

ENTHUSIAST | LEADER | ACHIEVER



Reaction Mechanism-I

ENGLISH MEDIUM

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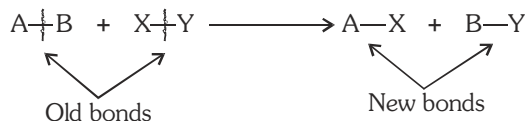
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REACTION MECHANISM : PART-I

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



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.

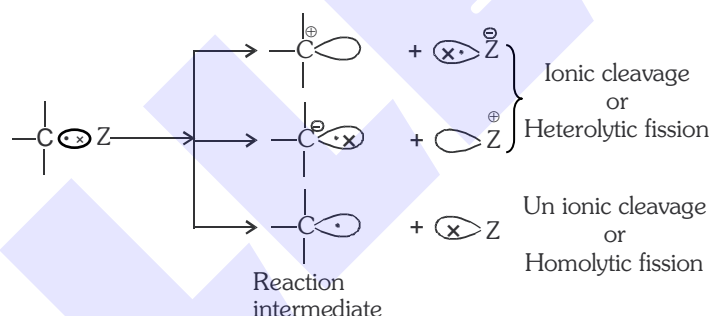
3.0 CONCEPTS TO UNDERSTAND REACTION MECHANISM :

- (1) Bond cleavage (2) Attacking reagent (3) Reaction intermediate (4) Electronic effect

3.1 TYPE OF BOND CLEAVAGE :

- (a) **Heterolytical cleavage/fission :** Cleavage in which unequal distribution of electrons takes place during the bond cleavage is known as heterolytical cleavage. Due to unequal distribution of electrons, ions are formed. That's why it is also known as ionic cleavage or heterolytical cleavage.
- (b) **Homolytical cleavage/fission :** Cleavage in which equal distribution of e^- s takes place during the chemical reaction, is known as homolytical cleavage.

Due to equal distribution of electrons, without charge unpaired electron containing species are formed, which are known as free radicals and cleavage is known as unionic cleavage/homolytical fission.



3.2 TYPES OF ATTACKING REAGENTS

These are of two types :

- (a) **Electrophilic reagent or electrophiles:**

Electrophilic (electro + philic)
 (electron + loving)

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

Electrophiles may be positively charged or neutral.

- (i) **Positively charged electrophiles :**



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

- (a) All Lewis acids as :
 $\text{BF}_3, \text{AlCl}_3, \text{SO}_3, \text{ZnCl}_2, \text{BeCl}_2, \text{FeCl}_3, \text{SnCl}_2, \text{CO}_2, \text{SnCl}_4.$
- (b) Carbenes and nitrenes act as electrophiles.

(b) Nucleophilic reagent or nucleophiles

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

Nucleophilic

(Nucleo + philes)

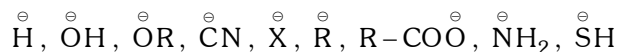


(Nucleus + loving)

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

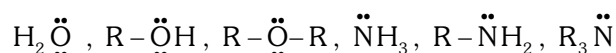
- Nucleophiles can be considered as Lewis base.

(i) Negatively charged nucleophiles.

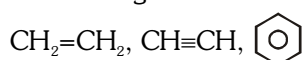


(ii) Neutral nucleophiles :

(a) Lone pair containing



(b) πe^- containing



(iii) $\text{R}^*-\text{Mg}-\text{X}$, LiAlH_4^* , NaBH_4^*

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

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

Examples :- $\text{K}^+\text{O}^--\text{N}=\text{O}$, $\text{NH}_2^--\ddot{\text{O}}\text{H}$, $\text{Na}^+\text{C}^-\equiv\text{N}$

3.3 REACTION INTERMEDIATE

□ Carbocation :

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

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

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

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

□ Free Radical :

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

□ Carbenes ($\text{CH}_2:$) :

Carbenes are neutral carbon species in which the carbon atom is bonded to two monovalent atoms or groups and carries two nonbonded electrons.

- It behaves as an electrophile.
- It is neutral.
- $6 e^-$ in outermost shell.
- $4 e^-$ are bonded and two are nonbonded e^- .

□ Nitrenes ($-\ddot{\text{N}}:$)

Nitrenes are neutral nitrogen species in which the nitrogen is bonded to one monovalent atom or group and carries four non-bonded electrons.

- It is monovalent radical.
- It is neutral.
- $6 e^-$ in outermost shell.
- Two are bonded and four are nonbonded electrons.

BEGINNER'S BOX-1

- Which of the following is ambident nucleophile :-
 (1) NH_2OH (2) NCO^\ominus (3) NO_2^\ominus (4) All of these
- $\text{CH}_3\text{CH}_2\text{-Cl}$ undergoes homolytic fission to produce :-
 (1) $\text{CH}_3\dot{\text{C}}\text{H}_2$ and $\dot{\text{C}}\text{H}_2\text{Cl}$ (2) $\text{CH}_3\dot{\text{C}}\text{H}_2$ and Cl^\ominus
 (3) $\text{CH}_3\overset{\oplus}{\text{C}}\text{H}_2$ and Cl^\ominus (4) $\text{CH}_3\overset{\ominus}{\text{C}}\text{H}_2$ and Cl^\oplus
- Which of the following intermediate has complete octet :-
 (1) Carbocation (2) Carbanion (3) Free radical (4) Carbene

3.4 ELECTRONIC EFFECTS :

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

- Inductive effect
- Mesomeric effect
- Hyperconjugation
- Electromeric effect

3.4.1 INDUCTIVE EFFECT (I-EFFECT) :

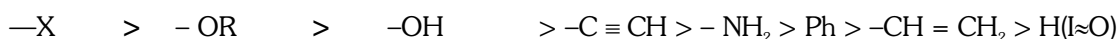
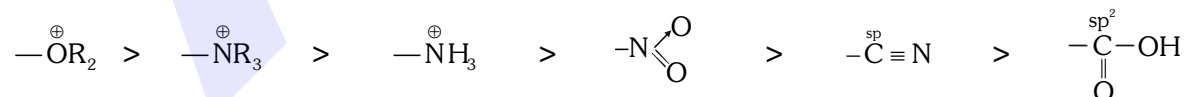
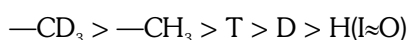
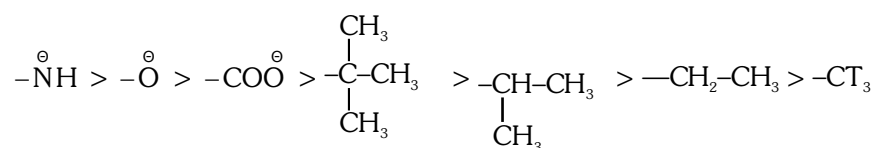
- Polarity induced in non polar σ bond due to presence of adjacent polar bond is known as inductive effect.

GOLDEN KEY POINTS

- In I-effect there is partial displacement of e^- .
- After 3 or 4 C-atom I-effect is considered to be zero.
- Inductive effect decreases on increasing distance.

So **Magnitude of I effect** $\propto \frac{1}{\text{distance}}$

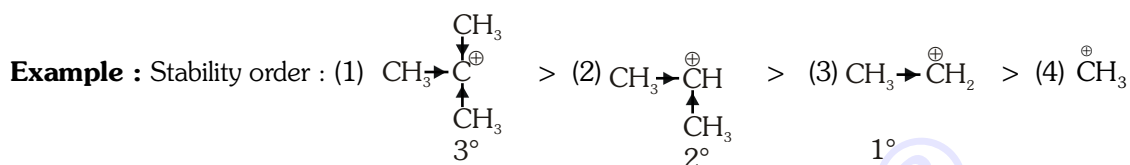
- I-effect of hydrogen is considered as zero.

-I groups :**+I groups :**

APPLICATION OF I-EFFECT
(1) Stability of carbocation :

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

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



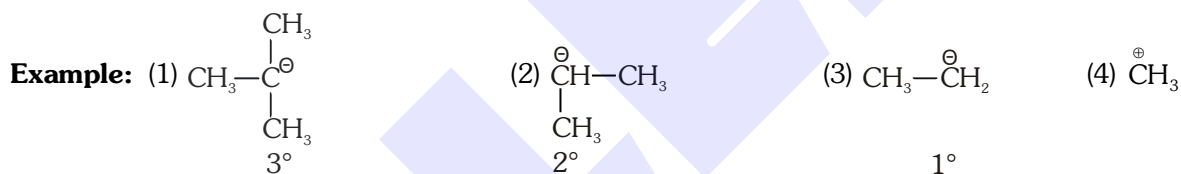
Reason : More no. of +I group.

more stable carbocation.

so stability order $1 > 2 > 3 > 4$.

(2) Stability of carbanion :

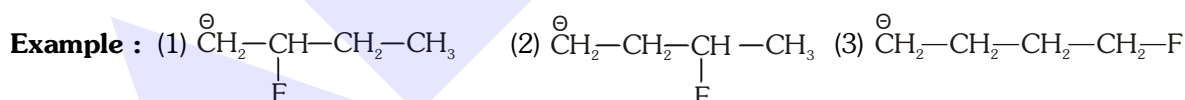
$$\text{Stability of Carbanion} \propto \frac{-I \text{ effect}}{+I \text{ effect}}$$



More No. of +I group.

Less stable carbanion.

So stability order $4 > 3 > 2 > 1$



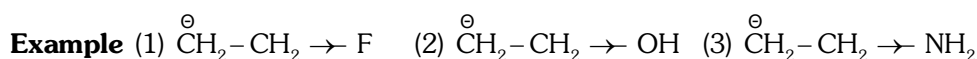
Minimum distance of -F.

Maximum -I of -F.

Minimum negative charge.

Maximum stable.

So stability order $1 > 2 > 3$



Maximum -I of F.

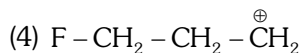
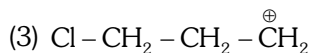
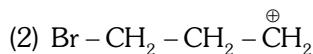
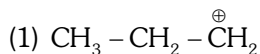
Negative charge will be minimum.

Maximum stable.

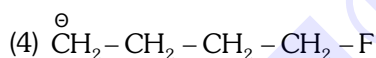
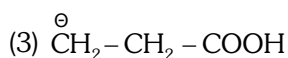
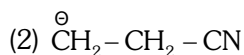
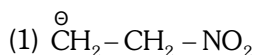
So stability order $1 > 2 > 3$

BEGINNER'S BOX-2

1. Most stable carbocation is :

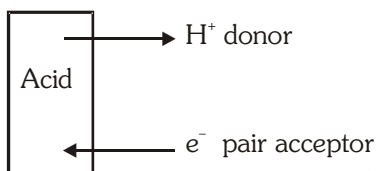


2. Most stable carbanion is :



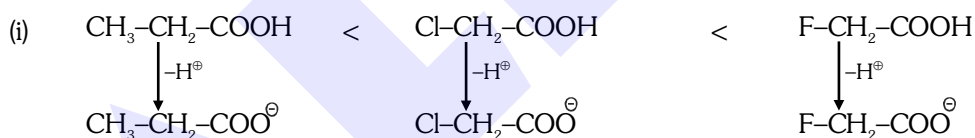
(3) Acidic and basic strength :

◆ Acidic strength :



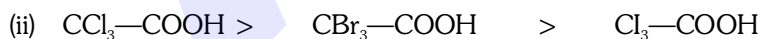
$$\text{Acidic strength} \propto \text{Stability of conjugate base (anion)} \propto \frac{-I \text{ effect}}{+I \text{ effect}}$$

Example :

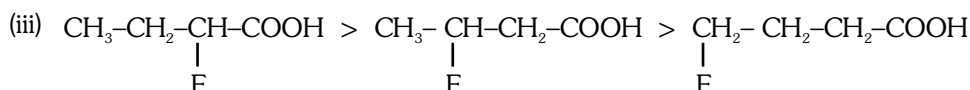


+I of $-\text{CH}_3$
anion is less stable

Maximum -I of $-\text{F}$
Maximum stable anion
Corresponding acid is maximum acidic.



maximum -I of Cl
so maximum acidic.

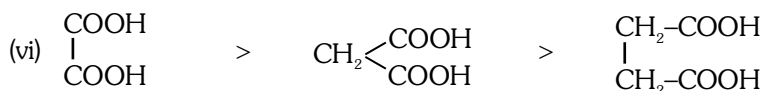
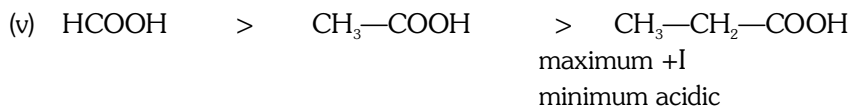
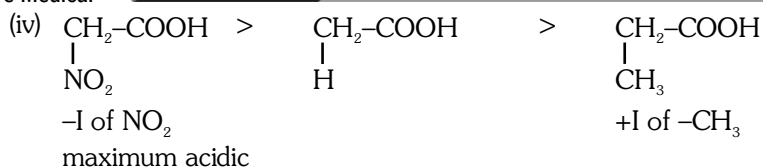


minimum distance of F from $-\text{COOH}$

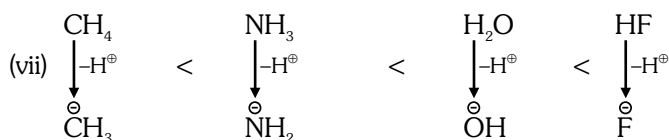
maximum -I of F.

So maximum acidic.

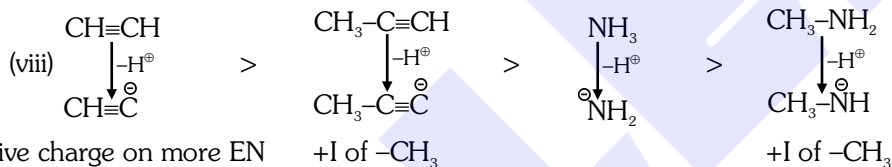
Pre-Medical



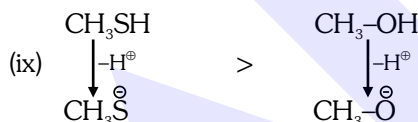
minimum distance of $-\text{COOH}$ from other
 maximum $-\text{I}$ of $-\text{COOH}$ on other
 maximum acidic



Negative charge on maximum E.N.
Maximum stable anion
So corresponding acid is most acidic

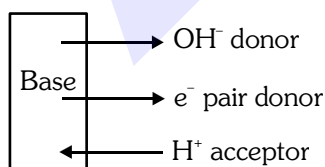


negative charge on more EN atom and no +I anion is maximum stable so corresponding acid is most acidic

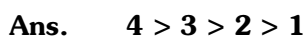


negative charge on big size atom
more stable anion
so corresponding acid is more acidic

◆ **Basic strength :**



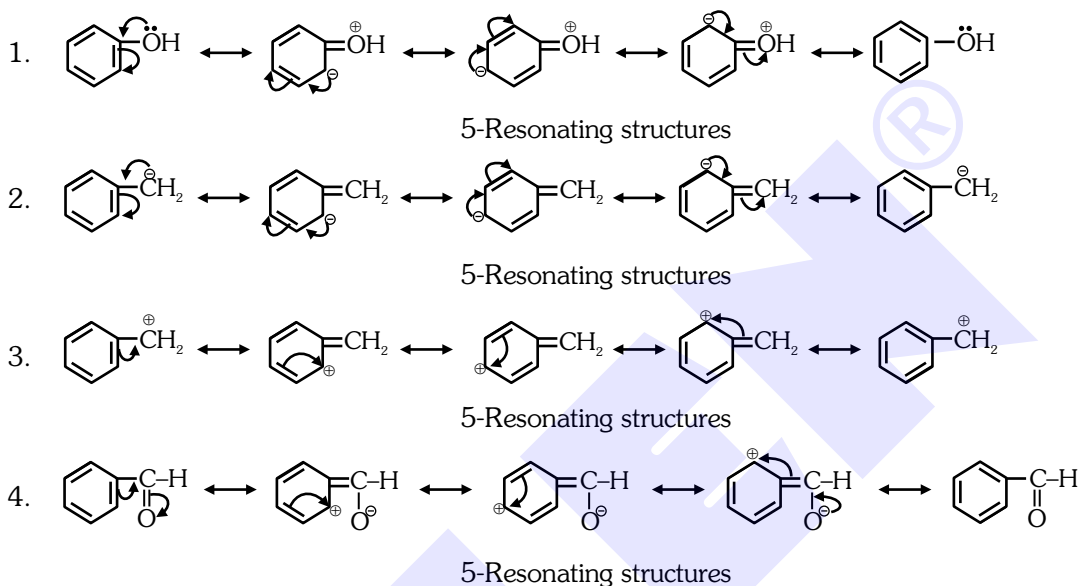
$$\text{Basic strength} \propto +I \text{ effect} \propto \frac{1}{-I \text{ effect}}$$



Maximum +I
so maximum basic

GOLDEN KEY POINTS
Conditions of Resonance :

- In resonance only e^- are delocalised not atoms.
- The number of e^- or number of unpaired or paired e^- in all resonating structures should be same.
- It is permanent effect.
- All the resonating or canonical structures must follow the Lewis structures.
- Resonating system should be in same plane.

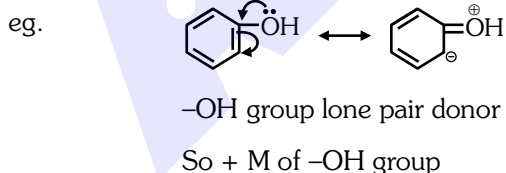
Draw resonating structures :


M-effect : Delocalisation of electron in conjugated system (due to presence of EWG or EDG) is known as 'M' effect.

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

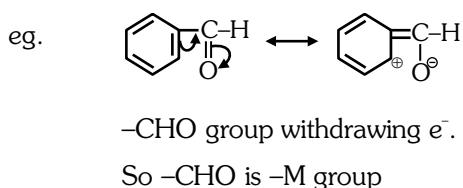
+M group : Lone pair containing group like

e.g. $-\ddot{\text{N}}\text{H}_2$, $-\ddot{\text{O}}\text{H}$, $-\ddot{\text{O}}\text{R}$, $-\ddot{\text{N}}\text{R}_2$, $-\ddot{\text{S}}\text{H}$, $-\ddot{\text{N}}\text{HR}$, $-\ddot{\text{X}}:$, $-\ddot{\text{N}}\text{HCOCH}_3$



(2) -M effect :- Group, that withdraws electron pair from the conjugated system, is known as -M effect exerting groups and the phenomena is known as -M effect.

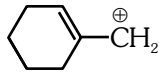
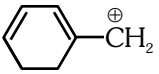
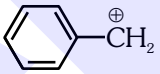
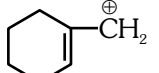
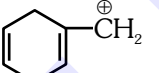
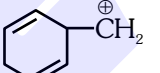
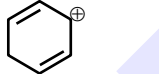

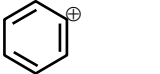
-M group : $-\text{CHO}$, $-\text{COOH}$, $-\text{COOR}$, $-\text{COR}$, $-\text{NO}_2$, $-\text{CN}$, $-\text{COX}$, $-\text{CONH}_2$, $-\text{SO}_3\text{H}$



APPLICATIONS OF RESONANCE EFFECT :

(1) Stability of carbocation.

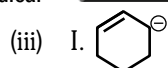
Ex. Give stability order for :-

- (i) $\text{CH}_2 = \text{CH} - \overset{\oplus}{\text{CH}}_2 > \text{CH}_3 - \text{CH}_2 - \overset{\oplus}{\text{CH}}_2 > \text{CH}_2 = \text{CH} - \text{CH} - \overset{\oplus}{\text{CH}}_2$
 stabilized by resonance (SBR) +I of Alkyl group -I of Alkenyl group
- (ii) $\text{CH}_3 - \overset{\oplus}{\underset{\text{CH}_3}{\text{C}}} - \text{CH} = \text{CH}_2 > \text{CH}_3 - \overset{\oplus}{\text{CH}} - \text{CH} = \text{CH}_2 > \overset{\oplus}{\text{CH}}_2 - \text{CH} = \text{CH}_2$
 SBR and +I of two $-\text{CH}_3$ SBR and +I of one $-\text{CH}_3$ SBR only
- (iii) $(\text{C}_6\text{H}_5)_3\overset{\oplus}{\text{C}} > (\text{C}_6\text{H}_5)_2\overset{\oplus}{\text{CH}} > \text{C}_6\text{H}_5\overset{\oplus}{\text{CH}}_2 > \text{CH}_2 = \text{CH} - \overset{\oplus}{\text{CH}}_2 > (\text{CH}_3)_3\overset{\oplus}{\text{C}} > (\text{CH}_3)_2\overset{\oplus}{\text{CH}} > \text{CH}_3 - \overset{\oplus}{\text{CH}}_2 > \overset{\oplus}{\text{CH}}_3 > \text{CH}_2 = \overset{\oplus}{\text{CH}} > \text{CH} \equiv \overset{\oplus}{\text{C}}$
- (iv)  $<$  $<$ 
 maximum resonance
- (v)  $>$  $>$ 
 SBR and +I SBR and -I No. reso.
- (vi)  $>$  $>$ 
 more resonance less resonance localized \oplus charge
- (vii) $\overset{\oplus}{\text{CH}}_2 - \overset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{H} < \overset{\oplus}{\text{CH}}_2 - \text{CH}_2 - \overset{\text{O}}{\underset{\parallel}{\text{C}}} - \text{H}$
 No reso. more -I of $-\text{CHO}$ so less stable No reso. less -I of $-\text{CHO}$

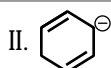
(2) Stability of carbanion :

Ex. Give stability order of :

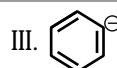
- (i) I. $\text{CH}_2 = \text{CH} - \overset{\ominus}{\text{CH}}_2$ II. $\text{CH}_2 = \overset{\ominus}{\text{CH}}$ III. $\text{CH}_3 - \overset{\ominus}{\text{CH}}_2$
 SBR negative on more EN
 stability order $\text{I} > \text{II} > \text{III}$
- (ii) $(\text{C}_6\text{H}_5)_3\overset{\ominus}{\text{C}} > (\text{C}_6\text{H}_5)_2\overset{\ominus}{\text{CH}} > \text{C}_6\text{H}_5\overset{\ominus}{\text{CH}}_2 > \text{CH}_2 = \text{CH} - \overset{\ominus}{\text{CH}}_2 > \overset{\ominus}{\text{CH}}_3 > \text{CH}_3 - \overset{\ominus}{\text{CH}}_2 > (\text{CH}_3)_2\overset{\ominus}{\text{CH}} > (\text{CH}_3)_3\overset{\ominus}{\text{C}}$

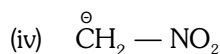


resonance stable

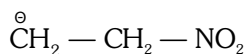


more resonance stable

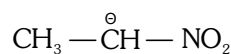

 localized \ominus charge

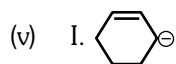
 stability order $\text{II} > \text{I} > \text{III}$


SBR

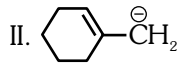


no. reso

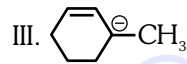

 SBR but +I of CH_3

 stability order $\text{I} > \text{III} > \text{II}$


SBR and +I



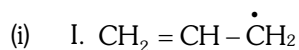
SBR



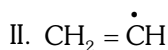
SBR and more +I

 stability order $\text{II} > \text{I} > \text{III}$

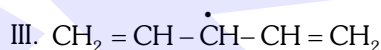
(3) Stability of free radicals.

Ex. Give stability order for :


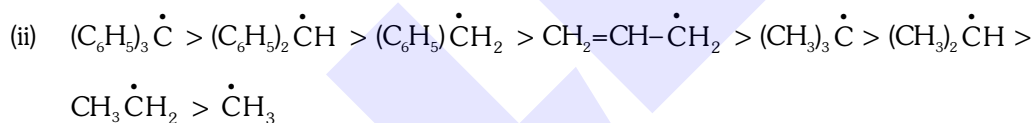
less resonance



no resonance

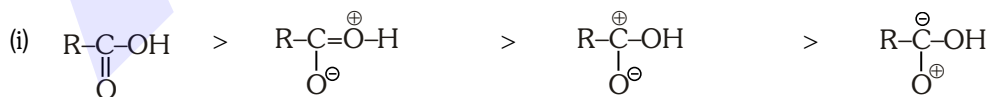


more resonance

 stability order $\text{III} > \text{I} > \text{II}$


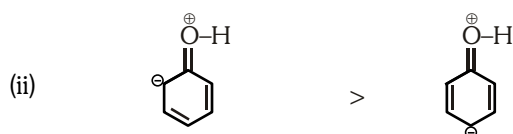
(4) Stability of resonating structures (R.S) Rules :

- Complete octet R.S. is more stable than incomplete octet.
- Nonpolar R.S. is more stable than polar resonating structures.
- For charged R.S. negative charge on more EN and positive charge on less EN is more stable.
- Opposite charge must be closer and same charge must be farther for greater stability.

Ex. Arrange the following for stability order.

 complete octet,
nonpolar

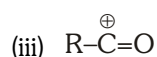
 complete octet,
polar

incomplete octet

 +ve charge on
more EN atom
(incomplete octet)


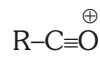
opposite charge closer

opposite charge farther

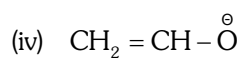


incomplete octet

<

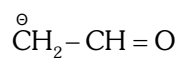


complete octet



(negative charge on more EN)

>



(negative charge on less EN)

(5) Aromaticity (Huckel's rule) : Cyclic, planar and completely conjugated system with $(4n+2)\pi$ electrons (where $n = 0, 1, 2, 3, \dots$) is known as aromatic compounds, these compound gains extra stability which is known as aromaticity.

Note : $[4n + 2] \pi$ electrons. (Odd number of π electron pairs) means

If $n = 0$ 2π electrons or 1 pair

$n = 1$ 6π electrons or 3 pairs

$n = 2$ 10π electrons or 5 pairs

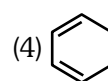
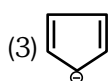
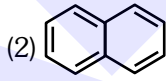
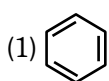
$n = 3$ 14π electrons or 7 pairs

S.No	Compound	Cyclic	Plannar	Cyclic Resonance	Huckel Rule $(4n+2) \pi e^-$	Aromatic Yes/No
1.		✓	✓	✓	$2\pi e^-$	Yes
2.		✓	✓	✓	$4\pi e^-$	No
3.		✓	✓	✓	$4\pi e^-$	No
4.		✓	✓	✓	$6\pi e^-$	Yes
5.		✓	✓	✓	$6\pi e^-$	Yes
6.		✓	✗	✗	$4\pi e^-$	No
7.		✓	✓	✓	$6\pi e^-$	Yes
8.		✓	✓	✓	$6\pi e^-$	Yes

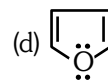
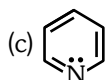
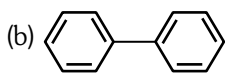
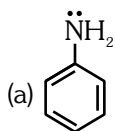
9.		✓	✓	✓	$6\pi e^-$	Yes
10.		✓	✓	✓	$6\pi e^-$	Yes
11.		✓	✓	✓	$6\pi e^-$	Yes
12.		✓	✓	✓	$10\pi e^-$	Yes
13.		✓	✓	✓	$14\pi e^-$	Yes
14.		✓	✓	✓	$6\pi e^-$	Yes
15.		✓	✗	✗	$6\pi e^-$	No
16.		✓	✓	✓	$6\pi e^- + 6\pi e^-$	Yes

BEGINNER'S BOX-4

1. Which of the following is nonaromatic



2. Which of the following compounds are aromatic in nature



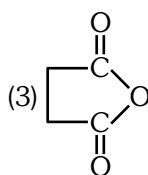
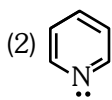
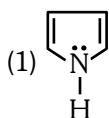
(1) Only a

(2) a and b

(3) a, b, d

(4) all of these

3. Which of the following is not aromatic compound



(4) All of these

(6) Acidic and Basic strength :

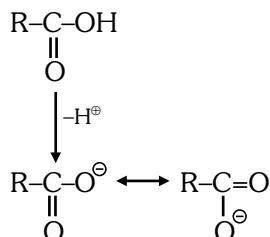
(a) Acidic strength :

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

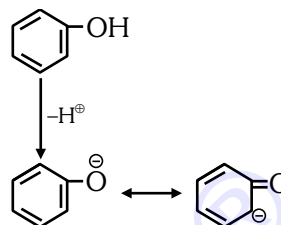
Illustrations

Illustration 1. Carboxylic acids are more acidic than phenols, why?

Solution.



2, equal R.S. more stable anion
so corresponding acid is more acidic.
Here, carboxylate ion is more stable
than phenoxide ion.

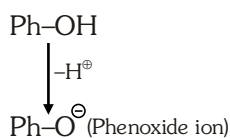


5, unequal R.S. less stable anion since $-ve$ charge is being shared by oxygen is less electronegative carbon.

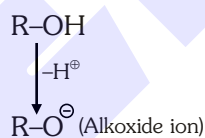
Note : The molecule having equivalent R.S. has more stability than the molecule having non equivalent R.S.

Illustration 2. Phenol is more acidic than alcohols why ?

Solution.



anion stable by resonance
So, corresponding acid is more acidic.



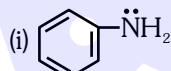
no resonance.
less stable anion

(b) Basic strength order :- Tendency to donate the electron pair by an atom or group is known as its basic strength. Compounds in which electron pair is delocalised will be less basic, while those in which electron pair is localised will be more basic.

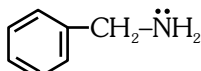
$$\left(\text{Basic strength} \propto \text{H}^{\oplus} \text{ accepting tendency} \propto \text{l.p. donating tendency} \propto \frac{+M, +I}{-M, -I} \right)$$

Ex.

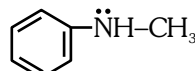
Give basic strength order :



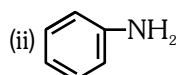
l.P. is stabilized by resonance
basic order —



II
no reso. of l.p.
so maximum basic
 $II > III > I$



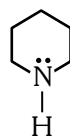
III
l.p. is stabilized by resonance
and +I of CH_3



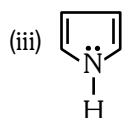
I
delocalized l.p.
basic order —



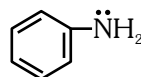
II
localized l.p.
on more EN
III > II > I



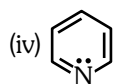
III
localized l.p.
on less EN



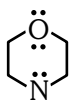
lone pair participate in aromatic sextet so less available



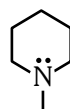
lone pair not participate in aromatic sextet so more available



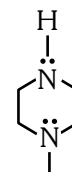
I
l.p. on more EN so least basic



II
more -I of oxygen



III
+I



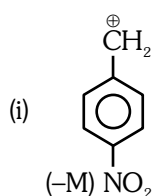
IV
less -I of nitrogen

basicity order

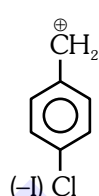
III > IV > II > I

Illustrations

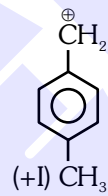
Illustration 3. Give stability order of :



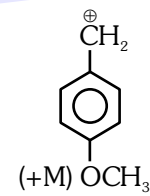
I
charge ↑
So stability order



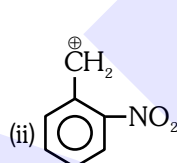
II
charge ↑
IV > III > II > I



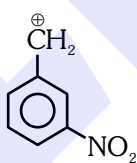
III
charge ↓



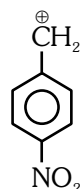
IV
charge ↓



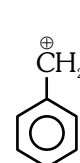
I
 $-M_o = -M_p$ and $-M_m = 0$
but $-I_o > -I_m > -I_p$, $-M$ and $-I$ increases positive charge.
stability order is



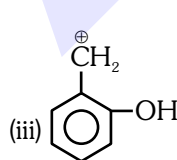
IV > II > III > I



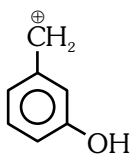
III



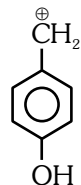
IV



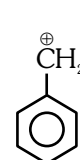
I
 $-OH$ group shows $+M$ effect
 $+M_o = +M_p$ and $+M_m = 0$ but $-I_o > -I_m > -I_p$ and $+M \gg -I$
So $+M$ stabilize the carbocation by decreasing positive charge
Stability order III > I > IV > II



II



III



IV

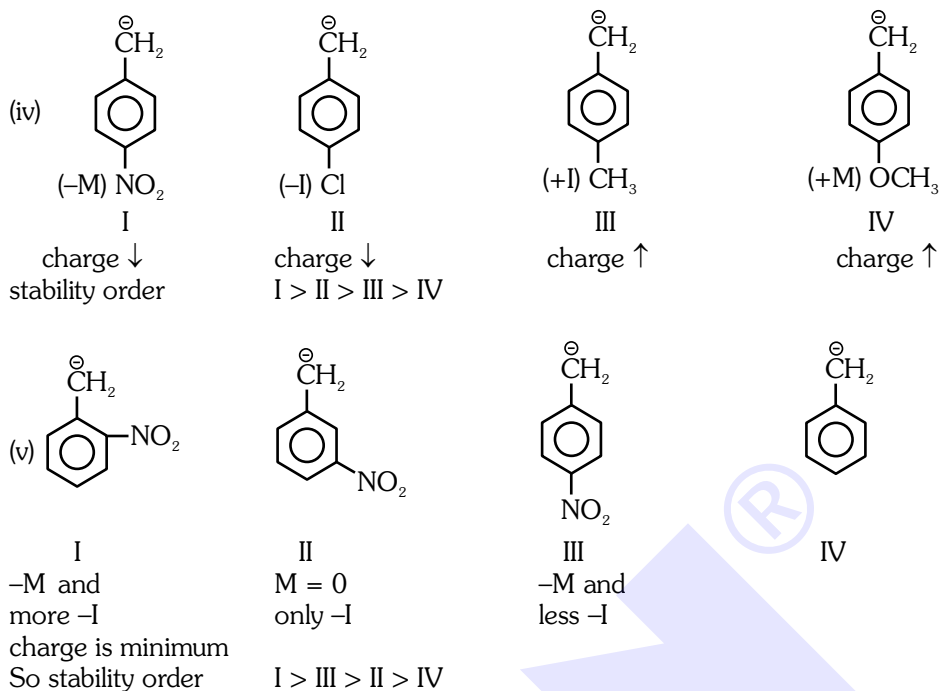
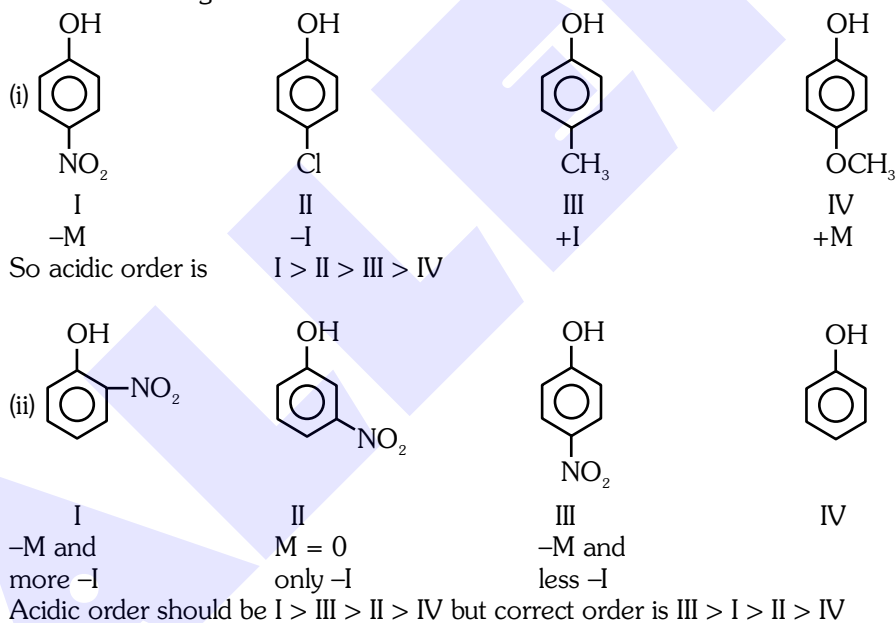
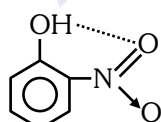


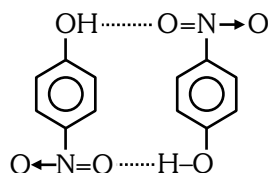
Illustration 4. Give acidic strength order for :



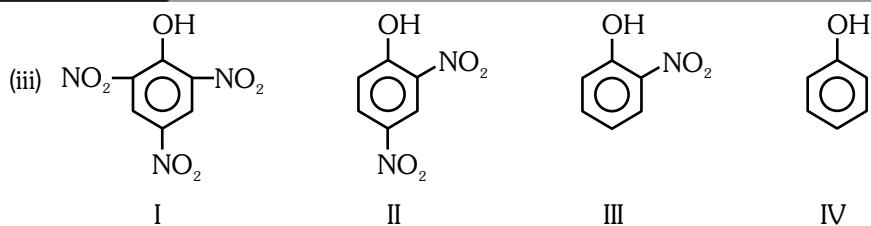
Reason : Due to intramolecular H-bonding in ortho nitrophenol, it is less acidic than para nitrophenol.



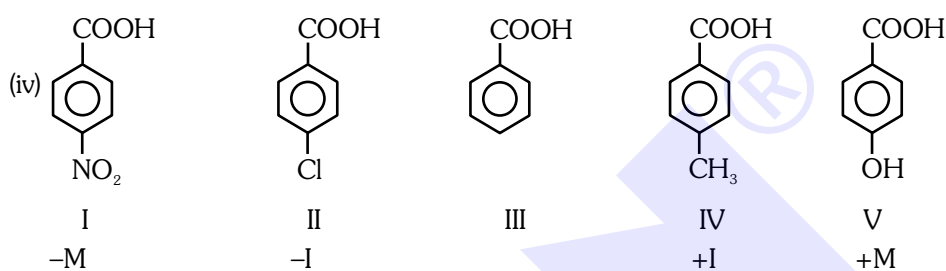
- intramolecular H-bonding
- less association
- less B.P.
- more volatile
- less acidic
- less soluble in water.



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



maximum -M and
maximum -I effect
so maximum acidic
Acidic order I > II > III > IV



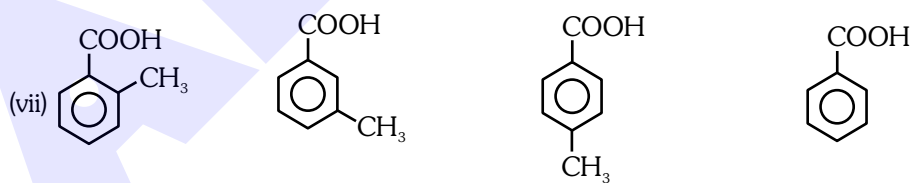
acidic order is I > II > III > IV > V



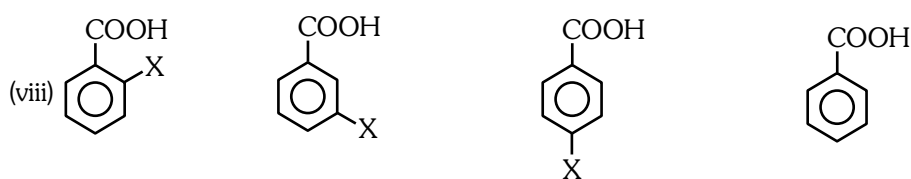
Acidic order is I > III > II



ortho effect only -I -I and -M
Acidic order is $\Rightarrow o > p > m > \text{benzoic acid}$

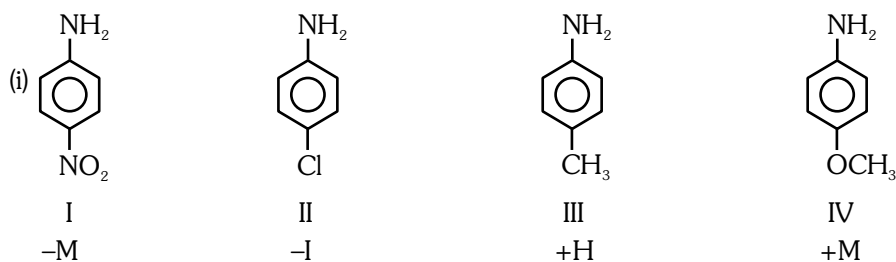


ortho effect only +I +I and +H
Acidic order is $\Rightarrow o > \text{benzoic acid} > m > p$



ortho effect -I (more) -I (less)
Acidic order is $\Rightarrow o > m > p > \text{benzoic acid}$

Illustration 5. Give basic strength order for :



Basic strength order $IV > III > II > I$



SIP
 -M and -I only -I -M and -I
 Basic strength order is \Rightarrow aniline $>$ m $>$ p $>$ o



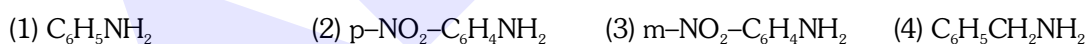
SIP only +I +H and +I
 Basic strength order is \Rightarrow p $>$ m $>$ aniline $>$ o

BEGINNER'S BOX-5

1. Most acidic among the following is :

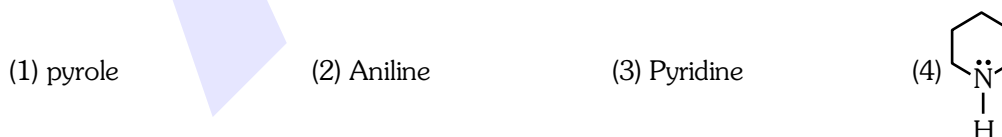


2. Among the following, the strongest base is :-

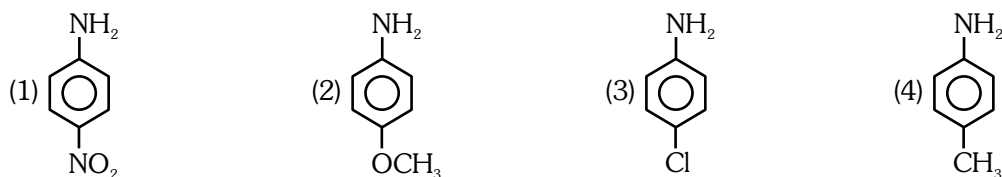


GC0023

3. Which is strongest base ?



4. Which of the following is least basic :-



GC0030

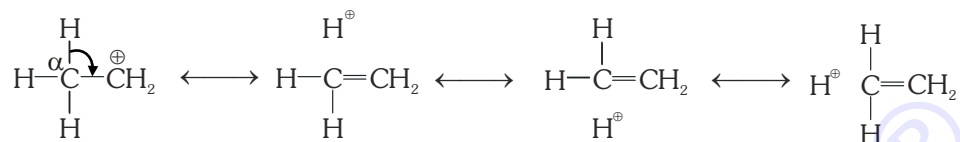
3.4.3 HYPERCONJUGATION EFFECT (H-EFFECT)

Complete transfer of e^- of C-H σ bond towards π bond or positive charge or unpaired electron is called as H-effect (permanent effect). It is also called as No bond resonance (given by Nathen and Baker).

□ CONDITIONS OF H-EFFECT :

1. If there is C-H σ bond and positive charge are in conjugation

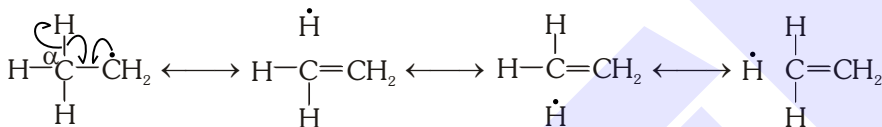
Carbon which is attached to positively charged carbon is called as α -C and H which is attached to α -C is called as α -H. So if number of α -H are more, then there will be more number of hyperconjugating structures, so more stable will be the carbocation.



all are called as hyperconjugating structures or canonical structures.

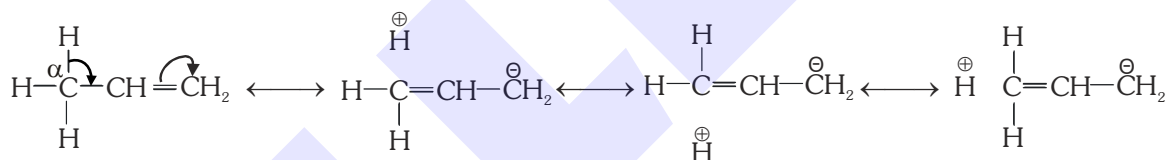
2. If there is C-H σ bond and unpaired electron are in conjugation then there will be H-effect.

Carbon, which is attached to C having unpaired e^- , is called as α -C and H which are attached to α -C are called as α -H.

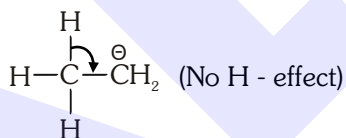


3. If there is C-H σ bond and π bond are in conjugation then there will be H-effect.

sp^3 carbon which is attached to double bonded C is called as α -C and H attached to α -C is called as α -H.



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



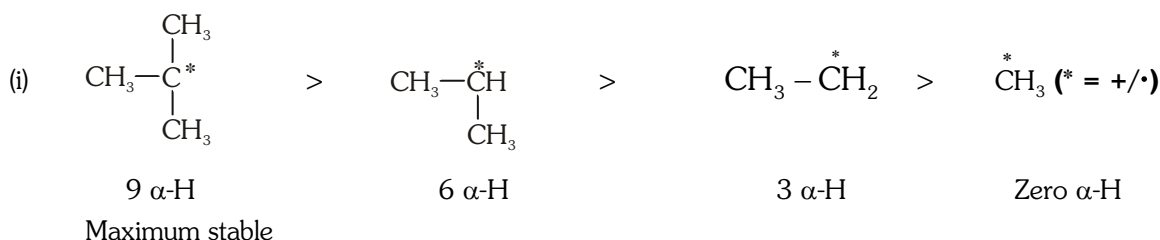
no shifting of C-H σ bond, because anion is having complete octet. ($8e^-$)

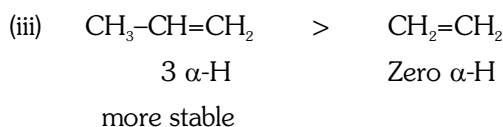
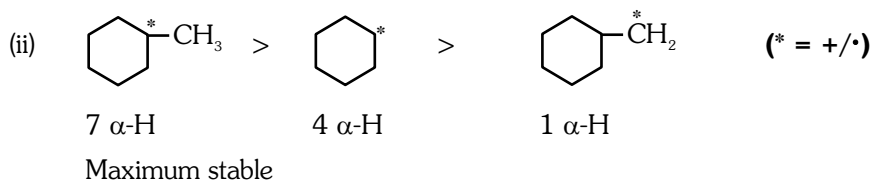
□ APPLICATION OF H-EFFECT

□ Stability of carbocation / Free Radical / Alkene

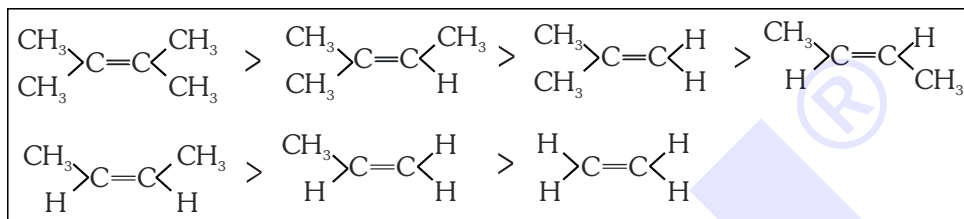
◆ Stability \propto No. of hyperconjugating structures \propto No. of α H.

Example : Give stability order for :-



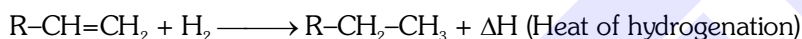


(iv) Stability order of alkenes will be



GOLDEN KEY POINTS

Heat of hydrogenation :



Heat evolved when one mole any unsaturated hydrocarbon is hydrogenated is called heat of hydrogenation (ΔH)

(If alkene is more reactive towards hydrogen then it will evolve more ΔH)

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

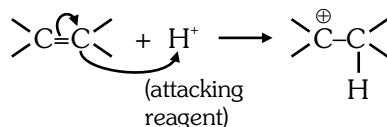
BEGINNER'S BOX-6

- Which of the following alkene is most stable ($\text{R} = \text{CH}_3$).
 (1) $\text{R}_2\text{C=CR}_2$ (2) R-CH=CR_2 (3) R-CH=CH-R (4) R-CH=CH_2
- Which of the following has minimum heat of hydrogenation.
 (1) ethene (2) Propene (3) cis-2-butene (4) trans-2-butene
- Which of the following is most stable.
 (1) Conjugated alkadiene ($\text{CH}_2\text{=CH-CH=CH}_2$) (2) Isolated alkadiene ($\text{CH}_2\text{=CH-CH}_2\text{-CH=CH}_2$)
 (3) Cumulated alkadiene ($\text{CH}_2\text{=C=CH}_2$) (4) All are equal.
- Among the following the strongest acid is :-
 (1) CH_3COOH (2) $\text{C}_6\text{H}_5\text{COOH}$ (3) $m\text{-CH}_3\text{OC}_6\text{H}_4\text{COOH}$ (4) $p\text{-CH}_3\text{OC}_6\text{H}_4\text{COOH}$

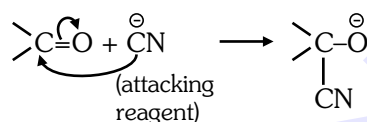
3.4.4 ELECTROMERIC EFFECT : (E Effect)

Complete transfer of a shared pair of π -electrons from one atom to another atom in presence of attacking reagent, is known as 'E' effect.

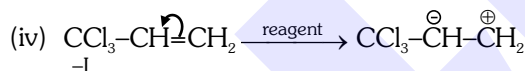
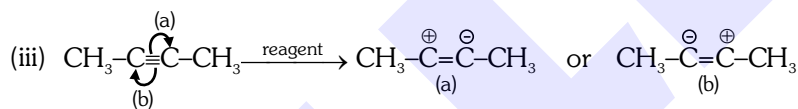
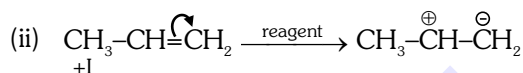
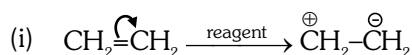
- (i) **Positive Electromeric Effect (+ E effect)** : In this effect the π -electrons of the multiple bond are transferred to that atom to which the reagent gets attached. For example :



- (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.

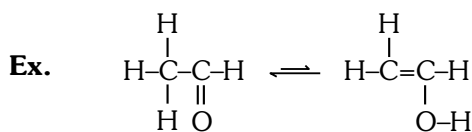
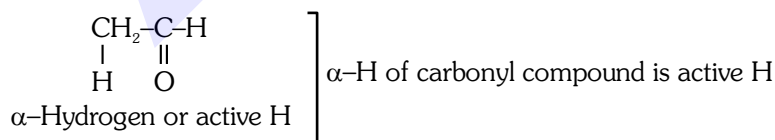


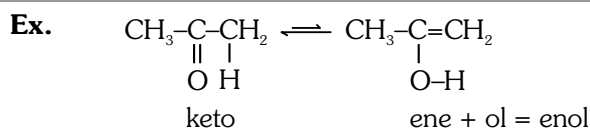
Shifting of π electrons :



3.5 TAUTOMERISM OR DESMOTROPISM

- Tautomers have same molecular formula but different structural formula due to migration of active hydrogen from one polyvalent atom to another polyvalent atom. This phenomena is known as tautomerism.
- Desmotropism means bond turning. [Desmos = Bond; Tropos = Turn]



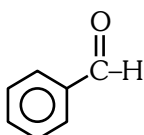
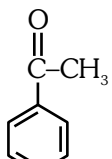
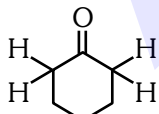
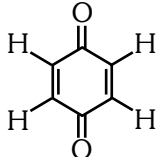


Note : (1) Tautomers exist in dynamic equilibrium.

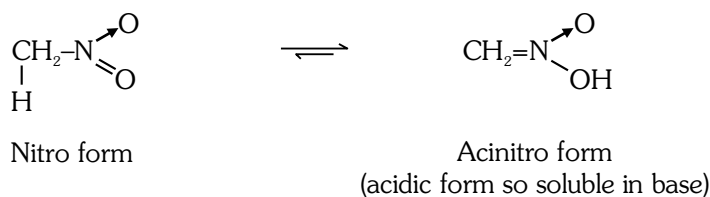
(2) By shifting of H-atom, π bond also changes its position.

(I) Condition for Tautomerism :

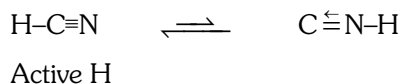
(a) For carbonyl compounds :- Carbonyl compounds having at least one active-H (α -H) show tautomerism

- | | | |
|------------------------------------------------------------------------------------------------------------------------------------|-----------------------------------------------------------------------------|----------------------------------|
| (i) $\text{CH}_3-\text{C}-\text{H}$
\parallel
O | 3 α H, | shows tautomerism. |
| (ii) $\text{CH}_3-\text{C}-\text{CH}_3$
\parallel
O | 6 α H, | shows tautomerism |
| (iii) $\text{CH}_3-\text{CH}-\text{C}-\text{H}$
$\quad \quad \parallel$
$\quad \quad \text{CH}_3 \quad \text{O}$ | 1 α H, | shows tautomerism |
| (iv) $\text{H}-\text{C}-\text{H}$
\parallel
O | No α H, | No tautomerism |
| (v)  | No α H, | No Tautomerism |
| (vi)  (Acetophenone) | 3 α H, | shows tautomerism (Acetophenone) |
| (vii) $\text{Ph}-\text{C}-\text{Ph}$ (Benzophenone)
\parallel
O | No α H, | No tautomerism (Benzophenone) |
| (viii) $\text{Ph}-\text{C}-\text{CH}_2-\text{C}-\text{Ph}$
$\parallel \quad \quad \parallel$
$\text{O} \quad \quad \text{O}$ | 2 α H, | shows tautomerism |
| (ix)  | 4 α H, | shows tautomerism |
| (x)  | α -H, attached sp^2 carbon does not initiate in tautomerism | |

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



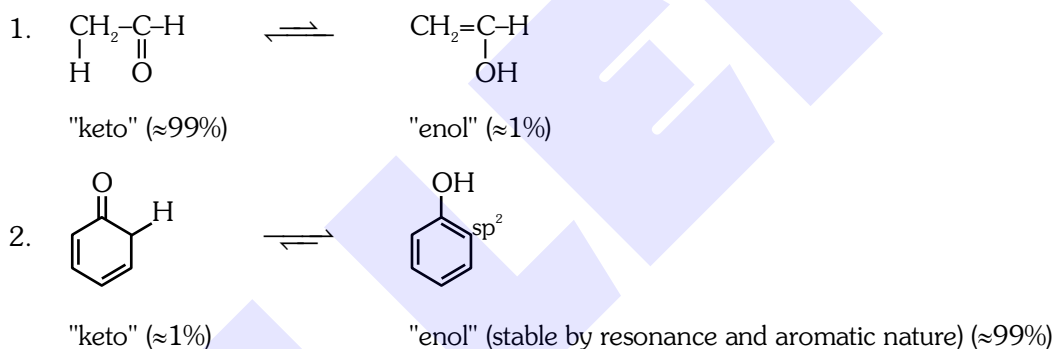
(c) $\text{H}-\text{C}\equiv\text{N}$ and $\text{H}-\text{N}\equiv\text{C}$ are tautomers [also Functional isomers] while $\text{R}-\text{C}\equiv\text{N}$ and $\text{R}-\text{N}\equiv\text{C}$ are only Functional isomers.



(d) $\text{H}-\text{N} \begin{array}{l} \nearrow \text{O} \\ \searrow \text{O} \end{array}$ and $\text{H}-\text{O}-\text{N}=\text{O}$ are tautomers.

Note : Nitro compounds with at least one α -H are soluble in NaOH.

(II) Enol Content :

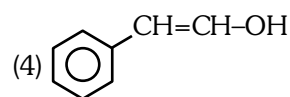
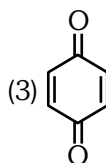
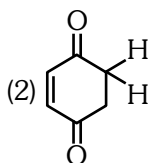
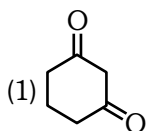


GOLDEN KEY POINTS

- More active the H, more will be its participation in tautomerism.
- Stability of enol form depends on (i) Resonance and (ii) H – Bond (iii) Aromaticity.

BEGINNER'S BOX-7

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

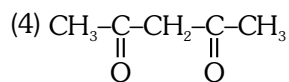
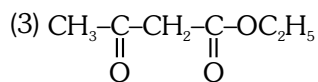
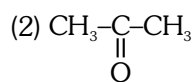
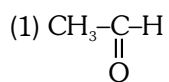


2. Tautomerism is due to :-

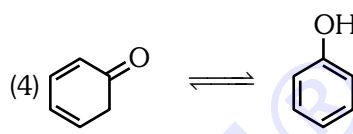
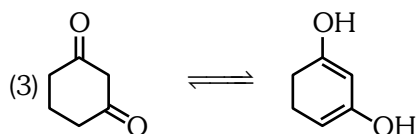
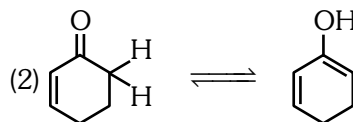
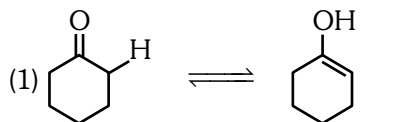
- | | |
|---------------------------------------|------------------------------------|
| (1) Delocalization of sigma electrons | (2) Delocalization of pi electrons |
| (3) Migration of active-H-atom | (4) None is correct |

GC0055

3. Which of the following has highest enol content.



4. In which of the following reaction most stable enol is present.



ANSWER'S KEY

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

BEGINNER'S BOX-2	Que.	1	2	
	Ans.	1	1	

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

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

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

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

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