GENERAL ORGANIC CHEMISTRY

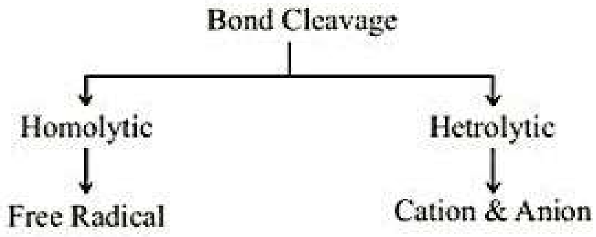
BOND CLEAVAGE

- Organic reaction is a process in which breaking and formation of covalent bonds takes place.
- In organic reaction, the organic compound which is converted into a new compound by breaking and formation of covalent bonds is known as the **reactant or substrate** and the new compound formed is known as the **product**.
- The chemical species (more reactive) which causes the change is called **reagent**.

$CH_3—CH_2—Br + {}^{-}OH \longrightarrow CH_3—CH_2—OH + Br^{-}$

substrate or Reactant — Reagent — Product

Breaking of covalent bond is known as **bond cleavage**. A bond can be broken by two ways :



Homolytic Fission or Homolysis

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

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

Heterolytic Bond Fission or Heterolysis

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

- Thus formation of opposite charged species takes place. In case of organic compounds, if positive charged is present on the carbon then cation is termed as **carbocation**. If negative charge is present on the carbon then anion is termed as **carbanion**.
- The factor which favours heterolysis is a greater difference of electronegativity between A and B.

REACTION INTERMEDIATES

Reaction intermediates are generated by the breaking of covalent bond of the substance. They are short -lived species (half life ≥ 10^{-6} sec.) and are highly reactive. few important types of reaction-intermediates are as follows.

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

Carbocations

An organic species which has a carbon atom bearing six electrons in its outermost shell and has a positive charge is called a carbocation.

Characteristics of Carbocation :

(i) Carbocation have a positive charge on carbon.

(ii) Positively charged carbocation has only 6 electrons in the outermost shell. It has an incomplete octet. So it behaves like a lewis acid.

(iii) Since all electrons are in paired state so carbocations are diamagnetic.

(iv) Carbocations are sp^2 hybridised.

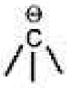
(v) Carbocations are planar with a perpendicular empty p-orbital. Due to planar structure carbocation leads racemization in stereogenic conditions.

(vi) Carbocations are formed in polar solvent.

(vii) It stabilize by presence of electron donating group (EDG)

Carbanions

Anion of carbon is known as carbanion. Carbanion carries three bond pairs and one lone pair, thus making the carbon atom negatively charged thus carbanion may be represented as



Characteristic of Carbanions :

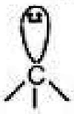
(i) It is formed by heterolytic bond fission.

(ii) There are eight electrons in the outermost orbit of carbanionic carbon hence its octet is complete.

(iii) It behaves as charged nucleophile.

(iv) It is diamagnetic in character because all eight electrons are paired.

(v) Hybridisation and geometry : Alkyl carbanion has three bond pairs and one lone pair. Thus hybridisation is sp^3 and geometry is pryamidal.



Note : Geometry of allyl and benzyl cabanion is almost planar and hybridisation is sp^2.

(vi) It reacts with electrophiles.

(vii) It stabilize by presence of electron withdrawing group (EWG)

Carbon Free Radical

(i) Carbon free radicals are odd electron species in which carbon atom bears the odd electron.

(ii) Homolytic bond fission of a covalent single bond gives rise to free radicals.

(iii) There are seven electrons in the outer most shell of carbon free radicals.

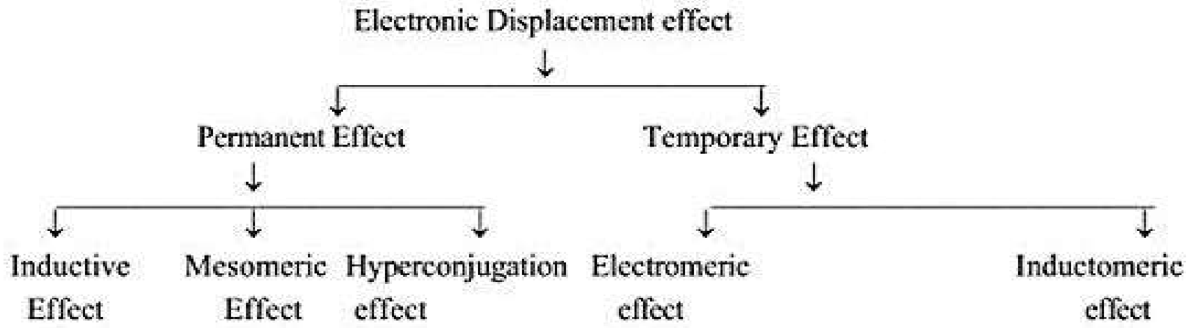
(iv) Owing to the presence of an odd electron; a carbon radical is paramagnetic in nature. Due to this reason free radicals are highly reactive.

(v) Carbon free radicals are normally sp^2 hybridized

(vi) Free radicals are neutral electrophiles.

(vii) It stabilize by presence of electron releasing group (ERG)

ELECTRONIC DISPLACEMENT EFFECTS (EDE)



INDUCTIVE EFFECT (I-EFFECT)

The displacement (shifting) of an electron (shared) pair along the carbon chain due to the diffrence in electronegativity of the groups present along with carbon chain is known as inductive effect.

- ➢ $C \overset{\delta\delta+}{\dashrightarrow} C \overset{\delta+}{\dashrightarrow} C \overset{\delta-}{\dashrightarrow} G$ (G : functional group)

$C \overset{\delta\delta-}{\dashleftarrow} C \overset{\delta-}{\dashleftarrow} C \overset{\delta+}{\dashleftarrow} G$

But the effect is insignificant beyond third carbon atom. (distance dependent effect)

- ➢ This effect is transmitted through the chain of σ bonds and diminishes, with increasing chain length.

Inductive effect is thus

(i) A permanent effect
(ii) The electrons never leave their original atomic orbital.
(iii) Operates through σ bonds
(iv) Polarisation of electrons is always in single direction.
(v) It is generally observed in saturated compounds.
(vi) Its magnitude (i.e., electron withdrawing or donating power) decreases with increase in distance.

On the basis of electron realising group (ERG) or elctron withdrawing group (EWG) inductive effect, can be of two types.

– *I* effect : The group which withdraws electrons is known as – *I* group and its effect is known as – *I* effect.

– I power of various group & cation.

$$-\overset{\oplus}{N}F_3 > -\overset{\oplus}{N}H_3 > -NO_2 > -SO_3H > -CN > -CHO > -\overset{\overset{\displaystyle O}{\|}}{C}-R > -COOH > -COOR >$$

$$-CONH_2 > -F > -Cl > -Br > I > -OH > -OR > -C \equiv CH > -C_6H_5 > -CH = CH_2 > -H$$

– I power of groups in decreasing order with respect to the reference H

+ *I* effect : The group which donates or gives electron is known as + *I* group and effect is known as + *I* effect.

e.g. Alkyl groups, $\overset{\ominus}{O}$, $-\overset{\overset{\displaystyle O}{\|}}{C}-O^-$ are + *I* groups. (Generally negative charged atoms or groups)

(a) **+ *I* power of different type groups and anions :**

$-\overset{-}{C}H_2 > -\overset{-}{N}H > -O^- > -COO^- >$ tertiary alkyl> secondary alkyl > primary-alkyl $> -CH_3 > -H$

+ *I* power in decreasing order with reference to H–atom

(b) **+ *I* power of same type of alkyl groups :**

+ *I* power ∝ number of C's in same type of alkyl group

For example

CH_3-CH_2-

$CH_3-CH_2-CH_2-$

$CH_3-CH_2-CH_2-CH_2-$

+ *I* power in increasing order ↓

APPLICATIONS OF INDUCTIVE EFFECT

(A) **Stability of reaction intermediates**

(i) Stability of carbocation (ii) Stability of free Radical (iii) Stability of carbanion

(i) **Stability of carbocation**

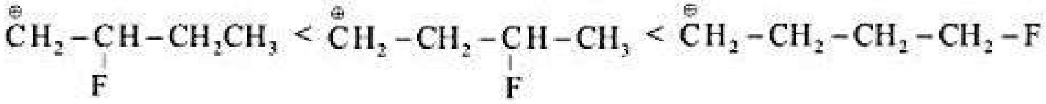
Stability of carbocation ∝ Presence of electron releasing group ∝ +I group ∝ $\frac{1}{-\text{I group}}$.

(a) $\underset{3^\circ}{(CH_3)_3C^+} > \underset{2^\circ}{(CH_3)_2CH^+} > \underset{1^\circ}{CH_3CH_2^+} > CH_3^+$

(b) $\overset{\ominus}{C}H_3 \rightarrow CH_3 > Br \leftarrow CH_2 - \overset{\oplus}{C}H_2 > Cl \leftarrow CH_2 - \overset{\oplus}{C}H_2 > F \leftarrow CH_2 - \overset{\ominus}{C}H_2$

Maximum –I of F

(c)



$\overset{\oplus}{C}H_2-\underset{F}{\underset{|}{C}}H-CH_2CH_3 < \overset{\oplus}{C}H_2-CH_2-\underset{F}{\underset{|}{C}}H-CH_3 < \overset{\ominus}{C}H_2-CH_2-CH_2-CH_2-F$

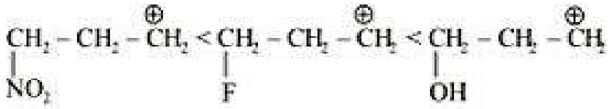
Maximum –I

Minimum distance

Minimum -I

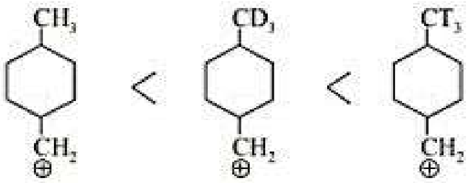
Maximum distance

(d)



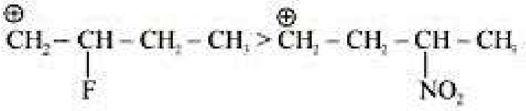
$\underset{NO_2}{\underset{|}{C}H_2}-CH_2-\overset{\oplus}{C}H_2 < \underset{F}{\underset{|}{C}H_2}-CH_2-\overset{\oplus}{C}H_2 < \underset{OH}{\underset{|}{C}H_2}-CH_2-\overset{\oplus}{C}H_2$

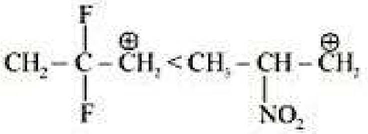
(e)

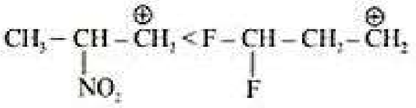


Note-1 : - DNP Rule : - (Distance Number Power Rule)

Example

(a) 
$\overset{\oplus}{C}H_2-\underset{F}{\underset{|}{C}H}-CH_2-CH_3 > \overset{\oplus}{C}H_2-CH_2-\underset{NO_2}{\underset{|}{C}H}-CH_3$ (Distance wins over power)

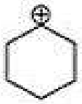
(b) 
$CH_3-\overset{F}{\underset{F}{C}}-\overset{\oplus}{C}H_2 < CH_3-\underset{NO_2}{\underset{|}{C}H}-\overset{\oplus}{C}H_2$ (Number wins over power)

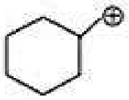
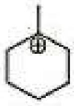
(c) 
$CH_3-\underset{NO_2}{\underset{|}{C}H}-\overset{\oplus}{C}H_2 < F-\underset{F}{\underset{|}{C}H}-CH_2-\overset{\oplus}{C}H_2$ (Distance wins over number)

Note-2

Bredt's Rule : Formation of carbocation, free radical and π-bond at bridge head position is not possible due to angle strain.

Examples :-

(a) (A)  (B) 

(C)  (D) 

Stability order : d > a > c > b

(b) 

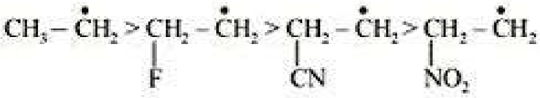
(ii) **Stability of free Radical**

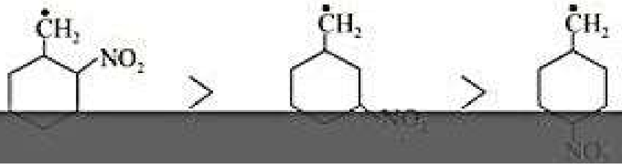
Stability of F.R. ∝ Presence of electron releasing group ∝ +I group ∝ $\frac{1}{-I\text{ group}}$.

Stability of F.R. decrease in the following order

(a) $\underset{3^\circ}{(CH_3)_3C^{\bullet}} > \underset{2^\circ}{(CH_3)_2CH^{\bullet}} > \underset{1^\circ}{CH_3CH_2^{\bullet}} > CH_3^{\bullet}$

(b) $\dot{C}H_2-CH_3 > Br-\dot{C}H_2-CH_2 > Cl-\dot{C}H_2-CH_2 > F-\dot{C}H_2-CH_2$
Maximum –I of F

(c) 
$CH_3-\dot{C}H_2 > \underset{F}{\underset{|}{C}H_2}-\dot{C}H_2 > \underset{CN}{\underset{|}{C}H_2}-\dot{C}H_2 > \underset{NO_2}{\underset{|}{C}H_2}-\dot{C}H_2$

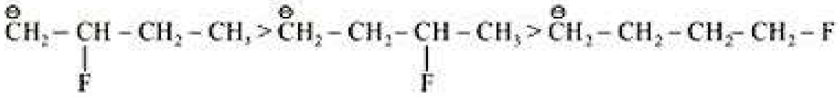
(d) 

(iii) Stability of carbanion

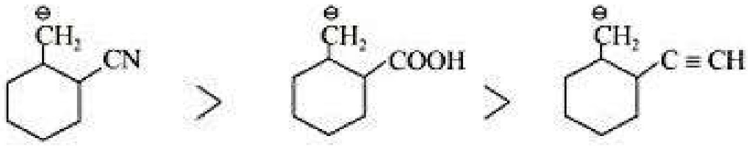
Stability of carbanion $\propto$ Presence of electron withdrowing group $\propto$ –I group $\propto \frac{1}{+\text{I group}}$.

(a) $\underset{3^\circ}{(CH_3)_3C^-} < \underset{2^\circ}{(CH_3)_2CH^-} < \underset{1^\circ}{CH_3CH_2^-} < CH_3^-$

(b) $\overset{\ominus}{C}H_2-CH_2\rightarrow NO_2 > \overset{\ominus}{C}H_2-CH_2\rightarrow F > \overset{\ominus}{C}H_2-CH_2\rightarrow OH > \overset{\ominus}{C}H_2-CH_2\rightarrow NH_2$

(c) 

$\overset{\ominus}{C}H_2-\underset{\underset{F}{|}}{CH}-CH_2-CH_3 > \overset{\ominus}{C}H_2-CH_2-\underset{\underset{F}{|}}{CH}-CH_3 > \overset{\ominus}{C}H_2-CH_2-CH_2-CH_2-F$

(d) 

(e) 

(B) Acidic Strength

Strength of Carboxylic Acid : Acid strength is measured by the position of equilibrium of ionisation in water.

$$HA \rightleftharpoons H^+ + \underset{\text{acid anion}}{A^-}$$

or $\quad K_a = \frac{[H^+][A^-]}{[HA]} \quad$ (K_a = acid ionisation constant)

or, $\quad$ acid strength $\propto [H^+] \propto K_a \propto \frac{1}{pK_a}$

(here $pK_a = -\log K_a$)

or $\quad$ Acid strength $\propto$ concentration of $[H^+]$

or $\quad$ Acid strength $\propto$ stability of acid anion

Thus strength of acid is the function of stability of acid anion.

$\because$ Stability of carbanion $\propto$ Presence of electron withdrowing group $\propto$ –I group $\propto \frac{1}{+\text{I group}}$

$\therefore$ acidic strength $\propto$ Presence of electron withdrowing group $\propto$ –I group $\propto \frac{1}{+\text{I group}}$

The influence of the inductive effect on acidity can be summarised as follows :

Acidic strength of carboxylic acid

(a) $HF < HCl < HBr < HI$

(b) $CH_4 < NH_4 < H_2O < HF$

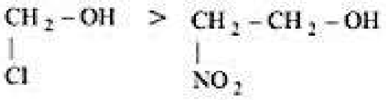
(c) $Cl{-}CH_2{-}COOH < Cl_2CH{-}COOH < CCl_3{-}COOH$

$-I \uparrow$ acid strength $\uparrow$

(d) $H{-}COOH > CH_3-COOH > CH_3-CH_2-COOH > CH_3-CH_2-CH_2-COOH$

$+I$ power of alkyl groups $\uparrow$ Acid strength $\downarrow$

(e)



$\underset{Cl}{CH_2-OH} > \underset{NO_2}{CH_2-CH_2-OH}$

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(f) $(CH_3)_3COH < (CH_3)_2CHOH < CH_3CH_2OH < CH_3OH$

(C) Basic Strength

Basicity of Amines :

Basicity is defined as the tendency to donate an electron pair for sharing. The difference in the base strength in various amines can be explained on the basis of +I - effect.

The groups producing +I effects (alkyl groups) tends to intensify electron density over N in amines thereby producing a base strengthening effect.

Thus, strength of base $\propto$ + I power of group present on $- NH_2 \propto K_b \propto \dfrac{1}{pKb}$

Whereas, a group producing -I effect [$-Cl$, $-NO_2$] tends to decrease electron density over N - atom in amines, thereby producing a base weakening effect.

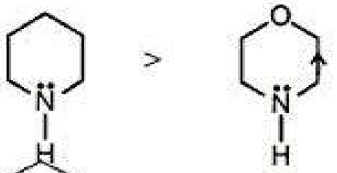
Thus, strength of base $\propto \dfrac{1}{-I \text{ power of group present on } -NH_2} \propto K_b$

Relative base strength of amines :

Examples

(a) $R - NH_2 < R_2NH < R_3N$ (b) $H_2O < NH_3 < NH_2^-$

(c)



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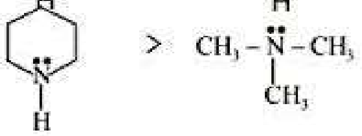
(e)



Order of basic strength in solvent phase

(f) $R = CH_3 \rightarrow R_2NH > RNH_2 > R_3N > NH_3$

(g) $R = C_2H_5 \rightarrow R_2NH > R_3N > RNH_2 > NH_3$

MCQ

Q.1 Homolytic fission of organic compound yields-
(A) Nucleophile (B) Carbanion (C) Free radical (D) Carbocation

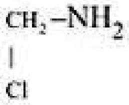
Q.2 The number of electrons present in the valence shell of carbon of $CH_3\overset{+}{C}H_2$ ion bearing +ve charge:
(A) 8 (B) 7 (C) 6 (D) 4

Q.3 Inductive effect refers to -
(A) σ electron displacement along a carbon chain
(B) complete transfer of one of the shared pair of electrons to one of the atoms joined by a double bond
(C) complete transfer of electron with the help of conjugation
(D) none of the above

Q.4 Most acidic hydrogen is present in-
(A) Ethyne (B) Ethene (C) Benzene (D) Ethane

Q.5 The least acidic among the following acids is-
(A) Trichloroacetic acid (B) Dichloroacetic acid
(C) Monochloroacetic acid (D) Acetic acid.

Q.6 Among the following which one is most basic-
(A) NH_3 (B) CH_3NH_2 (C) $CH_3CH_2NH_2$ (D)



$\underset{\displaystyle Cl}{\underset{|}{CH_2}}-NH_2$

Q.7 Which one is the characteristic feature of a free radical :
(A) presence of positive charge (B) presence of unpaired electron
(C) presence of even number of electrons (D) associated with high stability

Q.8 Benzoylperoxide, when heated to about 80°C gives a-
(A) Free radical (B) Carbanion (C) Carbocation (D) None of these

Q.9 Which one is a 1° carbocation of the following:
(A) $CH_3\overset{+}{C}H_2$ (B) $CH_3\overset{+}{C}H—C_2H_5$ (C) $(CH_3)_2\overset{+}{C}H$ (D) $(CH_3)_3\overset{+}{C}$

Q.10 $\overset{\ominus}{C}H_3$ is less stable than

(A) $CH_3-\overset{\ominus}{C}H_2$ (B) $CH_3-\overset{\ominus}{C}H-CH_3$ (C) $\overset{\ominus}{C}H_2-NO_2$ (D) $CH_3-\overset{\ominus}{C}H-C_2H_5$

Q.11 Which of the following groups has the highest +I effect ?
(A) $-CH$ (B) $CH-CH-$ (C) $(CH)CH-$ (D) $(CH)C-$

Q.12 Decreasing order of –I effect of the triad $\left[-NO_2, \overset{\oplus}{N}H_3, -CN\right]$ is

(A) $-\overset{\oplus}{N}H_3 > -NO_2 > -CN$
(B) $-\overset{\oplus}{N}H_3 > -CN > -NO_2$
(C) $-CN > -NO_2 > \overset{\oplus}{N}H_3$
(D) $-NO_2 > -CN > \overset{\oplus}{N}H_3$

Q.13 Maximum –I effect is exerted by the group-
(A) $-C_6H_5$
(B) $-OCH_3$
(C) $-Cl$
(D) $-NO_2$

Q.14 Choose the strong base from each of the following pair
(1) $^-OC_2H_5$, ^-OH (2) $HC \equiv C^-$, CH_3^- (3) Br^-, I^- (4) CH_3^-, NH_2^-

	(1)	(2)	(3)	(4)
(A)	$^-OC_2H_5$,	CH_3^-,	Br^-	CH_3^-
(B)	OH,	CH_3^-,	I^-	NH_2^-
(C)	OH^-,	$HC \equiv C^-$	Br^-	CH_3^-
(D)	OH^-,	CH_3^-,	I^-	NH_2^-

Q.15 Basic nature of H_3O^+, H_2O and OH^- is in order -
(A) $H_3O^+ < H_2O < OH^-$
(B) $H_2O < OH^- < H_3O^-$
(C) $OH^- < H_2O < H_3O^+$
(D) $OH^- = H_3O^+ = H_2O$

Q.16 Which is most stable carbocation

(A) $CH_3CH^+_2$
(B) CH_3^+
(C) $CH_3-\overset{+}{C}H-CH_3$
(D) $CH_3CH_2-\overset{+}{C}H_2$

Q.17 Among the following compounds, the weakest acid is-
(A) $HC{\equiv}CH$
(B) C_6H_6
(C) C_2H_6
(D) CH_3OH

Q.18 Most stable carbanion is

(A) $HC \equiv C^-$
(B) $C_6H_5^-$
(C) $(CH_3)_3C-CH_2^-$
(D) $(CH_3)_2C = CH^-$

Q.19 Which of the following compounds is most acidic ?
(A) CH_3COOH
(B) CH_3CH_2OH
(C) $CH_2ClCOOH$
(D) CCl_3COOH

Q.20 Which is the decreasing order of stability

(a) $CH_3-\overset{+}{C}H-CH_3$ (b) $CH_3-\overset{+}{C}H-O-CH_3$ (c) $CH_3-\overset{+}{C}H-CO-CH_3$

(A) a > c > b
(B) a > b > c
(C) c > b > a
(D) b > a > c

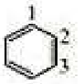
ANSWERS

Q.1	C	Q.2	C	Q.3	A	Q.4	A	Q.5	D	Q.6	C
Q.7	B	Q.8	A	Q.9	A	Q.10	C	Q.11	D	Q.12	A
Q.13	D	Q.14	A	Q.15	A	Q.16	C	Q.17	C	Q.18	A
Q.19	D	Q.20	D								

RESONANCE

Consider structures of benzene :

According to the given structure C_1–C_2 bond length should be smaller then C_2–C_3 bond length but C_1–C_2 and C_2–C_3 bond length must be equal. So this bond length data is not explained by single structure so we need two structures of benzene which is following



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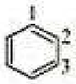


II

I and II are resonating structures of C_6H_6.

When a molecule or ion can not be represented by single lewis dot structure and more than one sturcture are needed to represent all properties of the molecule these structures are known as resonating structure and combined structure of all resonating structure are known as resonance hybrid and this phenomenon is known as resonance.

- Resonating structure have the same arrangement of atomic nuclei but differ in distribution of electrons, (only π electron delocalised)
- Resonating structure are hypothetical and actual structure is a resonance hybrid.
- Resonance generally occurs when there is a conjugation of π-bonds (alternate double - single - double bond arrangement)

Condition for Resonance :

(i) Planarity - Atoms considered in molecules must be sp^2 or sp–hybridised not sp^3 hybridised.

(ii) Conjugation - System in which p-orbitals are arranged parallel and continuous to each other is considered as conjugated system.

(1) Negative charge electron alternate to π electron conjugation
(2) Lone pair electron alternate to π electron conjugation
(3) π electron alternate to π electron conjugation
(4) π electron alternate to vacant orbital (Positive charge) conjugation
(5) π electron alternate to odd electron (free radical) conjugation
(6) Lone pair electron alternate to vacant orbital (Positive charge) conjugation

Conjugate positions of the molecule :

Alternate positions of the molecule having π bond, positive charge, negative charge, odd electron or lone pair of electrons are known as conjugative positions.

$$CH_3 - CH_2 - \underset{1}{CH} = CH - \underset{3}{CH} = CH - \underset{5}{CH} = CH_2$$

1, 3, 5 are alternate positions having π bonds. Hence these positons are known as conjugate positions.

$$\underset{1}{CH_2} = CH - \underset{3}{CH} = CH - \underset{5}{\overset{\oplus}{C}H} - CH_3$$

1, 3 and 5 are conjugate positons.

$$\underset{1}{CH_2} = CH - \underset{3}{CH} = CH - \underset{5}{CH} = CH - \underset{7}{\ddot{N}H_2}$$

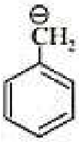
1, 3, 5, 7 are Conjugate positions

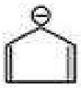
Note : Compound having at least two conjugate positions is known as conjugated compound.

TYPES OF CONJUGATIONS

(1) Negative charge electron alternate to π electron conjugation : If in a conjugated system π bond and Θ charge at alternate position so conjugation is known as negative charge electron alternate to π electron conjugation

$CH_2 = CH - \overset{\ominus}{C}H_2$ $\quad$ $CH_2 = CH - CH = CH - \overset{\ominus}{C}H_2$

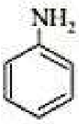


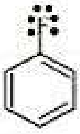


(2) Lone pair electron alteranate to π electron conjugation : If in a conjugated system π bond and lone pair at alternate position so conjugation is known as ℓp electron aternate to π electron conjugation.

$CH_2 = CH - \ddot{N}H_2$ $\quad$ $CH_2 = CH - \ddot{\underset{..}{X}}:$

$$\underset{1}{CH_2} = CH - \underset{3}{CH} = CH - \underset{5}{CH} = CH - \underset{7}{\ddot{N}H_2}$$

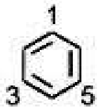


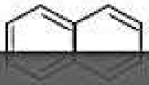


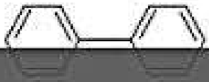
(3) π electron alternate to π electron conjugation : If π bond alternate with π bond so conjugation is known as π electron alternate to π electron conjugation

$$\underset{1}{CH_2} = CH - \underset{3}{CH} = CH_2$$

$$CH_3 - CH_2 - \underset{1}{CH} = CH - \underset{3}{CH} = CH - \underset{5}{CH} = CH_2$$







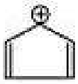
All of the above compounds have π - π conjugation.

(4) **π electron alternate to vacant orbital (Positive charge) conjugation :** If π bond alternate with vacent orbital so conjugation is known as positive charge alternate to π electron conjugation.

$$\underset{1}{CH_2} = CH - \underset{3}{\overset{\oplus}{C}H_2}$$

It has positive charge, π conjugation.

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



These species has two type of conjugation π electron alternate to π electron conjugation and positive charge alterante to π electron conjugation.

(5) **π electron alternate to odd electron (free radical) conjugation :** If π bond and odd e^- are in alternate position.

$$CH_2 = CH - \dot{C}H_2$$

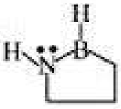
$$CH_2 = CH - CH = CH - \dot{C}H_2$$

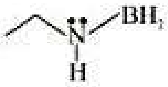
(6) **Lone pair electron alternate to vacant orbital (Positive charge) conjugation :** If lone pair and vacant orbital are alternate position

$$CH_3-\overset{\oplus}{C}H-\ddot{N}H_2 \longleftrightarrow CH_3-CH=\overset{\oplus}{N}H_2$$

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

$CH_3-\overset{\oplus}{C}H-\underset{\cdot\cdot}{\ddot{O}}-CH_3$

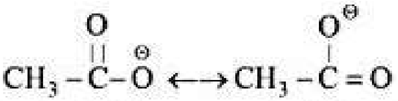




Rules to draw valid resonating structures

1. Electron flow occurs from high electron density to low electron density.
   Negative charge → Lone pair electron → π-bond electron → δ^+ → positive charge

2. Position of atom cannot be change, only the π-electrons are delocalised.

Ex. 

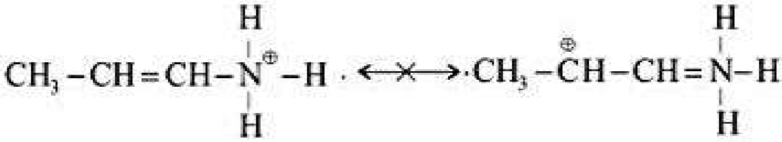
$$\underset{(A)}{CH_3-\overset{\overset{O}{||}}{C}-\overset{\ominus}{O}} \longleftrightarrow \underset{(B)}{CH_3-\overset{\overset{O^{\ominus}}{|}}{C}=O}$$

A & B are Resonance forms.

$$CH_3-\underset{\underset{\displaystyle O}{\|}}{C}-CH_3 \not\longleftrightarrow CH_2=\underset{\underset{\displaystyle OH}{|}}{C}-CH_3$$

Above forms are not resonating forms because position of H is changed.

3. Second period elements should not violate the octet rule while drawing resonating structures



$$CH_3-CH=CH-\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{\overset{\oplus}{N}}}-H \not\longleftrightarrow CH_3-\overset{\oplus}{C}H-CH=\overset{\overset{\displaystyle H}{|}}{\underset{\underset{\displaystyle H}{|}}{N}}-H$$

I II

Above structures are not resonance form because in structure II, nitrogen has 10 valence electrons which violates octet rule.

4. Each Resonating structures must have the same number of unpaired and paired electrons.

$$\underset{\text{I}}{CH_2=CH-\overset{\bullet}{C}H_2} \longleftrightarrow \underset{\text{II}}{\overset{\bullet}{C}H_2-CH=CH_2}$$

I & II are resonating structure because both have 8 paired electrons and 1 unpaired electron

5. Net charge should be conserved in all resonating structures.

$$\underset{\text{Net Charge}=0}{CH_2=CH-CH=CH_2} \longleftrightarrow \underset{\text{Net Charge}=0}{\overset{\oplus}{C}H_2-CH=CH-\overset{\ominus}{C}H_2}$$

Both structures have same net charge so both are resonance forms.

Rules for stability of resonating structures

1. Among various resonating structure non polar resonating structure is more stable than polar resonating structure more number of covalent bonds is considered to be more contributing than others.

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

2. If two resonance structures have same number of bonds then that structure in which octet of every atom is complete is more contributing than structure having incomplete octet.

$$CH_3-\overset{\oplus}{C}H-NH_2 \longleftrightarrow CH_3-CH=\overset{\oplus}{N}H_2$$

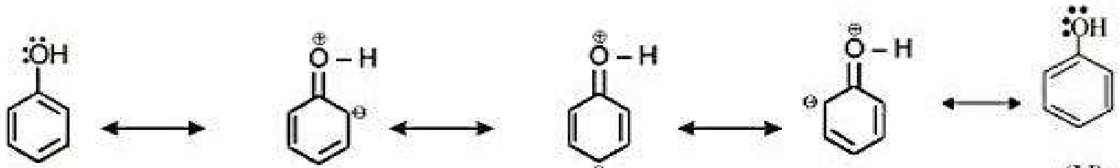
3. If resonating structures have same number of bonds then the neutral structure is more stable than charged structure and if both are charged Resonating structure then less charged resonating structure is more stable.

4. In case of charged resonating structures, the most stable one is that in which the positive and negative charge reside on the most electropositive and most electronegative atoms of the structure respectively.

$$\underset{\text{(A)}}{\overset{\ominus}{C}H_2-CH=O} \longleftrightarrow \underset{\text{(B)}}{CH_2=CH-O^{\ominus}}$$

stability of B > A

5. Resonating structure in which unlike charges are closer is more contributing than that structures in which



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

Hence stability of II and IV will be the same and both will be more stable than III. The order of stability of resonating structures in decreasing order will be as follows :

$$I = V > II \equiv IV > III$$

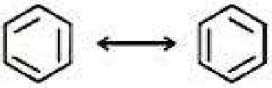
6. Resonating structure in which like charges are farer away is more contributing as compared to structure in which like charges are closer.

RESONANCE ENERGY

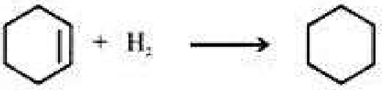
The energy differecnce between most stable resonating structure and resonance hybrid is known as resonance energy.

- It's the experimental value which is calculated by heat of hydrogenation (HOH)
- Higher the value of resonance energy, greater is the resonance stabilization.

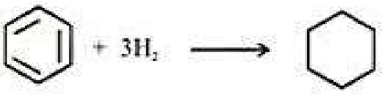
Resonance Energy of Benzene :



The resonance energy of benzene is calculated from the heat of hydrogenation as given below :



+ 29 Kcal.



$+ 3 \times 29$ Kcal. = 87 Kcal. (Theoretical value)

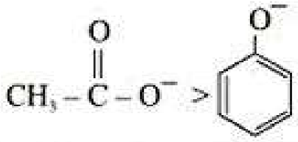
but experimental value for benzene is 51 Kcal. so,

Resonance energy = Calculated value – Experimental value
= 87 – 51
= 36 Kcal.

Resonance energy comparison

1. Consider better resonance or equivalent resonating structures, molecules having equivalent resonating structures must have more resonance energy, than non-equivalent resonating structures.

eg. R.E.

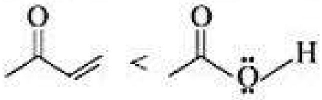


$CH_3-\overset{\overset{O}{\|}}{C}-O^- >$ C$_6$H$_5$O$^-$

2. Aromatic compound have more resonance energy than non-aromatic compound.

3. In case of larger conjugation, more will be the Resonance energy.

4. Resonance energy will be more, when π-bond, lone pair conjugation is present than π, π-conjugation



MCQ

Q.1 Which molecule does not show resonance

(A) CO (B) CO_2 (C) CO_3^{-2} (D) NO_3^-

Q.2 Polarization of electrons in acrolein may be written as -

(A) $\overset{\delta^+}{C}H_2 = CH - CH = \overset{\delta}{O}$

(B) $\overset{\delta^+}{C}H_2 = CH - \overset{\delta^-}{C}H = 0$

(C) $\overset{\delta^-}{C}H_2 = \overset{\delta^+}{C}H - CH = 0$

(D) $\overset{\delta^-}{C}H_2 = CH - CH = \overset{\delta^+}{O}$

Q.3 In pyridine ;  Number of conjugated electrons are -

(A) 6 (B) 8 (C) zero (D) 5

Q.4 In which compound delocalization is not possible -

(A) 2-butene (B) 1, 3-butadiene (C) 1, 3, 5-hexatriene (D) Benzene

Q.5 Consider the following compound :

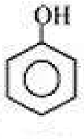
$$\underset{1}{C}H_2 = \underset{2}{C}H - \underset{3}{C}H = \underset{4}{C}H_2$$

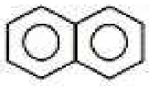
carbon-carbon bond length between C_2 and C_3 will be -

(A) 1.54 Å (B) 1.3 Å

(C) 1.21 Å (D) Less than 1.54 and greater than 1.33 Å

Q.6 Which compound has higher resonance energy in the following pairs

(A) 
(I)


(II)

(B) 
(I)

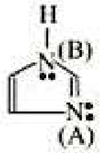

(II)

(C) $CH_2 = CH - F$ (I) $CH_2 = CH - Br$ (II)

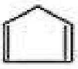
Q.7 Which is less stable canonical structure in the following pairs

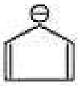
$\overset{\ominus}{C}H_2 - O - CH_3$ (I) $CH_2 = \overset{\oplus}{O} - CH_3$ (II)

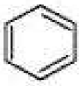
Q.8 Which marked atom's lone pair participate in resonance phenomenon

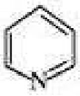


Q.9 Which molecules is not showing resonance

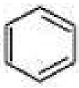
(A) 

(B) 

(C) 

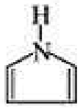
(D) 

Q.10 Which molecules is showing π-electron alternate to π-electron conjugation

(A) 

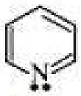
(B) $CH_2=CH-\overset{\oplus}{C}H_2$ (C) $CH_2=CH-\overset{\ominus}{C}H_2$ (D) $CH_2=CH-\overset{\bullet}{C}H_2$

Q.11 Correct order for resonance energy in the following molecules



(I)

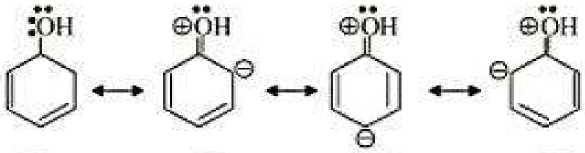
(II)



(III)

(A) III > I > II (B) III = I = II (C) III < I < II (D) III = I > II

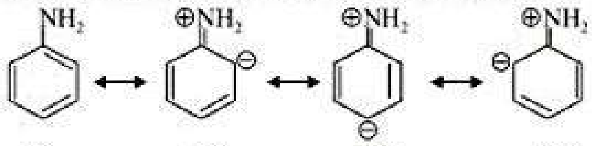
Q.12 In the following canonical structures which is most stable structure



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

(A) I (B) II (C) III (D) IV

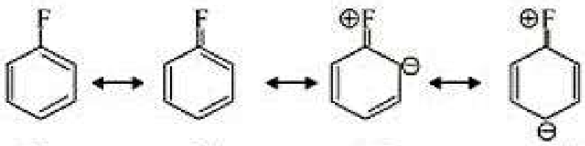
Q.13 In the following canonical structures which is least stable structure



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

(A) I (B) II (C) III (D) IV

Q.14 Which is incorrect canonical structure



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

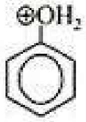
(A) I (B) II (C) III (D) IV

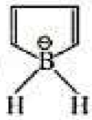
Q.15 In which molecules non-conjugation is present

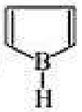
(A) (B) (C) (D)

Q.16 In which molecule resonance phenomenon operates-

(A) 

(B) 

(C) 

(D) 

ANSWERS

Q.1 A **Q.2** A **Q.3** A **Q.4** A **Q.5** D **Q.6** (A) II, (B) II, (C) I
Q.7 (A) II **Q.8** (B) **Q.9** A **Q.10** A **Q.11** A **Q.12** A
Q.13 C **Q.14** B **Q.15** C **Q.16** D

MESOMERIC EFFECT

(a) This is a permanent effect where the displacement of conjugational π electrons are influenced by the group attached to carbon chain.

(b) There is a push or pull of π electrons of the conjugated system of molecule.

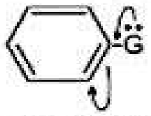
(c) M effect operates only in the conjugated system.

(d) If the conjugation is not available, M effect does not propagate further.

(e) M–effect has no correlation with the electronegativity of the connecting atom of the group

(f) M-effect is two type; +M and –M

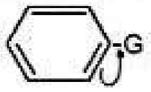
(g) **+M effect (+R) :** If the group pushes the electrons into the π electron system, the effect is said as +M effect and the group is called ERG (electron releasing group) or +M group.

e.g.  or 

+ M Effect is shown by : $-Cl$, $-Br$, $-NH_2$, $-NHR$, $-NR_2$, $-NHCOCH_3$, $-OH$, $-OR$

Condition : Electron pair must be present at first atom of group.

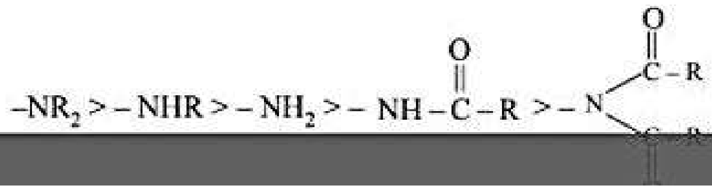
(h) **–M effect (–R) :** If the π electrons are present system is pulled by the group then the effect is called –M effect and the group is called EWG group (electron withdrawing group) or –M group.

e.g.  or 

–M effect is shown by :
$-CHO$, $C = O$, $-COOH$, $-NO_2$, $-CN$, $-SO_3H$, $-SO_2Cl$

Condition : (i) Vacant orbital must be present
(ii) Multiple bond with more electron negative second atom.

+ M – effect – order

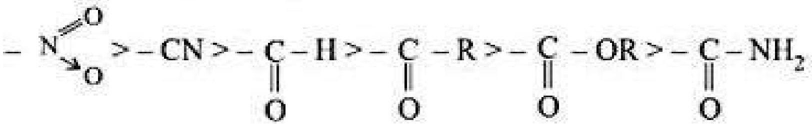
1. $-\bar{C}H_2 > -\bar{N}H > -O^-$
2. $-\bar{N}H > -NH$
3. 

$-NR_2 > -NHR > -NH_2 > -NH-\overset{\overset{O}{\|}}{C}-R > -N\begin{matrix}\diagup \overset{\overset{O}{\|}}{C}-R \\ \diagdown C-R\end{matrix}$

4. $-\mathrm{O}^- > -\mathrm{OR} > -\overset{-}{\mathrm{O}}-\mathrm{CH}=\mathrm{CH}_2$
5. $-\mathrm{NH}_2 > -\mathrm{OH} > -\mathrm{F}$
6. $-\mathrm{F} > -\mathrm{CL} > -\mathrm{Br} > -\mathrm{I}$

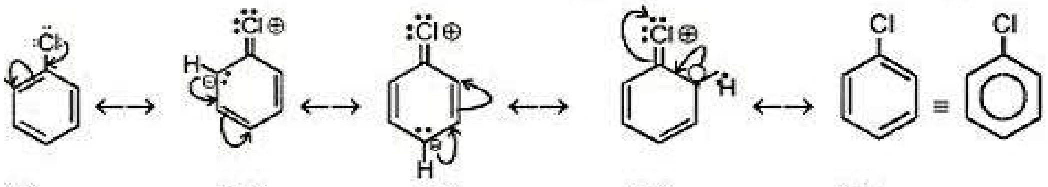
– M – effect order

1. $-\overset{\ominus}{\mathrm{C}}\mathrm{H}_2 > -\mathrm{BH}_2 > -\ddot{\mathrm{P}}\mathrm{H}_2$

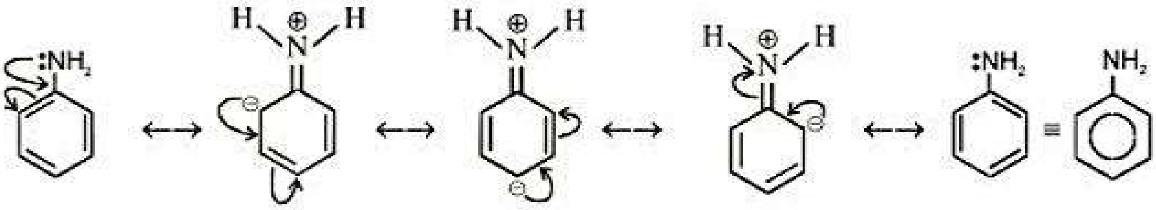
2. 

$-\mathrm{N}\overset{\nearrow \mathrm{O}}{\searrow \mathrm{O}} > -\mathrm{CN} > -\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}-\mathrm{H} > -\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}-\mathrm{R} > -\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}-\mathrm{OR} > -\underset{\mathrm{O}}{\underset{\|}{\mathrm{C}}}-\mathrm{NH}_2$

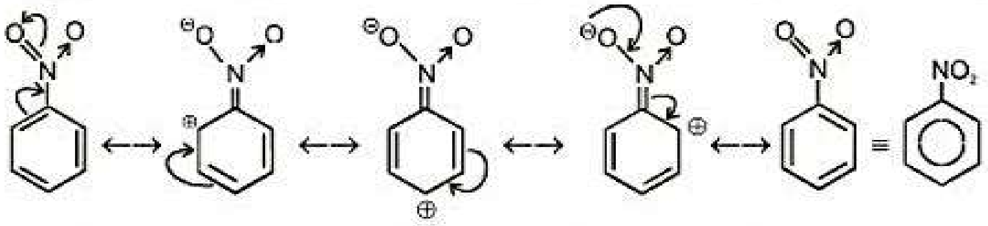
The various resonating structures of chlorobenzene, aniline and nitrobenzene are illustrated in following diagrams. Note that – Cl and – NH_2 show + M effect and – NO_2 show – M effect.



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



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



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

Note :

(i) Thus, mesomeric effect works at only ortho & para position, it is absent on meta position, while inductive effect works at all three position o, m, p however intensity of effect decreases as the distance increases.

(ii) Mesomeric effect always dominates on inductive effect except halogen (CL, Br, I, only).

APPLICATION OF MESOMERIC EFFECT

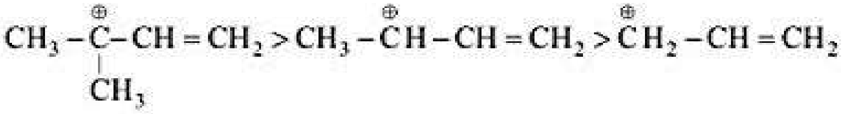
Stability of reaction intermediates

(i) Stability of carbocation

- More resonance in carbocation, more stability of carbocation.

Example: Stability order :

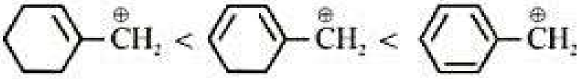
(i)



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

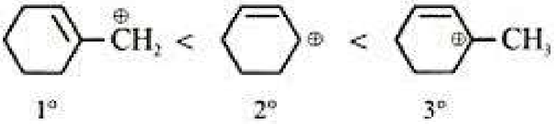
(ii) $CH_2=CH-\overset{\oplus}{C}H_2 > CH_3 \rightarrow CH_2-\overset{\oplus}{C}H_2 > CH_2=CH-CH_2 \leftarrow \overset{\oplus}{C}H_2$

(iii)

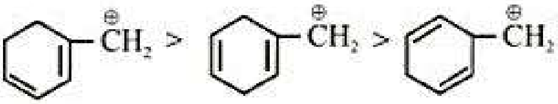


Maximum resonance

(iv)



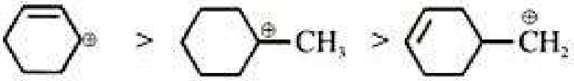
(v)



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

$CH_3-\overset{\oplus}{C}H_2 > \overset{\oplus}{C}H_3 > CH_2=\overset{\oplus}{C}H > CH\equiv\overset{\oplus}{C}$

(vii)

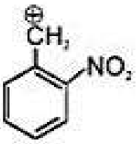


(viii) $CH_2=CH-\overset{\oplus}{C}H_2$ allyl carbocation, Number of resonating Structures = 2

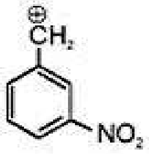
$C_6H_5-\overset{\oplus}{C}H_2$ benzyl carbocation, Number of resonating Structures = 4

Hence the benzyl carbocation is more stable than the allyl carbocation.

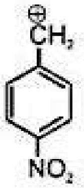
(ix)



(I)
Increase in
positive charge by
–I and – R effect



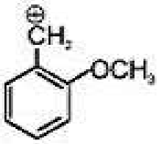
(II)
Increase in
positive charge
only by –I effect



(III)
Increase in
Positive charge by
–I and – R effect

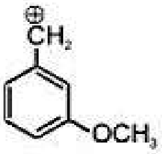
stability order II > III > I

(x)



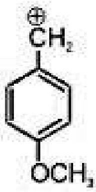
(I)

Stabilised by + R effect
destabilised by –I effect
–I power is maximum
(due to distance)



(II)

destabilised by
–I effect only



(III)

Stabilised by + R effect
destabilised by –I effect
–I power is minimum
(due to distance)

stability order III > I > II

(ii) Stability of carbanion : More resonance in carbanion, more stability of carbanion

Example: stability order for following

(i) $CH_2=CH-\overset{\ominus}{C}H_2,\ CH_2=\overset{\ominus}{C}H,\ CH_3-\overset{\ominus}{C}H_2$

I II III

stability order I > II > III

(ii) $\underset{\text{maximum}(-I)}{\overset{\ominus}{C}H_2-OH} > \overset{\ominus}{C}H_2-CH_2-OH > \underset{\text{Minimum }(-I)\text{ of OH}}{\overset{\ominus}{C}H_2-CH_2-CH_2-OH}$

(iii) $\overset{\ominus}{C}H_2-NO_2\quad \overset{\ominus}{C}H_2-CH_2-NO_2\quad CH_3-\overset{\ominus}{C}H_2-NO_2$

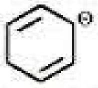
I II III

stability order I > III > II

(iv)

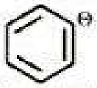
resonance

I



more resonance

II



localized ⊖ charge

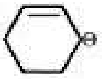
III

stability order II > I > III

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

$\overset{\ominus}{C}H_3 > CH_3-\overset{\ominus}{C}H_2 > (CH_3)_2-\overset{\ominus}{C}H > (CH_3)_3\overset{\ominus}{C}$

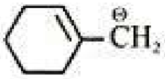
(vi)



2° anion

I

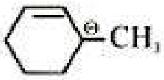
>



1° anion

II

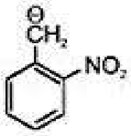
>



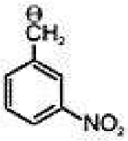
3° anion

III

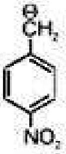
(vii)



I



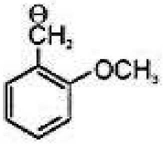
II

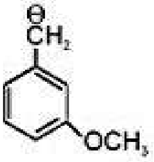


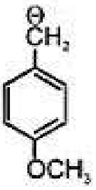
III

stability order I > III > II

(viii)


I


II


III

stability order II > I > III

(iii) Stability of free radicals.

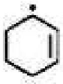
- More resonance, more stability of free radical.

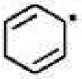
Example: Stability order

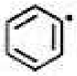
(i) $CH_2=CH-\dot{C}H_2$ (I) less resonance, $CH_2=\dot{C}H$ (II) no resonance, $CH_2=CH-\dot{C}H-CH=CH_2$ (III) more resonance

stability order III > I > II

(ii)


I
resonance


II
more resonance


III
localized

stability order II > I > III

(iii) $(C_6H_5)_3\dot{C} > (C_6H_5)_2\dot{C}H > (C_6H_5)\dot{C}H_2 > CH_2=CH-\dot{C}H_2 > (CH_3)_3\dot{C}$

$> (CH_3)_2\dot{C}H > CH_3\dot{C}H_2 > \dot{C}H_3$

ACIDIC STRENGTH

For an acid $HA_{(aq)} \rightleftharpoons H^+_{(aq)} + A^-_{(aq)}$

from law of mass action, $K_a = \dfrac{[H^+_{(aq)}][A^-_{(aq)}]}{[HA]}$

where , $K_a \rightarrow$ Acidity constant, or dissociation constant of acid

$K_a \rightarrow$ Explain the strength of acid

$pK_a = -\log K_a$, $K_a \propto$ Acidic strength $\propto 1/pK_a$

$pH = -\log[H^+]$

$$\boxed{\text{Acidic strength} \propto \text{stability of conjugate base} \propto -M \text{ effect} \propto \frac{1}{+M} \propto -I \propto \frac{1}{+I}}$$

Acidity of Phenol v/s alcohol

$C_6H_5OH \longrightarrow C_6H_5\overset{\ominus}{O} + \overset{\oplus}{H}$

Phenol stabilized by resonance

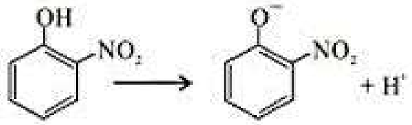
$$\mathrm{R-OH} \xrightarrow{-H^{\oplus}} R-O^{\ominus} + \mathrm{H}^{\oplus}$$

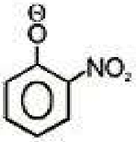
Alcohol no resonance

thus acidic strength of phenol > alcohol

more is the stability of phenoxide ion more will be the acidity of phenol

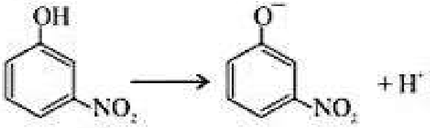
Acidity of Substituted Phenols : Acidity of substitued phenols depend on the stability of the phenoxide ion because acidity is the function of conjugate base.

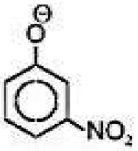




(I)

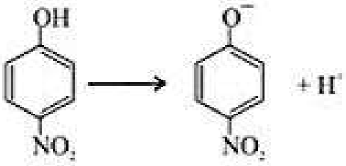
Stabilised by –R and –I effect and –I power is maximum

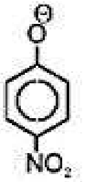




(II)

Stabilised by –I effect only



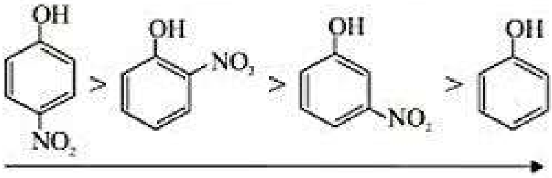


(III)

Stabilised by –R and –I effect and –I power is maximum

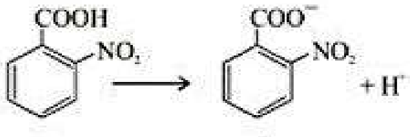
stability order should be I > III > II

Thus according to stability of anions o-derivative will be more acidic than p-derivative which will be more acidic than m-derivative. But result is as follows in case of nitrophenols, p-derivative is more acidic than o-derivative which is more acidic than m-derivative. In o-derivative , there is intramolecular hydrogen bonding which decrease acidity. Thus order of acidity is as follows :

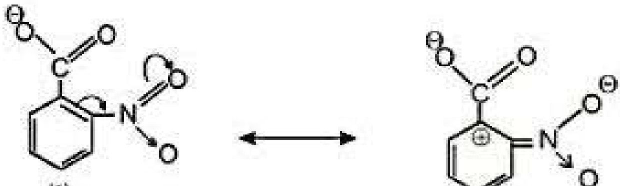


Acidity in decreasing order

Acidity of substituted benzoic acids Ortho substituted benzoic acid is always a stronger acid than m- and p-derivative. This is known as ortho effect

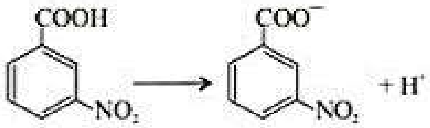


I

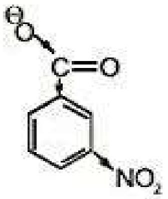


(I)

Thus, anion is stabilised by –R and –I effect and – I power is maximum.

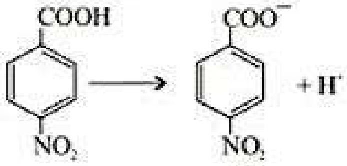


II

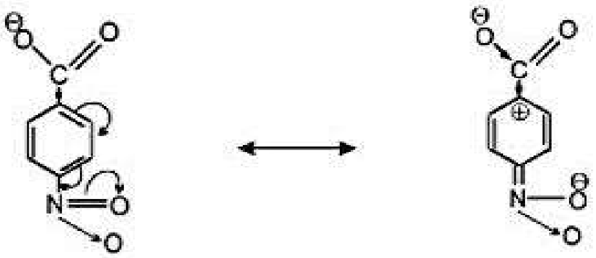


(II)

Anion is stabilised only by –I effect of NO_2 group

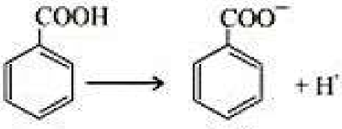


III

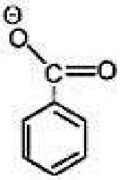


(III)

Anion is stabilised by -R and –I effect of NO_2 group



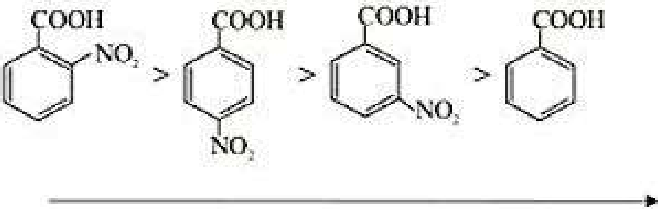
IV



(IV)

Thus decreasing order of the stability of these anions is follows : I > III> II > IV

We know that ortho derivative is the most acidic therefore decreasing order of acidity of these acids is as follows :



Acidity in decreasing order

BASIC STRENGTH

For an base, $BOH_{(aq)} \rightleftharpoons B^{+}_{(aq)} + OH^{-}_{(aq)}$

from law of mass action, $K_b = \dfrac{[B^{+}_{(aq)}][OH^{-}_{(aq)}]}{[BOH]}$

where , $K_b \rightarrow$ Basicity constant, or dissociation constant of base

$K_b \rightarrow$ Explains the strength of base

$K_b \propto$ Basic strength $\propto$ $1/\,pK_b$

$pK_b = -\log K_b$

$pOH = -\log [OH^-]$

basic strength $\propto$ +M $\propto \dfrac{1}{-M} \propto$ + I $\propto \dfrac{1}{-I}$

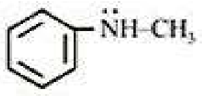
Basicity of Aromatic Amines : Basicity of nitrogen containing compounds $\propto$ Electron density on nitrogen.

In aromatic amines, lone pair of elecrons present on nitrogen is delocalised, hence electron density decrease due to resonance.

Ex. $C_6H_5NH_2$ is less basic than CH_3NH_2

lone pair is participating in resonance
(I)

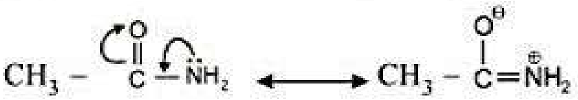
no resonance of lone pair so maximum basic
(II)



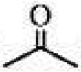
lone pair is participating in resonance and +I of CH_3
(III)

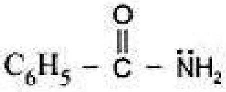
basic order II > III > I

Effect of cross conjugation on basicity :



$$CH_3-\overset{O}{\overset{\|}{C}}-\ddot{N}H_2 \longleftrightarrow CH_3-\overset{O^{\ominus}}{\overset{|}{C}}=\overset{\oplus}{N}H_2$$

Due to delocalisation and – I effect of  group, amides are less basic than amines.



$$C_6H_5-\overset{O}{\overset{\|}{C}}-\ddot{N}H_2$$

In this amide there is cross conjugation which increases basicity; thus $C_6H_5CONH_2$ is more basic than CH_3CONH_2. π bond of C = O group is in conjugation to benzene ring as well as lone pair of NH_2 group.

AROMATICITY

(a) **Aromatic Character of Compounds :** According to the **Huckel rule,** a compound will be aromatic if it fulfils the following four conditions :

(i) Compound should be cyclic

(ii) Compound should be planar or nearly planar.

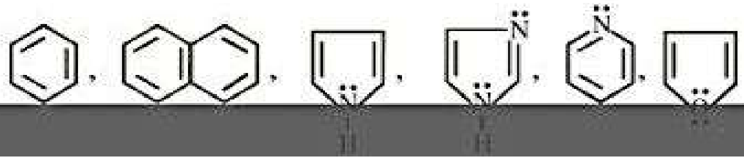
(iii) Compound should be conjugated through out ring

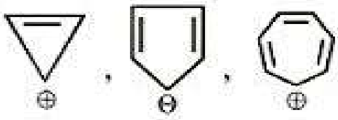
(iv) Compound should have $(4n+2)\pi$ conjugated or delocalised electrons where n is a whole number

n = 0, 1, 2, 3, 4, 5, 6, ...

	n =	0,	1,	2,	3,	4,	5......
$(4n+2)\pi$electron	=	2	6	10	14	18	22....

Examples :





(b) **Antiaromatic Compounds :** According to Huckel rule, compound will be antiaromatic if it fulfils the following four conditions :

(i) Compound should be cyclic

(ii) Compound should be planar.

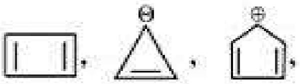
(iii) Compound should be conjugated through out ring and

(iv) Compound should have (4n)π conjugated or delocalised electrons where n is a whole number

n = 1, 2, 3, 4, 5, 6

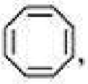
	n =	1,	2,	3,	4,	5......
(4n)πelectron	=	4	8	12	16	20......

Example

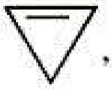


(c) **Non aromatic compounds :** these compounds are niether aromatic nor antiaromatic

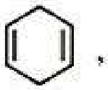
Example



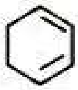
(I)



(II)



(III)



(IV)

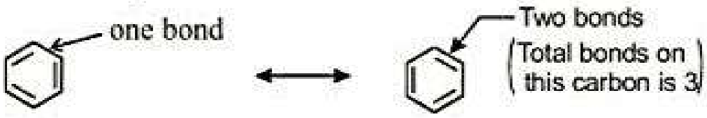
Although cyclooctatetraene has (4n)π electrons but even then it is not an antiaromatic. Geometry of this compound is non planar. Thus it is non aromatic. II^nd^, III^rd^ & IV^th^ compounds are not completely conjugated.

Note : Due to Aromatically extrastability is achieved by aromatic molecule, than non-aromatic or antiaromatic molecule.

(E) **Bond order :** Bond order in conjugated compound or bond order in compounds which exhibit resonance

$$\text{Bond order} = \frac{\text{Total number of bonds between two atoms}}{\text{Number of resonating structures}}$$

For examples :



Bond order of carbon in benzene = $\frac{2+1}{2}$ = 1.5

Example : Give the correct order of bond length of following mentioned compounds.

(i) $CH_3-CH_2\underset{a}{-}\ddot{N}H_2$ (ii) $CH_2=CH\underset{b}{-}\ddot{N}H_2$

no resonance(only single bond charecters) resonance(partial double bond characters)

bond length order a > b

MCQ

Q.1 Which of the following carboxylic acids is most acidic in character -
(A) o-methyl benzoic acid (B) m-methyl benzoic acid
(C) p-methyl benzoic acid (D) Benzoic acid

Q.2 Which one of the following is most acidic-
(A) p-nitrophenol (B) phenol (C) m-nitrophenol (D) o-nitrophenol

Q.3 Consider the follownig carbocations -

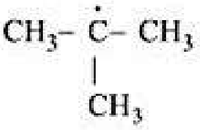
(a) $CH_3-\overset{\oplus}{C}H_2$ (b) $CH_2=\overset{\oplus}{C}H$ (c) $CH_2=CH-\overset{\oplus}{C}H_2$ (d) $C_6H_5-\overset{\oplus}{C}H_2$

Stability of these carbocations in decreasing order is -
(A) d > c > a > b (B) d > c > b > a (C) c > d > b > a (D) c > d > a > b

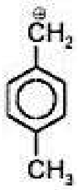
Q.4 Increasing order of acid strength among p - methoxy phenol, p-methyl phenol and p-nitrophenol is-
(A) p- nitrophenol, p-methoxyphenol, p- methylphenol
(B) p- methylphenol, p- methoxyphenol, p-nitrophenol
(C) p- nitrophenol, p- methylphenol, p- methoxyphenol
(D) p- methoxyphenol, p- methylphenol, p- nitrophenol.

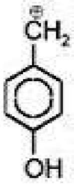
Q.5 The groups which when present in para position tend to decrease the acidity of phenol are-
(A) $-NO_2$ (B) $-CN$ (C) $-OCH_3$ (D) $-F$

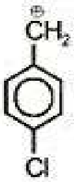
Q.6 Which free radical is the most stable -

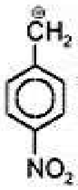
(A) $C_6H_5-\dot{C}H_2$ (B) $CH_2=CH-\dot{C}H_2$ (C) $CH_3-\dot{C}H-CH_3$ (D) 
$CH_3-\underset{CH_3}{\underset{|}{\dot{C}}}-CH_3$

Q.7 Which carbocation is the most stable -

(A) 

(B) 

(C) 

(D) 

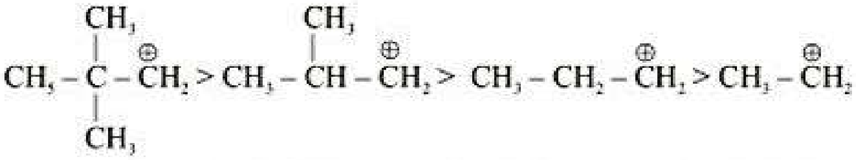
ANSWERS

Q.1 A **Q.2** A **Q.3** A **Q.4** D **Q.5** C **Q.6** A **Q.7** B.

HYPER CONJUGATION

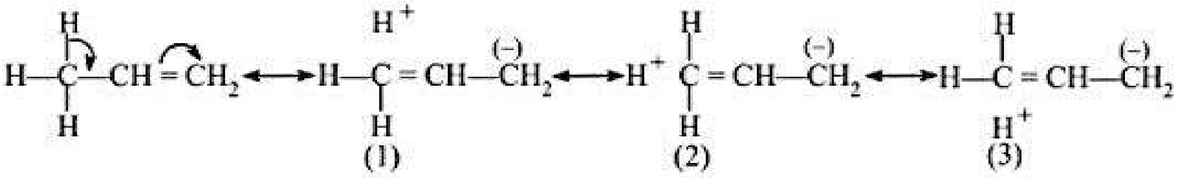
Introduction

According to inductive effect order of stability of cations should be



$$CH_3-\overset{CH_3}{\underset{CH_3}{C}}-\overset{\oplus}{C}H_2 > CH_3-\overset{CH_3}{C}H-\overset{\oplus}{C}H_2 > CH_3-CH_2-\overset{\oplus}{C}H_2 > CH_3-\overset{\oplus}{C}H_2$$

But acutally order should be reversed which is explained on the basis of hyper conjugation.



Definition :- Delocalization of conjugated (C–H) sigma electrons with π-bond or positive charge or free radical is called hyperconjugation or H-effect.

(i) hyperconjugating structures may be written involving "no bond" between the alpha carbon and hydrogen atoms so known as **"no bond resonance."**

(ii) Nathan baker observed this effect so known as "Nathan baker effect"

(iii) It is also permanent effect

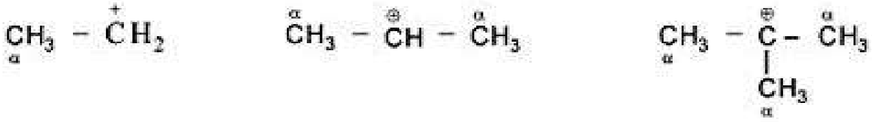
Condition for hyperconjugation:

(i) Compound should have at least one sp^2-hybrid carbon of either alkene, alkyl carbocation or alkyl free radical.

(ii) α-carbon with respect to sp^2 hybrid carbon should have at least one hydrogen. If both these conditions are fulfilled then hyperconjugation will take place in the molecule.

TYPES OF HYPERCONJUGATION

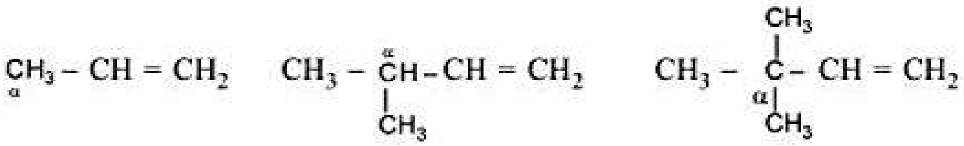
(i) **σ (C – H), vacant orbital (positive charge) hyperconjugation :** This type of conjugation occurs in alkyl carbocation.



$\underset{\alpha}{CH_3}-\overset{+}{C}H_2$ $\qquad$ $\overset{\alpha}{C}H_3-\overset{\oplus}{C}H-\overset{\alpha}{C}H_3$ $\qquad$ $\underset{\alpha}{CH_3}-\overset{\oplus}{\underset{\underset{\alpha}{CH_3}}{C}}-\overset{\alpha}{C}H_3$

no. of α H = 3 $\qquad$ no. of α H = 6 $\qquad$ no. of α H = 9

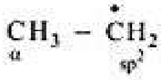
(ii) **σ (C – H), π hyperconjugation :** This type of conjugation occurs in alkenes.



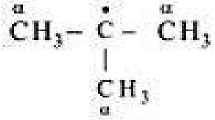
$\underset{\alpha}{CH_3}-CH=CH_2$ $\qquad$ $CH_3-\overset{\alpha}{\underset{CH_3}{C}}H-CH=CH_2$ $\qquad$ $CH_3-\overset{CH_3}{\underset{\alpha\,CH_3}{C}}-CH=CH_2$

no. of α H = 3 $\qquad$ no. of α H = 1 $\qquad$ no. of α H = 0

(iii) **σ (C – H), odd electron hyperconjugation :** This type of conjugation occurs in alkyl free radicals -



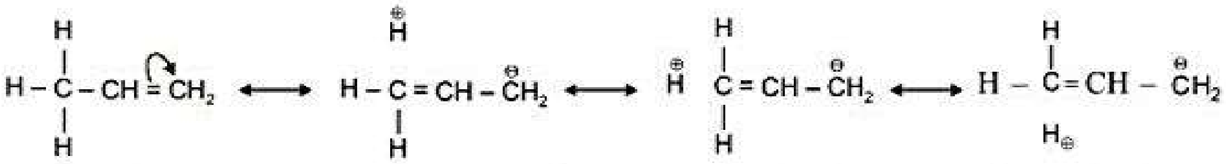
$\overset{\alpha}{CH_3} - \overset{\bullet}{\underset{sp^2}{C}}H_2$



$\overset{\alpha}{C}H_3 - \overset{\bullet}{C}(\overset{\alpha}{C}H_3) - \overset{\alpha}{C}H_3$

Note: Carbanion never shows hyper conjugation, if there is one –C–H sigma bond alternate with negative charge then there will be no H-effect

Hyper conjugating structures due to hyperconjugation may be written involving "no bond" between the alpha carbon and hydrogen atoms.



In the above hyper conjugating structures there is no covalent bond between carbon and hydrogen. From this point of view, hyperconjugation may be regarded as " **no bond resosnance** ".

ordere of effectiveness of hyperconjugation : α C–H bond > α C–D bond > α C–T bond

APPLICATION OF HYPERCONJUGATION

(A) **Stability of Alkyl Carbocations :** Stability of alkyl carbocations ∝ number of hyperconjugating structures ∝ number of α–hydrogens.

Ex. (i)

$\overset{\oplus}{C}H_3$

(I)

no. of α H = 0

$CH_3 - \overset{\oplus}{C}H_2$

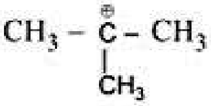
(II)

no. of α H = 3

$CH_3 - \overset{\oplus}{C}H - CH_3$

(III)

no. of α H = 6



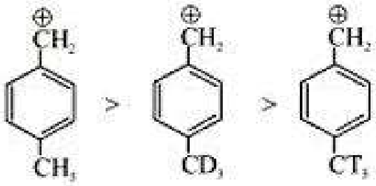
$CH_3 - \overset{\oplus}{C}(CH_3) - CH_3$

(IV)

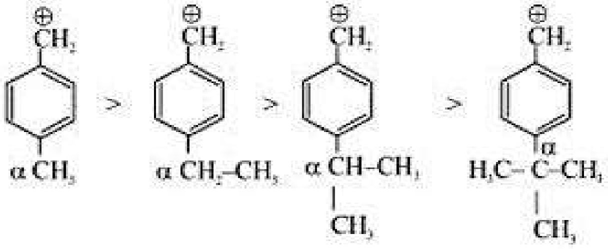
no. of α H = 9

stability order IV > III > II > I

(ii)



(iii)



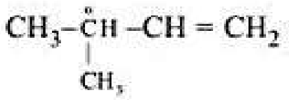
(3αH) (2αH) (1αH) (0αH)

(H effect dominates over I effect)

(B) **Stability of Alkenes :**Hyperconjugation explains the stability of certain alkenes over other alkenes:

Stability of alkenes ∝ Number of alpha hydrogens ∝ Number of hyperconjugating structures

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

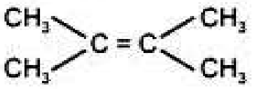


$CH_3-\underset{\displaystyle CH_3}{\overset{\alpha}{C}H}-CH=CH_2$

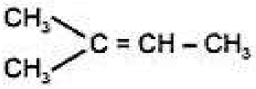
(III)

stability order I > II > III

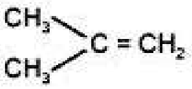
(ii)



(I)



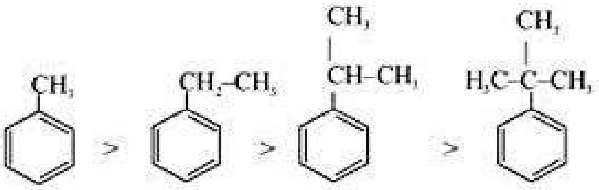
(II)



(III)

stability order I > II > III

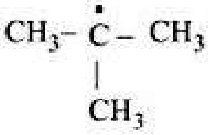
(iii)



(C) **Stability of Alkyl free radicals :** Stability of alkyl free radicals can be explained by hyperconjugation. Stability depends on the number of hyperconjugating structures.

structure

(I) $\dot{C}H_3$ (II) $CH_3-\dot{C}H_2$ (III) $CH_3-\dot{C}H-CH_3$



$CH_3-\underset{\displaystyle CH_3}{\dot{C}}-CH_3$

(IV)

	(I)	(II)	(III)	(IV)
	no. of α H = 0	no. of α H = 3	no. of α H = 6	no. of α H = 9
No of hyperconjugating Structure other then given structure	0	3	6	9

(i) Stability is in increasing order IV > III > II > I

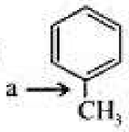
(D) **Bond length in alkenes:** More is the number of hyperconjugating structures, the more will be single bond character in carbon-carbon double bond.

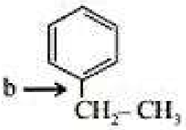
The bond length between carbon-carbon double bond ∝ number of hyperconjugating structures.

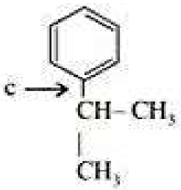
Ex. **(i)** $CH_3-CH\overset{\overset{a}{\downarrow}}{=}CH-CH_3,\ CH_3-CH\overset{\overset{b}{\downarrow}}{=}CH_2,\ CH_2\overset{\overset{c}{\downarrow}}{=}CH_2$

Bond length order ⇒ a > b > c

(ii)

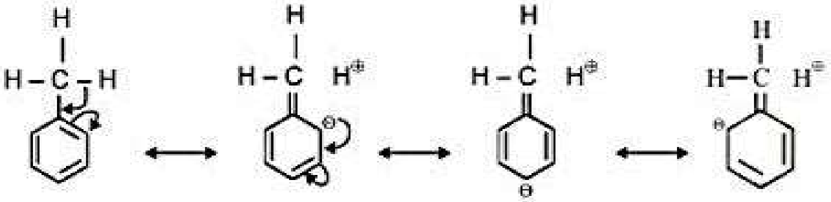




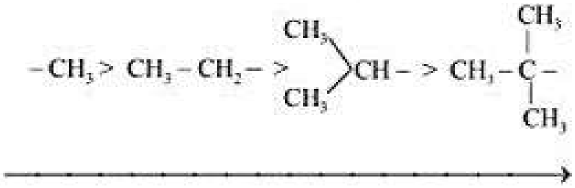


Bond length order ⇒ a > b > c

(E) **Electron releasing (or donating) power of (–R) in alkyl benzene :** CH_3 – (or alkyl group) is +H group, ortho-para directing group and activating group for electrophilic aromatic substitution reaction because of the hyperconjugation.



The electron donating power of alkyl group will depends on the number of hydrogens present on α-carbon. The electron releasing power of some groups are as follows -



$$-CH_3 > CH_3-CH_2- > \begin{matrix} CH_3 \\ CH_3 \end{matrix}\!\!\!\!\!\!>CH- > CH_3-\underset{CH_3}{\overset{CH_3}{\overset{|}{\underset{|}{C}}}}-$$

Electron donating power in decreasing order due to the hyperconjugation

(F) **Heat of hydrogenation (HOH) :**

$$R–CH=CH_2 + H_2 \longrightarrow R–CH_2CH_3 + \Delta H$$

(a) heat evolved when 1 mole of any unsaturated hydrocarbon are hydrogenated is called heat of hydrogenation (ΔH) If alkene is more reactive towards hydrogen then it will evolve more ΔH.

$$\text{So, } \boxed{\Delta H \propto \frac{1}{\text{stability of alkene}} \propto \frac{1}{\text{number of } \alpha\text{-H}}}$$

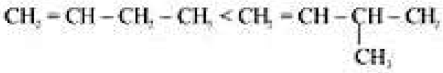
(b) $\Delta H \propto$ number of π bonds

(c) It is exothermic process (energy release)

Examples of HOH order

(i) $CH_2=CH-CH_2-CH_3 > CH_3-CH=CH-CH_3$

(ii)



$$CH_2=CH-CH_2-CH_3 < CH_2=CH-\underset{CH_3}{\underset{|}{CH}}-CH_3$$

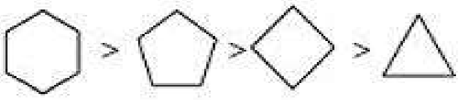
(iii)

Heat of combustion (HOC)

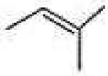
It is the energy liberated during complete combustion of organic compound.

HOC comparison

HOC ∝ No. of carbon–atoms

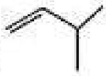
eg. 

$$HOC \propto \frac{1}{\text{Stability of hydrocarbon}}$$

(a)  9 α

(b)  5 α

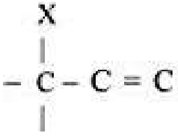
(c)  2 α

(d)  1 α

d > c > b > a

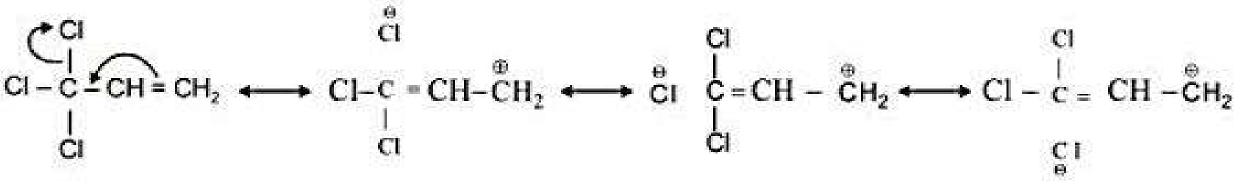
Note : Reverse Hyperconjugation (–H effect) :

The phenomenon of hyperconjugation is also observed in the system given below :

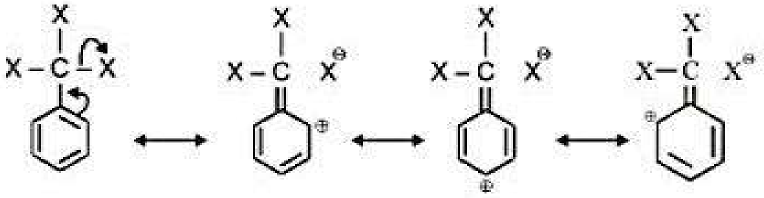


$-\overset{X}{\underset{|}{\overset{|}{C}}}-C=C$ where X - halogen

In such system the effect operates in the reverse direction. Hence the hyperconjugation in such system is known as reverse hyperconjugation.



The meta directing influence and deactivating effect of $-CX_3$ group for electrophilic aromatic substitution reaction can be explained by this effect.

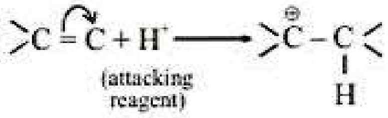


ELECTROMERIC EFFECT : (E-EFFECT)

- It is temporary effect.
- The organic compounds having a unsaturation (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

- The effect is annulled as soon as the attacking reagent is removed from the domain of the reaction.
- It is represented by E and the shifting of the electrons is shown by a curved arrow ($\curvearrowright$).
- When inductive and electromeric effect operate in opposite directions, the electomeric effect predominates.
- There are two distinct types of electromeric effect.

(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 :



(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.

ATTACKING REAGENTS

The species which attack on a substrate and form a product is called as attacking reagents.

Substrate - Reactant which is less reactive is generally taken in greater amount.

Attacking reagents are of two types

(A) Electrophile (B) Nucleophile

(A) **Electrophiles or electrophilic reagents ($E^{\oplus}$):**

(a) They are electron deficient species.

(b) They have a tendency to accept electron from another molecule

(c) In a reaction, an electrophile attacks the substrate at the point of maximum electron density.

(d) Neutral molecule having electron deficient centre, CCl_4, CO_2

Types of Electrophile :

(i) Positively charged electrophiles

$\overset{\oplus}{H}$, $\overset{\oplus}{N}O$, $\overset{\oplus}{R}(\overset{\oplus}{C}H_3, \overset{\oplus}{C}_2H_5)$, $\overset{\oplus}{S}O_3H$

(ii) Neutral electrophiles

(a) All Lewis acids as : BF_3, $AlCl_3$, SO_3, $ZnCl_2$, $BeCl_2$, $FeCl_3$, $SnCl_4$

(b) Free radicals, carbenes acts as electrophiles.

(c) Transition metal cations are electrophiles, e.g. Fe^{3+}, Fe^{+}, Ag^{+}, Cd^{2+} etc.]

(d) Neutral molecule having electron deficient center, eg. CCl, CO

(B) Nucleophlic reagents or nucleophiles :

(a) They are electron rich species so they have a tendency to donate electron pair.

(b) All nucleophiles are lewis bases.

(c) They attack the centre of minimum electron density in a molecule in a chemical reaction.

Types of Nucleophile :

(i) Negatively Charged nucleophiles :

$F^-, Cl^-, Br^-, I^-, OH^-, CN^-, RCOO^-, RO^-, R^-, R-C\equiv C^-, NH_2^-, SH^-$ etc.

(ii) Neutral nucleophile containing lone pair :

$H_2\ddot{\underset{..}{O}}, R-\ddot{\underset{..}{O}}H, R-\ddot{\underset{..}{O}}-R, \ddot{N}H_3, R-\ddot{N}H_2$

(iii) π electron containing compounds

$CH_2=CH_2, CH\equiv CH$

(C) Ambiphiles :

Ambiphiles are those which act as both electrophile and nucleophile.

Example :

$R-CH=\ddot{\underset{..}{O}}$, RCOR, RCOOH etc.

S. No.	Electrophile	Nucleophile
1	Accept electron	Supplies the electron pair
2	Electron deficient (electron loving)	Electron rich
3	Usually positively charged species	Usually negatively charged species
4	Attacks the points of high electron density	Attacks the point of low electron denisty
5	e.g., $\overset{\oplus}{H}, \overset{\oplus}{C}H_3, CO_2, \overset{\oplus}{N}O$	e.g., $F^-, Cl^-, Br^-, I^-, H_2O$

MCQ

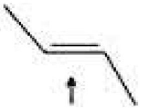
Q.1 Find out the correct statement(s) about given compound

$H_2C \underset{\uparrow}{=} CH_2$

(I)

$CH_3-CH \underset{\uparrow}{=} CH_2$

(II)



(III)

(IV)

(V)

(A) Order of Heat of Hydrogenation & Heat of combustion is same

(B) Order of Heat of Hydrogenation & Heat of combustion is different

(C) Order of rotation barrier energy for marked bond is I > II > V > IV > III

(D) Order of Boiling point is V > IV > III > II > I