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Bond fission or bond cleavage-

"The breakage of a covalent bond is called bond fission or bond cleavage."

It may be of following two types-

(1) Homolyticbond fission or homolysis- Such bond fission in which both the separating species take away their own electron from shared pair of electrons is called homolytic bond fission or homolysis.

Homolysis leads to the formation of the neutral species containing an unpaired electron which are called free radicals. It usually occurs in non-polar covalent bonds and is achieved either by heat or energetic light in gaseous phase. For example,

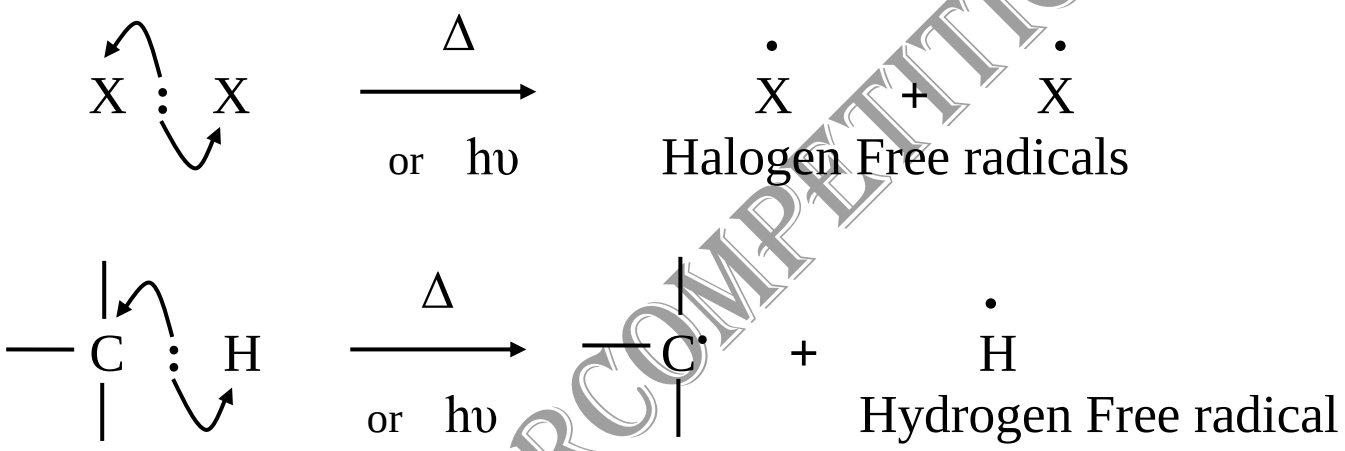
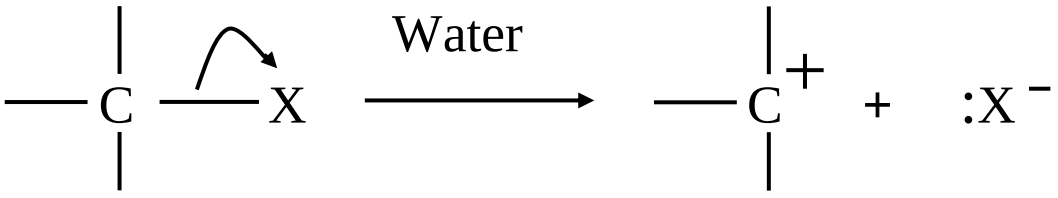


Fig.- Homolytic Bond fission

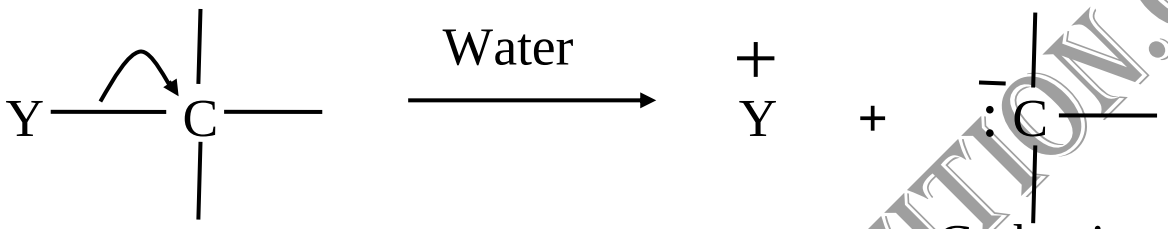
(ii)Heterolytic bond fission or bond cleavage- Such bond fission in which both the electrons of shared pair is taken away by only one of the separating species is called Heterolytic bond fission or heterolysis. It usually occurs in polar covalent bonds in solution phase and is facilitated by polar solvents like water, alcohol etc. Here, shared pair of electrons is taken away by more electronegative bonded atom. It leads to the formation of charged species (ions). Here, if carbon bears positive charge then the species is called carbonium ion or carbocation but if it bears negative charge then it is called carbanion. Both Carbonium ion and carbanion are short lived and highly reactive reaction intermediates. For example,

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Haloalkane Carbonium ion

(X is more electronegative than C)



Carbanion

(Y is less electronegative than C)

Reaction Intermediates

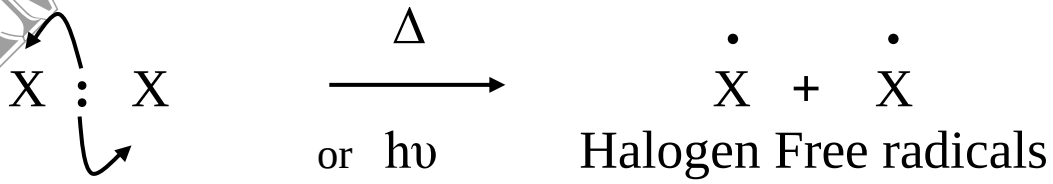
A reaction intermediate is a species which is formed from the reactants (or from preceding intermediates) and reacts further to give final products.

These are highly energetic, short lived and highly reactive in nature. Being short lived and highly reactive in general, they could not be isolated and stored.

(1) Free Radicals

The neutral species formed in hemolytic bond fission and containing an unpaired electron are called free radicals.

Formation of free radicals is achieved either by heat or energetic light in gaseous phase. For example,



Halogen Free radicals

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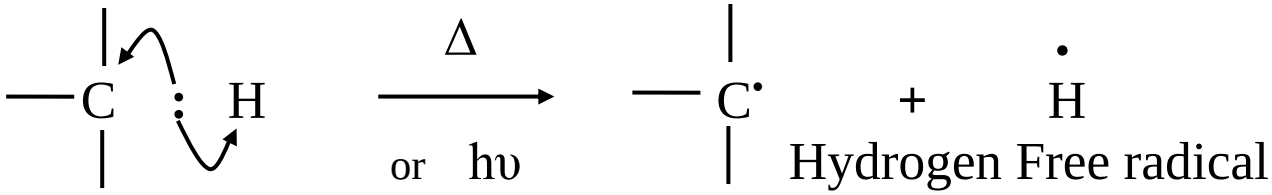


Fig.- Homolytic Bond fission

Formation of free radicals may also be achieved by using organic peroxides such as benzoyl peroxide at relatively low temperature.

Since, free radicals contain an unpaired electron, they are attracted in magnetic field and are paramagnetic in nature. Here, magnetic moment,

$$\mu = \sqrt{n\,(n+2)}\ \text{B.M.}$$

(Where, n = No. Of unpaired electrons)

$$= \sqrt{1\,(1+2)}\ \text{B.M.}$$

$$= \sqrt{3}\ \text{B.M.}$$

Characteristics of Free Radicals-

(1) The free radicals are neutral species formed by homolytic bond fission of a covalent bond.

(2) They contain an unpaired electron which has strong tendency to get paired up. Hence, they are highly reactive in nature..

(3) Formation of free radicals is achieved either by heat or energetic light in gaseous phase.

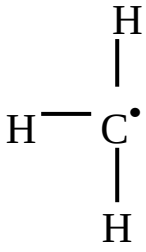
(4) In alkyl free radicals, carbon containing unpaired electron has seven electrons (septet) in its valence shell. Thus, they are electron deficient and always seek for electrons.

(5) In alkyl free radicals, carbon bearing unpaired electron is sp^2 hybridized. Hence, alkyl free radicals have trigonal planar geometry where, unpaired electron is present in unhybridized p-orbital which is perpendicular to the sp^2 hybridized orbitals.

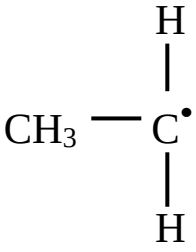
Types of Alkyl free radicals

Depending upon the nature of carbon atom bearing unpaired electron, alkyl free radicals may be primary (1^0), secondary (2^0) or tertiary (3^0) in nature. For example,

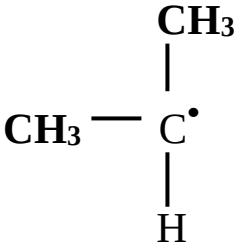
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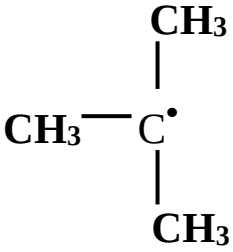
Methyl
free radical (1^0)



Ethyl
free radical (1^0)



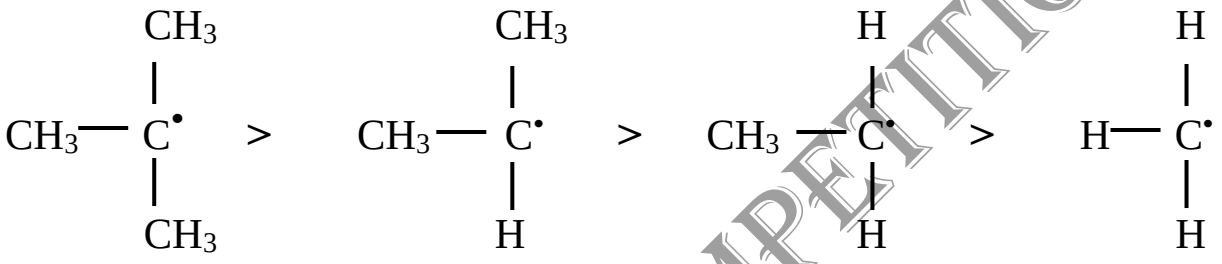
Iso propyl
free radical (2^0)



Tert. butyl
free radical (3^0)

Stability of Alkyl Free radicals

Stability of free radicals is explained on the basis of Hyperconjugation. The greater the number of Hyperconjugated forms possible for an alkyl free radical, more is its stability. For example, the order of stability of methyl, ethyl, isopropyl and tertiary butyl free radicals is as under-



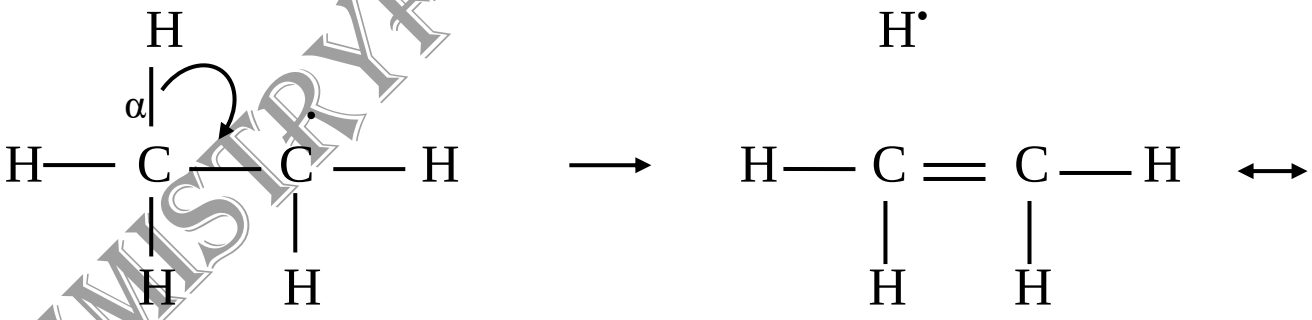
Tert butyl
free radical

Isopropyl
free radical

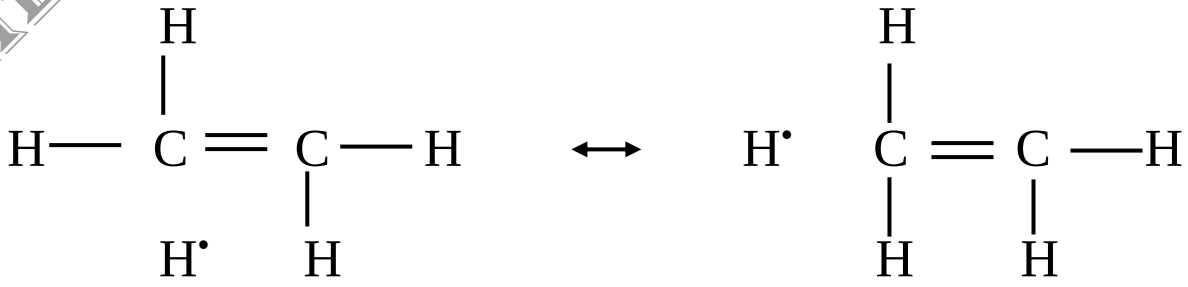
Ethyl
free radical

Methyl
free radical

Here, methyl free radical does not contain any α-hydrogen atom and therefore, it has no Hyperconjugated form while, ethyl free radical contains three α- hydrogen atoms and therefore, it has three Hyperconjugated forms. Thus, ethyl free radical will be more stable than methyl free radical.



Ethyl Free Radical (I)



(II) (III)

Fig.- Hyper-conjugation in Ethyl free radical

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Similarly, isopropyl free radical ($2^{\mathbf{0}}$) having six α-hydrogen atoms has six hyper-conjugated forms and is more stable than ethyl free radical ($1^{\mathbf{0}}$) and tertiary butyl free radical ($3^{\mathbf{0}}$) having nine hyper-conjugated forms is intern more stable than isopropyl free radical ($2^{\mathbf{0}}$).

There are certain free radicals which gain stability by resonance and are more stable than alkyl free radicals. For example, allyl free radical is more stable than tertiary butyl free radical.



Fig.-Resonance in allyl free radical

Similarly, benzyl free radical also gains stability by resonance and is more stable than allyl free radical due more extension of resonance.

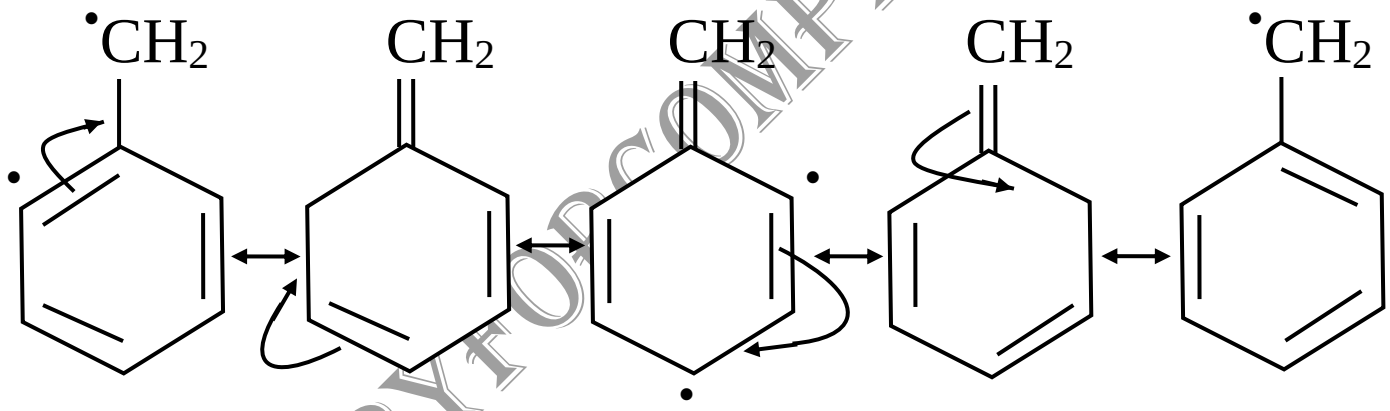
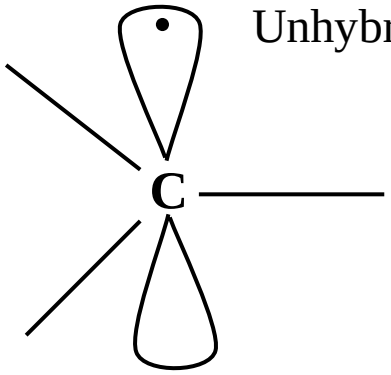


Fig.- Resonance in Benzyl Free radical

In the same way, diphenyl methyl free radical having 10 resonance forms is more stable than benzyl free radical and triphenyl methyl free radical is in turn more stable than diphenyl methyl free radical.

Geometry of Alkyl Free Radicals- In alkyl free radicals, carbon bearing unpaired electron is sp^2 hybridized. Hence, alkyl free radicals have trigonal planar geometry where, unpaired electron is present in unhybridized p-orbital which is perpendicular to the sp^2 hybridized orbitals.

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Unhybridized p-orbital containing Unpaired electron

Fig.- Geometry of alkyl free radical (Trigonal Planar)

In substituted alkyl free radicals, s-character in sp^2 hybridized orbital is relatively higher, so that they tend to take pyramidal geometry. For example, the order of s-character in sp^2 hybridized orbital of different fluorine substituted methyl free radicals is as under-

$$H_3C^{\bullet} < FH_2C^{\bullet} < F_2HC^{\bullet} < F_3C^{\bullet}$$

Here, trifluoromethyl free radical having the highest s-character in sp^2 hybridized orbital is essentially pyramidal.

Factors Affecting the Stability of Free Radicals

Free radicals are electron deficient species. Hence, any factor which donates electrons to their half filled orbital or causes dispersal of their unpaired electron i.e. delocalizes their unpaired electron, increases their stability.

Some important factors Affecting the stability of free radicals are as under-

(1) Bond dissociation energy-

Stability of free radicals is associated with the bond dissociation energy (BDE) of the bond undergoing homolysis during their formation. The larger the bond dissociation energy, more is the energy of free radical formed and therefore, lesser is stability of respective free radical. For example, stability of alkyl free radicals follows following order-

$$H_3C^{\bullet} < CH_3CH_2^{\bullet} < (CH_3)_2CH^{\bullet} < (CH_3)_3C^{\bullet}$$

The bond dissociation energy (BDE) of the bonds undergoing homolysis during formation of these free radicals are as under-

H_3C-H	104 kcal/mol
H_3C-CH_2-H	98 kcal/mol
$(CH_3)_2CH$-H	96 kcal/mol
$(CH_3)_3C$-H	93 kcal/mol

This order of bond dissociation energy is just opposite to the order of stability of free radicals formed after their homolysis.

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Similarly, methyl free radical is more stable than hydroxyl free radical.

$$CH_3^{\bullet} \quad > \quad {}^{\bullet}OH$$

The bond dissociation energy (BDE) of the bonds undergoing homolysis during formation of these free radicals are as under-

CH_3-H	104 kcal/mole
HO-H	119 kcal/mole

Here, oxygen atom is more electronegative than carbon atom. Hence, unpaired electron of hydroxyl free radical is more tightly held to the oxygen atom and is relatively less dispersed as compared to that in methyl free radical.

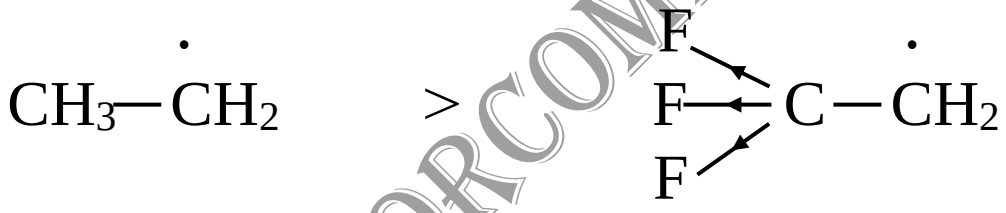
(2) Resonance- Resonance increases the stability of free radicals. The greater the extent of resonance for a free radical more is its stability. For example,

$$\mathbf{H_3C\text{-}\ H_2C^{\bullet} \ < \ CH_2{=}CH\text{-}H_2C^{\bullet} \ < \ CH_2{=}CH\text{-}CH^{\bullet}\text{-}CH{=}CH_2}$$

(stabilized by resonance) (doubly stabilized by resonance)

(3) Presence of electron withdrawing atoms or groups-

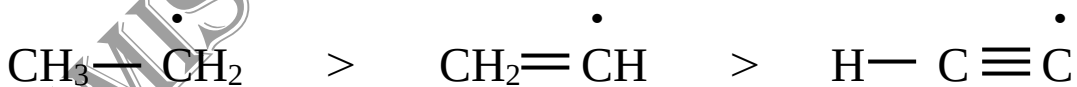
Electron withdrawing atoms or groups destabilize the free radicals. For example, trifluoroethyl free radical is less stable than ethyl free radical.



Ethyl Free Radical Trifluoroethyl Free Radical

(4) s-character in hybridised carbon-

Stability of free radicals is lesser, if the orbital containing unpaired electron is more closer to the nucleus. For example, the order of stability of ethyl, Ethenyl (vinyl) and ethynyl free radicals will be as under-



Ethyl Free Radical Vinyl Free Radical Ethynyl Free Radical

Here, ethynyl free radical contains sp hybridised carbon with 50% s-character. Hence, it is most electronegative and binds unpaired electron more firmly and prevents its dispersal.

In vinyl free radical carbon bearing unpaired electron is sp^2 hybridised with 33.33 % s-character. Here, carbon is relatively less electronegative and therefore, unpaired electron is more delocalized. Thus, vinyl free radical will be relatively more stable than ethynyl free radical.

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In the same way, in ethyl free radical carbon bearing unpaired electron is sp^3 hybridised with only 25% s-character. Here, carbon is the least electronegative and therefore, unpaired electron is the most delocalized. Thus, ethyl free radical will be the most stable amongst three.

(5) Atomic Size of atom having unpaired electron-Stability of free radicals decreases with decrease of atomic size bearing unpaired electron. For example,

$$H_3C^{\bullet} > H_2N^{\bullet} > HO^{\bullet} > F^{\bullet}$$

In fact, on moving left to right in a period, the atomic size decreases and electronegativity increases. Thus, unpaired electron goes closer to the nucleus and its dispersal becomes difficult.

(6) Electronegativity of atom having unpaired electron-

The greater the electronegativity of atom having unpaired electron lesser is the stability of respective free radical. On moving down the group in periodic table, stability of free radicals increases. For example, order of stability of halogen free radicals will be as under-

$$F^{\bullet} < Cl^{\bullet} < Br^{\bullet} < I^{\bullet}$$

In fact, on moving down the group atomic size increases and electronegativity of atoms decreases, so that the orbital containing unpaired electron is more dispersed. It results in more dispersal of unpaired electron i.e. increase of stability of free radical.

(7) Presence of adjacent atom having one or more lone pair of electrons

Atoms having one or more lone pair of electrons stabilize the free radicals. For example, the order of stability of methyl and different substituted methyl free radicals is as under-

$$H_3C^{\bullet} < F\text{-}H_2C^{\bullet} < HO\text{-}H_2C^{\bullet} < H_2N\text{-}H_2C^{\bullet}$$

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