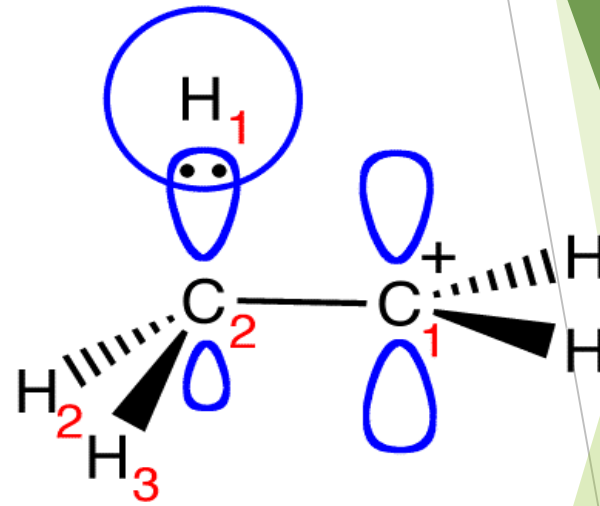
Silent features of hyperconjugation.

- According to classical resonance theory, electron delocalization could occur only via parallel overlap of p orbitals.
- But in hyperconjugation, which is considered as special case of resonance, electron delocalization occur via parallel overlap of p orbitals with hybridized orbitals participating in sigma bonds.
- Stability of molecule is directly proportional to the no of beta hydrogens. Greater the np of beta hydrogens, higher is the stability of molecule.
- Due to hyperconjugation shortening of carbon-carbon single bonds adjacent to multiple bonds are observed.
- This is because some double bond character appears in C-C single bond due to hyperconjugation.
- It lowers the overall energy of the system.
- Net charge positive charge on C becomes much less than it would have been in absence of hyperconjugation.
- Similarly the free electron gets delocalized on all beta hydrogens resulting the increase in stability of free radical.
- The double bond of the olefines also get delocalized due to hyperconjugation making the molecule stable.

Hyperconjugation in ethyl carbocation.

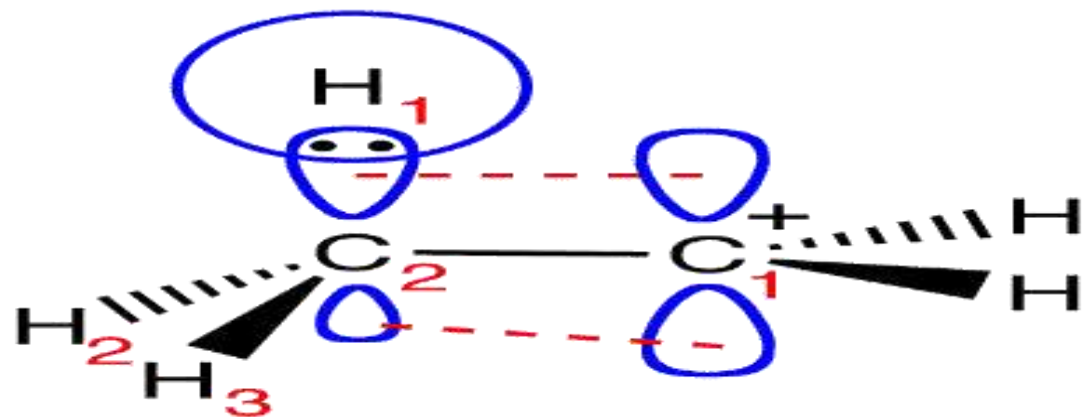


1

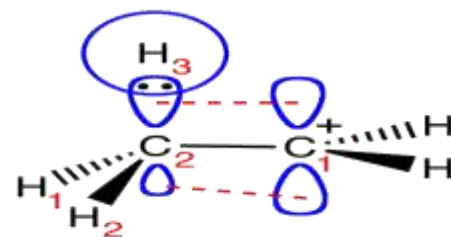
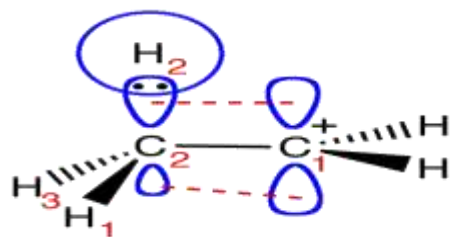


2

In **2**, the empty p orbital on C₁ and the sp³-hybridized orbital on C₂ participating in C₂—H₁ bond are more or less parallel, allowing parallel overlap, which lowers the electron deficiency at C₁ but makes the H₁ electron deficient.

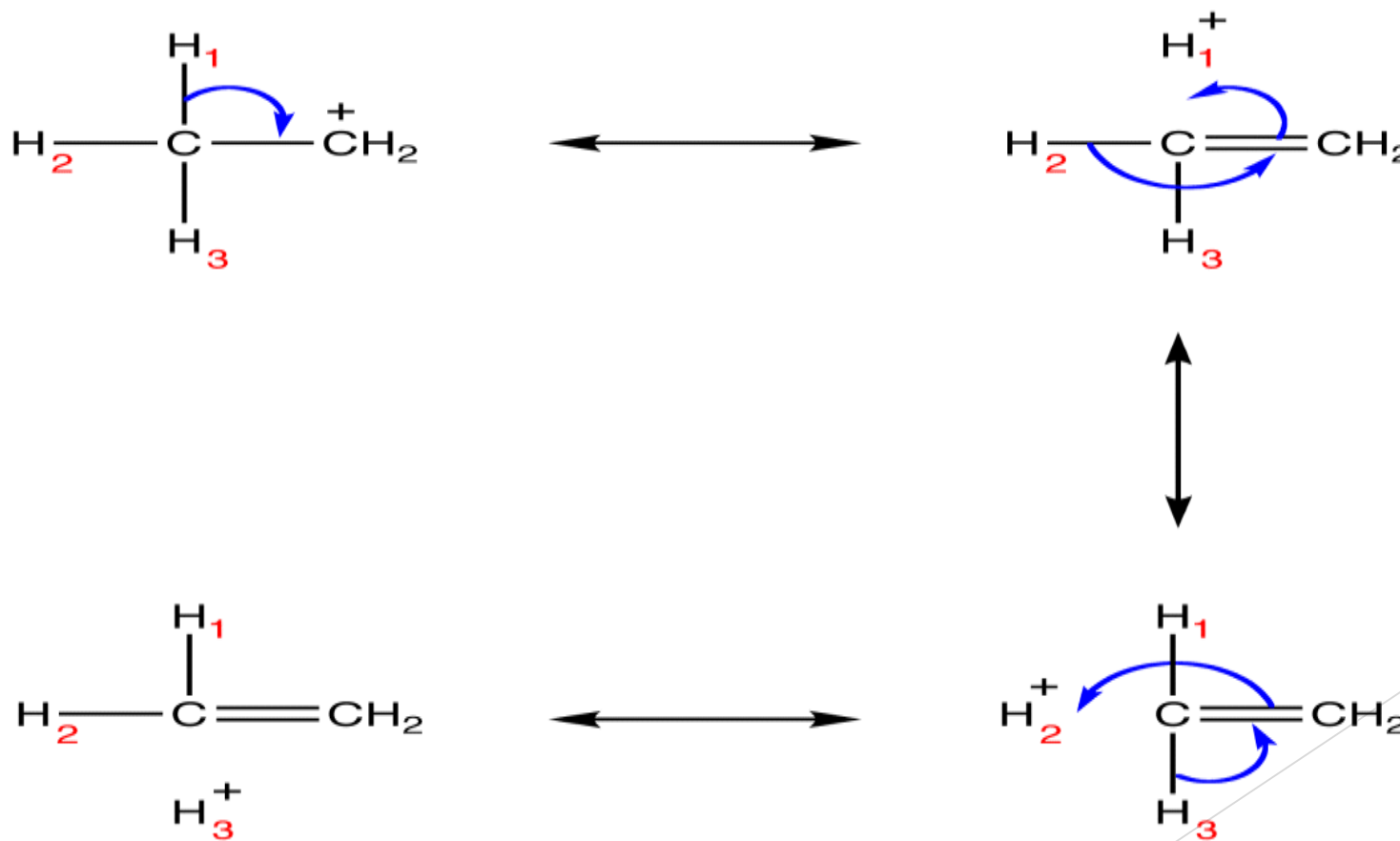


This overlap is not strong enough to completely prevent the free rotation around the C_1-C_2 bond. Consequently, C_2-H_2 bond and C_2-H_3 bond could also share electrons with the empty p orbital on C_1 .



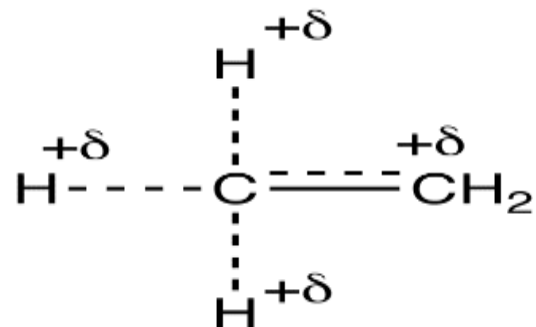
Various hyperconjugating structures of Ethyl carbocation

- Various hyperconjugating structures can be represented as follows

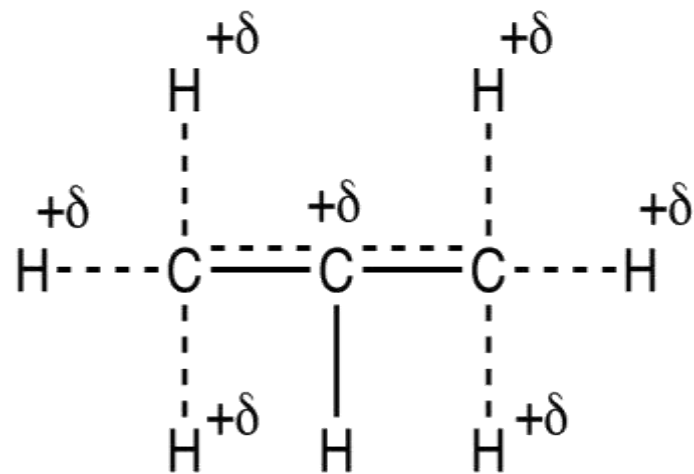


Conti.....

- On the basis of various hyperconjugating structures of Ethyl carbocation its structure can be represented as below



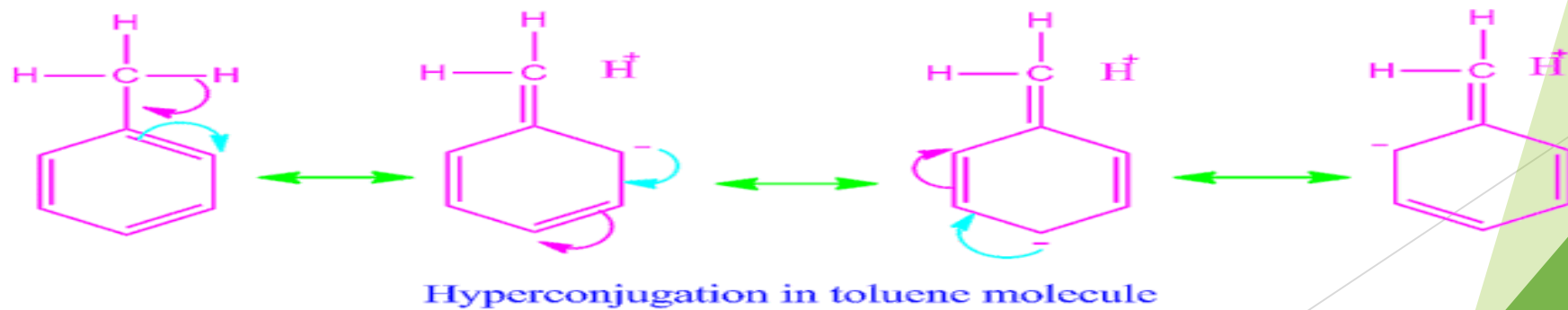
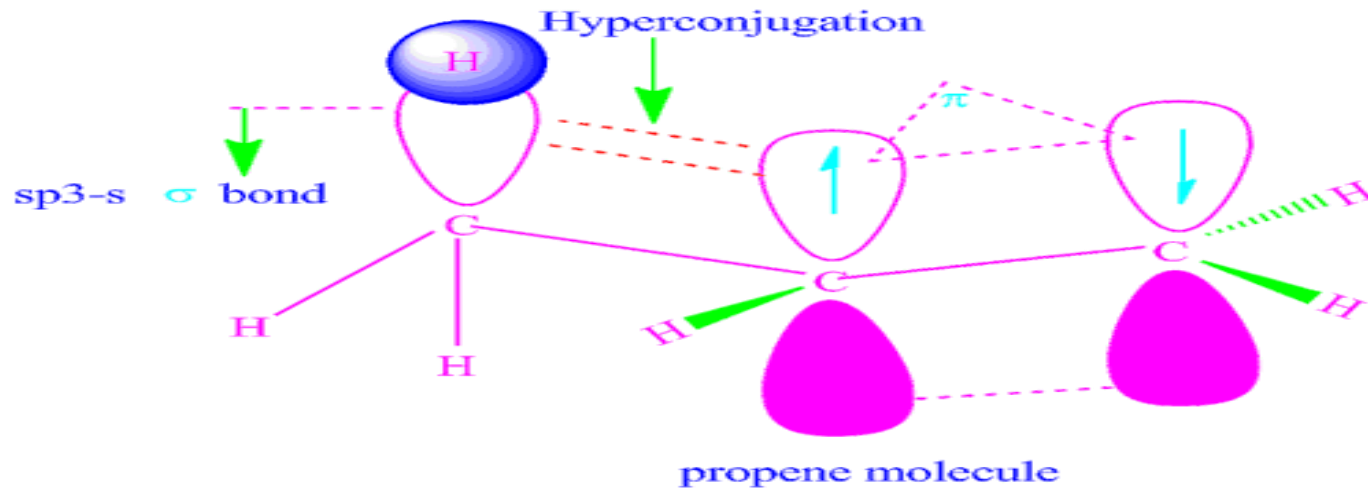
- Due to hyperconjugation, in the ethyl carbocation, the net charge of +1 is shared by a total of four atoms, one carbon atom and three hydrogen atoms.
- Similarly on the basis of various hyperconjugating structures, the hybrid structure of isopropyl carbocation can be written as follows



From the above hybrid structures it is clear that +1 charge of carbon is shared by total of 7 atoms including 6 hydrogen and 1 C. This makes the isopropyl much more stable than it would have been due to +I effect only. Hyperconjugation also explains the exceptional stability of t-butyl carbocation which could have been due to +I effect only.

Thus it is evident that higher the number of beta hydrogens, higher will be the the number of atoms sharing the positive charge resulting in the increase in the stability of carbocation

Hyperconjugation in unsaturated systems

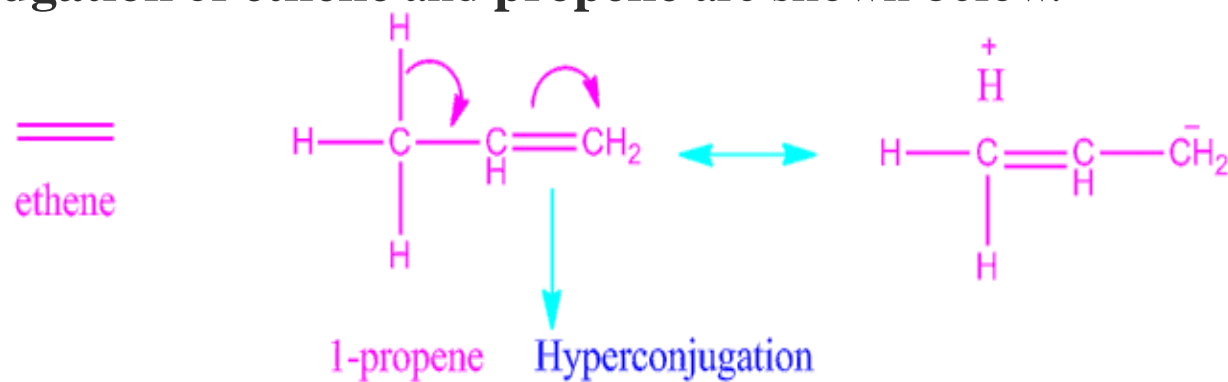


Why propene is more stable than ethene ?

- ▶ **Propene** is more stable than ethene due to greater **hyper-conjugation effect** for **propene**. But this effect is absent in ethene.

For this, the heat of hydrogenation value of ethene is greater than propene.

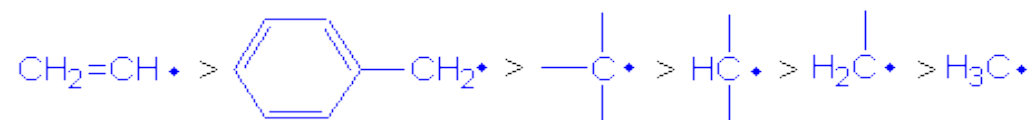
- ▶ The **hyper-conjugation** of **ethene** and **propene** are shown below.



- ▶ Similarly stability of 2-methyl-but-2-ene can be explained on the basis of hyperconjugation.

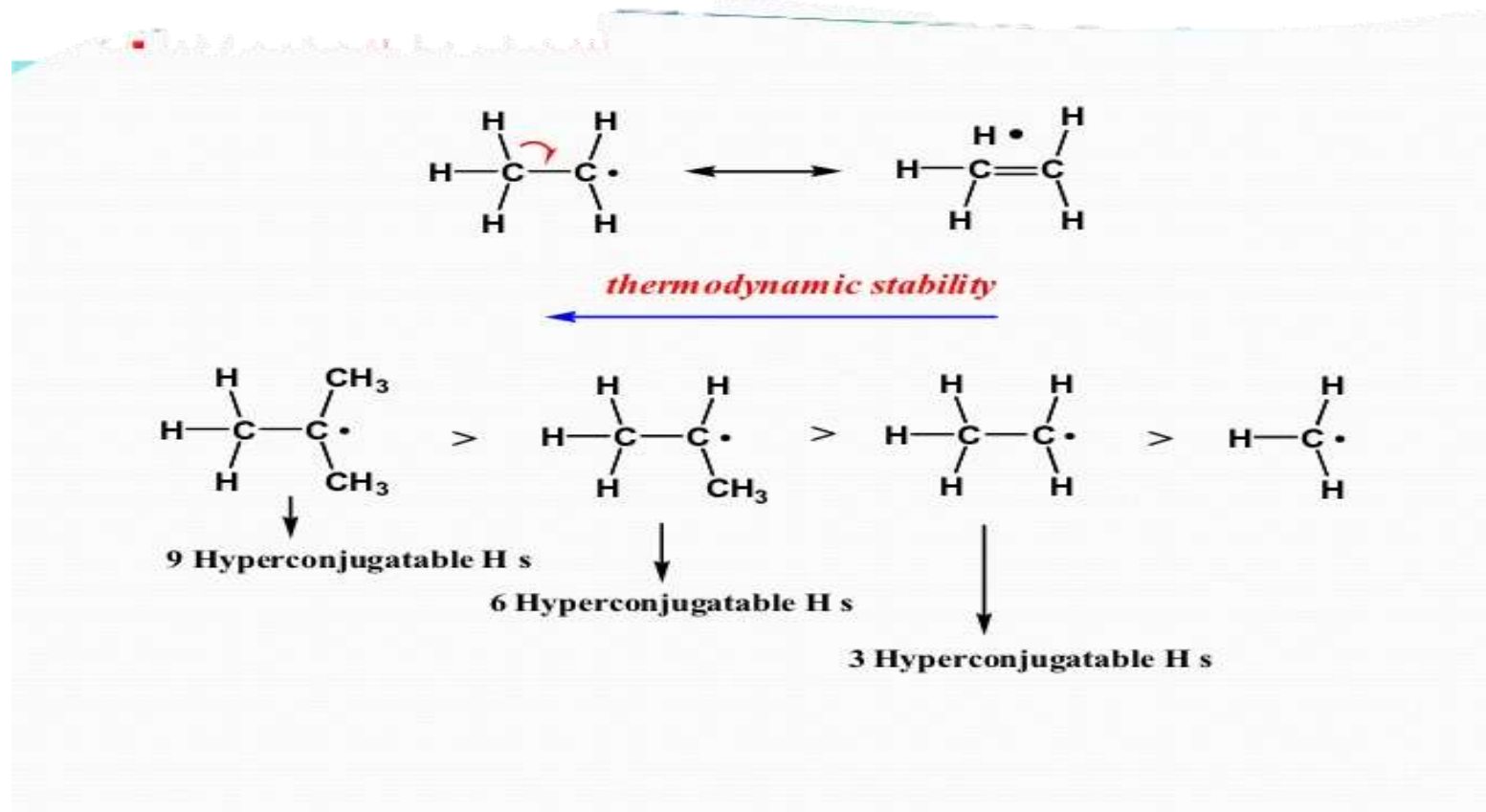
Hyperconjugation in free radicals

- Stability order of some free radicals are as follows:



- The sequence of radical stability may be explained by the differing amounts of hyperconjugation. The more alkyl substituents a radical carbon atom possesses, the more stabilized it becomes from hyperconjugation.
- The interaction of the double-occupied C-H σ bonding orbital with the single-occupied, non-bonding p orbital of the radical carbon atom is comparable to the stabilization by hyperconjugation in carbenium ions. However, they differ greatly in one important factor. The stabilization of carbenium ions, for example, is the result of the overlapping of a double-occupied C-H bonding orbital with an **unoccupied**, non-bonding 2p orbital. In radicals, on the other hand, this stabilization is obtained by the overlapping of a C-H bonding orbital with a **single-occupied**, non-bonding 2p orbital.

Relation between no of hyperconjugating structures and stability order of free radicals



Stability of free radicals

- Among various other factors, hyperconjugation plays very important role in describing stability of free radicals
- Higher the number of beta hydrogen, higher is the no of hyperconjugating structures of radical.
- Higher the number of hyperconjugating structure, higher is the delocalization of free electron, thus higher is the stability of free radical.
- t-butyl carbocation has 9 hyperconjugating structures therefore more stable than secondary carbocation which has 6 hyperconjugating structures .primary carbocation is least stable.
- Stability order of some free radical are as follows:-



Hyper conjugation – Important Postulates:

- Hyperconjugation is a stabilizing factor, which involves delocalization of σ and π electrons and exists in the molecules having the following framework, i.e either alkenes or carbocations or free radicals having at least one σ -H atom, but not in carbanions.
- Hyper conjugation depends on the presence of no of alpha-hydrogen atoms. More the no of σ alpha-hydrogen atoms \square \square more the no of Hyper conjugated structures, more the no of Hyper conjugated structures more its electron releasing nature. Thus the methyl group shows 3 Hyper conjugated structures, ethyl group shows 2 Hyper conjugated structures, isopropyl group shows 1 Hyper conjugated structure and t-butyl group shows 0 Hyper conjugated structures. So the order of electron – release patterns for simple alkyl groups connected to an unsaturated system is as follows methyl > ethyl > isopropyl > t-butyl. Hence methyl group is the strongest electron releasing group and t-butyl group is the weakest electron releasing group.
- 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 or delocalization of charge.
- The stronger effective order of Mesomeric effect, Hyper conjugation and Inductive effect is as follows.
- Mesomeric effect > Hyper conjugation > Inductive effect

Continued....

- 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.
- 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.
- In Hyper conjugation, all the σ C – H bonds of an alkyl group can polarizes to the adjacent π bond. Hence the contributing or canonical structures are polar in nature and are responsible for the dipole momentum.
- In Hyper conjugation, as the no of Hyper conjugated structures increases, stability of the molecule will also increases.
- In Hyper conjugation the substrates can act as nucleophile, and the electrophilic attack takes place at the terminal CH₂ group.
- Hyper conjugation explains stability of olefins, carbocations (carbonium ions), free radicals, alkyl benzene, carbonyl group, heat of hydrogenation, Dipole moment & bondlength, Reactivity and orientation of electrophilic substitution on benzene ring. and Anomeric effect.

Classification of Hyper conjugation:

- **Sacrificed Hyper conjugation:** The Hyper conjugation in which loss of one σ bond is called as Sacrificed Hyper conjugation.
- **Isovalent hyper conjugation:** The Hyper conjugation in which total no of σ bonds are retained during resonance is called as Isovalent hyper conjugation.
- **Reverse Hyper conjugation:** The Hyper conjugation in which, the delocalization of electrons takes place towards the halogen group through hyperconjugative mechanism is called as Reverse Hyper conjugation.
Reverse Hyper conjugation happens in the case of α -halo alkenes. Reverse Hyper conjugation is because of electron withdrawing nature of halogen. The dipole moments of α -halo alkenes are remarkably increased because of this phenomenon.

Hyper conjugation – Consequences and Applications:

- Hyper conjugation explains stability of olefins
- Hyper conjugation explains stability of carbocations (carbonium ions).
- Hyper conjugation explains stability of free radicals
- Hyper conjugation explains stability of alkyl benzene
- Hyper conjugation explains stability of carbonyl group
- Hyper conjugation explains stability of heat of hydrogenation
- Hyper conjugation explains Dipole moment & bond length.
- Hyper conjugation explains Reactivity and orientation of electrophilic substitution on benzene ring.
- Hyper conjugation explains Anomeric effect.

References

- ▶ I L Finar, Organic Chemistry, Vol. 1
- ▶ R T Morison & R N Boyd, Organic Chemistry
- ▶ J Singh & L D S Yadav, Organic Chemistry
- ▶ Bahl & Bahl, Organic Chemistry