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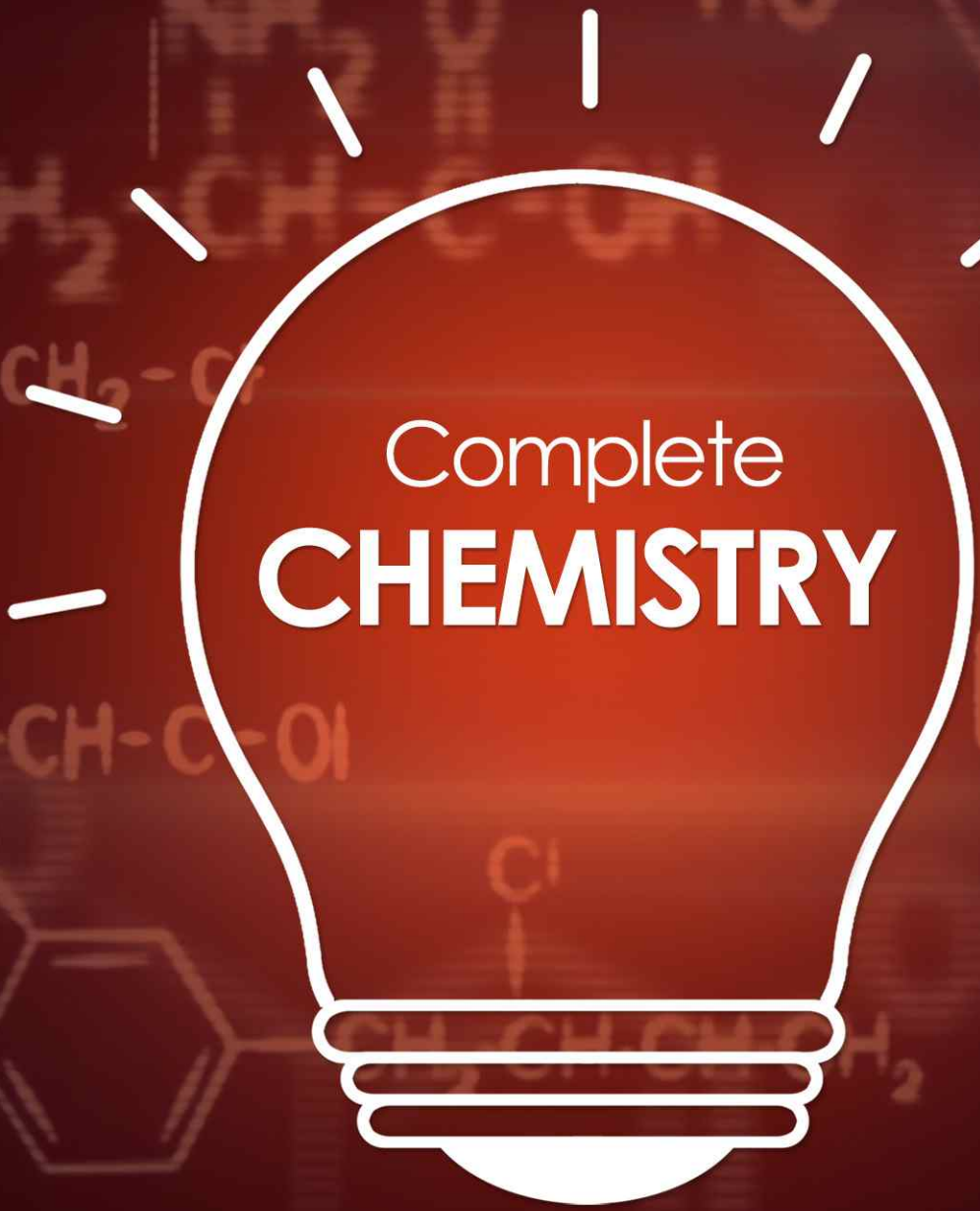

Complete CHEMISTRY

IIT-JEE · NEET · CBSE eBOOKS

CLASS 11&12th

CLASS 11th

General Organic Chemistry

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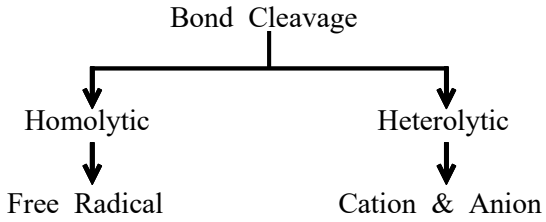
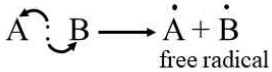
01. Bond Cleavage

In organic reaction, the organic compound which is converted into a new compound by breaking and formation of covalent bonds is known as the **reactant** or **substrate** and the new compound formed is known as the **product**.
The chemical species (more reactive) which causes the change is called **reagent**.
Breaking of covalent bond is known a **bond cleavage**. A bond can be broken by two ways:



Homolytic Fission or Homolysis

- The covalent bond is broken in such a way that each resulting species gets its own electron. This leads to the formation of odd electron species known as **free radical**.
- Homolytic bond fission gives free radical as the reaction intermediate.



- The factor which favours homolysis is zero or a small difference in electronegativity between A and B. Homolytic bond fission takes place in gaseous phase or in the presence of non polar solvents (CCl_4, CS_2)

Heterolytic Bond Fission or Heterolysis

- In heterolysis, the covalent bond is broken in such a way that one species (i.e., less electronegative) loses its own electron, while the other species (i.e., more electronegative) gains both the electrons.

Thus formation of opposite charged species take place. In case of organic compounds, if positive charged is present on the carbon then cation is termed as **carbocation**. If negative charge is present on the carbon then anion is termed as **carbanion**.

- The factor which favours heterolysis is a greater difference of electronegativity between A and B.

02. Reaction Intermediates

Most of the organic reaction occur through the involvement of certain chemical species. These are generally *short-lives* (10^{-6} seconds to a few seconds) *and highly reactive and hence cannot be isolated. These short-lived highly reactive chemical species through which the majority of the organic reactions occur are called* **reactive intermediates.** Some important examples of reactive intermediates are : *carbocations, carbanions, free-radicals, carbenes and nitrenes.*

Carbocations

Chemical species bearing a positive charge on carbon and carrying six electrons in its valence shell are called **carbocations** or **carbenium ions.** Earlier these were called **carbonium ions.** These are formed by heterolytic cleavage of the covalent bonds in which the leaving group takes away with it the shared pair of electrons (of the covalent bond). For example,

i.e., $(CH_3)_3C-Cl \longrightarrow (CH_3)_3\overset{+}{C} + Cl^-$

tert-Butyl chloride → *tert*-Butyl carbocation

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

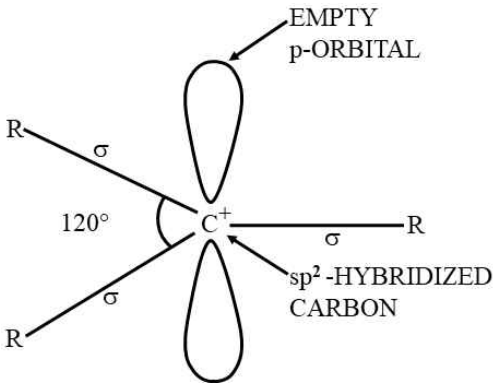
$CH_3-\overset{+}{C}H_2$ Ethyl carbocation (1°)

$CH_3-\overset{+}{C}H-CH_3$ Isopropyl carbocation(2°)

$CH_3-\overset{+}{\underset{CH_3}{\underset{|}{C}}}-CH_3$ *tert.* Butyl carbocation(3°)

Reactivity : The order of reactivity of carbocations follows the sequence: *1° > 2° > 3°.*

Orbital structure : *The carbocations are planar chemical species.* The carbon atom carrying the positive charge is sp^2–hybridized orbitals of this carbons 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 unhybridized 2*p*-orbital which is perpendicular to the plane of the three σ-bonds is, however, empty



Carbanions : *Chemical species bearing a negative charge on carbon and possessing eight electrons in its valence shell are called* **carbanions.**

Classification : Like carbocations, carbanions are also classified as primary (1°), secondary (2°) and tertiary (3°) according as the negative charge is present on a primary, secondary and a tertiary carbon atom respectively. For example.

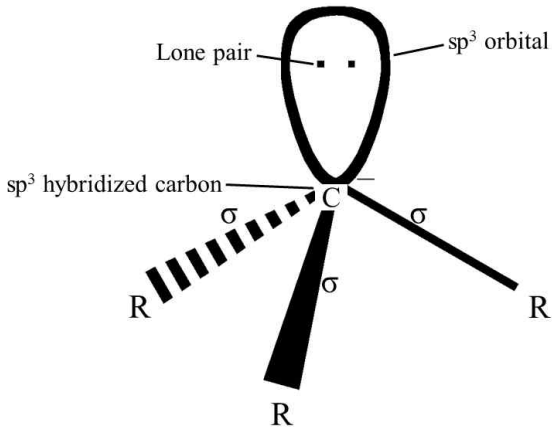
$R-CH_2^-$ Primary carbanion (1°)

R_2CH^- Secondary carbanion (2°)

R_3C^- Tertiary carbanion (3°)

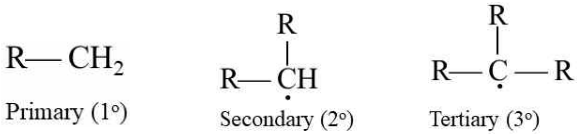
Reactivity : The order of reactivity of carbanions is reverse of the order of stability, *i.e.,* $3° > 2° > 1° > CH^-_3$.

Orbital structure : *The structure of simple alkyl* carbanions is usually pyramidal just like those of ammonia and amines. The carbon atom carrying the negative charge is sp^3-hybridized. Three of the four sp^3-hybridized orbitals form three σ-bonds with monovalent atoms or groups while the fourth sp^3-orbital contains the lone pair of electrons.

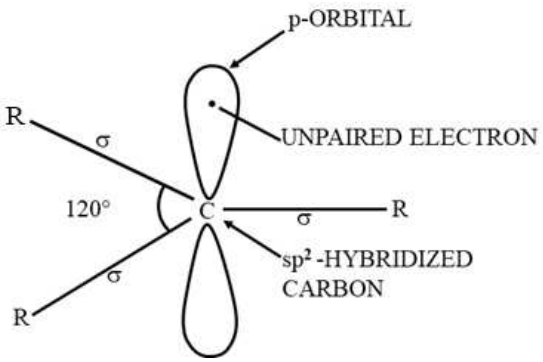


Free Radicals : *A free radical may be defined as an atom or a group of atoms having an odd or upaired electron.*

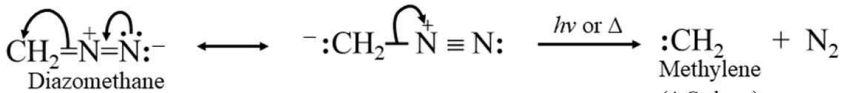
Classification. Like carbocations and carbanions, free radicals are also classified as *primary* (1°), *secondary* (2°) *and tertiary* (3°) according as the carbon atom carrying the unpaired electron is primary, secondary and tertiary respectively. For example,

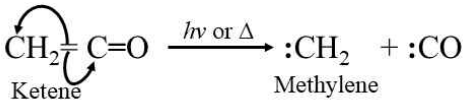


Orbital structure : *Alkyl free radicals like carbocations are planar chemical species.* The only difference being that in carbocations, the unhybridized *p*- orbital is empty while in free radicals, it contains the odd electron



(i) Carbenes : *Neutral divalent carbon species in which the carbon atom is bonded to two monovalent atoms or groups and also contains two non-bonding electron are called* **carbenes.** These are generally produced either by photolysis (irradiation with UV light) or thermolysis or pyrolysis (action of heat) of diazoalkanes or ketenes. Thus,





Like carbocations, carbenes are short-lived highly reactive chemical species since the central carbon atom has only six electrons in its valence shell and thus has a strong tendency to complete its octet by gaining two more electrons. *Carbenes, thus, behave as Lewis acids or electrophiles.*