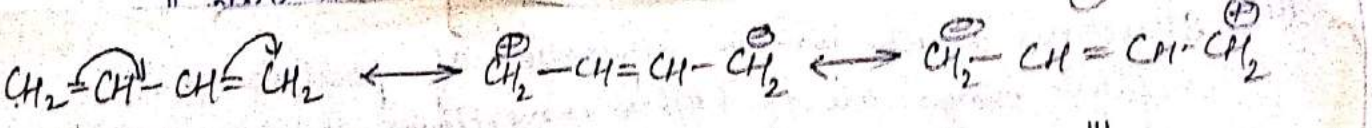
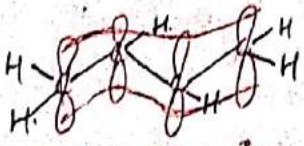
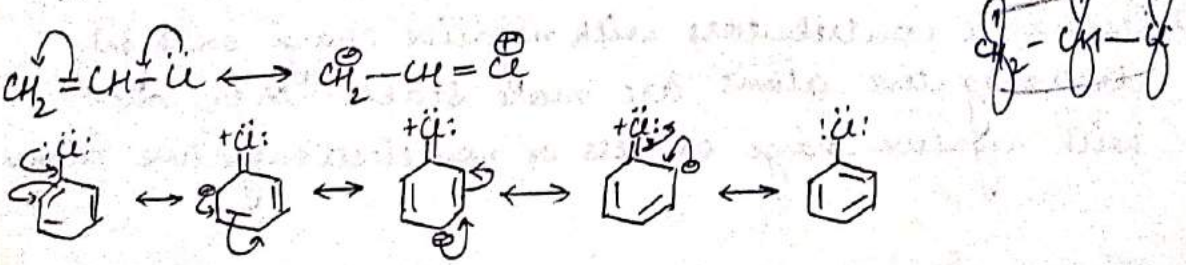




π-π overlap in buta-1,3-diene

* The groups or atoms, which during delocalization release electrons towards ring or conjugated system are said to exhibit +R effect or +M effect. for example, halogens (-Ẍ:), -ÖH, -NH$_2$, -ÑHR, -ÑR$_2$, -ÖCH$_3$

* The group or atoms, which during delocalization withdraw electrons from ring or conjugated system are said to exhibit -R effect or -M effect. example - >C=O, -CHO, -C(=O)-OH, -NO$_2$, -C≡N



p-π overlap in vinyl Chloride & chlorobenzene

Necessary Condition of resonance!

(i) All resonating structures must have the same arrangement of atomic nuclei.

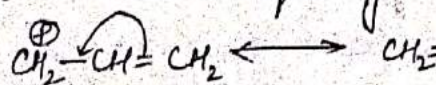
(ii) The resonating structures must have same no. of paired or unpaired electrons. However they differ in a way of distribution of electrons.

(iii) All resonating structures have same total charge

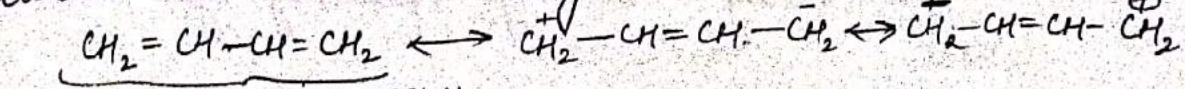
(iv) The energies of various structures must be same or nearly same

Main characteristics :- (Contributions)

(i) Structures which are indistinguishable are of equal energy and hence contribute equally towards the resonance hybrid.



(ii) More the no. of covalent bonds in a resonating (canonical) structures more is its stability



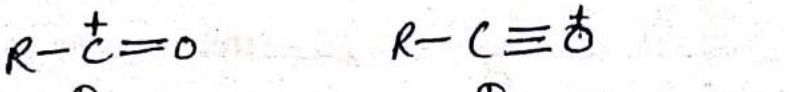
This structure is more stable

(iii) Structures which involve separation of positive and negative charges are of higher energy (lower stability) and hence contribute little toward resonance hybrid

I II

Structure I more stable compare to II

(iv) Structures in which all the atoms have a complete valence shell of electrons (i.e noble gas structure) are especially stable and make contributions to the hybrid.



I II

C - has 6 electron C - has 8 electrons

Structure II is more stable than I

(v) Resonance contributors with negative charge on highly electronegative atoms are more stable than ones with negative charge on less or non-electronegative atoms.

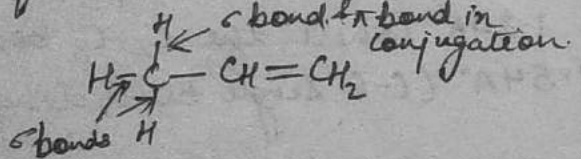
Hyperconjugation

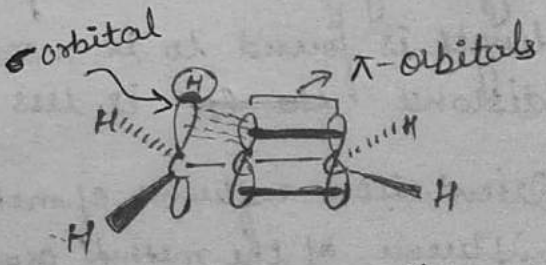
Delocalisation of σ electrons through σ-π or σ-p overlap, Known as hyperconjugation.

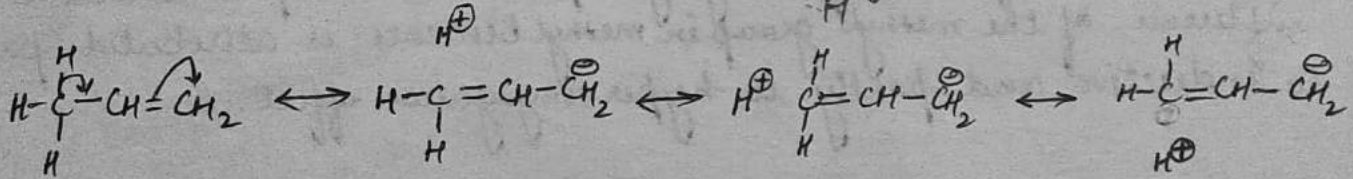
* Hyperconjugation involves delocalization of C-H Sigma electrons into adjacent π-system.

For example, in propene, the three C-H σ-bonds of CH_3 group are in conjugation with π-bond. The σ electrons are transferred in the process to adjacent Carbon-carbon bond, in turn π-electrons are shifted to terminal CH_2 Carbon.

There are three C-H σ bonds so three contributing structures are possible for propene. Due to participation of σ-electrons in delocalization, the bond between carbon and hydrogen does not exist in contributing structures and for this reason hyperconjugation is referred as no bond resonance.







Hyperconjugation explains the stability of substituted alkenes. A more substituted alkene is more stable due to availability of more number of conjugated C-H σ bonds which can participate in hyperconjugation.

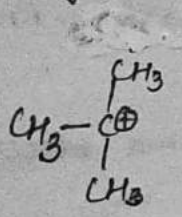
In ethene hyperconjugation does not occur due to non-availability of conjugated C-H σ bonds.

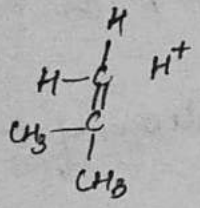
Effects of hyperconjugation :-

(1) Stability of Carbonium ions : The order of stability of carbonium ions as follows

Tertiary > Secondary > Primary

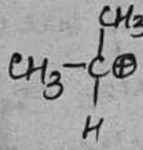
Above order of stability can be explained by hyperconjugation. In general greater the no. of hydrogen atoms attached to α-Carbon atoms, the more hyperconjugative forms can be written and thus greater will be stability of carbonium ions.

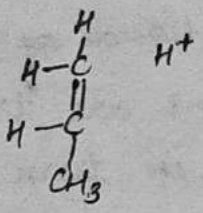




3° Carbonium ion

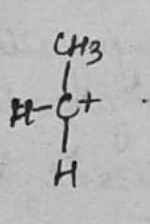
(9 equivalent forms)

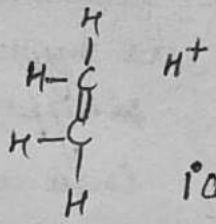




2° Carbonium ion

(6 equivalent forms)





1° Carbonium ion

(3 equivalent forms)

(2) Stability of free radicals can also be explained as that of Carbonium ions.

$$(CH_3)_3\dot{C} > (CH_3)_2\dot{C}H > CH_3\dot{C}H_2 > \dot{C}H_3$$

(3) Bond length: The bond length in a molecule changes if there is hyperconjugation ex- in propene $\overset{3}{C}H_3-\overset{2}{C}H=\overset{1}{C}H_2$, the C_1-C_2 bond length is found to be more than 1.34A° while the C_2-C_3 bond distance is less than 1.54A° (C-C Single bond length)

(4) Orientation influence of methyl group: The ortho, para directive influence of the methyl group in methyl benzenes is attributed partly to inductive and partly to hyperconjugation effect.

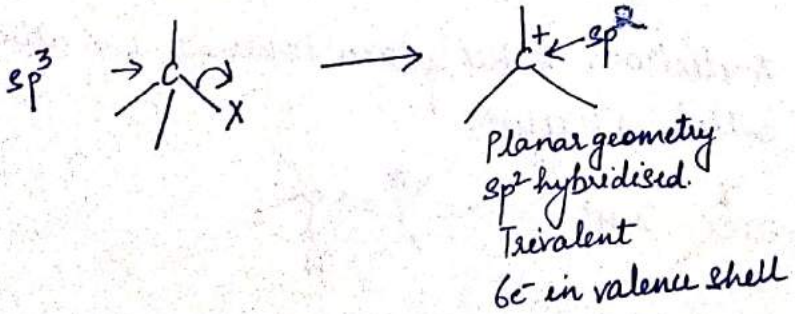
Reactive Intermediates :-

Most of the organic reactions occur through the involvement of certain chemical species. These are generally short lived (10^{-6} Sec to a few Sec) and highly reactive and hence can not be isolated. These short-lived highly reactive chemical species through which the majority of the organic reactions occur are called reactive intermediates. Various reaction intermediates that we came across in the study of organic reactions are:

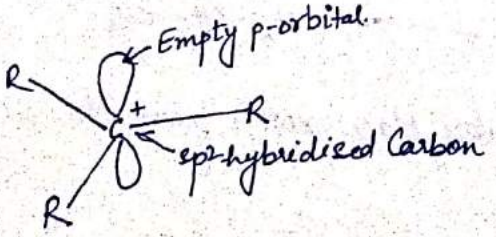
1. Carbocations
2. Carboanions
3. Free radicals
4. Carbenes
5. Nitrenes
6. Arynes (Benzyne)

Carbocations:-

These are defined as chemical species in which the positive charge is carried by the carbon atom with six electrons in its valence shell. These are formed by heterocyclic cleavage of the covalent bond in which an atom or group along with its pair of electron leaves the carbon. (The shared pair of electrons between two atoms goes to one atom only)

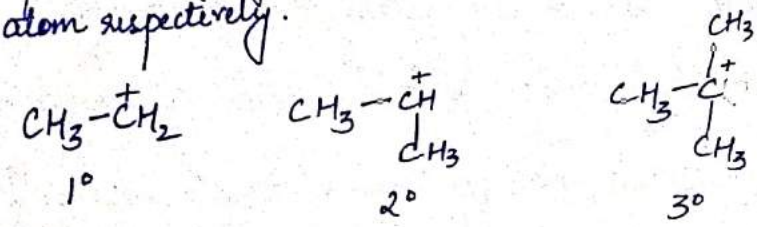


Planar geometry
sp^2 hybridised.
Trivalent
6e⁻ in valence shell



* The carbon atom carrying the positive charge is sp^2 hybridised. The three sp^2 hybridised orbitals of this carbon form three σ bonds with monovalent atoms or groups which lie in a plane and are inclined to one another at an angle of 120°. The unhybridised 2p-orbital which is perpendicular to the plane of the three σ bonds is however empty.

Carbocations are classified as primary (1°) secondary (2°) and tertiary (3°) according as the positive charge is present on primary, secondary and a tertiary carbon atom respectively.



1° 2° 3°

The order of stability of carbocations follow sequence : 3°>2°>1°

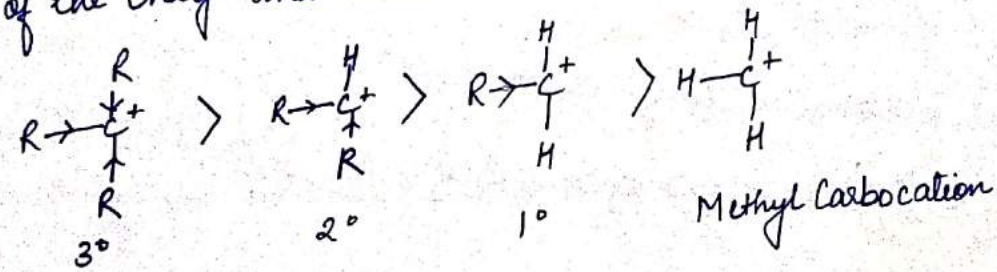
There are two factors which determines the stability.

① Inductive Effect ② Hyperconjugation.

Inductive Effect:-

Electron donating effect of alkyl groups increases the electron density around tvely charged carbon atom. This results in reducing the magnitude of positive charge on it and thus charge is delocalised on carbon. Dispersal of positive charge increases the stability. Greater the number of alkyl groups on the carbon atom carrying positive charge, greater would be dispersal of the charge and hence more stable would be the carbocation

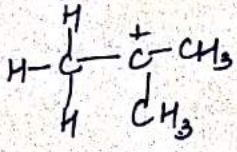
Thus,



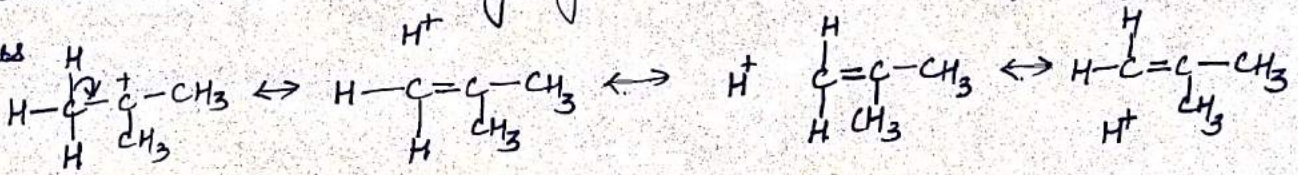
3° 2° 1° Methyl Carbocation

HyperConjugation:-

A large number of cathonical forms can be written for tertiary carbocation compared to those for secondary and primary

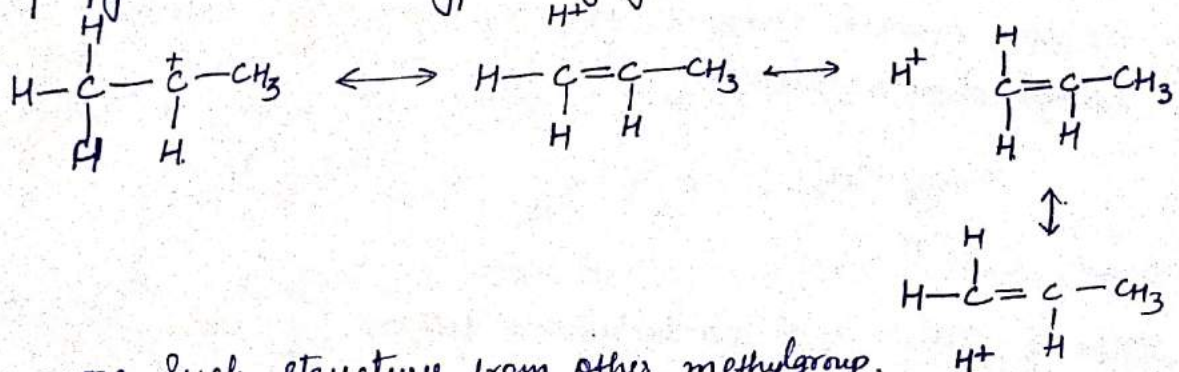


tert-Butyl Carbocation has nine α-hydrogens and hence nine hyperconjugation structures



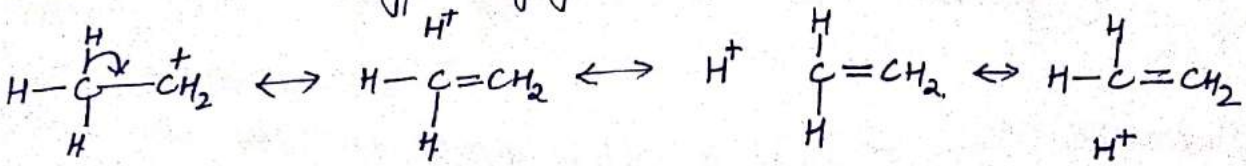
Six more such structures from other two methyl groups.

For isopropyl Cation Six hyperconjugation structures can be written.



There more Such structures from other methylgroup.

For ethyl Carbocation three hyperconjugation structures.



For CH_3^+ Carbocation, no hyperconjugation structure can be written. Thus the order of stability is

$$(CH_3)_3\overset{+}{C} > (CH_3)_2\overset{+}{C}H > CH_3\overset{+}{C}H_2 > \overset{+}{C}H_3$$

Stability of Carbonium ions (Carbocations)

$$R_3\overset{+}{C} > C_6H_5\overset{+}{C}H_2 > \overset{+}{C}H_2-CH=CH_2 > R_2\overset{+}{C}H > R\overset{+}{C}H_2 > \overset{+}{C}H_3 > CH_2=\overset{+}{C}H_2$$

Benzyl Allyl Vinyl

Allyl and Benzyl Carbocations are resonance stabilized.

$$\overset{+}{C}H_2-CH=CH_2 \longleftrightarrow CH_2=CH-\overset{+}{C}H_2$$