03 General Organic Chemistry

General Organic Chemistry :

Reaction : Breaking of old bond and formation of new bond is known as chemical reaction

$$\text{Organic molecule (substrate)} \xrightarrow{\text{Attacking Reagent}} \text{(Intermediate)} \longrightarrow \text{Product (s)}$$

A sequential account of each step, describing details of electron movement, energetics during bond cleavage and bond formation, and the rates of transformation of reactants into products (kinetics) is referred to as reaction mechanism. Reactants are of two types substrate and reagent.

Substrate is that reactant which supplies carbon to the new bond and the other reactant is called reagent. If both reactants supply carbon to the new bond then choice is arbitrary and in that case the molecule on which attention is focused is called substrate.

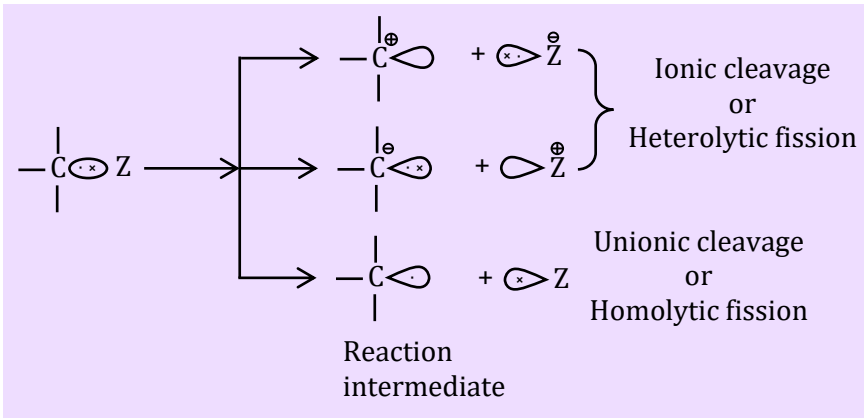
Bond Cleavage :

Type of Bond Cleavage :

(a) Heterolytic cleavage/fission : Cleavage in which unequal distribution of electrons takes place during the bond cleavage is known as heterolytic cleavage. Due to unequal distribution of electrons, ions are formed. That's why it is also known as ionic cleavage or heterolytic cleavage.

(b) Homolytic cleavage/fission : Cleavage in which equal distribution of e⁻s takes place during the chemical reaction is known as homolytic cleavage.

In homolytic cleavage, one of the electrons of the shared pair in a covalent bond goes with each of the bonded atoms. Thus, in homolytic cleavage, the movement of a single electron takes place instead of an electron pair. The single electron movement is shown by 'half-headed' (fish hook: ⇀) curved arrow. Such cleavage results in the formation of neutral species (atom or group) which contains an unpaired electron. These species are called free radicals.



Type of Reagents (Electrophiles and Nucleophiles) :

These are of two types :

(a) Electrophilic reagent or electrophiles :

Electrophilic (electro + philic)
(electron + loving)

A reagent that takes away an electron pair from reactive site is called electrophile (E^+) i.e., electron seeking.

Electrophiles may be positively charged or neutral.

(i) Positively charged electrophiles :

$\overset{\oplus}{H}, \overset{\oplus}{S}O_3H, \overset{\oplus}{N}O, \overset{\oplus}{N}O_2, \overset{\oplus}{X}, \overset{\oplus}{R}, R—\underset{\underset{O}{\|}}{\overset{\oplus}{C}}, C_6H_5—\overset{\oplus}{N}_2$

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

All Lewis acids as :

$BF_3, AlCl_3, SO_3, ZnCl_2, BeCl_2, FeCl_3, SnCl_2, CO_2, SnCl_4$, carbene $(\ddot{C}H_2)$

- Oxygen in H_3O^+ and nitrogen in NH_4^+ are not electrophile due to their complete octet.

(b) Nucleophilic reagent or nucleophiles :

A reagent that brings an electron pair to the reactive site is called a nucleophile (Nu:) i.e., nucleus seeking.

Nucleophiles may be negatively charged ions or possess lone pair of electron or π e^-.

(i) Negatively charged nucleophiles.

$\overset{\ominus}{H}, \overset{\ominus}{O}H, \overset{\ominus}{O}R, \overset{\ominus}{C}N, \overset{\ominus}{X}, \overset{\ominus}{R}, R—C\overset{\ominus}{O}O, \overset{\ominus}{N}H_2, \overset{\ominus}{S}H$

(ii) All Lewis bases which contain lone pairs or πe^-

$H_2\ddot{O}, R—\ddot{O}H, R—\ddot{O}—R, \ddot{N}H_3, R—\ddot{N}H_2, R_3\ddot{N}, CH_2=CH_2, CH\equiv CH$.

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

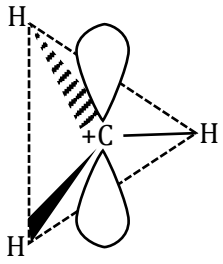
Examples :- $\overset{\ominus}{\ddot{O}}—N=O, \overset{\ominus}{C}\equiv\ddot{N}$

Introduction of Reaction Intermediates :

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 rich site.
- It has incomplete octet because it has six electron in outer most shell.
- All electrons are paired therefore they are diamagnetic.

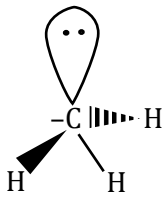
The shape of $\overset{\oplus}{C}H_3$ may be considered as being derived from the overlap of three equivalent $C(sp^2)$ hybridised orbitals with 1s orbital of each of the three hydrogen atoms. Each bond may be represented as $C(sp^2)$–H(1s) sigma bond. The remaining carbon orbital (2p) is perpendicular to the molecular plane and contains no electrons.



Shape of methyl carbocation

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

- It has eight electron in outermost shell so it has complete octet.
  Carbon in carbanion is generally sp^3 hybridised and its geometry is distorted tetrahedron.



geometry of methyl carbanion

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.
- It has incomplete octet so it is also electron deficient species.

BEGINNER'S BOX-1

1. Which of the following species is not electrophilic in nature :-

(1) BH_3 (2) $H_3O^{\oplus}$ (3) $\overset{\oplus}{N}O_2$ (4) $\overset{\oplus}{Cl}$

CGC106

2. CH_3CH_2-Cl undergoes homolytic fission to produce :-

(1) $CH_3\dot{C}H_2$ and $\dot{Cl}$ (2) $CH_3\dot{C}H_2$ and $Cl^{\ominus}$

(3) $CH_3\overset{\oplus}{C}H_2$ and $Cl^{\ominus}$ (4) $CH_3\overset{\ominus}{C}H_2$ and $Cl^{\oplus}$

CGC107

3. Which of the following intermediate has complete octet :-

(1) Carbocation (2) Carbanion (3) Free radical (4) Carbene

CGC108

4. Which of the following is ambident nucleophile?

(1) NH_2OH (2) $NCO^{\ominus}$ (3) $NO_2^{\ominus}$ (4) All of these

CGC109

5. Which of the following is not a nucleophile?

(1) Br^- (2) $\ddot{N}H_3$ (3) SO_3 (4) C_6H_6 (benzene)

CGC110

6. Which of the following species is paramagnetic in nature?

(1) Free radical (2) Carbonium ion (3) Carbanion (4) All the above

CGC111

7. Which of the following contains four pairs of electrons?

(1) Carbocation (2) Carbanion

(3) Carbon free radical (4) None of these

CGC112

Electronic Effects :

There are four effects which affect the chemical reaction due to transfer of electron

(1) Inductive effect (2) Mesomeric effect

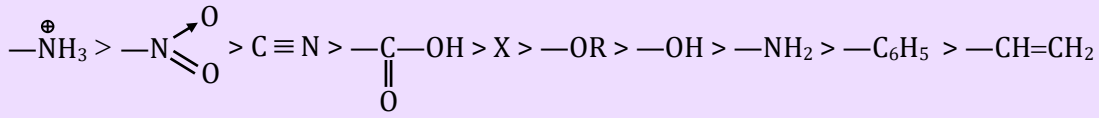
(3) Hyperconjugation effect (4) Electromeric effect

The electron displacements due to the influence of an atom or a substituent group present in the molecule cause permanent polarisation of the bond. Inductive effect and resonance effects are examples of this type of electron displacements. Temporary electron displacement effects are seen in a molecule when a reagent approaches to attack on it. This type of electron displacement is called electromeric effect or polarizability effect. In the following sections we will learn about these types of electronic displacements.

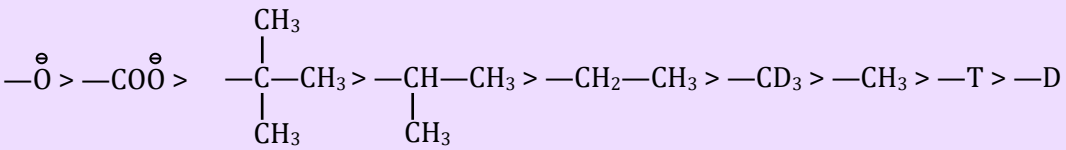
1. Inductive Effect (I-Effect) :

Polarisation of non-polar (C–C) σ-bond caused by the polarisation of adjacent σ-bond is referred to as the inductive effect. This effect is passed on to the subsequent bonds also but the effect decreases rapidly as the number of intervening bonds increases and becomes vanishingly small after three bonds.

–I groups :



+I groups :



Application of I-Effect

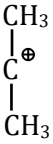
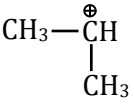
(I) Stability of carbocation :

$$\text{Energy} \propto \text{charge} \propto \frac{1}{\text{stability}}$$

$$\text{Stability of carbocation} \propto \frac{+\text{I effect}}{-\text{I effect}}$$

Illustration 1

Stability order :

(1)  (2)  (3) $CH_3-\overset{\oplus}{C}H_2$ (4) $\overset{\oplus}{C}H_3$

More no. of +I group.

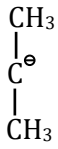
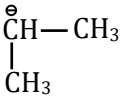
More stable carbocation.

So stability order 1 > 2 > 3 > 4.

(II) Stability of carbanion :

$$\text{Stability of carbanion} \propto \frac{\text{-I effect}}{\text{+I effect}}$$

Illustration 2

(1)  (2)  (3) $CH_3-\overset{\ominus}{C}H_2$ (4) $\overset{\ominus}{C}H_3$

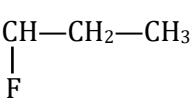
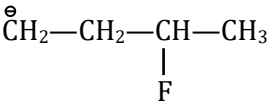
3° 2° 1°

More No. of +I group.

Less stable carbanion.

So, stability order 4 > 3 > 2 > 1

Illustration 3

(1)  (2)  (3) $\overset{\ominus}{C}H_2-CH_2-CH_2-CH_2-F$

Minimum distance of –F.

Maximum –I of –F.

So stability order 1 > 2 > 3

Illustration 4

(1) $\overset{\ominus}{C}H_2-CH_2-F$ (2) $\overset{\ominus}{C}H_2-CH_2-OH$ (3) $\overset{\ominus}{C}H_2-CH_2-NH_2$

Maximum –I of F.

Negative charge will be minimum.

Maximum stable.

So stability order 1 > 2 > 3

BEGINNER'S BOX-2

1. Most stable carbocation is :

(1) $I-CH_2-\overset{\oplus}{C}H_2$ (2) $Br-CH_2-\overset{\oplus}{C}H_2$ (3) $Cl-CH_2-\overset{\oplus}{C}H_2$ (4) $F-CH_2-\overset{\oplus}{C}H_2$

CGC113

2. Most stable carbanion is :

(1) $\overset{\ominus}{C}H_2-CH_2-NO_2$ (2) $\overset{\ominus}{C}H_2-CH_2-CN$

(3) $\overset{\ominus}{C}H_2-CH_2-COOH$ (4) $\overset{\ominus}{C}H_2-CH_2-CH_2-CH_2-F$

CGC114

3. Inductive effect involves

(1) Displacement of σ-electrons (2) Delocalisation of π-electrons

(3) Delocalisation of σ-electrons (4) Displacement of π-electrons

CGC115

4. +I effect is shown by

(1) $-NO_2$ (2) – Cl (3) – Br (4) $-CH_3$

CGC116

5. Maximum –I effect is exerted by the group

(1) C_6H_5- (2) $-OCH_3$ (3) –Cl (4) –CN

CGC117

(III) Acidic Strength :

Acids are substances which can donate $H^{\oplus}$

$HA(aq) \rightleftharpoons H^{\oplus}(aq) + A^{-}(aq)$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$K_a \rightarrow$ Acid dissociation constant.

$[H^+] \uparrow K_a \uparrow pK_a \downarrow pH \downarrow \rightarrow$ Strong acid

$[H^+] \downarrow K_a \downarrow pK_a \uparrow pH \uparrow \rightarrow$ Weak acid

- Acidic strength $\propto$ stability of conjugate base
- Stronger the acid, weaker its conjugate base

  Acid $\xrightarrow{-H^{\oplus}}$ Conjugate base

  $HCl \xrightarrow{-H^{\oplus}} Cl^{\ominus}$
- Acidic Strength $\propto \frac{\text{-I effect}}{\text{+I effect}}$

Illustration 5

(i) $CH_4 \xrightarrow{-H^{\oplus}} \overset{\ominus}{C}H_3$ < $NH_3 \xrightarrow{-H^{\oplus}} \overset{\ominus}{N}H_2$ < $H_2O \xrightarrow{-H^{\oplus}} \overset{\ominus}{O}H$ < $HF \xrightarrow{-H^{\oplus}} \overset{\ominus}{F}$

Negative charge on maximum EN atom
Most stable anion
So corresponding acid is most acidic

(ii) CH_3SH > $CH_3—OH$

$CH_3S^{\ominus}$ (from CH_3SH by $-H^{\oplus}$) ; $CH_3—O^{\ominus}$ (from $CH_3—OH$ by $-H^{\oplus}$)

negative charge on big size atom
more stable anion
so corresponding acid is more acidic

(iii) $CH_2(NO_2)—COOH$ > $CH_2(H)—COOH$ > $CH_2(CH_3)—COOH$

–I of NO_2 **+I of $-CH_3$**
maximum acidic

(iv) $CH_3—CH_2—\underset{F}{CH}—COOH$ > $CH_3—\underset{F}{CH}—CH_2—COOH$ > $CH_2(F)—CH_2—CH_2—COOH$

minimum distance of F from –COOH
maximum –I of F.
So maximum acidic.

(v) $CH{\equiv}CH$ > $CH_3—C{\equiv}CH$ > NH_3 > $CH_3—NH_2$

$CH{\equiv}C^{\ominus}$ (from $CH{\equiv}CH$ by $-H^{\oplus}$) ; $CH_3—C{\equiv}C^{\ominus}$ (from $CH_3—C{\equiv}CH$ by $-H^{\oplus}$) ; $NH_2^{\ominus}$ (from NH_3 by $-H^{\oplus}$) ; $CH_3—NH^{\ominus}$ (from $CH_3—NH_2$ by $-H^{\oplus}$)

negative charge on **+I of $-CH_3$** **+I of $-CH_3$**
more EN atom
and no +I
anion is maximum stable
so corresponding acid is
most acidic

(IV) Basic Strength :

Base – Species which can share lone pair of electron to H^+

Basic Strength $\propto K_b \propto \frac{1}{pK_b} \propto$ Stability of conjugate acid

$\propto$ ability to donate electron

$\propto \frac{1}{EN} \propto \frac{+I \text{ effect}}{-I \text{ effect}}$

$\ddot{N}H_2 \rightarrow$ EWG	$\ddot{N}H_2 \leftarrow$ EDG
Electron density ↓	Electron density ↑
Ability to donate ↓	Ability to donate ↑
Basic strength ↓	Basic strength ↑

Note:

Generally, 1st check EN and then effects.

Illustration 6

(A) $CH_3-CH_2-NH_2$ (B) $CH_3-CH=NH$ (C) $CH_3-C\equiv N$

Solution:

(A) $CH_3—\underset{\uparrow}{CH_2}—NH_2$ (sp^3 nitrogen)

(B) $CH_3—\underset{\uparrow}{CH}=NH$ (sp^2 nitrogen)

(C) $CH_3—C\equiv\underset{\uparrow}{N}$ (sp nitrogen)

$$\text{Basic strength} \propto \frac{1}{\text{electronegativity}}$$

So Basic strength order :- A > B > C

Illustration 7

(A) $CH_3-CH_2-CH_2-NH_2$ (B) $CH_3-CH_2-NH_2$ (C) CH_3-NH_2 (D) CH_3-OH

Solution:

$$\text{Basic strength} \propto \frac{1}{\text{electronegativity}} \propto +I \text{ effect}$$

More number of Alkyl groups ; more +I effect

So Basic strength order:- A > B > C > D

Illustration 8

(A) $H_2C(Cl)—CH_2—NH_2$ (B) $H_2C(NO_2)—CH_2—NH_2$ (C) $H_2C(\overset{\oplus}{N}H_3)—CH_2—NH_2$

Solution:

–I effect order $-\overset{\oplus}{N}H_3 > -NO_2 > -Cl$

$$\text{Basic strength} \propto \frac{+I \text{ effect}}{-I \text{ effect}}$$

So Basic strength order:- A > B > C

Illustration 9

Basic Strength of 1°, 2°, 3° Amines

NH_3 $R—NH_2$ $R—\underset{R}{\underset{|}{N}}—H$ $R—\underset{R}{\underset{|}{N}}—R$

Solution:

(a) In gaseous phase/non-polar solvent

$R—\underset{R}{\underset{|}{N}}—R$ $R—\underset{R}{\underset{|}{N}}—H$ $R—NH_2$ NH_3

($3^o > 2^o > 1^o > NH_3$)

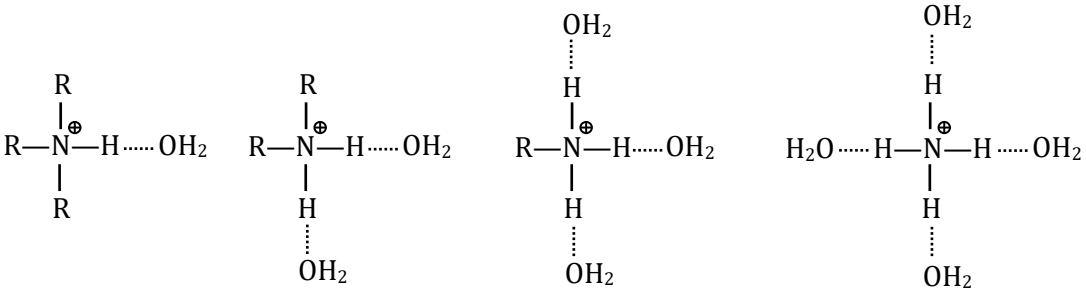
(b) In aqueous phase following factors affect basic strength

(i) Inductive effect ($3° > 2° > 1° > NH_3$)

(ii) Solvation (stability of conjugate acid)

(iii) Steric hindrance

(ii) Solvation (stability of conjugate acid)



- More solvation
- More stable conjugate acid
- More strong base

$NH_3 > 1° > 2° > 3°$

(iii) Steric hindrance

Due to steric hindrance solvation decreases.

Result

$R \rightarrow CH_3$ $(2° > 1° > 3° > NH_3)$

$R \rightarrow C_2H_5$ $(2° > 3° > 1° > NH_3)$

Note:

If nothing mentioned, then consider aqueous phase.

BEGINNER'S BOX-3

1. Which of the following is most acidic :

(1) $Cl_3C—COOH$ (2) $Cl_2CH—COOH$ (3) $ClCH_2—COOH$ (4) CH_3COOH

CGC118

2. Which of the following is most acidic :

(1) $\underset{F}{\overset{|}{C}}H_2—COOH$ (2) $\underset{Cl}{\overset{|}{C}}H_2—COOH$ (3) $\underset{Br}{\overset{|}{C}}H_2—COOH$ (4) $\underset{I}{\overset{|}{C}}H_2—COOH$

CGC119

3. Which is most basic among the following :

(1) $CH_3CH_2–NH_2$ (2) $Cl–CH_2CH_2NH_2$ (3) $O_2N–CH_2CH_2–NH_2$ (4) $CH_3–CH_2CH_2–NH_2$

CGC120

4. Conjugate base of which of the following is maximum stable?

(1) $CH_3—CH_2—OH$ (2) $CH_3—\underset{CH_3}{\overset{|}{C}}H—OH$

(3) $Cl—CH_2—CH_2—OH$ (4) $CH_3—CH_2—CH_2—OH$

CGC121

5. Which is more basic than $CH_3—\overset{\ominus}{N}H$

(1) $CH_3—\overset{\ominus}{C}H_2$ (2) $CH_3—\overset{\ominus}{O}$ (3) $CH\equiv\overset{\ominus}{C}$ (4) All of these

CGC122

2. Resonance

When all the properties of a molecule / ion cannot be explained by a single structure and to explain its properties, more than one structure is required then the molecule/ion is said to have resonance.

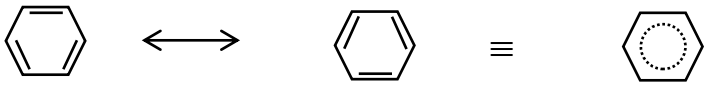
The different structures are called resonating structures/canonical forms.

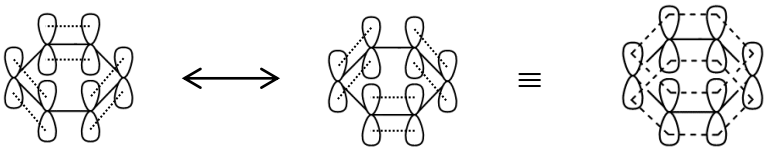
According to Resonance Theory,

When two or more structures are possible for a molecule/ion due to electron transfer, the actual molecule/ion will be a hybrid of all the structures.

Resonating Structures / Canonical forms

Resonance Hybrid

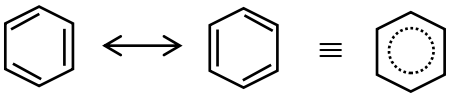




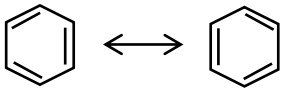
Resonance Hybrid

Note:

1. Resonating structures are completely hypothetical/imaginary.



2. The real structure is known as Resonance Hybrid.
3. The two resonating structures of benzene are equivalent and equivalent resonating structures have equal contribution in resonance hybrid.



4. Resonance involves 'delocalization' of π electrons.
5. In resonance only electrons are transferred.
6. In all the resonating structures number of unpaired electrons are same.
7. All resonating structures should follow Lewis dot structure.

(1) = — = (π - π conjugation)

Ex.

(i) $CH_2 = CH - CH = CH_2 \longleftrightarrow \overset{\oplus}{C}H_2 - CH = CH - \overset{\ominus}{C}H_2 \longleftrightarrow \overset{\ominus}{C}H_2 - CH = CH - \overset{\oplus}{C}H_2$

(a) (b) (a) (b)

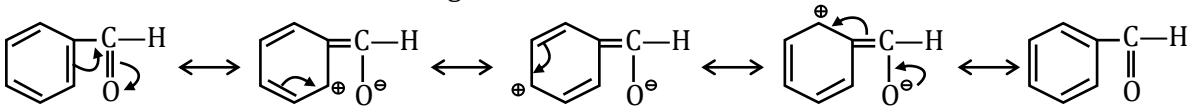
(ii) $CH_2 = CH - C(=O) - H \longleftrightarrow \overset{\oplus}{C}H_2 - CH = C(-O^{\ominus}) - H$

(Acrolein)

Note:

Movement of e^- towards more electronegative atom

Ex.

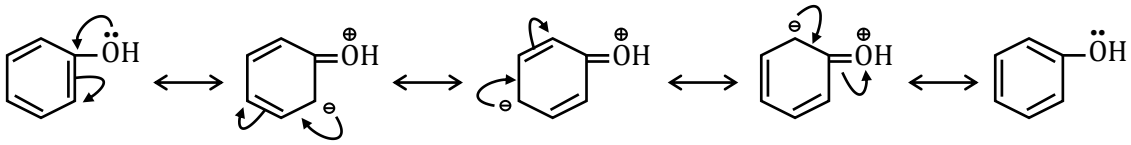


(5-Resonating structures)

(2) = — •• (π - lone pair conjugation)

Ex. $CH_2=CH-\ddot{O}H \longleftrightarrow \overset{\ominus}{C}H_2-CH=\overset{\oplus}{O}H$

Ex.



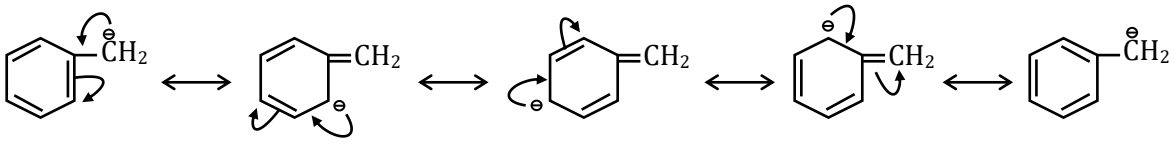
(5-Resonating structures)

(3) = — ⊖ (π - negative conjugation)

Ex. $CH_2=CH-\overset{\ominus}{C}H_2 \longleftrightarrow \overset{\ominus}{C}H_2-CH=CH_2$

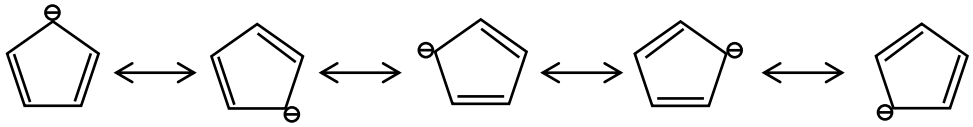
(Allyl carbanion)

Ex.



(5-Resonating structures)

Ex.



(Cyclopentadienyl carbanion)

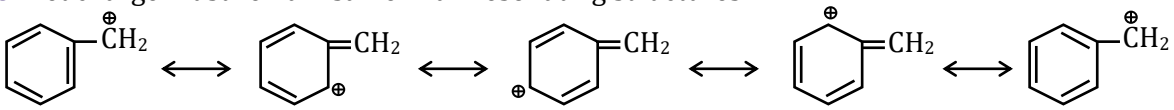
(4) = — ⊕ (π - positive conjugation)

Ex. $CH_2=CH-\overset{\oplus}{C}H_2 \longleftrightarrow \overset{\oplus}{C}H_2-CH=CH_2$

(Allyl carbocation)

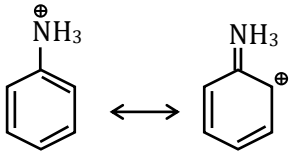
Note: Net charge must remain same in all resonating structures.

Ex.



(5-Resonating structures)

Ex.



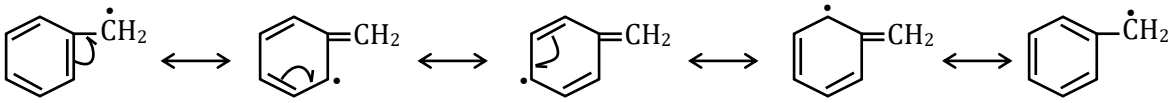
Is not valid resonating structure (nitrogen cannot be pentavalent), hence positive (+ve) charge is localized.

(5) = — • (π - free radical conjugation)

Ex. $CH_2=CH-\dot{C}H_2 \longleftrightarrow \dot{C}H_2-CH=CH_2$

(Allyl carbon free radical)

Ex.



(5-Resonating structures)

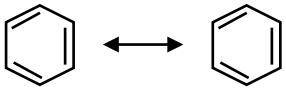
••/⊖ – ⊕/vacant orbital

(6) A——B

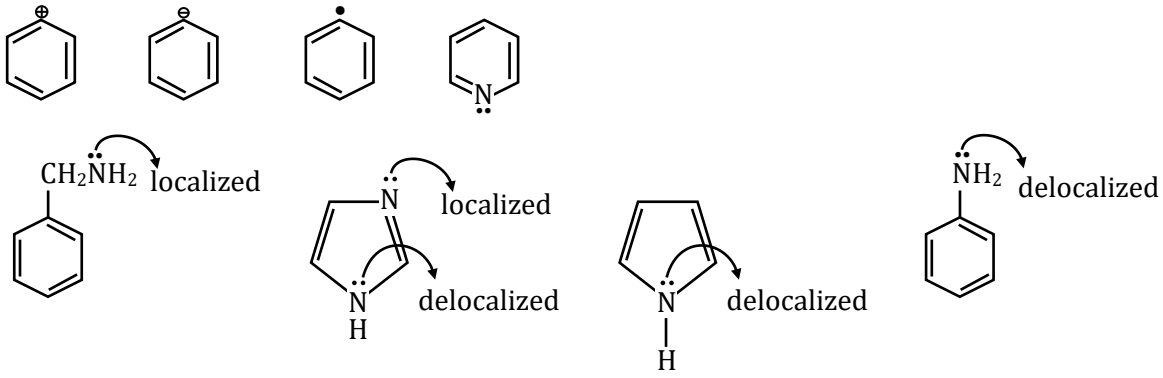
Ex. $\overset{\oplus}{C}H_2-\ddot{O}H \longleftrightarrow CH_2=\overset{\oplus}{O}H$

Note:

1. When conjugated π bonds are enclosed in a ring of alternating double bonds and single bonds we push all the π bonds over by one position to draw its resonating structure with no charge separation.



2. –ve/+ve/free radical/lone pair on double bonded atom in ring, does not take part in resonance. They are said to be localized.



BEGINNER'S BOX-4

1. Mesomeric effect involves

(1) Delocalisation of σ electrons
(2) Partial displacement of σ electrons
(3) Delocalisation of π electrons
(4) Delocalisation of π and σ-electrons

CGC123

2. $\overset{\ominus}{C}H_2-\underset{\underset{O}{\|}}{C}-CH_3$ and $H_2C=\underset{\underset{O^{\ominus}}{|}}{C}-CH_3$ are

(1) Resonating structures
(2) Tautomers
(3) Geometrical isomers
(4) Optical isomers

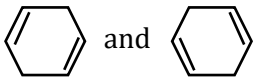
CGC124

3. Which of the following cation is involved in resonance?

(1) $\overset{\oplus}{C}H_2-C\equiv N$
(2) $\overset{\oplus}{C}H_2-CH=O$
(3) $CH_2=CH-\overset{\oplus}{C}H_2$
(4) $CH_2=CH-\overset{\oplus}{N}H_3$

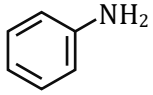
CGC125

4. Which are valid resonating structures?

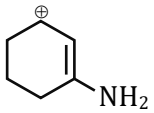
(1) $CH_2=CH-\overset{\oplus}{O}H_2$ and $\overset{\oplus}{C}H_2-CH=OH_2$
(2) $CH_3-\underset{\underset{O}{\|}}{C}-H$ and $CH_2=\underset{\underset{OH}{|}}{C}-H$
(3)  and
(4) $CH_2=N-\ddot{O}H$ and $\overset{\ominus}{C}H_2-N=\overset{\oplus}{O}H$

CGC126

5. Lone pair of nitrogen is localized in

(1) 

(2) 

(3) 

(4) 

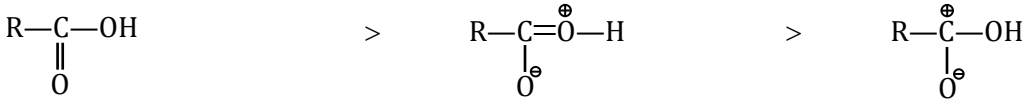
CGC127

Stability of Resonating Structures

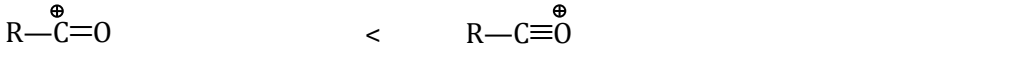
Rules for deciding stability of resonating structures :

1. Resonating structure having octet complete of all atoms is more stable.
2. Non polar resonating structure (uncharged) is more stable than polar resonating structure (charged).
3. If both resonating structures are charged then resonating structure in which negative charge is on more electronegative atom and positive charge on less electronegative atom is more stable.
4. Resonating structures in which unlike charges are at minimum separation or like charges are at maximum separation are more stable.

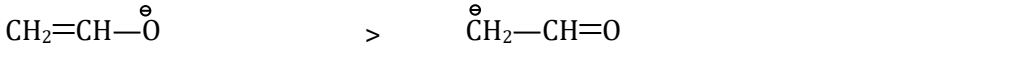
Ex. Arrange the following for stability order.

(i)  > >

complete octet, nonpolar **complete octet, polar** **incomplete octet**

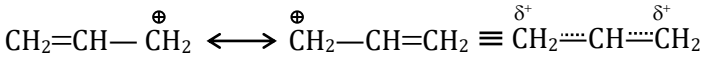
(ii) 

incomplete octet **complete octet**

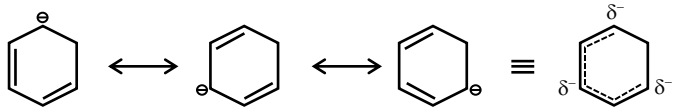
(iii) 

(negative charge on more EN) **(negative charge on less EN)**

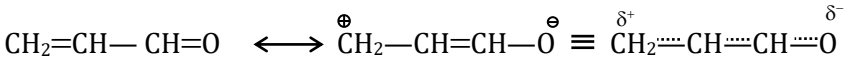
Resonance hybrid:



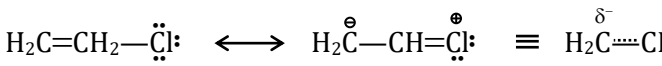
Resonance hybrid



Resonance hybrid



Resonance hybrid



Resonance hybrid

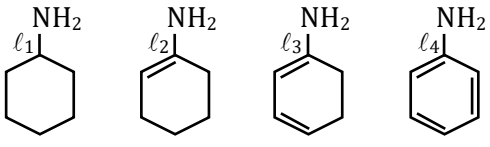
Note:

More stable resonating structure have more contribution to resonance hybrid.

Bond Length Comparison:

1. If a single bond gets more double bond character due to resonance then less will be the bond length.

Illustration 10



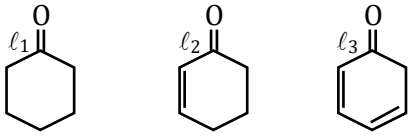
Solution:

In ℓ_4 there is more double bond character so bond length is decreased

Bond length order :- $\ell_1 > \ell_2 > \ell_3 > \ell_4$

2. If a double bond gets more single bond character due to resonance then more will be the bond length.

Illustration 11



Solution:

From left to right, single bond character increases due to more resonance.

Bond length order :- $\ell_3 > \ell_2 > \ell_1$

BEGINNER'S BOX-5

1. Polarisation in acrolein may be written as

(1) $\overset{\delta-}{C}H_2=CH-\overset{\delta+}{C}H=O$ (2) $\overset{\delta-}{C}H_2=CH-CH=\overset{\delta+}{O}$

(3) $\overset{\delta-}{C}H_2=\overset{\delta+}{C}H-CH=O$ (4) $\overset{\delta+}{C}H_2=CH-CH=\overset{\delta-}{O}$

CGC128

2. Which one of the following resonating structure is most stable?

(1) $CH_2=CH—CH=O$ (2) $\overset{\ominus}{C}H_2-\overset{\oplus}{C}H-CH=O$ (3) $CH_2=CH-\overset{\oplus}{C}H-\overset{\ominus}{O}$ (4) $\overset{\oplus}{C}H_2-CH=CH-\overset{\ominus}{O}$

CGC129

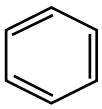
3. Determine bond length order?

$CH_3—CH_2—CH_2\overset{\alpha}{—}NH_2$ $CH_3—CH_2=CH\overset{\beta}{—}NH_2$ $CH_3—CH_2—CH_2\overset{\gamma}{=}NH$

(1) $\alpha > \beta > \gamma$ (2) $\beta > \alpha > \gamma$ (3) $\alpha = \beta = \gamma$ (4) None of these

CGC130

4. Correct order of bond length is

(a) CH_3-CH_3 (b) $CH_2=CH_2$ (c)  (d) $HC \equiv CH$

(1) a > b > c > d (2) a > c > b > d (3) a> c > d > b (4) None of these

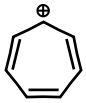
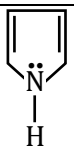
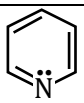
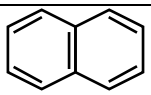
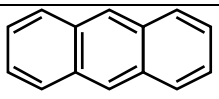
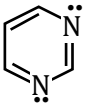
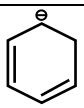
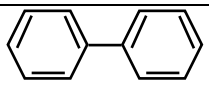
CGC131

Aromaticity :

Aromatic Compound	Anti Aromatic Compound
1. Cyclic	1. Cyclic
2. Planar	2. Planar
3. Completely conjugated.	3. Completely conjugated.
4. It must have $[4n + 2]\pi$ e^- in cycle (Huckle Rule) (where n can be 0,1,2,3,.....) If n = 0 2π electrons n = 1 6π electrons n = 2 10π electrons	4. It must have $[4n]\pi$ e^- in cycle. (where n can be 1,2,3,.....) If n = 1 4π electrons n = 2 8π electrons n = 3 12π electrons

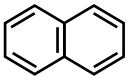
Note:

Non aromatic - cyclic compounds which are neither aromatic nor anti-aromatic.

S.No	Compound	Cyclic	Planar	Cyclic Resonance	Number of πe^-	Type
1.		✓	✓	✓	$2\pi e^-$	Aromatic
2.		✓	✓	✓	$4\pi e^-$	Anti-aromatic
3.		✓	✓	✓	$4\pi e^-$	Anti-aromatic
4.		✓	✓	✓	$6\pi e^-$	Aromatic
5.		✓	✓	✓	$6\pi e^-$	Aromatic
6.		✓	×	×	$4\pi e^-$	Non-aromatic
7.		✓	✓	✓	$6\pi e^-$	Aromatic
8.		✓	✓	✓	$6\pi e^-$	Aromatic
9.		✓	✓	✓	$6\pi e^-$	Aromatic
10.		✓	✓	✓	$6\pi e^-$	Aromatic
11.		✓	✓	✓	$6\pi e^-$	Aromatic
12.		✓	✓	✓	$10\pi e^-$	Aromatic
13.		✓	✓	✓	$14\pi e^-$	Aromatic
14.		✓	✓	✓	$6\pi e^-$	Aromatic
15.		✓	×	×	$6\pi e^-$	Non-aromatic
16		✓	✓	✓	$6\pi e^-$ +$6\pi e^-$	Aromatic

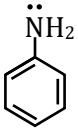
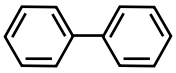
BEGINNER'S BOX-6

1. Which of the following is nonaromatic

(1)  (2)  (3)  (4) 

CGC132

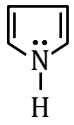
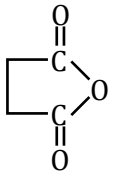
2. Which of the following compounds are aromatic in nature

(a)  (b)  (c)  (d) 

(1) Only a (2) a and b (3) a,b,d (4) All of these

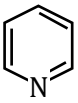
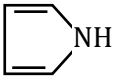
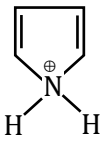
CGC133

3. Which of the following is not aromatic compound

(1)  (2)  (3)  (4) All of these

CGC134

4. Which species is anti aromatic?

(1)  (2)  (3)  (4) 

CGC135

5. Which of the following is not aromatic?

(1) Benzene (2) Cyclopentadienyl anion
(3) Tropylium cation (4) Cyclopentadienyl cation

CGC136

M-effect are of two types :

(1) +M-effect :- Group that donates the electron pair to conjugated system is known as +M group and the phenomenon is known as +M effect.

+M group : Lone pair containing group like

—$\ddot{N}H_2$, —$\ddot{O}H$, —$\ddot{O}R$, —$\ddot{N}R_2$, —$\ddot{S}H$, —$\ddot{N}HR$, —$\ddot{X}$, —$\ddot{N}HCOCH_3$, —$\ddot{O}$—$COCH_3$

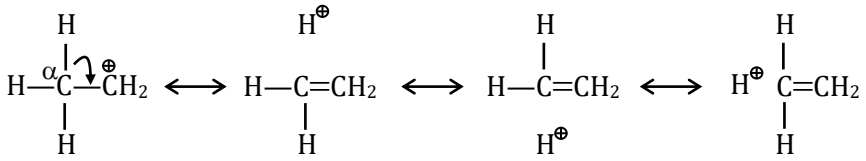
(2) – M-effect :- Group that withdraws the electron pair from conjugated system is known as –M group and the phenomenon is known as –M effect.

–M group : —CHO, —COOH, —COOR, —COR, —NO_2, —CN, —COX, —$CONH_2$, —SO_3H

(3) Hyperconjugation Effect (H-Effect)

Complete transfer of electrons of C–H σ-bond towards positive charge or free radical or π bond is called H-effect. It is also known as no bond resonance/Baker Nathan effect.

(I) Hyperconjugation in carbocation



Conditions:

1. α carbon must be sp^3 hybridized.
2. α H must be present

Note:

Number of hyperconjugative structures ∝ number of α-H.

Illustration 12

Find the stability order of carbocation?

(A) $H_3C-\overset{\oplus}{C}(CH_3)-CH_3$ (B) $H_3C-\overset{\oplus}{C}H-CH_3$ (C) $H_3C-\overset{\oplus}{C}H_2$

Solution:

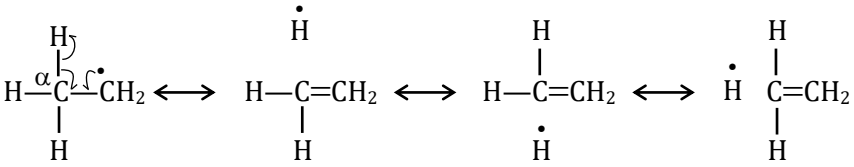
Stability of carbocation ∝ H-Effect ∝ number of α–H

(A) $H_3C-\overset{\oplus}{C}(CH_3)-CH_3$ (B) $H_3C-\overset{\oplus}{C}H-CH_3$ (C) $H_3C-\overset{\oplus}{C}H_2$

9α-H 6α-H 3α-H

Ans. A > B > C

(II) Hyperconjugation in free radical



Conditions:

1. α carbon must be sp^3 hybridized.
2. α–H must be present

Illustration 13

Find the stability order of carbon free radical ?

(A) $H_3C-\overset{\bullet}{C}(CH_3)-CH_3$ (B) $H_3C-\overset{\bullet}{C}H-CH_3$ (C) $H_3C-\overset{\bullet}{C}H_2$

Solution:

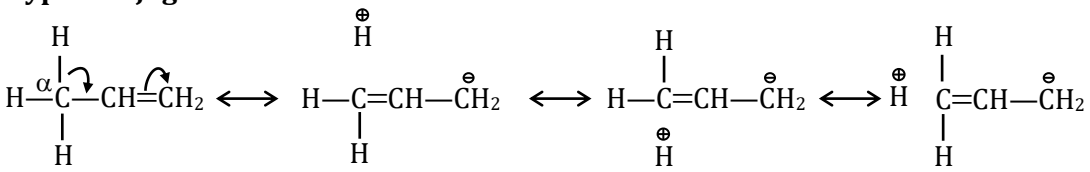
Stability of carbon free radical ∝ H-Effect ∝ number of α–H

(A) $H_3C-\overset{\bullet}{C}(CH_3)-CH_3$ (B) $H_3C-\overset{\bullet}{C}H-CH_3$ (C) $H_3C-\overset{\bullet}{C}H_2$

9α-H 6α-H 3α-H

Ans. A > B > C

(III) Hyperconjugation in alkene



Conditions:

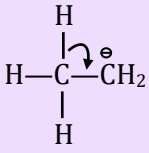
1. α carbon must be sp^3 hybridized.
2. α–H must be present.

Note:

H Effect involves delocalization of both σ and π e^-.

Note:

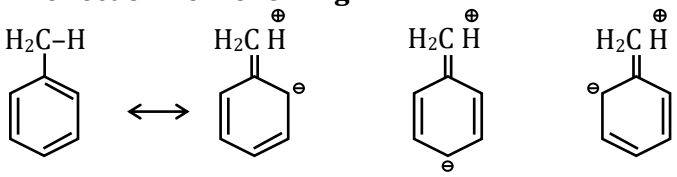
If there is C—H σ bond and negative charge in conjugation then there will be no H-effect.



(No H - effect)

no shifting of C—H σ bond, because anion is having complete octet. ($8e^-$)

(IV) +H effect on Benzene Ring



1. Alkyl groups directly attached to benzene ring increase the electron density in the ring through hyperconjugation.
2. Electron density increases at ortho/para position.

Note:

1. Hyperconjugation is distance independent effect.
2. It is a permanent effect
3. Generally, It is more dominant than inductive effect but less dominant than mesomeric/ resonance effect.
4. Inductive effect order: $-CT_3 > -CD_3 > -CH_3$
   But H-effect order: $-CH_3 > -CD_3 > -CT_3$
   Bond strength: –C–T > –C–D > –C–H

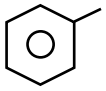
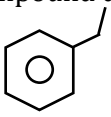
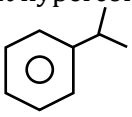
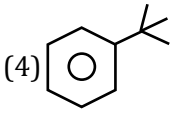
BEGINNER'S BOX-7

1. Which has maximum H-effect?

(1) $CH_3—CH_2—\overset{\oplus}{C}H—CH_3$ (2) $CH_3—\overset{\oplus}{C}H—CH_3$ (3) $Ph—\overset{\oplus}{C}H_2$ (4) $CH_3—\underset{CH_3}{\underset{|}{CH}}—\overset{\oplus}{C}H_2$

CGC137

2. Which of the following compound does not exhibit hyperconjugation?

(1)  (2)  (3)  (4) 

CGC138

3. Hyperconjugation occurs in :-

(1) $CH_3—\overset{\ominus}{C}H_2$ (2) $(CH_3)_3\,C—\dot{C}H_2$ (3) $CH_2=CH_2$ (4) $Ph—\overset{\oplus}{C}H—CH_3$

CGC139

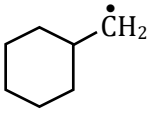
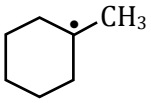
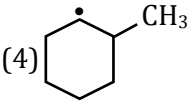
4. Which of the following cation is most stable?

(1) $CH_3—CH_2—\overset{\oplus}{C}H_2$ (2) $CH_3—\overset{\oplus}{C}H—CH_2—CH_3$

(3) $CH_3—\overset{\oplus}{C}H_2$ (4) $CH_3—\overset{\oplus}{C}H—CH_3$

CGC140

5. Which is minimum stable?

(1)  (2)  (3)  (4) 

CGC141

Stability of alkene by H-effect

Stability of alkene $\propto$ H-Effect $\propto$ number of α–H

Illustration 14

Find the stability order of alkene ?

(i) (A) $CH_3—CH=CH—CH_3$ (B) $CH_2=CH—CH_3$ (C) $CH_2=CH_2$

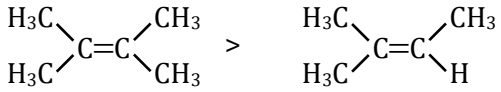
Solution:

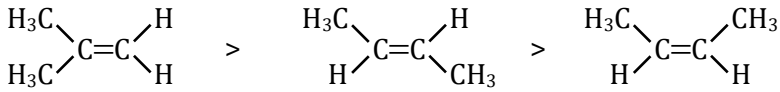
Stability of alkene $\propto$ H-Effect $\propto$ number of α–H

(A) $CH_3—CH=CH—CH_3$ (B) $CH_2=CH—CH_3$ (C) $CH_2=CH_2$

6α-H 3α-H 0α-H

Ans. A > B > C

(ii) 



Isobutylene trans-but-2-ene cis-but-2-ene

BEGINNER'S BOX-8

1. Which of the following alkene is maximum stable (R=CH_3)

(1) $R_2C=CR_2$ (2) $R—CH=CR_2$ (3) $R—CH=CH—R$ (4) $R—CH=CH_2$

CGC142

2. Which of the following is maximum stable?

(1) $CH_2=CH—CH=CH_2$ (2) $CH_2=CH—CH_2—CH=CH_2$

(3) $CH_2=CH_2$ (4) All are equal.

CGC143

3. Correct order of stability is

(1) Isobutene > trans–2–butene > cis–2–butene

(2) trans–2–butene > Isobutene > cis–2–butene

(3) trans–2–butene > cis–2–butene > Isobutene

(4) cis–2 butene > trans–2–butene > Isobutene

CGC144

4. The correct order of increasing stability of the given alkenes is

(1) 1 – pentene > cis –2– pentene > trans – 2–pentene > 2 – methyl – 2 – butene

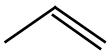
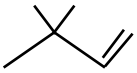
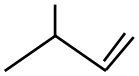
(2) 1 – pentene > trans –2– pentene > cis –2– pentene > 2 – methyl – 2 – butene

(3) 1 – pentene < cis –2– pentene < trans – 2–pentene < 2 – methyl – 2 – butene

(4) 1 – pentene < trans – 2–pentene < cis –2– pentene < 2 – methyl – 2 – butene

CGC145

5. Which of the following alkene is most stable?

(1)  (2)  (3)  (4) $CH_2=CH_2$

CGC146

Heat of Hydrogenation (HOH) :

Amount of heat released during complete hydrogenation of 1 mole of unsaturated hydrocarbon in the presence of a metal catalyst.

$$H_2C=CH_2+H_2 \xrightarrow{Pt/Ni/Pd} H_3C—CH_3 \qquad \Delta H < 0$$

Generally, HOH $\propto$ Number of π bonds $\propto \frac{1}{\text{stability of alkene}}$ (If number of π bonds are same)

Illustration 15

Compare HOH

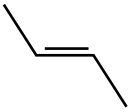
(A)  (B) 

Solution:

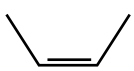
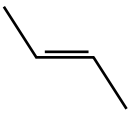
HOH $\propto$ number of π bonds; HOH order: B > A

Illustration 16

Compare HOH

(A)  (B) 

Solution:

(A)  (B) 

More steric repulsion — Less steric repulsion

Stability of alkene:- B > A

$\text{HOH} \propto \frac{1}{\text{Stability of alkene}}$; HOH order :- A > B

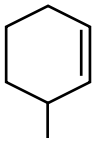
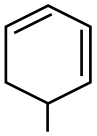
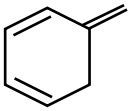
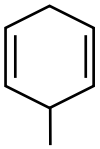
BEGINNER'S BOX-9

1. Which of the following has minimum heat of hydrogenation.
(1) Ethene (2) Propene (3) cis-2-butene (4) trans-2-butene

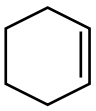
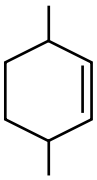
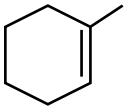
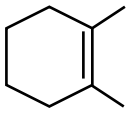
CGC147

2. Which of the following has minimum heat of hydrogenation?
(1) Ethene (2) Propene (3) 1-butene (4) cis-2-butene

CGC148

3. Which compound has maximum heat of hydrogenation?
(1)  (2)  (3)  (4) 

CGC149

4. Which of the following has minimum heat of hydrogenation?
(1)  (2)  (3)  (4) 

CGC150

Applications of Electronic Effects :

Stability of Intermediates

(1) Stability of carbocation :

Stability $\propto +M \propto +H \propto +I$

$$\Rightarrow \propto \frac{1}{-M} \propto \frac{1}{-H} \propto \frac{1}{-I}$$

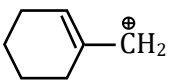
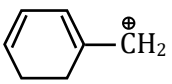
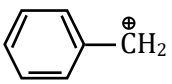
Ex. Give stability order for :-

(i) $CH_2=CH-\overset{\oplus}{C}H_2$ > $CH_3-CH_2-\overset{\oplus}{C}H_2$ > $\overset{\oplus}{C}H_3$

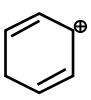
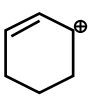
stable by resonance (SBR) **+I of Alkyl group**

(ii) $CH_3-\overset{\oplus}{\underset{\displaystyle CH_3}{C}}-CH=CH_2$ > $CH_3-\overset{\oplus}{C}H-CH=CH_2$ > $\overset{\oplus}{C}H_3-CH=CH_2$

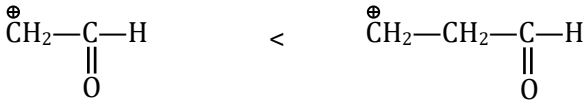
SBR and more α-H **SBR and less α-H** **SBR only**

(iii)  <  < 

maximum resonance

(iv)  >  > 

more resonance **less resonance** **localized ⊕ charge**

(v)  <

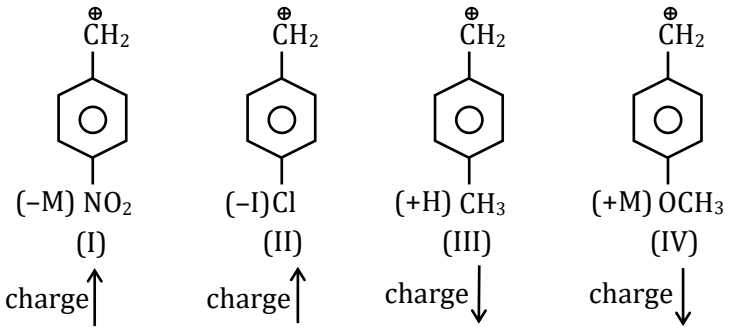
No reso. more –I of —CHO No reso. less –I of —CHO

so less stable

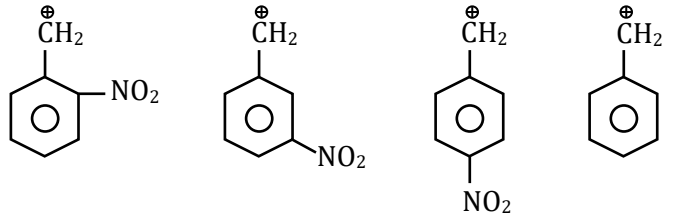
Stability of Benzyl Carbocation

Mesomeric effect is observed at ortho and para position only and $M_{ortho} = M_{para}$

Mesomeric effect at meta position will be zero, only I^- effect is observed at meta position.

(i) 

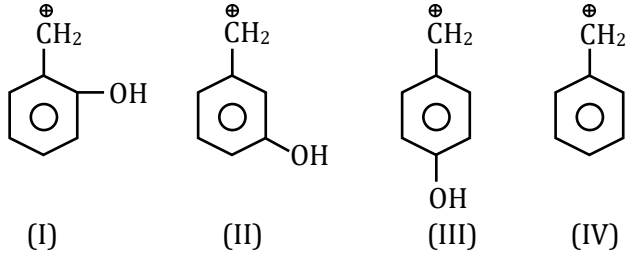
So, stability order IV > III > II > I

(ii) 

$M_o = M_p$ and $M_m = 0$

but $I_o > -I_m > -I_p$, –M and –I increases positive charge.

stability order is IV > II > III > I

(iii) 

–OH group shows +M effect

$+M_O = +M_P$ and $+ M_m=0$ but $-I_O > -I_m > -I_P$ and $+ M >> - I$

So +M stabilize the carbocation by decreasing positive charge

Stability order III > I > IV > II

(iv) $(C_6H_5)_3\overset{\oplus}{C} > (C_6H_5)_2\overset{\oplus}{C}H > C_6H_5\overset{\oplus}{C}H_2 > CH_2{=}CH{-}\overset{\oplus}{C}H_2 > (CH_3)_3\overset{\oplus}{C} > (CH_3)_2\overset{\oplus}{C}H > CH_3{-}\overset{\oplus}{C}H_2 > \overset{\oplus}{C}H_3$

BEGINNER'S BOX-10

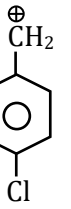
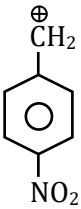
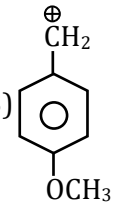
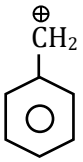
1. Arrange the following intermediate in their stability order ?

(A) $CH_2=CH-\overset{\oplus}{C}H_2$ (B) $CH_2=CH-\overset{\oplus}{C}H-CH=CH_2$ (C) $Ph-\overset{\oplus}{C}H_2$

(1) A > B > C (2) C > B > A (3) B > C > A (4) A > C > B

CGC151

2. Most stable carbocation is?

(1)  (2)  (3)  (4) 

CGC152

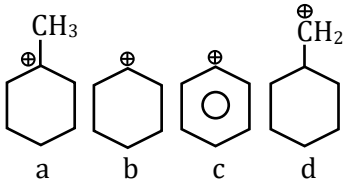
3. Which is incorrect stability order?

(1) $CH_2=CH-\overset{\oplus}{C}H_2 > CH_3-\overset{\oplus}{C}H-CH_3$ (2) $CH_2=\overset{\oplus}{C}H < CH_3-\overset{\oplus}{C}H_2$

(3) $CH_3-CH_2-\overset{\ominus}{C}H_2 > CH_3-\overset{\ominus}{C}H-CH_3$ (4) $CH_3-\overset{\oplus}{C}H_2 > CH_3O-\overset{\oplus}{C}H_2$

CGC153

4. The stability order of following carbocation is



a b c d

(1) a > b > d > c (2) c > a > b > d (3) d > b > c > a (4) b > d > c > a

CGC154

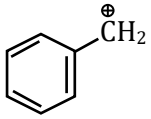
5. Which carbocation is most stable?

(1) $CH_3-CH=CH-\overset{\oplus}{C}H_2$ (2) $CH_3-CH=CH-\overset{\oplus}{C}H-CH_3$

(3) $CH_3-CH=CH-\overset{\oplus}{\underset{\displaystyle CH_3}{\underset{|}{C}}}-CH_3$ (4) All have same stability

CGC155

6. Which is least stable cation?

(1)  (2)  (3)  (4) 

CGC156

(2) Stability of anion :

Generally,

EN / Size > Resonance > Effects (M, H, I)

EN: Negative on more electronegative atom is more stable across the period.

Size: Negative on bigger size is more stable down the group.

Stability $\propto -M \propto -H \propto -I$

$$\propto \frac{1}{+M} \propto \frac{1}{+H} \propto \frac{1}{+I}$$

Ex. Give stability order of :

(i) I. $CH_2=CH-\overset{\ominus}{C}H_2$ II. $\overset{\ominus}{C}H_3$ III. $CH_3-\overset{\ominus}{C}H_2$

SBR

stability order I > II > III

(ii) $(C_6H_5)_3\overset{\ominus}{C} > (C_6H_5)_2\overset{\ominus}{C}H > C_6H_5\overset{\ominus}{C}H_2 > CH_2=CH-\overset{\ominus}{C}H_2 > \overset{\ominus}{C}H_3 > CH_3-\overset{\ominus}{C}H_2 > (CH_3)_2\overset{\ominus}{C}H > (CH_3)_3\overset{\ominus}{C}$

(iii) I.  II.  III. 

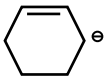
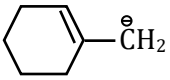
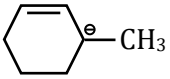
resonance stable **more resonance stable** **localized ⊖ charge**

stability order II > I > III

(iv) I. $\overset{\ominus}{C}H_2-NO_2$ II. $\overset{\ominus}{C}H_2-CH_2-NO_2$ III. $CH_3-\overset{\ominus}{C}H-NO_2$

SBR **no. reso** **SBR but +I of CH_3**

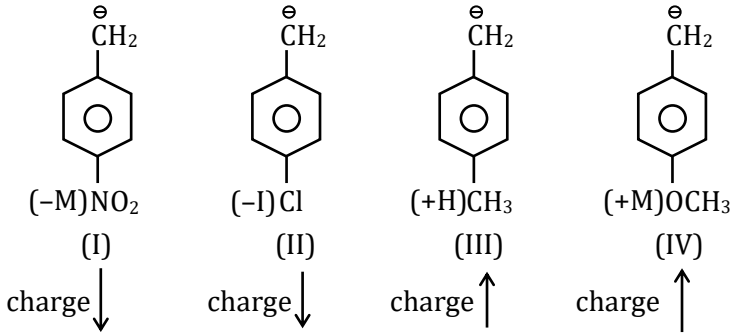
stability order I > III > II

(v) I.  II.  III. 

SBR and +I **SBR** **SBR and more +I**

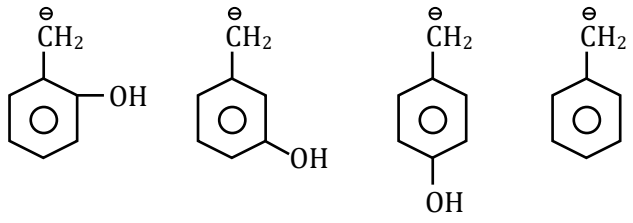
stability order II > I > III

(vi)



stability order I > II > III > IV

(vii)



(I) (II) (III) (IV)

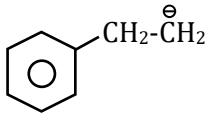
+M M = 0 +M

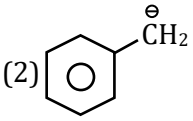
–I more only –I –I less

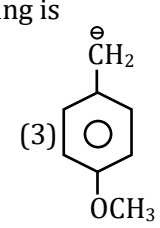
So stability order II > IV > I > III

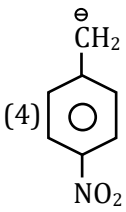
BEGINNER'S BOX-11

1. The least stable carbanion among the following is

(1) 

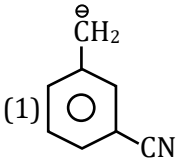
(2) 

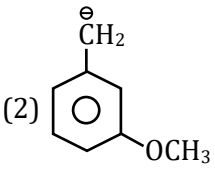
(3) 

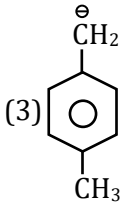
(4) 

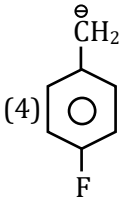
CGC157

2. Which is the least stable anion?

(1) 

(2) 

(3) 

(4) 

CGC158

3. Which is incorrect order of stability?

(1) $CH_3-\underset{\underset{O}{\|}}{C}-\overset{\ominus}{C}H-\underset{\underset{O}{\|}}{C}-CH_3 > \overset{\ominus}{C}H_2-\underset{\underset{O}{\|}}{C}-CH_2-\underset{\underset{O}{\|}}{C}-CH_3$

(2) $CH_3-\underset{\underset{O}{\|}}{C}-\overset{\ominus}{C}H_2 > Ph-\overset{\ominus}{C}H_2$

(3) $Ph-\overset{\ominus}{O} > CH_3-COO^{\ominus}$

(4) $Ph-\overset{\ominus}{C}H_2 > CH_2=CH-\overset{\ominus}{C}H_2$

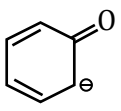
CGC159

4. $Cl-\overset{\ominus}{C}H_2$ is more stable than

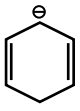
(1) $CH_3-\overset{\ominus}{C}H_2$ (2) $F-\overset{\ominus}{C}H_2$ (3) $CH_3-\overset{\ominus}{C}H-CH_3$ (4) All

CGC160

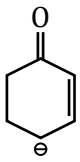
5. Correct stability order of



(I)



(II)

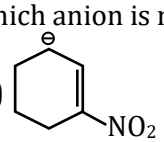


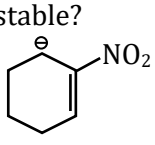
(III)

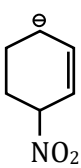
(1) I > II > III (2) I > III > II (3) II > III > II (4) III > I > II

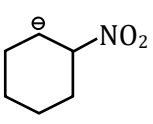
CGC161

6. Which anion is maximum stable?

(1) 

(2) 

(3) 

(4) 

CGC162

(3) Stability of carbon free radical and bond dissociation energy :

Stability of free radical $\propto$ number of α-H

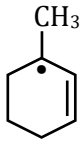
$\propto$ resonance

Ex. Give stability order of

(i) $CH_3-\dot{C}H_2$ **3 α-H** (I) $CH_3-\dot{C}H-CH_3$ **6 α-H** (II) $CH_2=CH-\dot{C}H_2$ **Resonance maximum stable** (III)

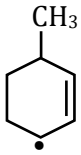
Stability order $\rightarrow$ III > II > I

(ii)



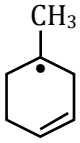
Resonance 3°, more α-H

(I)



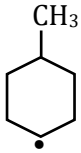
Resonance 2°, less α-H

(II)



No Resonance 3°, more α-H

(III)



No Resonance 2°, less α-H

(IV)

Stability order $\rightarrow$ I > II > III > IV

Bond dissociation energy $\rightarrow$ It is the energy required to break a bond homolytically.

$$\text{B.D.E.} \propto \frac{1}{\text{stability of free radical}}$$

Illustration 17

Compare C–H bond dissociation energy

(A) $H_3C-CH_2 \xrightarrow{E_1} H$ (B) $H_3C-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-\xrightarrow{E_2} H$

Solution:

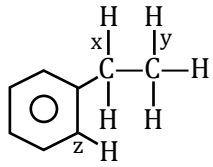
(A) $H_3C-CH_2 \xrightarrow{E_1} H \xrightarrow{-H^{\bullet}} H_3C-\dot{C}H_2$ 3α-H

(B) $H_3C-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}-\xrightarrow{E_2} H \xrightarrow{-H^{\bullet}} H_3C-\underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{\overset{|}{\underset{|}{C}}}}{}^{\bullet}$ 9α-H

Stability order :- B > A

B.D.E. order :- A > B

BEGINNER'S BOX-12

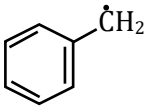
1. 

Correct bond dissociation energy order of C—H bond is

(1) y > x > z (2) z > x > y (3) x > z > y (4) z > y > x

CGC163

2. Which is maximum stable free radical?

(1)  (2)  (3)  (4) 

CGC164

3. Which C—H bond have maximum bond dissociation energy?

(1) $CH_3—CH_2—H$ (2) $CH_2=CH—CH_2—H$ (3) $Ph—CH_2—H$ (4) 

CGC165

4. Correct stability order of

(a) $Ph—\dot{C}H_2$ (b) $CH_2=CH-\dot{C}H-CH_3$ (c) $CH_2=CH—\dot{C}H_2$

(1) a > b > c (2) b > c > a (3) a > c > b (4) b > a > c

CGC166

(4) Acidic strength :

Acids are substances which can donate $H^{\oplus}$.

$HA(aq) \rightleftharpoons H^{\oplus}(aq) + A^{-}(aq)$

$$K_a = \frac{[H^+][A^-]}{[HA]}$$

$K_a \rightarrow$ Acid dissociation constant.

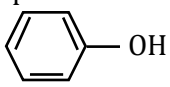
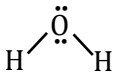
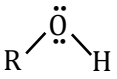
$[H^+] \uparrow k_a \uparrow$ pka $\downarrow$ pH $\downarrow \rightarrow$ Strong acid

$[H^+] \downarrow k_a \downarrow$ pka $\uparrow$ pH $\uparrow \rightarrow$ Weak acid

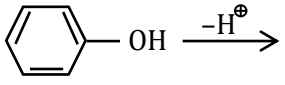
$$\text{Acidic strength} \propto \text{Stability of conjugate base (anion)} \propto \frac{-M,-I}{+M+I}$$

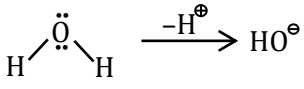
Illustration 18

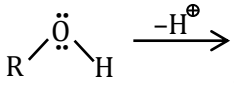
Compare acidic strength

(A)  (B)  (C) 

Solution:

(A)  having resonance

(B) 

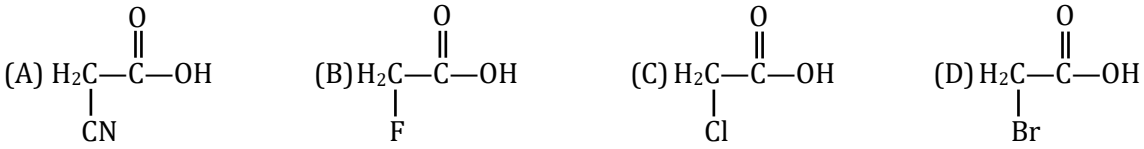
(C) 

+I effect of alkyl group

Acidic strength: A > B > C

Illustration 19

Compare acidic strength



Solution:

–I effect order:- —CN > —F > —Cl > —Br

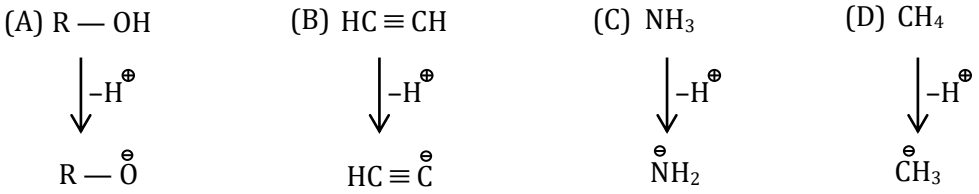
Acidic strength: A > B > C > D

Illustration 20

Compare acidic strength

(A) R — OH (B) $HC \equiv CH$ (C) NH_3 (D) CH_4

Solution:



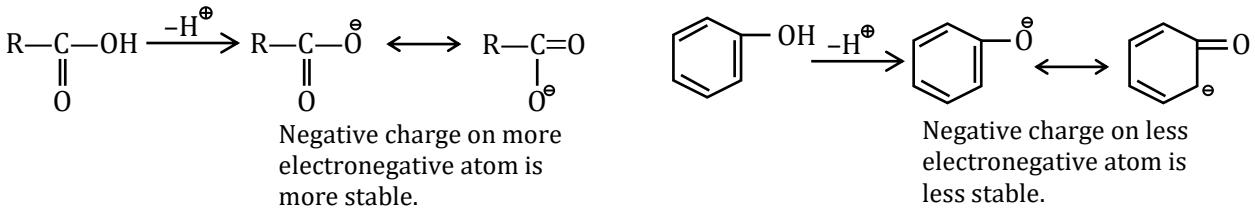
Electronegativity decreases from left to right

Acidic strength: A > B > C > D

Illustration 21

Compare acidic strength

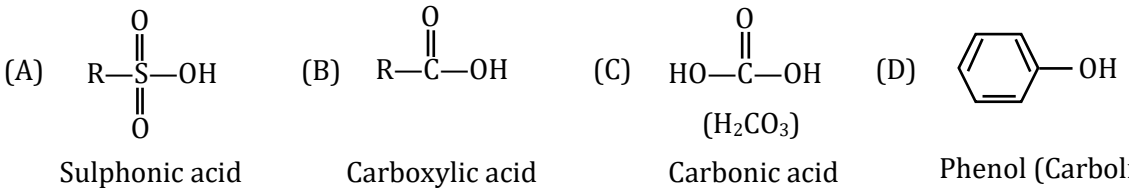
Solution:



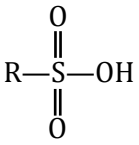
Here, carboxylate ion is more stable than phenoxide ion. So carboxylic acid is more acidic than phenol.

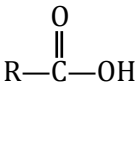
Illustration 22

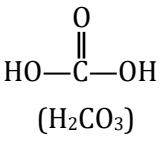
Compare acidic strength

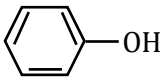


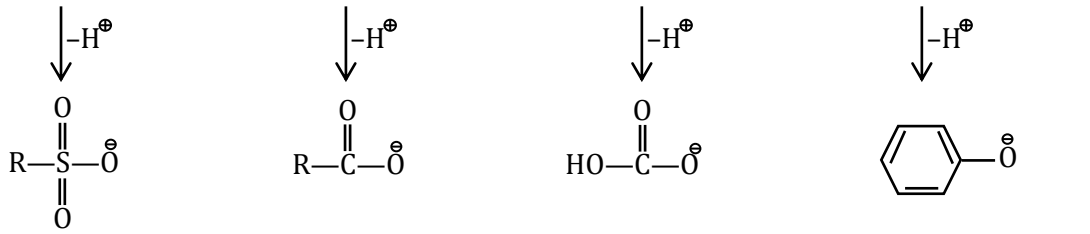
Solution:

(A)  Sulphonic acid

(B)  Carboxylic acid

(C)  (H_2CO_3) Carbonic acid

(D)  Phenol (Carbolic acid)



Sulphonate ion
3 equivalent
resonating structures

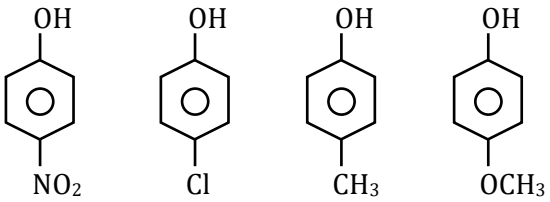
Carboxylate ion
2 equivalent
resonating structures

Bicarbonate ion
(–)ve on two oxygen
and +M of –OH

Phenoxide ion
(–)ve on one oxygen

Acidic Strength :- A > B > C > D

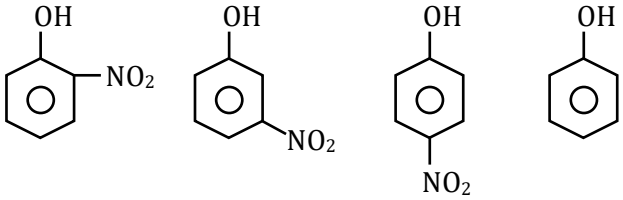
Acidic Strength of Phenol & Substituted Phenol

Ex. 

(I) (II) (III) (IV)

–M –I +H +M

So acidic order is I > II > III > IV

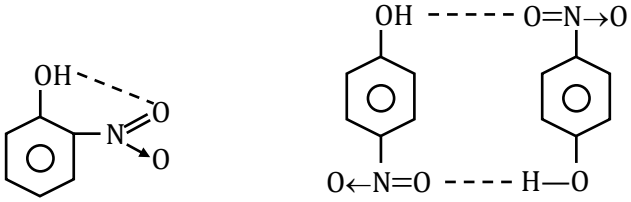
Ex. 

(I) (II) (III) (IV)

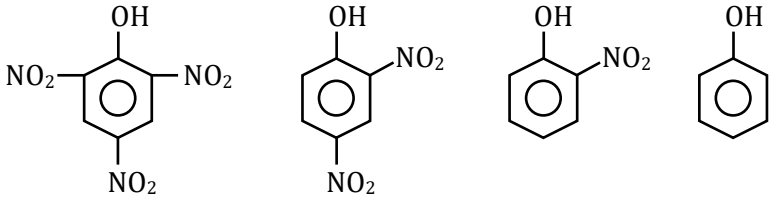
–M and more –I | M = 0 only –I | –M and less –I

Acidic order should be I > III > II > IV but correct order is III > I > II > IV

Reason: Due to intramolecular H-bonding in ortho nitrophenol, it is less acidic than para nitrophenol.



- intramolecular H-bonding — intermolecular H-bonding
- less association — more association
- less B.P. — more B.P.
- more volatile — less volatile
- less soluble in water. — more soluble in water.

Ex. 

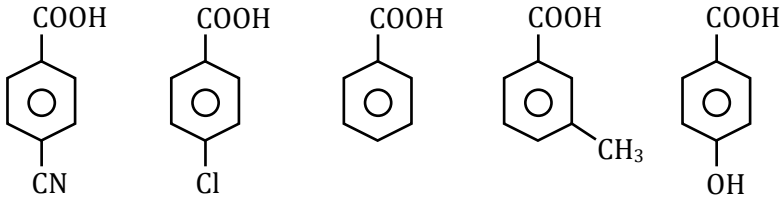
(I) (II) (III) (IV)

maximum –M and

maximum –I effect

so maximum acidic

Acidic order I > II > III > IV

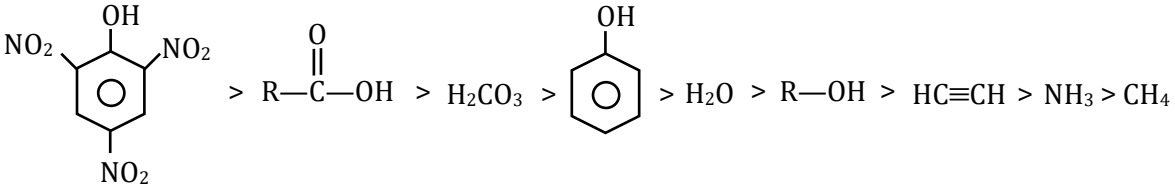
Ex. 

(I) (II) (III) (IV) (V)

–M –I +H +M

acidic order is I > II > III > IV > V

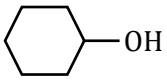
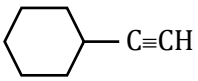
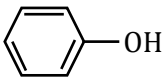
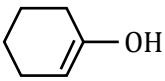
Acidic Strength Order



Picric acid

BEGINNER'S BOX-13

1. Most acidic among the following is

(1)  (2)  (3)  (4) 

CGC167

2. In the following compounds

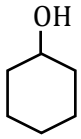
(I) (II) (III) (IV)

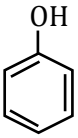
The order of acidity is

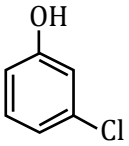
(1) III > IV > I > II (2) I > IV > III > II (3) II > I > III > IV (4) IV > III > I > II

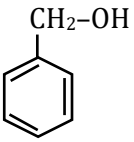
CGC168

3. Most acidic among the following is

(1) 

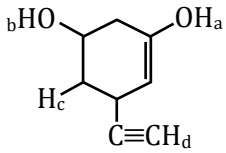
(2) 

(3) 

(4) 

CGC169

4. In a, b, c and d which is most acidic?



(1) a (2) b (3) c (4) d

CGC170

5. Which is incorrect statement?

(1) $CH_3—\underset{\underset{O}{\|}}{C}—CH_2—COOH$ is less acidic than $O_2N—CH_2—COOH$

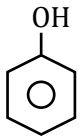
(2) Carboxylic acid is more acidic than carbonic acid (H_2CO_3)

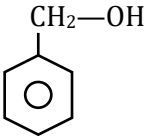
(3) Phenol is more acidic than alcohol

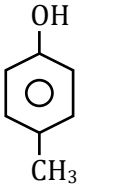
(4) Picric acid is less acidic than acetic acid

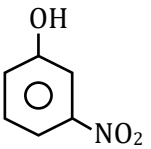
CGC171

6. Which is minimum acidic?

(1) 

(2) 

(3) 

(4) 

CGC172

(5) Basic strength :

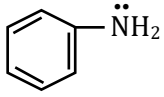
Base – Species which can share lone pair of electron to H^+

Basic Strength $\propto K_b \propto \frac{1}{pK_b} \propto$ Stability of conjugate acid

Basic strength $\propto H^{\oplus}$ accepting tendancy $\propto$ l.p. donating tendancy $\propto \frac{+M,+I}{-M,-I}$

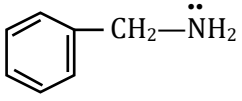
Ex. Give basic strength order :

(i)



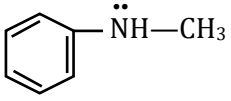
I

Delocalized lone pair (resonance)



II

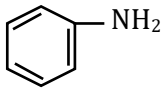
Localized lone pair (no resonance) so maximum basic



III

Delocalized lone pair (resonance) and +I of CH_3

basic strength order — II > III > I

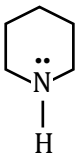
(ii) 

I

delocalized lone pair (resonance)

II

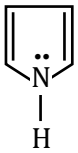
localized lone pair on more EN



III

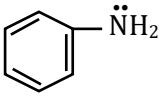
localized lone pair on less EN

Basic strength order — III > II > I

(iii) 

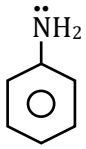
Lone pair is involved in aromaticity so less basic

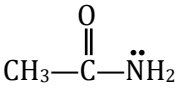
<



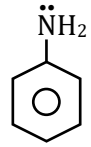
Lone pair is not involved in aromaticity so more basic

Illustration 23

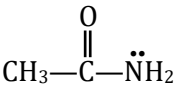
(A) 

(B) 

Solution:

(A) 

After resonance, negative charge comes on carbon

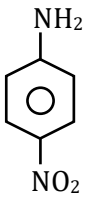
(B) 

After resonance, negative charge comes on oxygen

In (B) lone pair involved in quality resonance; So doesn't accept proton rapidly than (A)

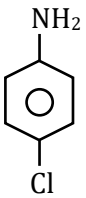
Basic strength order : A > B

Illustration 24



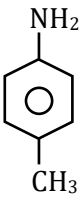
(I)

–M



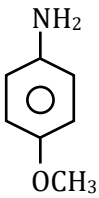
(II)

–I



(III)

+H



(IV)

+M

Solution:

Basic strength order IV > III > II > I

BEGINNER'S BOX-14

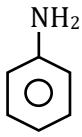
1. Which is least basic?

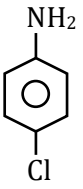
(1) $CH_3—CH_2—NH—CH_3$ (2) $O_2N—CH_2—NH—CH_3$

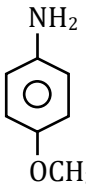
(3) $CH_3—CH_2—NH—CHO$ (4) $Ph—CH_2—NH—CH_3$

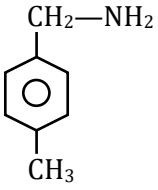
CGC173

2. Which is maximum basic?

(1) 

(2) 

(3) 

(4) 

CGC174

3. Correct order of basic strength is

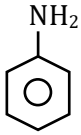
(1) $Ph—\ddot{N}H_2 > Ph—\ddot{N}H—CH_3$ (2) $CH_3—CH_2—\ddot{N}H_2 > CH_3—C\equiv\ddot{N}$

(3) $CH_3—\ddot{O}—CH=CH_2 > CH_3—CH_2—\ddot{O}H$ (4) $CH_3—\underset{\displaystyle CH_3}{\overset{\displaystyle |}{\ddot{N}}}—CH_3 > CH_3—\ddot{N}H—CH_3$

CGC175

4. Which is stronger base than $CH_3—CH_2—NH_2$?

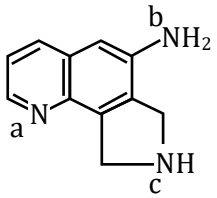
(1) 

(2) 

(3) $CH_2=CH—NH_2$ (4) $CH_3—CH_2—NH—CH_3$

CGC176

5. Correct basic order of a, b and c is?

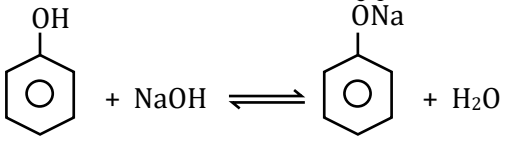


(1) a > b > c (2) c > a > b (3) a > c > b (4) c > b > a

CGC177

Feasibility of Acid-Base Reaction :

An acid-base reaction will be feasible, if it goes from strong acid to weak acid.

(a) 

SA **WA**

$HC\equiv CH + NaOH \rightleftharpoons HC\equiv\overset{\ominus\oplus}{C}Na + H_2O$ (not feasible)

WA **SA**

Note:

Reaction with NaOH is feasible if acidic strength of acid is more than H_2O.

(b) $CH_3COOH + NaHCO_3 \rightleftharpoons H_2CO_3 + CH_3COO^{\ominus}\overset{\oplus}{Na}$

SA WA

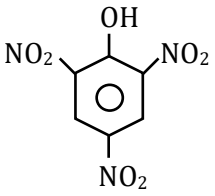
$H_2CO_3 \rightarrow H_2O + CO_2$

Note:

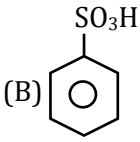
1. Reaction with $NaHCO_3$ is feasible if acidic strength of acid is more than H_2CO_3.
2. 'C' of CO_2 comes from $NaHCO_3$.
3. Acids which are more acidic than H_2CO_3 are soluble in aqueous $NaHCO_3$ due to salt formation.

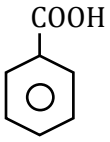
Illustration 25

Which of the following is not soluble in sodium hydrogen carbonate($NaHCO_3$)?

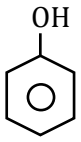
(A) 

Picric acid

(B) 

(C) 

Benzoic acid

(D) 

Phenol

Solution:

Ans. (D)

Because K_a order:- H_2CO_3 > phenol

(c) $HC{\equiv}CH + NaNH_2 \rightleftharpoons NH_3 + HC{\equiv}C^{\ominus}\overset{\oplus}{Na}$

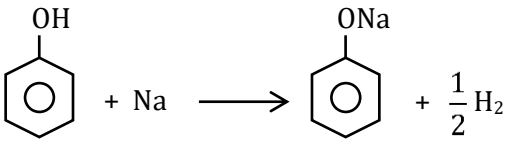
Note:

Reaction with $NaNH_2$ is feasible if acidic strength of acid is more than NH_3.

Note:

Amines and those compounds which are more acidic than amines can produce hydrogen gas on treatment with sodium.

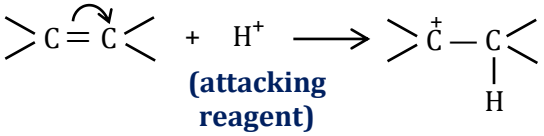
$NH_3 + Na \longrightarrow NaNH_2 + \frac{1}{2}H_2$



Electromeric Effect :

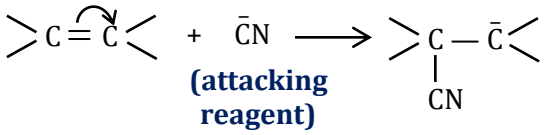
It is a temporary effect. The organic compounds having a multiple bond (a double or triple bond) show this effect in the presence of an attacking reagent only. It is defined as the complete transfer of a shared pair of π-electrons to one of the atoms joined by a multiple bond on the demand of an attacking reagent.

(i) Positive Electromeric Effect (+E effect) :- In this effect the π–electrons of the multiple bond are transferred to that atom to which the reagent gets attached. For example :



(attacking reagent)

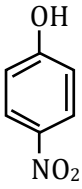
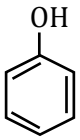
(ii) Negative Electromeric Effect (–E effect) :- In this effect the π–electrons of the multiple bond are transferred to that atom to which the attacking reagent does not get attached. For example:



When inductive and electromeric effects operate in opposite directions, the electomeric effect predominates.

BEGINNER'S BOX-15

1. Which of the following is not soluble in NaOH?

(1) CH_3COOH (2)  (3) CH_3CH_2–OH (4) 

CGC178

2. Which acid base reaction is feasible?

(i) $HC\equiv CH + NaNH_2 \rightarrow HC\equiv \overset{\ominus\oplus}{C}Na + NH_3$ (ii) $HC\equiv CH + NaOH \rightarrow HC\equiv \overset{\ominus\oplus}{C}Na + H_2O$

(1) Only (i) (2) Only (ii) (3) Both (i) & (ii) (4) None of these

CGC179

3. Which of the following will not show electromeric effect?

(1) $CH_2=CH_2$ (2) $CH_3–CH_3$ (3) $HC\equiv CH$ (4) All of these

CGC180

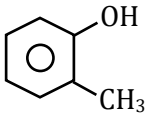
4. Which of the following is an example of +E effect ?

(1) $CH_3—CH=O \xrightarrow{HSO_3^{\ominus}} CH_3—\underset{\displaystyle SO_3H}{\underset{|}{CH}}—\overset{\ominus}{O}$ (2) $CH_3—C\equiv N \xrightarrow{\overset{\ominus}{C}H_3} CH_3—\underset{\displaystyle CH_3}{\underset{|}{C}}=\overset{\ominus}{N}$

(3) $CH_3—CH=CH_2 \xrightarrow{\overset{\oplus}{H}} CH_3—\overset{\oplus}{C}H—CH_3$ (4) None of these

CGC181

5. Which can react with $NaHCO_3$?

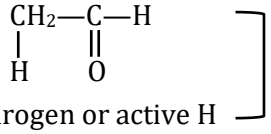
(1) Ph–OH (2) $CH_3–CH_2–OH$ (3) $CH_3–COOH$ (4) 

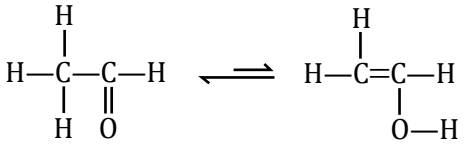
CGC182

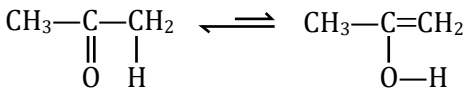
Tautomerism :

Tautomerism or Desmotropism

- Tautomers have same molecular formula but different structural formula due to migration of active hydrogen between two atoms of a molecule.
- Desmotropism means bond turning. [Desmos = Bond; Tropos = Turn]



Ex. 

Ex. 

keto **ene + ol = enol**

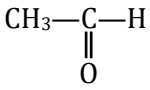
Note :

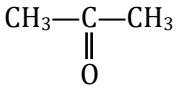
(1) Tautomers exist in dynamic equilibrium.

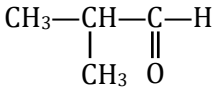
(2) By shifting of H–atom, π bond also changes its position.

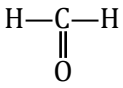
(I) Condition for Tautomerism :

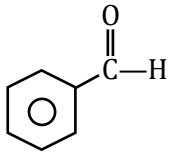
(a) For carbonyl compounds :- Carbonyl compounds having at least one active-H (α–H) show tautomerism

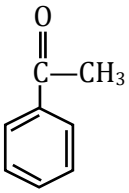
(i)  3 α H, **shows tautomerism.**

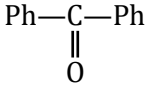
(ii)  6 α H, **shows tautomerism**

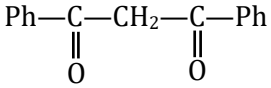
(iii)  1 α H, **shows tautomerism**

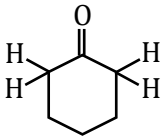
(iv)  No α H, **No tautomerism**

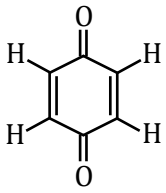
(v)  No α H, **No tautomerism**

(vi)  (Acetophenone) 3 α H, **shows tautomerism (Acetophenone)**

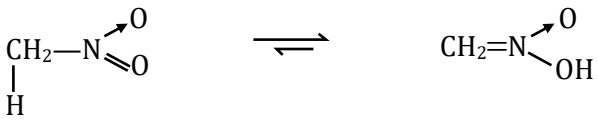
(vii)  Benzophenone) No α H, **No tautomerism (Benzophenone)**

(viii)  2 α H, **shows tautomerism**

(ix)  4 α H, **shows tautomerism**

(x)  α–H, **attached to sp^2 carbon does not participate in tautomerism**

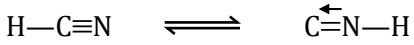
(b) For nitro compounds : Nitro compounds having at least one active-H (α – H) show tautomerism



Nitro form **Acinitro form**

(acidic form so soluble in base)

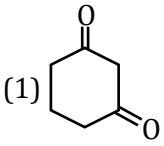
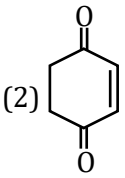
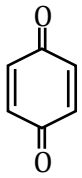
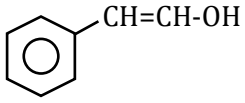
(c) H—C≡N and H—N⇉C are tautomers [also Functional isomers] while R—CN and R—NC are only Functional isomers.



Active H

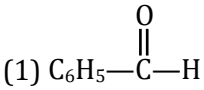
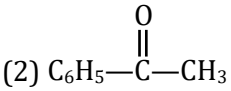
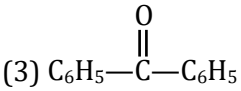
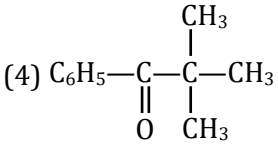
BEGINNER'S BOX-16

1. Which of the following does not show keto enol tautomerism?

(1)  (2)  (3)  (4) 

CGC183

2. Keto-Enol tautomerism is observed in

(1)  (2)  (3)  (4) 

CGC184

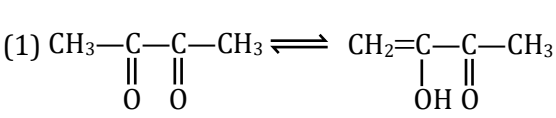
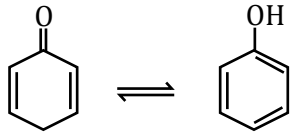
3. Enolic form of acetone contains

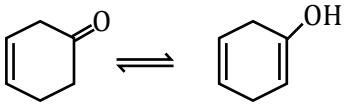
(1) 8σbonds, 1πbond and 2 lone pairs (2) 8σbonds, 2πbond and 2 lone pairs

(3) 10σbonds, 1πbond and 1 lone pair (4) 9σbonds, 1πbond and 2 lone pairs

CGC185

4. Which are keto-enol isomers?

(1)  (2) 

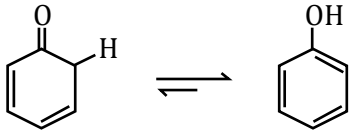
(3)  (4) All of these

CGC186

(II) Enol Content :

1. $CH_2(H)-C(=O)-H \rightleftharpoons CH_2=C(OH)-H$

"keto" (≈ 99%) "enol" (≈ 1%)

2. 

"keto" (<0.1%) "enol" (stable by resonance and aromatic nature) (> 99.9%)

BEGINNER'S BOX-17

1. Which has maximum enol content:

(1) $CH_3-C(=O)-H$

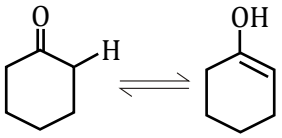
(2) $CH_3-C(=O)-CH_3$

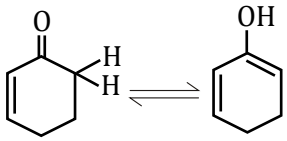
(3) $CH_3-C(=O)-CH_2-C(=O)-OC_2H_5$

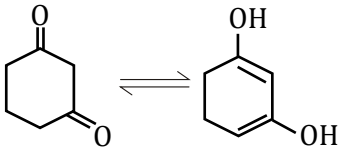
(4) $CH_3-C(=O)-CH_2-C(=O)-CH_3$

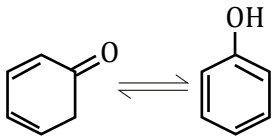
CGC187

2. Which has maximum stable enol form

(1) 

(2) 

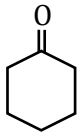
(3) 

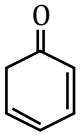
(4) 

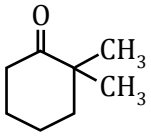
CGC188

3. Highest enol content is in

(1) $CH_3-C(=O)-H$

(2) 

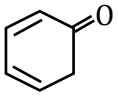
(3) 

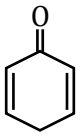
(4) 

CGC189

4. Which of the following has more stable enol form than it's keto form?

(1) $CH_3-C(=O)-CH_2-C(=O)-CH_3$

(2) 

(3) 

(4) All of these

CGC190

BEGINNER'S BOX ANSWERS KEY

BEGINNER'S BOX-1	Que.	1	2	3	4	5	6	7
	Ans.	2	1	2	4	3	1	2

BEGINNER'S BOX-2	Que.	1	2	3	4	5
	Ans.	1	1	1	4	4

BEGINNER'S BOX-3	Que.	1	2	3	4	5
	Ans.	1	1	4	3	1

BEGINNER'S BOX-4	Que.	1	2	3	4	5
	Ans.	3	1	3	4	2

BEGINNER'S BOX-5	Que.	1	2	3	4
	Ans.	4	1	1	2

BEGINNER'S BOX-6	Que.	1	2	3	4	5
	Ans.	4	4	3	2	4

BEGINNER'S BOX-7	Que.	1	2	3	4	5
	Ans.	2	4	4	4	2

BEGINNER'S BOX-8	Que.	1	2	3	4	5
	Ans.	1	1	1	3	1

BEGINNER'S BOX-9	Que.	1	2	3	4
	Ans.	4	4	3	4

BEGINNER'S BOX-10	Que.	1	2	3	4	5	6
	Ans.	2	3	4	1	3	3

BEGINNER'S BOX-11	Que.	1	2	3	4	5	6
	Ans.	1	3	3	4	2	1

BEGINNER'S BOX-12	Que.	1	2	3	4
	Ans.	4	4	1	1

BEGINNER'S BOX-13	Que.	1	2	3	4	5	6
	Ans.	3	4	3	1	4	2

BEGINNER'S BOX-14	Que.	1	2	3	4	5
	Ans.	3	4	2	4	2

BEGINNER'S BOX-15	Que.	1	2	3	4	5	
	Ans.	**3**	**1**	**2**	**3**	**3**	

BEGINNER'S BOX-16	Que.	1	2	3	4	
	Ans.	**3**	**2**	**4**	**4**	

BEGINNER'S BOX-17	Que.	1	2	3	4	
	Ans.	**4**	**4**	**3**	**4**	