

❖ Hyperconjugation

The phenomenon of hyperconjugation (or σ -conjugation) may simply be defined as the delocalization of electrons with the participation of bonds of primarily σ -character.

Typically, the phenomenon of hyperconjugation involves the interaction of the σ -electrons from the C–H bond with an adjacent empty nonbonding p or antibonding σ^* or π^* orbitals to give a pair of extended molecular orbitals. Nevertheless, antibonding σ^* orbitals, which are low-lying energetically, may also interact with fully-filled orbitals of lone pair character (n), which in that case is called as 'negative hyperconjugation'. Increased delocalization of electron density associated with the phenomenon of hyperconjugation raises the stability of the system. Particularly, the new bonding orbital is stabilized, resulting in high overall stabilization of the molecular system. The Baker-Nathan effect, which is also sometimes synonymously used for hyperconjugation, is an explicit application employed to some reactions or structure types.

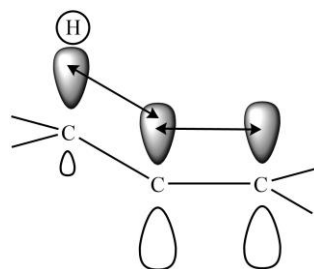
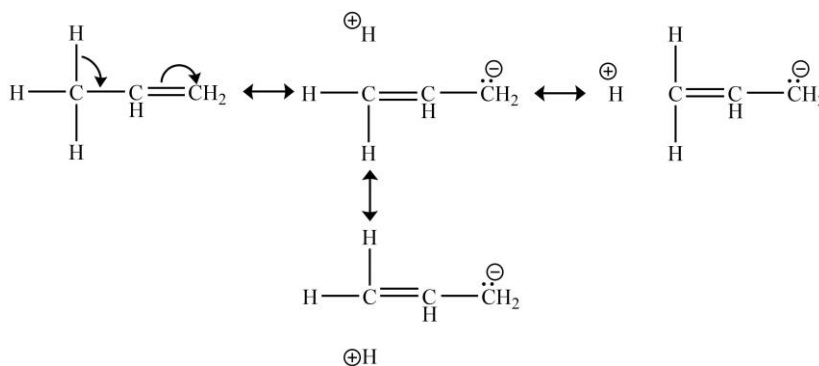


Figure 12. The orbital picture of hyperconjugation.

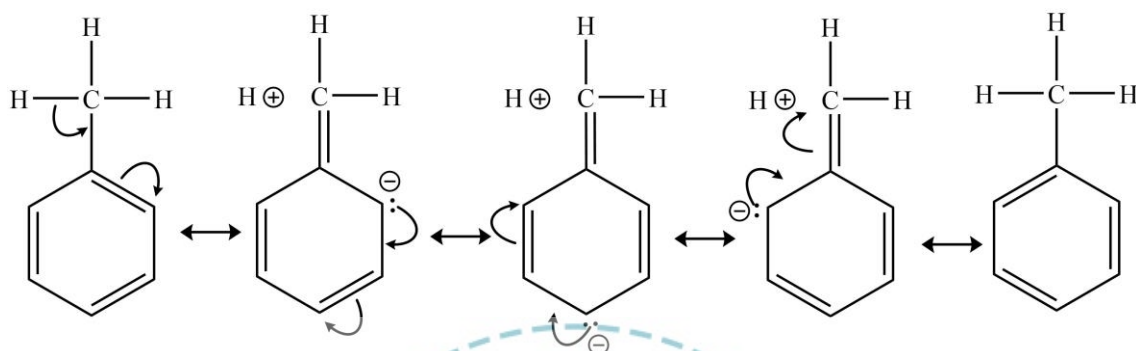
This effect also reverses the order of the +I effect of alkyl groups if they are attached to an unsaturated carbon. The general order of +I effect is $(\text{CH}_3)_3\text{C}- > (\text{CH}_3)_2\text{CH}- > \text{CH}_3-\text{CH}_2- > -\text{CH}_3$. However, consider the hyperconjugation after attaching them to unsaturated carbon i.e.



Therefore, the greater the number of hydrogen at the carbon attached to unsaturated carbon, the more will be the number of possible hyper conjugative structures resulting in a larger electron-donating effect. The number of α -hydrogens in $(\text{CH}_3)_3\text{C}-$, $(\text{CH}_3)_2\text{CH}-$, CH_3-CH_2- and $-\text{CH}_3$ are 0, 1, 2 and 3, respectively; and thus, the new order of electron donating strength becomes is $(\text{CH}_3)_3\text{C}- < (\text{CH}_3)_2\text{CH}- < \text{CH}_3-\text{CH}_2- < -\text{CH}_3$.

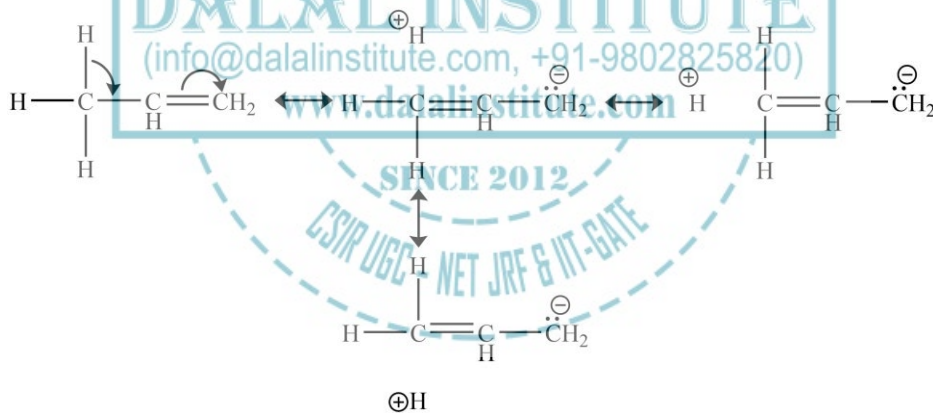
Applications of hyperconjugation effect: Some of the important applications of the hyperconjugation effect that affect the properties to a great extent are given below.

i) *Directive influence of alkyl groups:* The existence of the hyperconjugation effect can be used to rationalize the *o*- and *p*-directing influence of alkyl groups as shown below.

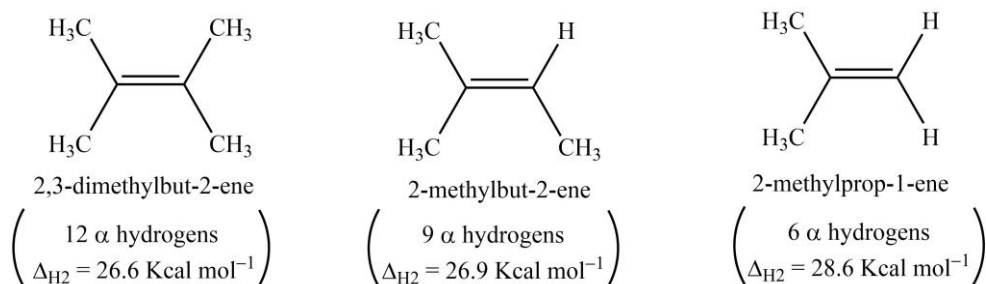


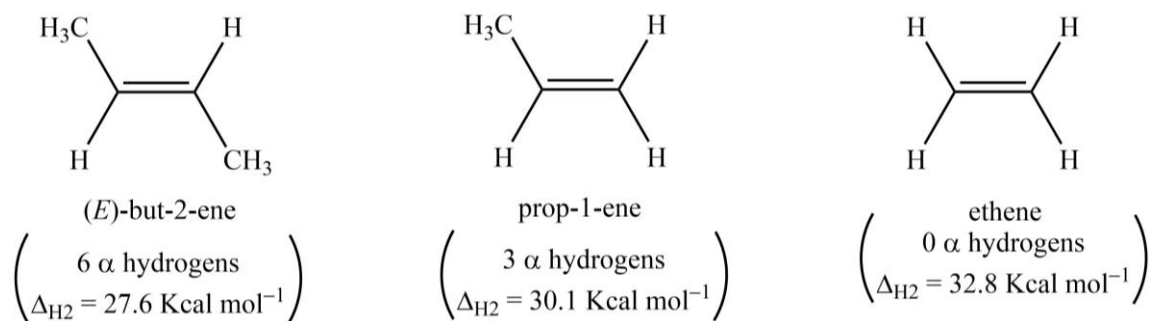
Similarly, six more hyperconjugative structures can also be written for two other H-atoms; and it is obvious that the electron density is increased at *o*- and *p*-sites.

ii) *Shortening of C–C bond adjacent to multiple bonds:* The existence of hyperconjugation effect can be used to rationalize the shortening of C–C bond adjacent to multiple bonds as shown below.

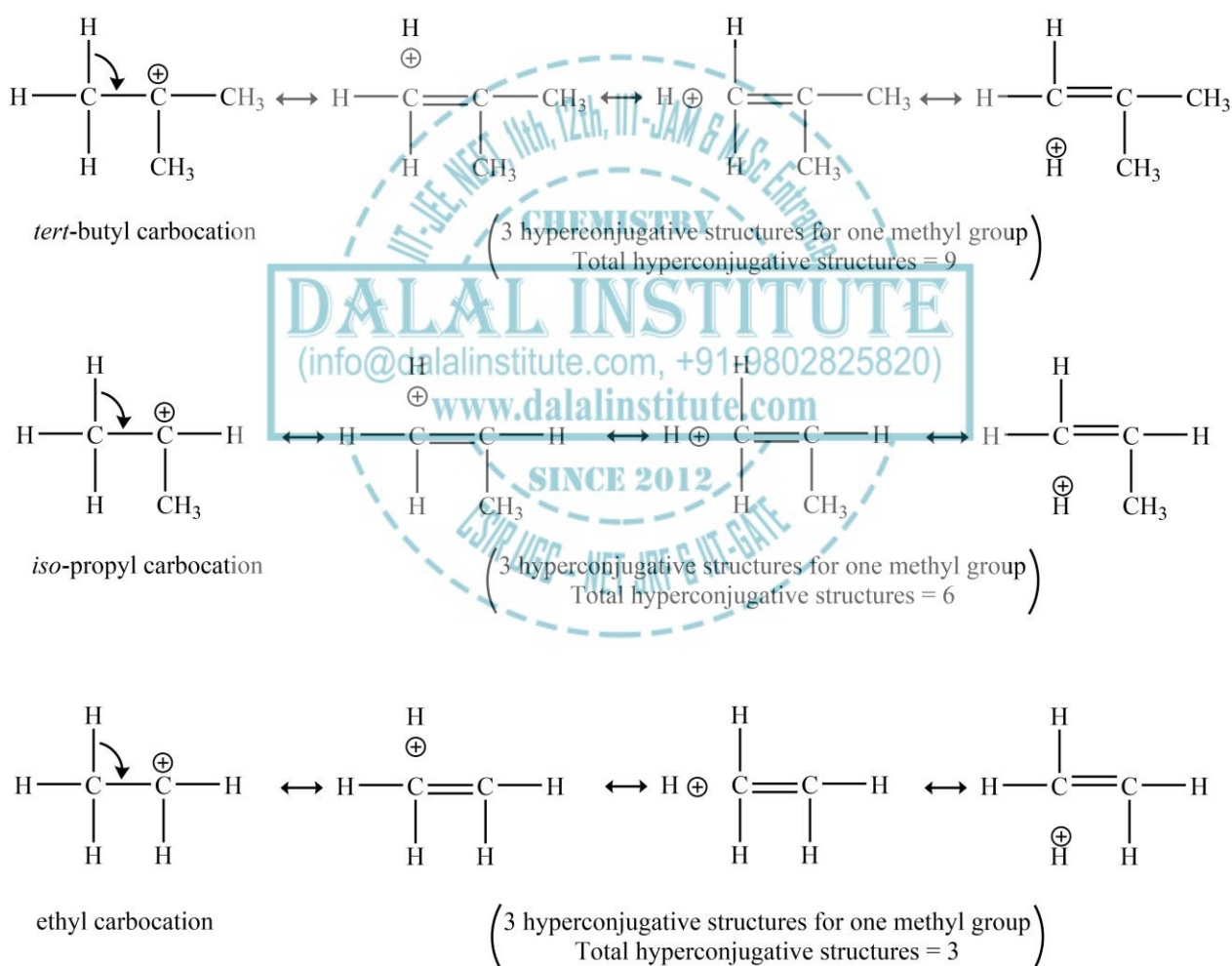


iii) *Relative stability of different alkenes:* The existence of hyperconjugation effect can be used to rationalize the relative stability of different alkenes as shown below.



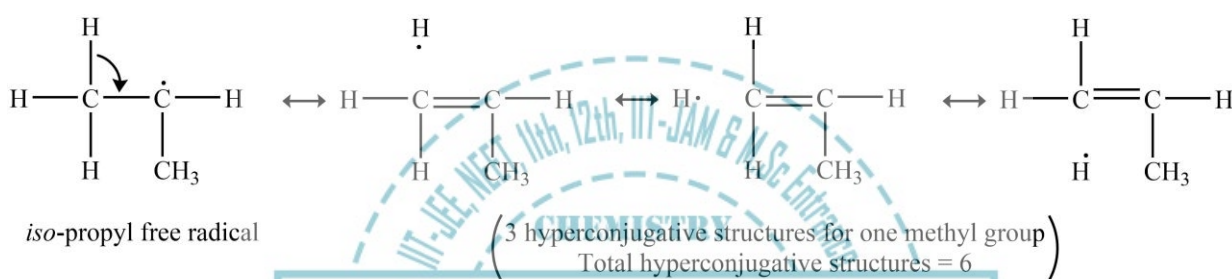
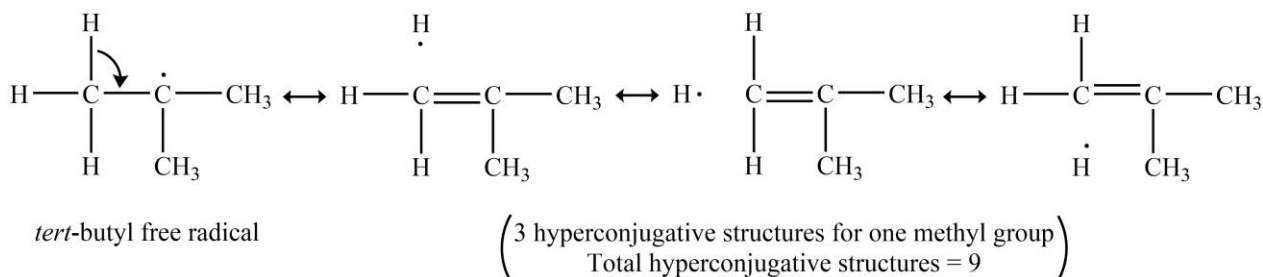


iv) *Relative stability of different carbocations*: The existence of hyperconjugation effect can be used to rationalize the relative stability of different carbocations as shown below.



Hence, as far as the number of possible hyperconjugative structures possible is concerned, tertiary carbocation should be more stable than secondary, which in turn should be more stable than primary.

v) *Relative stability of different free radicals*: The existence of hyperconjugation effect can be used to rationalize the relative stability of different free radicals as shown below.



Hence, as far as the number of possible hyperconjugative structures possible is concerned, tertiary free radicals should be more stable than secondary, which in turn should be more stable than primary.

The phenomenon of hyperconjugation can also clarify numerous other effects where explanations may also not be as clear as that for the rotational barrier of C_2H_6 . For instance, the Lewis structure for an ammonium ion shows a positive charge on the N atom; though, the hydrogen atoms are more electropositive than is nitrogen atoms, and therefore, are the more genuine carriers of the positive charge. We have known this fact since bases eliminate the protons instead of the nitrogen atom. The matter of the ethane's rotational barrier is not settled by the scientific community till now. An investigation of quantitative molecular orbital theory demonstrates that 2-orbital-4-electron (steric) repulsions are much more dominant over the phenomenon of hyperconjugation. The valence bond theory also put a strong emphasis on the steric significance.

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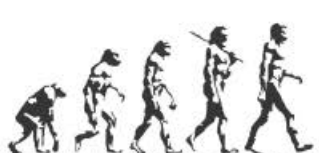
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A TEXTBOOK OF ORGANIC CHEMISTRY

Volume I

MANDEEP DALAL



First Edition

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