

3.12.3 Carbon Radicals

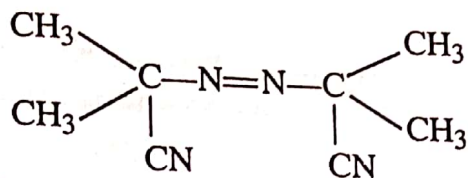
Carbon radicals are odd electron species in which a carbon atom bears the odd electron. Homolytic fission of a covalent single bond gives rise to free radicals. This cleavage is initiated either by physical aid or by chemical reagents.

(a) Physical aid : heat and light

(b) Chemical reagent :

(i) Organic peroxides mainly benzoyl peroxide $\text{C}_6\text{H}_5-\overset{\text{O}}{\parallel}{\text{C}}-\text{O}-\text{O}-\overset{\text{O}}{\parallel}{\text{C}}-\text{C}_6\text{H}_5$

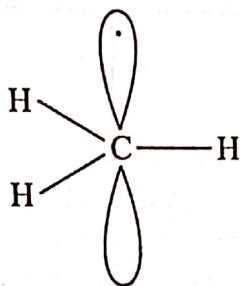
(ii) Azo compounds, mainly azobis-isobutyronitrile.



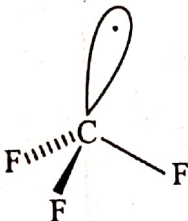
(iii) Reductant and oxidant, *i.e.*, metal.

Owing to the presence of odd electron, a carbon radical is paramagnetic in nature. Due to this reason free radicals are highly reactive.

The structure of the carbon radicals are very difficult to predict. They have planar to pyramidal geometry depending on the groups and atoms attached to the carbon atom having the odd electron. For example, methyl free radical is essentially planar.

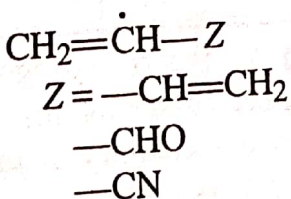


On the other hand, trifluoromethyl free radical is pyramidal.



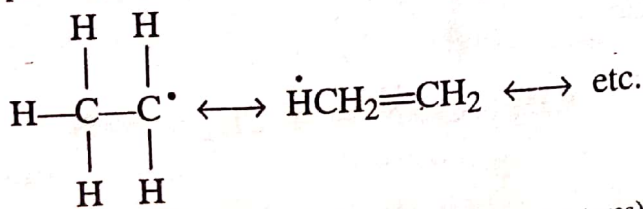
Tertiary butyl radical has also pyramidal geometry. Simple alkyl radical has pyramidal geometry. Radical geometry is significantly affected by substituent groups that can act as π -donors.

Presence of oxygen substituent or fluorine on radical carbon favours a pyramidal structure. The vinyl radical has bent geometry with bond angle 137° . Substituents affect the preferred geometry of vinyl radicals. Conjugation with π acceptor substituents favour a planar geometry, whereas σ donor substituents favour a bent geometry.



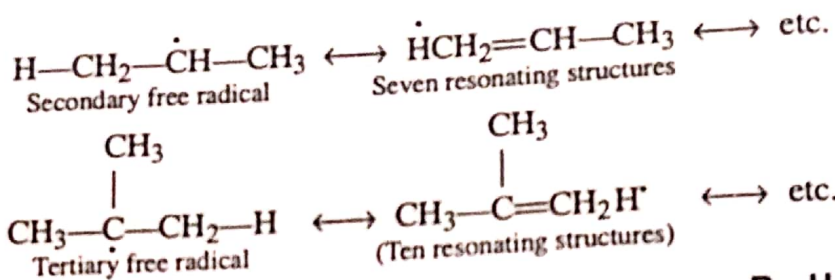
where

(A) Stability : Since bond dissociation energies give us an idea of the ease with which radicals can form, they can also give us an idea of the stability of those radicals once they have formed. Thus, dissociation energy of $R\text{---}H$ bonds provides a measure of the relative stability of free radical R . Table-3.9 lists such values. The lower the bond dissociation energy, the higher will be the stability. The stability order of alkyl free radicals is tertiary > secondary > primary > CH_3 . This stability order can be explained by hyperconjugation.



Primary free radical

(Four resonating structures)

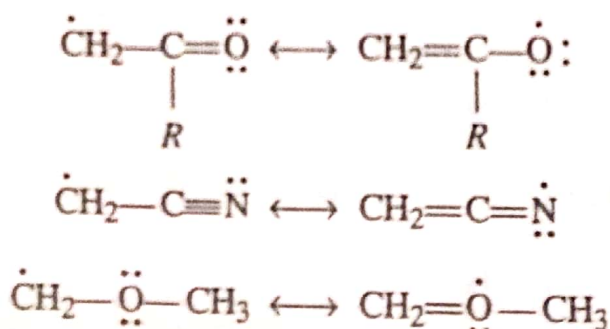

Table 3.9 : Bond dissociation energy value of some R—H bonds.

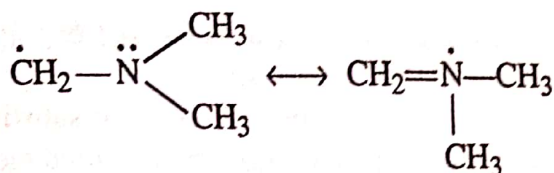
Bond	Bond dissociation energy in kJ/mole
CH ₃ —H	439
CH ₃ —CH ₂ —H	423
$\begin{array}{c} \text{CH}_3-\text{CH}-\text{H} \\ \\ \text{CH}_3 \end{array}$	410
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3-\text{C}-\text{H} \\ \\ \text{CH}_3 \end{array}$	397
CH ₂ =CH—CH ₂ —H	364
C ₆ H ₅ —CH ₂ —H	372
$\begin{array}{c} \text{CH}_3 \\ \\ \text{C}_2\text{H}_5\text{O}-\text{C}-\text{H} \\ \\ \text{H} \end{array}$	385
CH ₃ —CO—CH ₂ —H	385
CN—CH ₂ —H	360

The unpaired electron is shared by the α-hydrogen atoms. The number of hyperconjugative structures for the tertiary radical is more than that for secondary and primary radicals. Hence the tertiary free radicals are more stable than secondary or primary radicals.

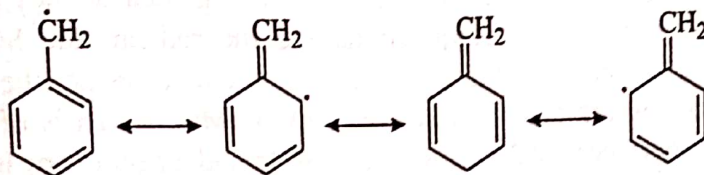
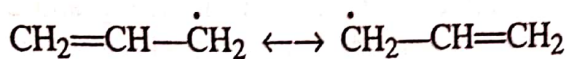
Both electron-attracting groups such as carbonyl, cyano and nitro and electron-donating groups such as methoxy and dimethylamino have a stabilising effect on a radical intermediate at an adjacent carbon.

This is called the **push-pull** or **captodative** effect. The effect arises from increased resonance structures.



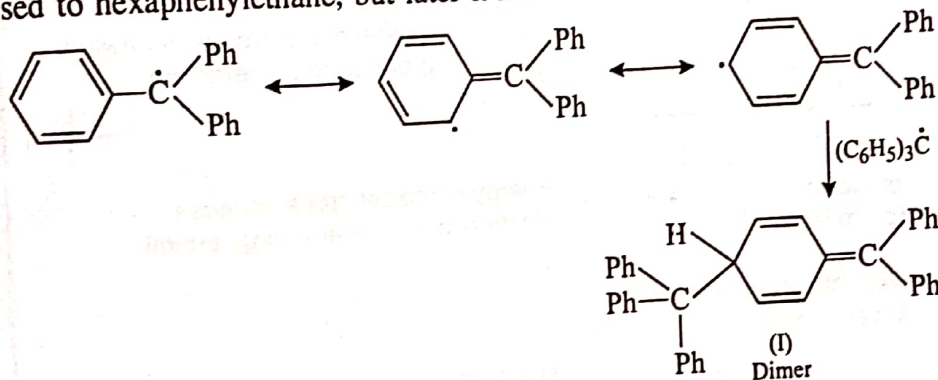


The stabilising effects of vinyl groups (in allyl radicals) and phenyl groups (in benzyl radicals) are very significant and can be satisfactorily explained by resonance.



Allyl and benzyl free radicals are more stable than alkyl free radicals but still have only a transient existence under ordinary conditions. However, the triphenylmethyl and similar radicals are stable enough to exist in solution at room temperature, through equilibrium with a dimeric form. The concentration of triphenylmethyl radical in benzene solution is about 2% at room temperature.

For many years it was assumed that triphenylmethyl free radical, the first stable free radical known, dimerised to hexaphenylethane, but later it has been found that it is not the case.



Although triphenylmethyl-type radicals are stabilised by delocalisation, it is steric hindrance to dimerisation and not resonance that is the major cause of their stability.

Simple alkyl radicals are extremely short-lived but some radicals survive almost indefinitely. Such radicals are known as **persistent radicals**. As mentioned the triphenylmethyl radical is very stable which exists as yellow solution in equilibrium with its dimer.

