CHAPTER 23

GENERAL ORGANIC CHEMISTRY

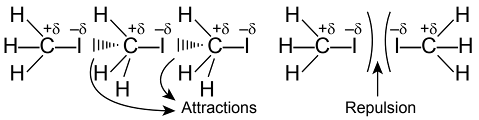
23.1 INTRODUCTION

In covalent compounds, the structural units (molecules) are covalent molecules. These molecules are held together by very weak forces. These forces are termed as **intermolecular forces, intermolecular non-bonding attractions or secondary forces.** Secondary forces are of the following types:

1. Dipole–Dipole interactions
2. Van der Waal's forces
3. Hydrogen bond

23.1.1 Dipole–Dipole Interactions

Except in a highly dispersed gas, molecules attract and repel each other. These attractions and repulsions arise primarily from molecular dipole–dipole interactions. E.g., in the liquid state, molecules of methyl iodide can either attract or repel each other, depending on the orientation of the molecules. When iodine ends of two molecules approach closely, the two molecules repel each other.



Dipole–dipole interaction can only be possible if molecule has a permanent dipole. An ordinary covalent bond has energy in the range of 30 to 100 kcal/mole. Dipole–dipole interactions are much weaker, approximately 1 to 3 kcal/mole. Magnitude of dipole-dipole interactions depends on the dipole moment of the bond of the compound and intermolecular distance $\mathrm{DDE} \propto \frac{1}{d^2}$.

23.1.2 Van der Waal's Forces

These forces of attractions exist between non-polar molecules. This force of attraction is intermolecular attraction due to the electrostatic attractions between nuclei of one molecule and electrons of the other molecule.

Van der Waal's forces are very weak and are significant only when the molecules are very close together, i.e., between the surface molecules. Van der Waal's force of interaction $VF \propto \frac{1}{d^7}$. They are effective only over short intermolecular distances.

Magnitude of Van der Waal interaction depends on number of electrons and protons in the molecule as well as on the intermolecular distance.

Note:

VF $\propto$ number of electrons and protons $\propto$ molecular weight

$\propto$ Surface area of the molecule

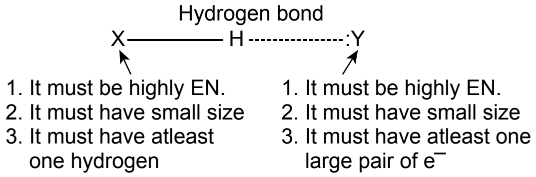
$\propto$ Symmetry of the molecule

If structure of a molecule is symmetrical then molecules are packed well in the crystal lattice (solid and liquid phases) which decreases distance, hence increases van der Waal's attraction.

23.1.3 Hydrogen Bonding

The strongest secondary force is of interaction of the hydrogen bond, which consists of bond between an H attached to a highly electronegative atom, X and an electronegative atom bearing an unshared pair of electrons, either in another molecule or in a different part of the same molecule.

23.1.3.1 Condition for H-bonding



Classification of hydrogen bonding: Hydrogen bonding is of two types.

(i) Intermolecular hydrogen bonding
(ii) Intramolecular hydrogen bonding

23.1.4 Substrate and Reagent

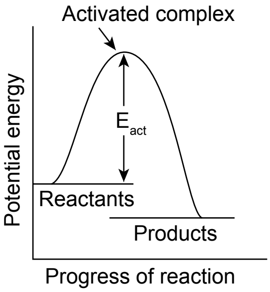
Whenever a chemical reaction occurs between two or more substance, new compounds are formed. The substances with which we start a reaction are called **reactants** or starting materials and the new compounds formed as a result of a chemical reaction are called **products.** The reactants are further classified as substrates and reagents.

Substrate + Reagent → Products

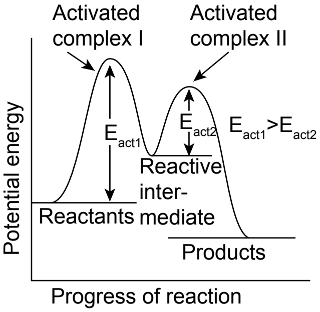
(i) **Reagent:** A more reactive reactant which is usually present in small amounts is called a reagent.
(ii) **Substrate:** A less reactive reactant which is usually present in large amounts is called a substrate.

23.1.5 Reaction Mechanism

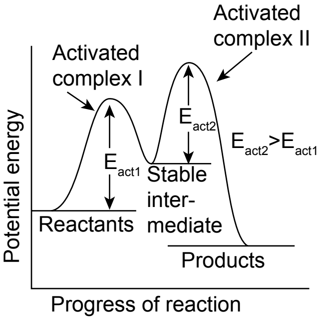
A chemical reaction is believed to occur through collision between substrate and reagent molecules. As a result of these collisions, a highly energetic species called the **activated complex** or the **transition state** is first formed which subsequently decomposes to give the products.



(a)
A one-step or
concerted reaction



(b)
A two-step reaction with
a reactive intermediate



(c)
A two-step reaction with
a stable intermediate

Alternatively, in some cases a relatively less energetic but more stable chemical species than the activated complex may be first formed. This chemical species which is relatively less energetic but more stable than the activated complex is called the **reaction intermediate.** This reaction intermediate then gets converted into the product through another activated complex.

Thus, a two-step reaction occurs through two activated complexes. If the energy of activation of the first activated complex is more than that of the second, then the intermediate rapidly gets converted into the products, i.e., the intermediate cannot be isolated. In such cases, the first step is the rate-determining step of the reactions.

If, however, the energy of activation of the second activated complex is higher than that of the first then the intermediate is quite stable and hence can be isolated. In such cases, the second step is the rate-determining step of the reaction. In the light of the above discussion, a reaction may follow either of the following two paths:

Path I: Substrate + Reagent → Activated complex → Products

Path II: Substrate + Reagent → Activated complex → Reaction intermediate → Activated complex$_2$ → product

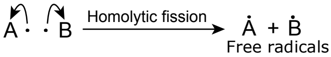
A detailed step-by-step description of a chemical reaction showing as to how reactants are converted into products is called mechanism of the reaction. If a reaction involves simultaneous making and breaking of bonds without the formation of any intermediate, it is said to be a **concerted reaction.** Such a reaction occurs through a single **activated complex** or **transition state**. On the other hand, if a reaction occurs in two or more steps with the formation of a reactive or isolable intermediate it is said to be a step wise or **non-concerted reaction.**

- Concerted reaction is also called elementary or simple reaction while non-concerted reactions are termed as non-elementary as complex reaction.

23.1.6 Type of Bond Cleavage

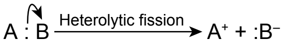
(a) **Symmetrical cleavage or homolysis:** If a covalent bond breaks in such a way that each atom takes away one electron of the shared pair, it is called symmetrical cleavage or **homolysis.**

The neutral chemical species (such as A and B) which contain an unpaired electron and which are produced by homolytic fission of covalent bonds are called free radicals.

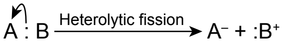


- **Condition for homolysis:** Homolytic fission usually occurs in non-polar bonds and is favoured by high temperature, ultra-violet (UV) radiations and by the presence of radical initiators such as peroxides, diazo compounds, etc. in gaseous phase and in non-polar solvents.

(b) **Unsymmetrical cleavage or heterolysis:** When a covalent bond joining two atoms A and B breaks in such a way that both the electrons of the covalent bond (i.e., shared pair) are taken away by one of the bonded atoms, then the mode of bond cleavage is called **unsymetrical cleavage** or **heterolysis.**



(when B is more electronegative than A)



$A^- + B^+$ (when A is more electronegative than B)

- **Condition of heterolysis:** It usually occurs in polar covalent bonds and is favoured by polar solvents in presence of polar reagents like acids or bases at low temperature.

23.2 TYPES OF REAGENTS

23.2.1 Electrophiles

They are electron-deficient species. They attack at the centre of high electron density acts as Lewis acid and have oxidizing tendency.

(a) **Classification of electrophiles:**

   (i) **Positive electrophiles:** H^+, H_3O^+, Cl^+, Br^+, I^+, NO_2^+, NO^+, R^+ (carbocation), etc.

   (ii) **Neutral electrophiles:** R, $:CR_2$, $:\ddot{N}R$, BF_3, $AlCl_3$, $ZnCl_2$, $FeCl_2$, $SnCl_4$, PCl_5, IF_7, $SnCl_2$, CO_2, SO_3, $BeCl_2$, etc.

- Alkali and alkaline earth metal cations as well as NH_4^+ cannot act as electrophiles.

23.2.2 Nucleophiles

They are electron-rich species, they attack at the centre of low electron density, i.e., +ve charge centre. They acts as Lewis bases and have reducing tendency.

(a) Classification of nucleophiles:

   (i) **Charged nucleophiles:** H^-, Cl^-, Br^-, I^-, R^-, $RC{\equiv}C^-$, OH^-, OR^-, SR^-, $C_6H_5O^-$, NH_2^-, NO_2^-, CN^-, $RCOO^-$, etc.

   (ii) **Neutral nucleophiles:** $H_2\ddot{O}:$, $\ddot{N}H_3$, $R\ddot{N}H_2$, $R\ddot{O}H$, $R\ddot{S}H$, $R\ddot{O}R$, $R\underset{\bullet\bullet}{\ddot{S}}R$, R–MgX, R–Li, $NaBH_4$, $LlAlH_4$.

   - Organic compound having carbon–carbon multiple bond also act as neutral nucleophile.

(b) Factors affecting nucleophilic character:

   (i) Negatively charged species are better nucleophiles in comparison to neutral species.

   E.g., $H_2O < OH^{\ominus} < CH_3-O^{\ominus}$.

(ii) Among base and its conjugate acids, nucleophilic character of base is greater.
E.g., $OH^{\ominus} > H_2O$ $NH_2^{\ominus} > NH_3$

(iii) In a polar protic solvent, nucleophilic character and basic character are antiparallel to each other while moving from top to bottom, i.e., nucleophilic character increases while basic character decreases.

Basic character $\xleftarrow{F^{\text{È}}\ Cl^{\text{È}}\ Br^{\text{È}}\ I^{\text{È}}}$

Nucleophilic character →

(iv) While moving from left to right in a period, nucleophilicity and basicity are parallel to each other, i.e., both decreases from left to right

Basic character $\xleftarrow{CH_3^{\text{È}}\ NH_2^{\text{È}}\ OH^{\text{È}}\ F^{\text{È}}}$

Nucleophilic character ←

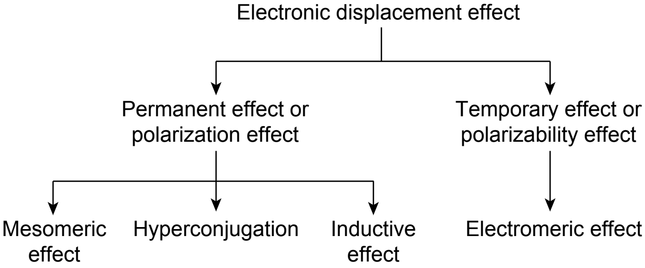
(v) In a group of nucleophile in which the nucelophilic atom is same, nucleophilicity parallels basicities.

Basic character $\xleftarrow{RO^{\text{È}}\ OH^{\text{È}}\ RCOO^{\text{È}}\ ROH\ H_2O}$

Nucleophilic character ←

(vi) When adjacent atom to nucelophilic site has lone pair of electrons, nucelophilic character increases. $H\underset{\cdot\cdot}{\ddot{O}}O^{\ominus} > OH^{\ominus}$ $\ddot{N}H_2\ddot{N}H_2 > \ddot{N}H_3$

23.3 ELECTRONIC DISPLACEMENT EFFECT



23.3.1 Inductive Effect

The permanent displacement of σ-electrons along a saturated carbon chain towards the more electronegative substitutent (atom or group) resulting in development of polarity is termed as inductive effect. The effect weakens steadily with increasing distance from the substituent and actually becomes negligible after two carbon atoms.

$$—C \rightarrow C_3^{\delta\delta\delta+} \rightarrow C_2^{\delta\delta+} \rightarrow C_1^{\delta+} \rightarrow C^{\delta-};\ \text{where } \delta^+ > \delta\delta^+ > \delta\delta\delta^+$$

Groups or atoms which withdraw electrons of the σ-bond towards themselves as compared to hydrogen are said to have electron-withdrawing or electron-attracting or -I effect. The order of -I effect of some substitutuents relative to hydrogen is:

$R_3\overset{\oplus}{N}$ – > $-NO_2$ > –CN > $-SO_3H$ > –COOH > –F > –Cl > –Br > –I > –OR > –OH > $-NH_2$

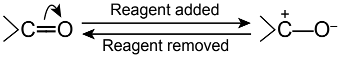
Groups or atoms which donate electrons to the carbon chain are said to have electron-releasing or electron-donating or +I effect.

E.g., $-\overset{-}{O} > -CO\overset{-}{O} < (CH_3)_3C- > (CH_3)_2CH- > CH_3CH_2-CH_3-D- > H-$. Now little space between different substituents.

- Inductive effect is a permanent effect and is responsible for change in physical and chemical properties of the compounds.

23.3.2 Electromeric Effect

It involves the complete transfer of electrons of a multiple bond (double or triple bond) to one of the bonded atoms (usually more electronegative) in presence of an attacking reagent. It is called E-effect.

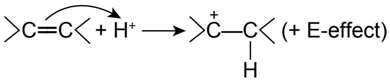


$>C=O \underset{\text{Reagent removed}}{\overset{\text{Reagent added}}{\rightleftharpoons}} >\overset{+}{C}-O^-$

- This effect is temporary and takes place only in the presence of a reagent. As soon as the reagent is removed, the molecule reverts back to its original position.

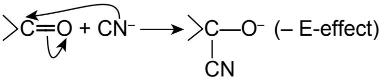
(a) Classification of electromeric effect:

(i) +E effect: If the electrons of the π-bond are transferred to that atom of the double bond to which the reagent gets finally attached, the effect is called +E-effect. Reaction which proceeds through the attack of an electrophile belongs to this category.



$>C=C< + H^+ \longrightarrow >\overset{+}{C}-\underset{H}{\underset{|}{C}}<$ (+ E-effect)

(ii) –E effect: If the attack of an attacking reagent and transfer of π-electron occurs to two different atoms, then reaction is known as -E effect. Reaction which occurs through the attack of nucleophile belongs to this category.



$>C=O + CN^- \longrightarrow >\underset{CN}{\underset{|}{C}}-O^-$ (– E-effect)

23.3.3 Resonance

The phenomenon in which more than one electronic structure of a compound is written but none of them is able to represent all the observed properties of the compound completely is termed as resonance. The actual structure of the compound is termed as resonance hybrid while various alternative structures are termed as resonating structures or canonical structures. Resonance phenomenon is further classified into two categories.

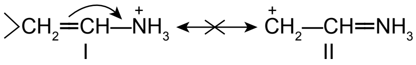
(i) Mesomeric effect (ii) Hyperconjugation

23.3.3.1 Condition for resonance

(i) The various resonating structures should differ only in the position of electrons and not in the position of atoms or nuclei.

(ii) All the resonating structures should have the same number of unpaired electrons.

(iii) In case of atoms of the second period in the periodic table, such resonating structures which violate octet rule should not be considered.



$\underset{\text{I}}{>CH_2=CH-\overset{+}{N}H_3} \not\longleftrightarrow \underset{\text{II}}{\overset{+}{C}H_2-CH=NH_3}$

(iv) Resonance occurs only in planar molecule or planar part of the molecule, any structural feature which affects the planarity of the molecules also affect the resonance.

(iv) Resonance occurs only in conjugated system, i.e., a system having any one of the following structural feature.

(i) π σ π (ii) π σ ⊕ (iii) π σ ⊖ (iv) π σ odd electron (v) lone pair σ ⊕.

(a) **Stability of resonating structures:**
   - (i) Non-polar structure, i.e., uncharged structures are more stable in comparison to polar structure.
   - (ii) Resonating structures having greater number of covalent bond are more stable in comparison to resonating structures having lesser number of covalent bond.
   - (iii) Resonating structures in which octet of all atoms is complete are more stable in comparison to the resonating structure where octet of some atom is incomplete.
   - (iv) Among polar structures greater the charge separation between like charges greater will be their stability.
   - (v) Among polar structures greater the charge separation between unlike charges lesser will be their stability.
   - (vi) Among polar structure in which –ve charge is present on more electronegative atom and +ve charge is present on less electronegative atom will be more stable.

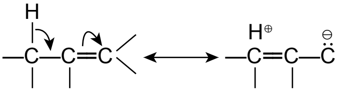
23.3.4 Hyperconjugation Effect

The phenomenon of displacement of electrons by conjugative mechanism involving σ, π and p-electrons is called hyperconjugation. Nathan and Baker pointed out that alkyl groups having atleast one hydrogen atom on the carbon atom, attached to an unsaturated carbon atom either having a double bond odd electron free radical, positively charged carbonium ions are able to release electrons due to delocalization of σ and π-bonds (or p-orbitals).

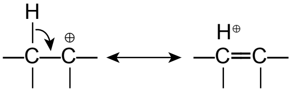
- Hyperconjugation is also called Boher Nathan–effect or no bond resonance or sacrificial conjugation.

(a) **Classification of conjugation:** Because number of covalent bonds is not equal in all hyperconjugating structures.

(i) σ-π **conjugation or heterovalet hyperconjugation:**

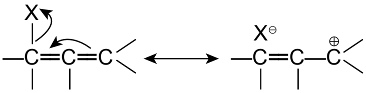


(ii) σ-**p conjugation or isovalent hyperconjugation:**



Because number of covalent bonds is equal in all hyperconjugating structures.

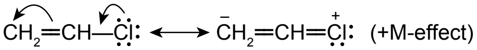
Reverse hyperconjugation:



(iii) **Mesomeric effect:** In case of conjugated systems (having alternate σ-and π-bonds) π-electrons can flow from one part of the molecule to the other due to resonance. As a result, centres of low and high electron density are created in such molecules. This flow of electron (or generation of centres of low and high electron density) in conjugated systems as a result of the phenomenon of resonance is called mesomeric effect (M-effect).

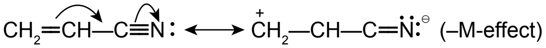
(b) **Classification of mesomeric effect:**

(i) **+M effect:** Groups which donate electrons to the double bond of a conjugated system are said to have + M effect. For example, –OH, –OR, –SH, –SR, –NH_2, –NHR, –NR_2, X (halogens), etc. Thus,



$$CH_2{=}CH{-}\ddot{\underset{\cdot\cdot}{Cl}}{:} \longleftrightarrow \overset{-}{C}H_2{=}CH{=}\overset{+}{\underset{\cdot\cdot}{Cl}}{:}\ \text{(+M-effect)}$$

(ii) **–M effect:** Groups which withdraw electrons from the double bond or from a conjugated system towards themselves due to resonance are said to have -M effect. For example, > C=O, —CHO,— COOR, —CN, —NO_2 —SO_3H, —COR, —$CONH_2$.



$$CH_2{=}CH{-}C{\equiv}N{:} \longleftrightarrow \overset{+}{C}H_2{-}CH{-}C{=}\ddot{N}{:}^{\ominus}\ \text{(–M-effect)}$$

23.4 REACTION INTERMEDIATES

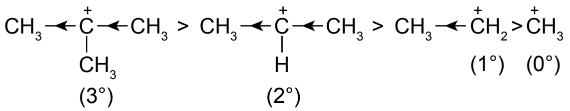
The highly reactive short-lived (10^{-6} s to a few seconds) chemical species through which majority of the organic reactions occur are called the reaction intermediates. They are formed by the action of a suitable reagent on the substrate molecule. E.g., carbocations, carbanions, free-radicals, carbenes, nitrenes and benzynes.

23.4.1 Carbocations

Chemical species bearing a positive charge on carbon atom and carrying six electrons in its valence shell are called carbocations. They are formed by heterolytic cleavage of covalent bonds. The carbocations are planar species. The carbon atom carrying the positive charge is sp^2-hybridized. The unhybridized p-orbital which is perpendicular to the plane of the three σ-bonds is, however, empty.

- Stability of carbocation $\propto \dfrac{1}{\text{Intensity of positive charge}}$ on carbon atom

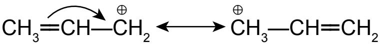
(a) **Stability of alkyl carbocations:** Order of stability of alkyl carbocation depends upon (i) + I-effect and (ii) hyperconjugation. The relative stability of simple alkyl carbocations follows the sequence: 3° > 2°> 1°, i.e.



$$\underset{(3^\circ)}{CH_3{\rightarrow}\underset{CH_3}{\overset{+}{C}}{\leftarrow}CH_3} > \underset{(2^\circ)}{CH_3{\rightarrow}\underset{H}{\overset{+}{C}}{\leftarrow}CH_3} > \underset{(1^\circ)}{CH_3{\rightarrow}\overset{+}{C}H_2} > \underset{(0^\circ)}{\overset{+}{C}H_3}$$

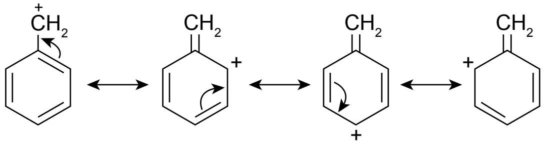
(b) **Stability of allyl and benzyl carbocation:** Allyl and benzyl carbocations are stabilized by resonance.

Allyl carbocation:



$$CH_3{=}CH{-}\overset{\oplus}{C}H_2 \longleftrightarrow \overset{\oplus}{C}H_3{-}CH{=}CH_2$$

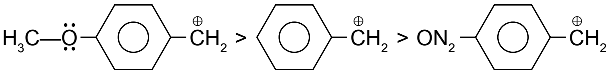
Benzylcarbocation:



Greater the number of phenyl groups attached to the carbon atom bearing the positive charge, larger the number of resonating structures, more stable is the carbocation.

e.g., $(C_6H_5)_3C^+ > (C_6H_5)_2CH^+ > C_6H_5CH_2^+ > CH_2=CH-\overset{\oplus}{C}H_2$

- Electron-donating substituents in the benzene ring tend to stabilize the substituted carbocation relative to benzyl carbocation by dispersal of the positive charge. Conversely, electron withdrawing groups in the benzene ring tend to destabilize the substituted carbocations relative to benzyl carbocation by intensification of the positive charge. E.g.,



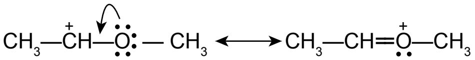
(c) **Stability of vinyl carbocation:** Carbocations in which the positive charge is located on a doubly bonded carbon such as vinyl $(CH_2=\overset{+}{C}H)$ and phenyl $C_6H_5^+$ cannot be stabilized by resonance and hence are quite unstable.

- As the s-character of the carbon bearing the positve charge increases, the stability of the carbocation decreases.

E.g., $\underset{\text{sp. (50\% s)}}{CH\equiv C+} < \underset{\text{sp}^2\text{. (33.3\% s)}}{CH_2=\overset{+}{C}H} < \underset{\text{sp}^3\text{. (25\% s)}}{CH_3-\overset{+}{C}H_2}$

(d) **Stabilization due to heteroatom:** If a heteroatom (O, N, Cl, etc.) having a lone pair of electrons is present next to the carbon atom bearing the positive charge, the stability of the carbocation increases due to resonance.

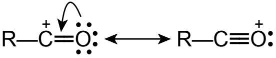
E.g.,



$CH_3-\overset{+}{C}H-\ddot{\underset{\cdot\cdot}{O}}:-CH_3 \longleftrightarrow CH_3-CH=\overset{+}{\underset{\cdot\cdot}{O}}-CH_3$

- Because of resonance, acylium ion is almost as stable as tert-butyl carbocation.

Acylium ion:



$R-\overset{+}{C}=\ddot{\underset{\cdot\cdot}{O}}: \longleftrightarrow R-C\equiv\overset{+}{O}:$

23.4.2 Carbanions

Chemical species in which the carbon atoms bears a negative charge and is surrounded by an octet of electrons are called carbanions. They are produced by heterolytic cleavage of covalent bonds. The structure of simple carbanions is usually pyramidal. The carbon atom carrying the negative charge is sp^3-hybridized.

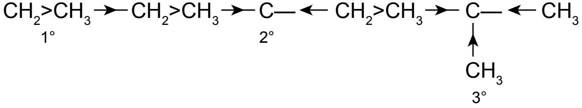
However, if carbanion is present in conjugation, then its hybridization is assumed to be sp^2.

E.g., $CH_2=CH-\overset{\cdot\cdot\ominus}{C}H_2$ Pseudo sp^2 - hybridisation

(a) **Stability of carbanions.**

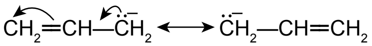
- Stability of carbanion $\propto \dfrac{1}{\text{Intensity of } -\text{ve charges}}$ of carbon atom

(i) **Stability of alkyl carbanions:** It follows a sequence which is exactly reverse of that of alkyl free radicals and carbocations, i.e., primary > secondary > tertiary, i.e.,



As the number of alkyl groups increases the intensity of the negative charge on the central carbon atom increases and hence the stability decreases accordingly.

(ii) **Allyl and benzyl carbanions:** Though they are primary, still are more stable than simple primary alkyl carbanions due to resonance.



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

As the number of phenyl groups attached to the carbon atom bearing the negative charge increases the stability increases accordingly.

$$(C_6H_5)_3\overset{\bar{\cdot\cdot}}{C} > (C_6H_6)_2\overset{\bar{\cdot\cdot}}{C}H > C_6H_5\overset{\bar{\cdot\cdot}}{C}H_2$$

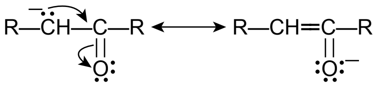
(iii) Electron-donating substituents in the benzene ring tend to decrease while electron-wthdrawing substituents tend to increase the stability of substituted carbanions relative to benzyl carbanion.

$$p\text{-}O_2N{-}C_6H_4{-}\overset{\bar{\cdot\cdot}}{C}H_2 > C_6H_4{-}\overset{\bar{\cdot\cdot}}{C}H_2 > p\text{-}CH_3O{-}C_6H_4{-}\overset{\bar{\cdot\cdot}}{C}H_2$$

(iv) If the α-position of a carbanion has a functional group which contains a multiple bond C = C, C= O, C ≡ N, NO_2, etc.) or carries an electronegative atom, such carbanions are stabilized by resonance and hence are more stable than simple aryl carbanions.

E.g., the stabilizing effect of the various α-substituents follows the order: NO_2 > RCO > COOR > CN > X (halogen).

(v) If the α-position of a carbanion has a functional group which contains a multiple bond C = C, C = O, C ≡ N, NO_2, etc.) or carries an electronegative atom, such carbanions are stabilized by resonance and hence are more stable than simple aryl carbanions. E.g., the stabilizing effect of the various α-substituents follows the order: NO_2 > RCO > COOR > CN > X (halogen).



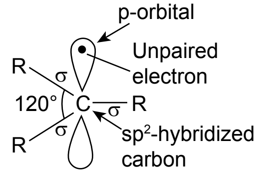
$$R{-}\overset{\bar{\cdot\cdot}}{C}H{-}\underset{\underset{:\ddot{O}:}{\|}}{C}{-}R \longleftrightarrow R{-}CH{=}\underset{\underset{:\ddot{O}:^-}{\|}}{C}{-}R$$

- The stability of the carbanion increases as the per cent s-character of carbon holding the negative charge increases.

$$\underset{sp\ (50\%\ s)}{H{-}C{\equiv}\overset{\bar{\cdot\cdot}}{C}} > \underset{sp^2\ (33.3\%\ s)}{CH_2{=}\overset{\bar{\cdot\cdot}}{C}H} > \underset{sp^3\ (25\%\ s)}{CH_3{-}\overset{\bar{\cdot\cdot}}{C}H_2}$$

23.4.3 Free Radicals

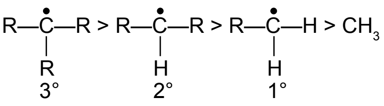
An atom or a group of atoms carrying an odd or unpaired electron is called a free radical. They are paramagnetic due to the presence of an unpaired electron and are formed by homolysis of covalent bonds either by heat or by light. Free radicals like carbocations are planar chemical species. The carbon atom carrying the unpaired electron is sp^2-hybridized. The unhybridized 2p-orbital which is perpendicular to the plane of three σ-bonds contains the unpaired electron.



Orbital structure of free radicals

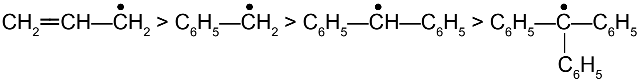
Stability of free radicals:

(i) The order of stability of free radicals is the same as that of carbocations i.e., this order of stability can be easily explained on the basis of hyperconjugation effect of the alkyl groups.



$$\underset{3^\circ}{R{-}\underset{R}{\overset{\bullet}{C}}{-}R} > \underset{2^\circ}{R{-}\underset{H}{\overset{\bullet}{C}}{-}R} > \underset{1^\circ}{R{-}\underset{H}{\overset{\bullet}{C}}{-}H} > CH_3$$

(ii) Allyl and benzyl free radicals are stabilized by resonance and hence are more stable than alkyl free radicals. Further, as the number of phenyl groups attached to the carbon atoms holding the odd electron increases, the stability of the free radicals increases accordingly.



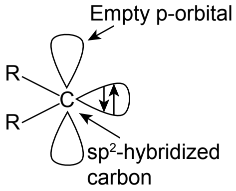
$$CH_2{=}CH{-}\dot{C}H_2 > C_6H_5{-}\dot{C}H_2 > C_6H_5{-}\dot{C}H{-}C_6H_5 > C_6H_5{-}\underset{C_6H_5}{\dot{C}}{-}C_6H_5$$

23.4.4 Carbenes

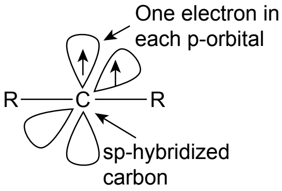
Neutral divalent carbon species in which the carbon is bonded to two monovalent atoms or groups and is surrounded by a sextet of electrons are called carbenes.

E.g., CH_2 (methylene), CCl_2 (dichlorocarbene), etc.

Like in carbocations, the central carbon atom in carbenes has only a sextet of 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 and electrophiles.



Singlet carbene



Triplet carbene

Classification of carbenes:

1. **Singlet carbene**
2. **Triplet carbene**

In **singlet carbenes**, the central carbon atom is sp^2-hybridized and two of the sp^2-hybridized orbitals form two σ-bonds with two monovalent atoms or groups while the third sp^2-hybridized orbital contains two non-bonding electrons. The unhybridized p-orbital is, however, empty. Thus, a singlet carbene has a bent structure. They are also called excited-state carbene because they exist in higher energy state.

In **triplet carbenes**, the central carbon is sp-hybridized and the two sp-hybridized orbitals form two σ -bonds with two monovalent atoms or groups while the two unhybridized p-orbitals have one electron each.Thus, a triplet carbene has a linear structure and behaves as a diradical. They are also called ground state carbene.

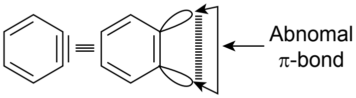
- It may be noted that a triplet carbene is always more stable than a singlet carbene.

Stability: Due to interelectronic repulsions between the two electrons present in the same orbital in a singlet carbene, a triplet carbene is generally more stable than a singlet carbene by about 38–46 kJ mol^{-1}.

- The decreasing order of stability of different types of singlet carbenes is as follows: $\ddot{C}H_2 > \ddot{C}F_2 > \ddot{C}Cl_2 > \ddot{C}Br_2$

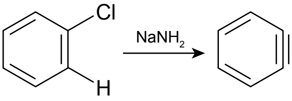
23.4.5 Benzyne

1. 1, 2-didehydrobenzene, C_6H_4, and its derivatives are called benzyne or arynes and the simplest member is benzyne.

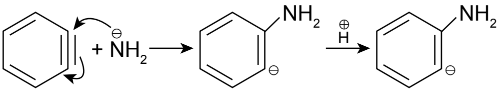


Two sp²-orbitals outisde the ring

2. It is a neutral reaction intermediate derived from benzene ring by removing two substituents, of ortho positions, one in the form of electrophile and other in the form of nucleophile leaving behind two electrons to be distributed between two orbitals.



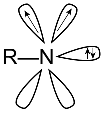
3. Benzyne intermediate is aromatic in character.
4. When halobenzene is heated with sodamide, formation of benzyne takes place.
5. (i) It behaves as a dienophile and gives Diels-Alder reaction with diene.
   (ii) It reacts with strong nucleophile like NH_2.



23.4.6 Nitrenes ($R-\ddot{N}$)

1. The nitrogen analogue of carbenes are called nitrenes.
2. There is a possibility of two spin states for nitrenes depending on whether the two non-bonding electrons (the normal nitrogen lone pair remains paired) have their spins paired or parallel.

$R-\underset{\cdot\cdot}{\ddot{N}}$ These two are lone pair of electrons.
↑



Sptriplet nitrene

These two may be paired or unpaired.

3. In general, nitrenes obey Hund's rule and are ground state triplets with two degenerate sp-orbitals containing a single electron each.