REACTION INTERMEDIATES

The substances formed when bonds are broken are known as reaction intermediates. These are usually brief in existence and very reactive, making it difficult to isolate them. The common intermediates include:

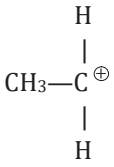
Carbocation

Cation in which positive charge is present on carbon atom is called carbocation.

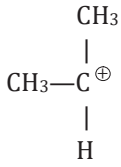
- Due to electron deficiency, it acts as an electrophile and always attack on electron richer site.
- It is incomplete octet species because it has six electrons in outer most shell.
- All electrons are paired.

Types of Carbocations

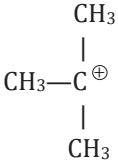
Carbocations are grouped into three types: primary (1°), secondary (2°), and tertiary (3°) carbocations.



Ethyl carbocation (1°)



Isopropyl carbocation (2°)



Tertiary butyl carbocation (3°)

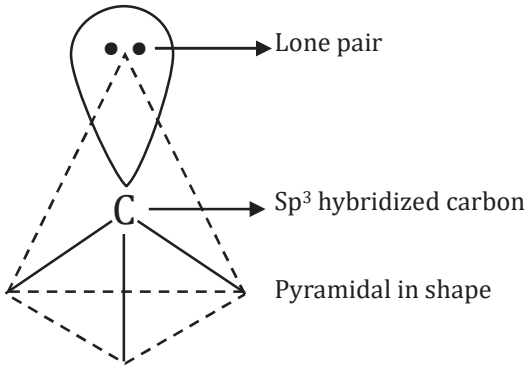
Carbanions

Anion in which negative charge is present on carbon atom is called carbanion.

- It has eight electrons in outermost shell so it is complete octet species.
- It is an electron richer species because it has extra electron.
- Due to presence of nonbonding electrons, it acts as a nucleophile.

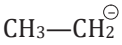
Orbital Structure of Carbanion

In a carbanion, the carbon atom carries a negative charge and has sp^3 hybridization. Three out of the four sp^3-hybridized orbitals create three σ bonds with monovalent atoms or groups, and the fourth sp^3-orbital holds the lone pair of electrons. As a result, the shape of a carbanion is pyramidal.

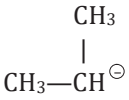


Classification of Carbanions

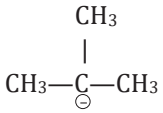
Similar to carbocations, carbanions are categorized as primary (1°), secondary (2°), and tertiary (3°) based on the type of carbon atom involved.



Ethyl carbanion (1°)



Isopropyl carbanion (2°)



Tertiary butyl carbanion (3°)

Free Radical

- Electrically neutral species in which unpaired electron is present on carbon atom is known as carbon free radical.
- It has seven electron or odd electron in outermost shell of unpaired electron containing carbon.
- It is electron deficient species due to incomplete octet.

Orbital Structure of Free Radical

Alkyl free radicals, similar to carbocations, have a flat structure. However, in free radical species, the unhybridized orbital holds the unpaired electron.

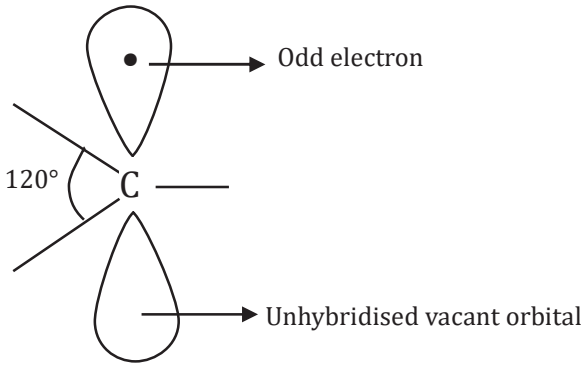
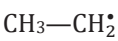


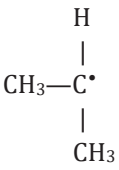
Fig: Orbital structure of free radicals

Classification:

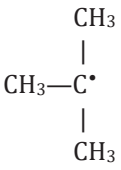
Free radicals are categorized as primary (1), secondary (2°), and tertiary (3°).



Ethyl free radical (1°)



Isopropyl free radical (2°)



Tertiary butyl free radical (3°)

Types Of Attacking Reagents

These are of two types:
(i) Electrophilic
(ii) Nucleophilic

(i) Electrophilic reagent or electrophiles:

Electrophilic (electro + phallic)
(electron + loving)

The reagent which attacks on the negative part of the molecule or having attraction for electrons are called electrophiles.

Electrophiles may be positively charged or neutral.

(i) Positively charged electrophiles:

$\overset{\oplus}{H}$, $\overset{\oplus}{SO_3H}$, $\overset{\oplus}{NO}$, $\overset{\oplus}{NO_2}$, $\overset{\oplus}{X}$, $\overset{\oplus}{R}$, $R-\overset{\oplus}{C}(=O)$, $C_6H_5-\overset{\oplus}{N_2}$

(ii) Neutral electrophiles: - central atom e^- deficient

(a) All Lewis acids as:

BF_3, $AlCl_3$, SO_3, $ZnCl_2$, $BeCl_2$, $FeCl_3$, $SnCl_2$, CO_2, SnC_{14}.

(b) Free radicals, carbenes and nitrenes act as electrophiles

(ii) Nucleophilic reagent or nucleophiles.

Which attacks on the positive site of the substrate or loves nucleus or having attraction towards nucleus.

Nucleophilic (Nucleon + phials)
↓
(Nucleus + loving)

Nucleophiles may be negatively charged ions or possess a lone pair of electrons or πe^-.

(i) Negatively charged nucleophiles.

$\overset{\ominus}{H}, \overset{\ominus}{OH}, \overset{\ominus}{OR}, \overset{\ominus}{CN}, \overset{\ominus}{X}, \overset{\ominus}{R}, R-\overset{\ominus}{COO}, \overset{\ominus}{NH_2}, \overset{\ominus}{SH}$

(ii) All Lewis base which contains lone pairs or π e^-.

$H_2\ddot{O}$, R–$\ddot{O}$H, R–$\ddot{O}$–R, $\ddot{N}H_3$, R–$\ddot{N}H_2$, $CH_2=CH_2$, $CH\equiv CH$.

(iii) $\overset{*}{R}$–Mg–X, LiAl$\overset{*}{H}_4$, NaB$\overset{*}{H}_4$

The star (*) indicates the atom which donates electrons to the substrate.

Ambident nucleophile: - Nucleophiles which have two sites of electron rich centre or in which two or more atoms bear a lone pair of electrons.

Examples:- $K^{\oplus\ominus}O-N=O$, $\ddot{N}H_2-\ddot{O}H$, $\overset{\oplus}{N}a\overset{\ominus}{C}\ddot{N}$