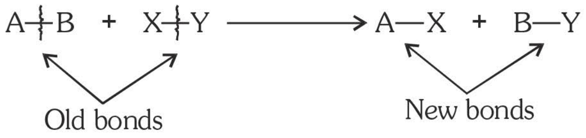
GENERAL ORGANIC CHEMISTRY

- **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 :

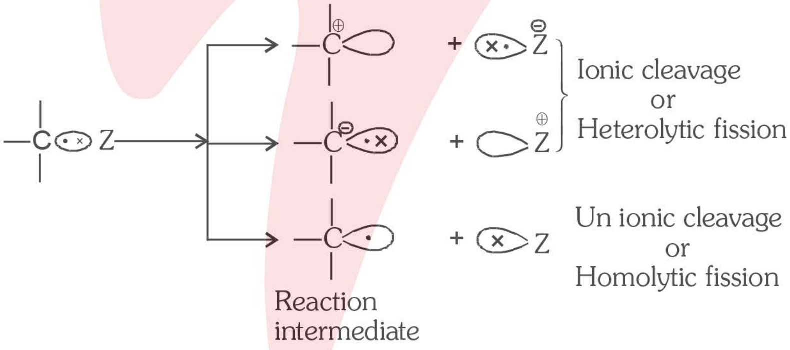
(1) Bond cleavage (2) Attacking reagent (3) Reaction intermediate (4) Electronic effect

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 :

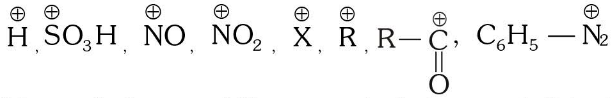
(a) Electrophilic reagent or electrophiles:

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 :



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

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

(a) All Lewis acids as :
BF_3, $AlCl_3$, SO_3, $ZnCl_2$, $BeCl_2$, $FeCl_3$, $SnCl_2$, CO_2, $SnCl_4$.

(b) Free radicals, 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.

$$\text{Nucleophilic} \qquad \begin{array}{c}(\text{Nucleo} + \text{philes}) \\ \downarrow \\ (\text{Nucleus} + \text{loving})\end{array}$$

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

- Nucleophiles can be considered as Lewis base.

(i) Negatively charged nucleophiles.

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

(ii) Neutral nucleophiles :

(a) Lone pair containing

$$H_2\underset{\cdot\cdot}{\ddot{O}}, R-\underset{\cdot\cdot}{\ddot{O}}H, R-\underset{\cdot\cdot}{\ddot{O}}-R, \ddot{N}H_3, R-\ddot{N}H_2, R_3\ddot{N},$$

(b) πe^- containing

$CH_2=CH_2$, $CH\equiv CH$, 

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

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

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

Examples :- $K^{\oplus\ominus}O—N=O, \ddot{N}H_2–\underset{\cdot\cdot}{\ddot{O}}H, \overset{\oplus}{Na}\overset{\ominus}{\ddot{C}}\equiv\ddot{N}$

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 (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 ($-\ddot{N}:$)

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.

3.4 ELECTRONIC EFFECTS :

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

(1) Inductive effect
(2) Mesomeric effect
(3) Hyperconjugation
(4) Electromeric effect

3.4.1 INDUCTIVE EFFECT (I-EFFECT) :

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

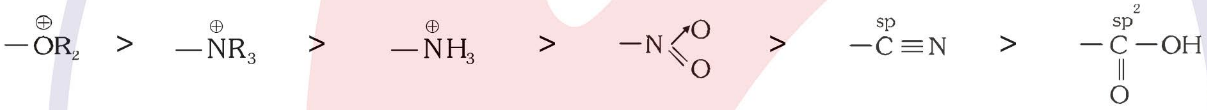
GOLDEN KEY POINTS

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

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

- I-effect of hydrogen is considered as zero.

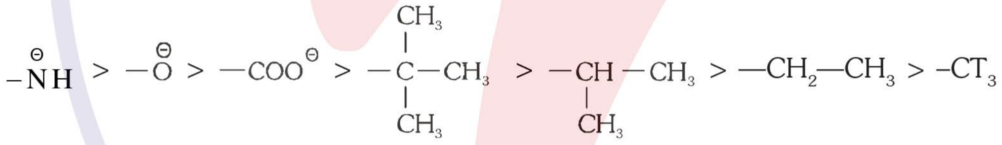
–I groups :



$-\overset{\oplus}{O}R_2 > -\overset{\oplus}{N}R_3 > -\overset{\oplus}{N}H_3 > -NO_2 > -\overset{sp}{C}\equiv N > -\underset{\underset{O}{\|}}{\overset{sp^2}{C}}-OH$

$—X > -OR > -OH > -C\equiv CH > -NH_2 > Ph > -CH=CH_2 > H(I\approx O)$

+I groups :



$-\overset{\ominus}{N}H > -\overset{\ominus}{O} > -COO^{\ominus} > -\underset{CH_3}{\overset{CH_3}{C}}-CH_3 > -\underset{CH_3}{CH}-CH_3 > -CH_2-CH_3 > -CT_3$

$—CD_3 > —CH_3 > T > D > H(I\approx O)$

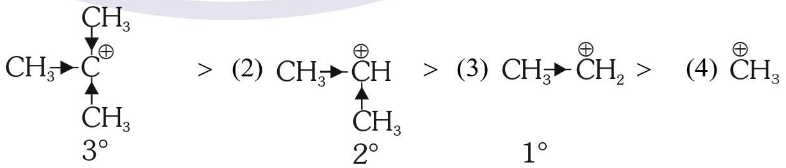
APPLICATION OF I-EFFECT

(1) Stability of carbocation :

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

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

Example : Stability order : (1)

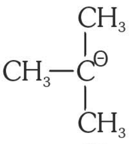


(1) $CH_3\rightarrow\underset{\underset{CH_3}{\uparrow}}{\overset{\overset{CH_3}{\downarrow}}{\overset{\oplus}{C}}}$ 3° > (2) $CH_3\rightarrow\underset{\underset{CH_3}{\uparrow}}{\overset{\oplus}{C}H}$ 2° > (3) $CH_3\rightarrow\overset{\oplus}{C}H_2$ 1° > (4) $\overset{\oplus}{C}H_3$

Reason : More no. of +I group.
more stable carbocation.
so stability order 1 > 2 > 3 > 4.

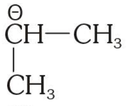
(2) Stability of carbanion :

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

Example: (1)


$CH_3-\overset{\ominus}{C}(CH_3)_2$

3°

(2)


$\overset{\ominus}{C}H(CH_3)-CH_3$

2°

(3) $CH_3-\overset{\ominus}{C}H_2$

1°

(4) $\overset{\ominus}{C}H_3$

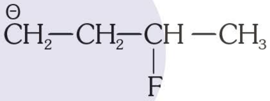
More No. of +I group.

Less stable carbanion.

So stability order 4 > 3 > 2 > 1

Example : (1)


$\overset{\ominus}{C}H_2-CH(F)-CH_2-CH_3$

(2)


$\overset{\ominus}{C}H_2-CH_2-CH(F)-CH_3$

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

Minimum distance of –F.

Maximum –I of –F.

Minimum negative charge.

Maximum stable.

So stability order 1 > 2 > 3

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

Maximum –I of F.

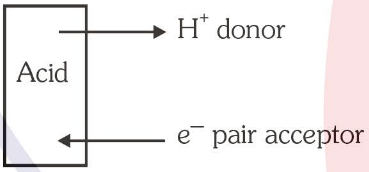
Negative charge will be minimum.

Maximum stable.

So stability order 1 > 2 > 3

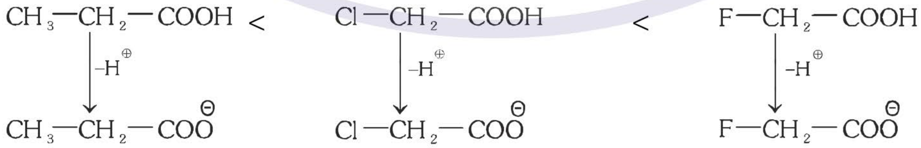
(3) Acidic and basic strength :

◆ **Acidic strength :**



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

Example :

(i)


$$CH_3-CH_2-COOH \xrightarrow{-H^{\oplus}} CH_3-CH_2-COO^{\ominus} \quad < \quad Cl-CH_2-COOH \xrightarrow{-H^{\oplus}} Cl-CH_2-COO^{\ominus} \quad < \quad F-CH_2-COOH \xrightarrow{-H^{\oplus}} F-CH_2-COO^{\ominus}$$

+I of $-CH_3$

anion is less stable

Maximum –I of –F

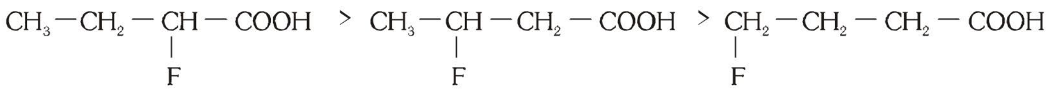
Maximum stable anion

Corresponding acid is maximum acidic.

(ii) $CCl_3-COOH > CBr_3-COOH > CI_3-COOH$

maximum –I of Cl
so maximum acidic.

(iii)



$$CH_3-CH_2-\underset{\large F}{\underset{|}{CH}}-COOH > CH_3-\underset{\large F}{\underset{|}{CH}}-CH_2-COOH > \underset{\large F}{\underset{|}{CH_2}}-CH_2-CH_2-COOH$$

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

(iv)

$$\underset{NO_2}{\underset{|}{CH_2}}-COOH > \underset{H}{\underset{|}{CH_2}}-COOH > \underset{CH_3}{\underset{|}{CH_2}}-COOH$$

–I of NO_2 maximum acidic

+I of $-CH_3$

(v) $HCOOH > CH_3-COOH > CH_3-CH_2-COOH$

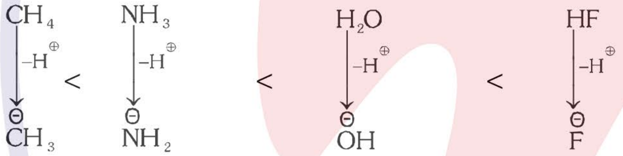
maximum +I
minimum acidic

(vi)

$$\begin{array}{c} COOH \\ | \\ COOH \end{array} > CH_2\begin{array}{l} \diagup COOH \\ \diagdown COOH \end{array} > \begin{array}{l} CH_2-COOH \\ | \\ CH_2-COOH \end{array}$$

minimum distance of –COOH from other
maximum –I of –COOH on other
maximum acidic

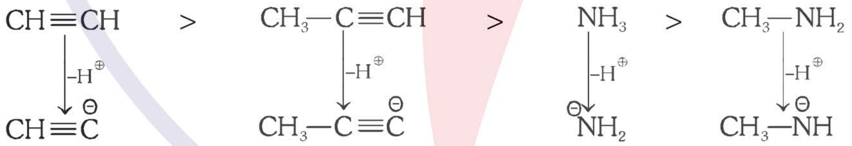
(vii)



$$\begin{array}{c} CH_4 \\ \downarrow {\scriptstyle -H^{\oplus}} \\ \overset{\ominus}{C}H_3 \end{array} < \begin{array}{c} NH_3 \\ \downarrow {\scriptstyle -H^{\oplus}} \\ \overset{\ominus}{N}H_2 \end{array} < \begin{array}{c} H_2O \\ \downarrow {\scriptstyle -H^{\oplus}} \\ \overset{\ominus}{O}H \end{array} < \begin{array}{c} HF \\ \downarrow {\scriptstyle -H^{\oplus}} \\ \overset{\ominus}{F} \end{array}$$

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

(viii)



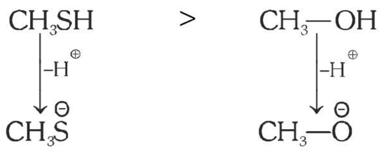
$$\begin{array}{c} CH\equiv CH \\ \downarrow {\scriptstyle -H^{\oplus}} \\ CH\equiv\overset{\ominus}{C} \end{array} > \begin{array}{c} CH_3-C\equiv CH \\ \downarrow {\scriptstyle -H^{\oplus}} \\ CH_3-C\equiv\overset{\ominus}{C} \end{array} > \begin{array}{c} NH_3 \\ \downarrow {\scriptstyle -H^{\oplus}} \\ \overset{\ominus}{N}H_2 \end{array} > \begin{array}{c} CH_3-NH_2 \\ \downarrow {\scriptstyle -H^{\oplus}} \\ CH_3-\overset{\ominus}{N}H \end{array}$$

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

+I of $-CH_3$

+I of $-CH_3$

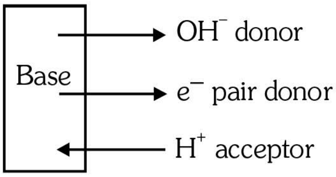
(ix).



$$\begin{array}{c} CH_3SH \\ \downarrow {\scriptstyle -H^{\oplus}} \\ CH_3\overset{\ominus}{S} \end{array} > \begin{array}{c} CH_3-OH \\ \downarrow {\scriptstyle -H^{\oplus}} \\ CH_3-\overset{\ominus}{O} \end{array}$$

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

- **Basic strength :**



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

Ex.: (1) CH_3NH_2 (2) $C_2H_5NH_2$ (3) $C_3H_7NH_2$ (4) $C_4H_9NH_2$

Ans. 4 > 3 > 2 > 1

Maximum +I

so maximum basic

3.4.2 RESONANCE OR MESOMERIC EFFECT

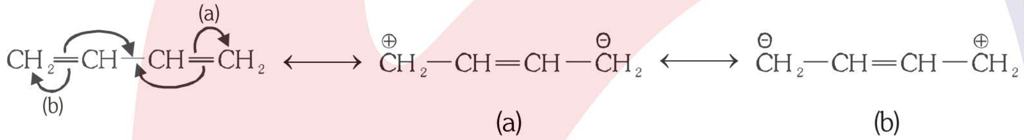
Delocalization of π e^- is called as resonance or complete transfer of πe^- from one atom to another atom when they are in conjugation with difference of only one σ bond is called as **Resonance**.

Types of conjugations :

(1) π–π conjugation.

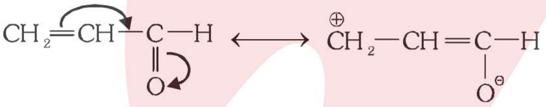
If there are two π bonds in conjugation then e^- of one π bond are transferred towards another π bond.

Ex. (i)



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

(ii)



$CH_2=CH-\underset{\underset{O}{\|}}{C}-H \longleftrightarrow \overset{\oplus}{C}H_2-CH=\underset{\underset{O^{\ominus}}{|}}{C}-H$

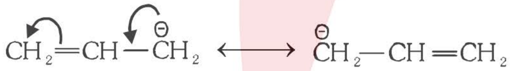
(2) π– lone pair conjugation

If there is lone pair or a negative charge and π bond are in conjugation then lone pair of e^- or negative charge are transferred towards π bond.

Ex. (i)

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

(ii)



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

(3) π– vacant orbital conjugation

If there is positive charge (vacant orbital) and π bond are in conjugation then e^- of π bond are transferred towards positive charge.

Ex.

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

(4) π– unpaired electron conjugation

If there is unpaired e^- and π bond are in conjugation.

Ex.

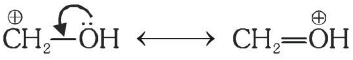
$CH_2=CH-\dot{C}H_2 \longleftrightarrow \dot{C}H_2-CH=CH_2$

[⌒ = transfer of unpaired e^-]

(5) lone pair - vacant orbital conjugation

If there is lone pair or negative charge and positive charge (vacant orbital) are in conjugation then e^- of lone pair or negative charge are transferred towards positive charge.

Ex.



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

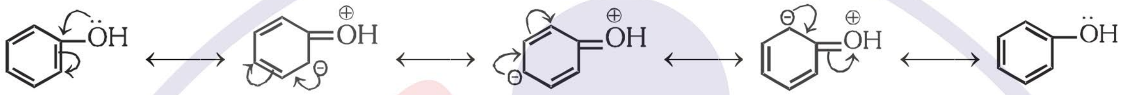
GOLDEN KEY POINTS

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.

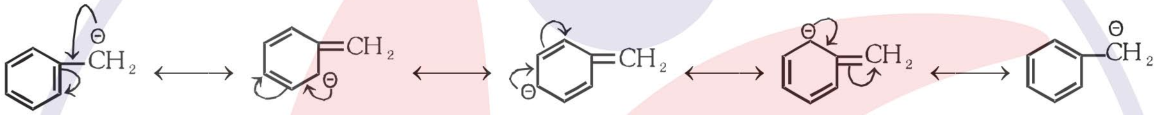
Draw resonating structures :

1.



5-Resonating structures

2.

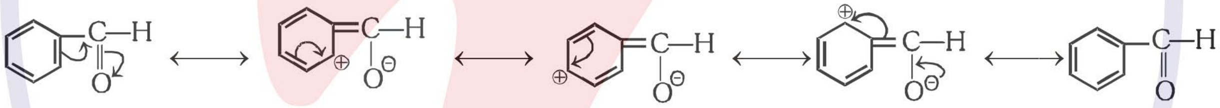


5-Resonating structures

3.

5-Resonating structures

4.



5-Resonating structures

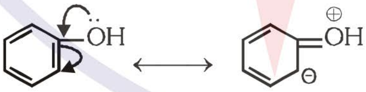
M-effect : Delocalisation of electron in conjugated system (due to presence of EWG or EDG) is known as 'M' effect.

(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. $-\ddot{N}H_2$, $-\ddot{\underset{..}{O}}H$, $-\ddot{\underset{..}{O}}R$, $-\ddot{N}R_2$, $-\ddot{\underset{..}{S}}H$, $-\ddot{N}HR$, $-\ddot{\underset{..}{X}}\!:$, $-\ddot{N}HCOCH_3$

eg.



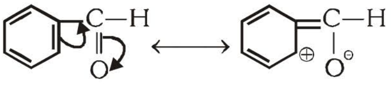
–OH group lone pair donor

So + M of –OH group

(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 : —CHO, —COOH, —COOR, —COR, $—NO_2$, —CN, —COX, $—CONH_2$, $—SO_3H$

eg.



–CHO group withdrawing e^-.

So –CHO is –M group

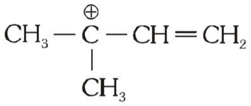
APPLICATIONS OF RESONANCE EFFECT :

(1) Stability of carbocation.

Ex. Give stability order for :-

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

stabilized by resonance (SBR) | +I of Alkyl group | –I of Alkenyl group

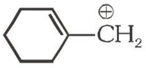
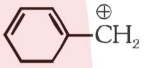
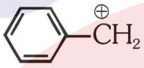
(ii) 

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

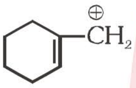
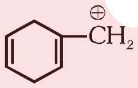
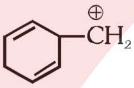
SBR and +I of two $-CH_3$ | SBR and +I of one $-CH_3$ | SBR only

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

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

(iv)  <  < 

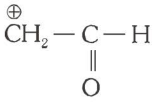
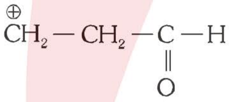
maximum resonance

(v)  >  > 

SBR and + I | SBR and – I | No. reso.

(vi)  >  > 

more resonance | less resonance | localized ⊕ charge

(vii)  < 

$\overset{\oplus}{C}H_2-\underset{\underset{O}{\|}}{C}-H$ < $\overset{\oplus}{C}H_2-CH_2-\underset{\underset{O}{\|}}{C}-H$

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

No reso.
less –I of —CHO

(2) Stability of carbanion :

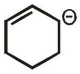
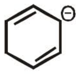
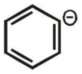
Ex. Give stability order of :

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

SBR | negative on more EN

stability order I > II > III

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

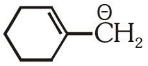
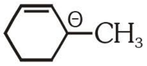
(iii) I.  II.  III. 

resonance stable | more resonance stable | localized ⊖ charge

stability order II > I > III

(iv) $\overset{\ominus}{C}H_2-NO_2$ SBR $\overset{\ominus}{C}H_2-CH_2-NO_2$ no. reso $CH_3-\overset{\ominus}{C}H-NO_2$ SBR but +I of CH_3

stability order I > III > II

(v) I.  II.  III. 

SBR and +I SBR SBR and more +I

stability order II > I > III

(3) Stability of free radicals.

Ex. Give stability order for :

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

stability order III > I > II

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

$CH_3\dot{C}H_2 > \dot{C}H_3$

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

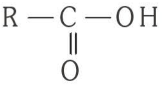
(i) Complete octet R.S. is more stable than incomplete octet.

(ii) Nonpolar R.S. is more stable than polar resonating structures.

(iii) For charged R.S. negtive charge on more EN and positive charge on less EN is more stable.

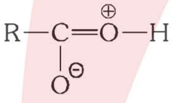
(iv) Opposite charge must be closer and same charge must be farther for greater stability.

Ex. Arrange the following for stability order.

(i) 

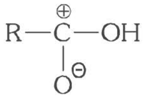
$R-\underset{\underset{O}{\|}}{C}-OH$

>



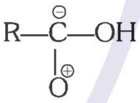
$R-\underset{\underset{O^{\ominus}}{|}}{C}=\overset{\oplus}{O}-H$

>



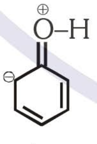
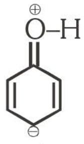
$R-\underset{\underset{O^{\ominus}}{|}}{\overset{\oplus}{C}}-OH$

>



$R-\underset{\underset{O^{\oplus}}{|}}{\overset{\ominus}{C}}-OH$

complete octet, nonpolar complete octet, polar incomplete octet more EN atom incomplete octet

(ii)  > 

opposite charge closer opposite charge farther

(iii) $R-\overset{\oplus}{C}=O$ < $R-C\equiv\overset{\oplus}{O}$

incomplete octet complete octet

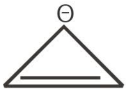
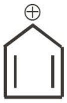
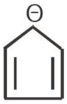
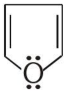
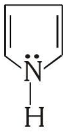
(iv) $CH_2=CH-\overset{\ominus}{O}$ > $\overset{\ominus}{C}H_2-CH=O$

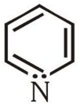
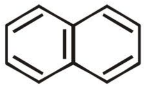
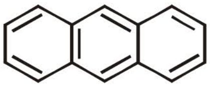
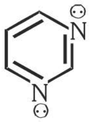
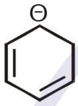
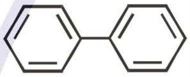
(negative charge on more EN) (negative charge on less EN)

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

Note : $[4n + 2]$ π 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

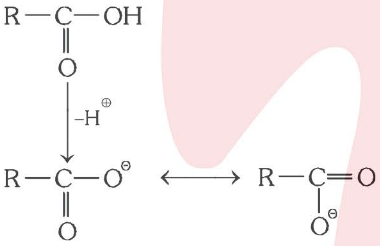
S.No	Compound	Cyclic	Plannar	Cyclic Resonance	Huckel Rule $(4n+2)$ πe^-	Aromatic Yes/No
1.		✔	✔	✔	$2\pi e^-$	Yes
2.		✔	✔	✔	$4\pi e^-$	No
3.		✔	✔	✔	$4\pi e^-$	No
4.		✔	✔	✔	$6\pi e^-$	Yes
5.		✔	✔	✔	$6\pi e^-$	Yes
6.		✔	✘	✘	$4\pi e^-$	No
7.		✔	✔	✔	$6\pi e^-$	Yes
8.		✔	✔	✔	$6\pi e^-$	Yes
9.		✔	✔	✔	$6\pi e^-$	Yes
10.		✔	✔	✔	$6\pi e^-$	Yes

11.		✔	✔	✔	6πe⁻	Yes
12.		✔	✔	✔	10πe⁻	Yes
13.		✔	✔	✔	14πe⁻	Yes
14.		✔	✔	✔	6πe⁻	Yes
15.		✔	✘	✘	6πe⁻	No
16.		✔	✔	✔	6πe⁻ + 6πe⁻	Yes

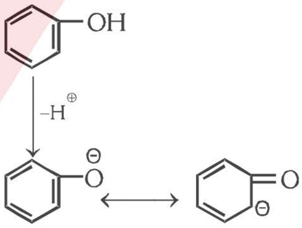
Illustrations

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.

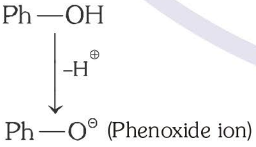


5, unequal R.S. less stable anion since –ve charge is being shared by oxygen is less electronegative carbon.

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

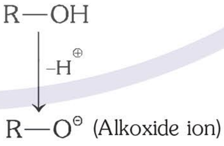
Illustration 2. Phenol is more acidic than alcohols why ?

Solution.



anion stable by resonance

So, corresponding acid is more acidic.



no resonance.

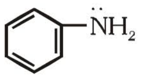
less stable anion

(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.

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

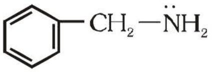
Ex. Give basic strength order :

(i)



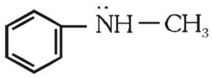
I

l.P. is stabilized by resonance



II

no reso. of l.p. so maximum basic

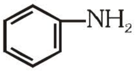


III

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

basic order — II > III > I

(ii)



I

delocalized l.p.

II

localized l.p. on more EN

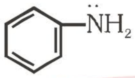
III

localized l.p. on less EN

basic order — III > II > I

(iii)

<



lone pair participate in aromatic sextet so less available

lone pair not participate in aromatic sextet so more available

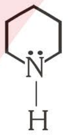
(iv)

I

l.p. on more EN so minimum basic

II

more –I of oxygen



III

+I

IV

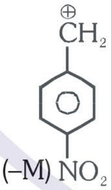
less – I of nitrogen

So, basic order III > IV > II > I

Illustrations

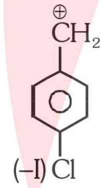
Illustration 3. Give stability order of :

(i)



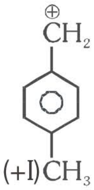
I

charge ↑



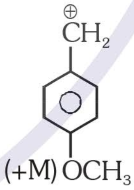
II

charge ↑



III

charge ↓

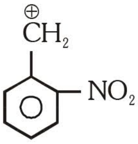


IV

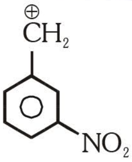
charge ↓

So stability order IV > III > II > I

(ii)

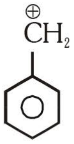


I



II

III

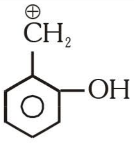


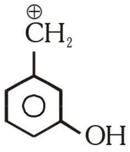
IV

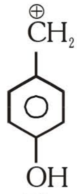
$-M_O = -M_P$ and $-M_m = 0$

but $-I_O > -I_m > -I_P$, –M and –I increases positive charge.

stability order is IV > II > III > I

(iii) 





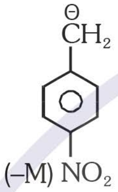
I	II	III	IV

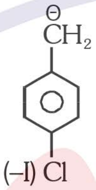
–OH group shows +M effect

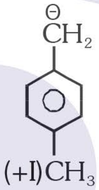
$+\,M_O = +\,M_P$ and $+\,M_m = 0$ but $-I_O > -I_m > -I_P$ and $+\,M >> -\,I$

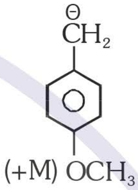
So +M stabilize the carbocation by decreasing positive charge

Stability order III > I > IV > II

(iv) 

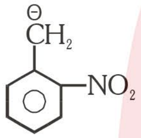


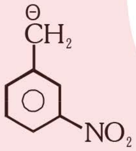


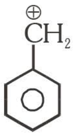


I	II	III	IV
charge ↓	charge ↓	charge ↑	charge ↑

stability order I > II > III > IV

(v) 





I	II	III	IV
–M and more –I	M = 0 only –I	–M and less –I	

charge is minimum

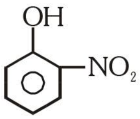
So stability order I > III > II > IV

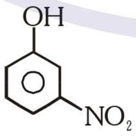
Illustration 4. Give acidic strength order for :

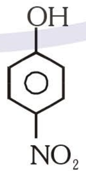
(i) 

I	II	III	IV
–M	–I	+I	+M

So acidic order is I > II > III > IV

(ii) 

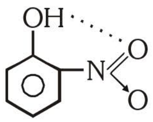


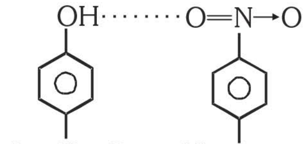


I	II	III	IV
–M and more –I	M = 0 only –I	–M and less –I	

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

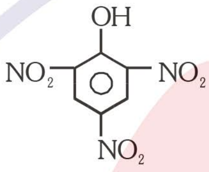
Reason : Due to intramolecular H-bonding in ortho nitrophenol, it is less acidic than para nitrophenol.

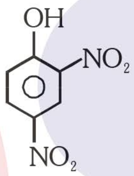


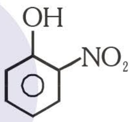


• intramolecular H-bonding	intermolecular H-bonding
• less association	more association
• less B.P.	more B.P.
• more volatile	less volatile
• less acidic	more acidic
• less soluble in water.	more soluble in water.

(iii)



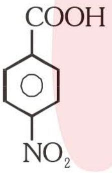


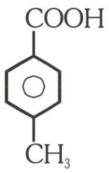


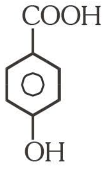
I II III IV

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

(iv)







I –M

II –I

III

IV +I

V +M

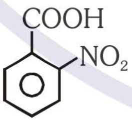
acidic order is I > II > III > IV > V

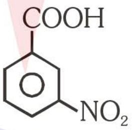
(v) H—COOH CH_3COOH C_6H_5—COOH

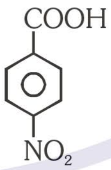
I II III

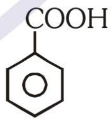
Acidic order is I > III > II

(vi)





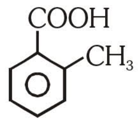


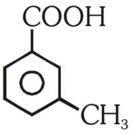


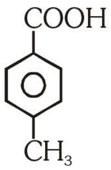
ortho effect only –I –I and –M

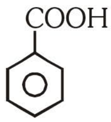
Acidic order is ⇒ o > p > m > benzoic acid

(vii)





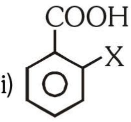


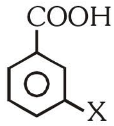


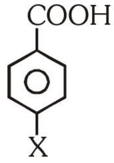
ortho effect only +I +I and +H

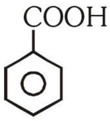
Acidic order is ⇒ o > benzoic acid > m > p

(viii)







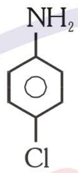


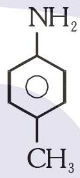
ortho effect –I (more) –I (less)

Acidic order is ⇒ o > m > p > benzoic acid

Illustration 5. Give basic strength order for :

(i)



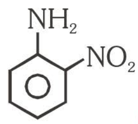


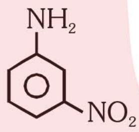
I II III IV

–M –I +H +M

Basic strength order IV > III > II > I

(ii)



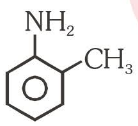


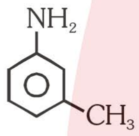
SIP

–M and –I only –I –M and –I

Basic strength order is ⇒ aniline > m > p > o

(iii)





SIP only +I +H and +I

Basic strength order is ⇒ p > m > aniline > o

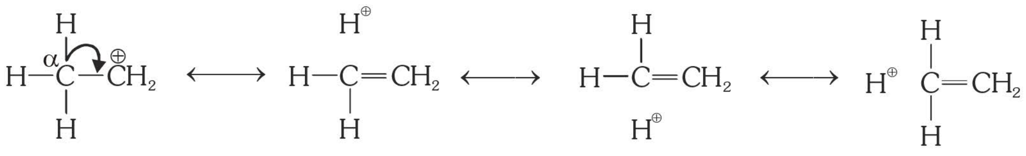
3.4.3 HYPERCONJUGATION EFFECT (H-EFFECT)

Complete transfer of e^- of C–H σ bond towards π bond or positive charge or free 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 :

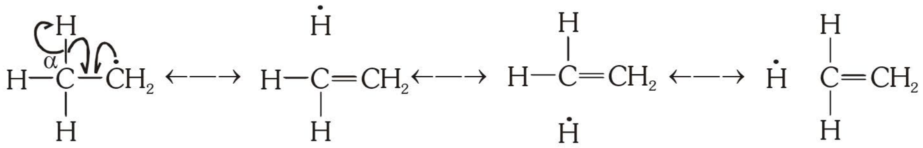
1. If there is C–H σ bond and positive charge are in conjugation

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.

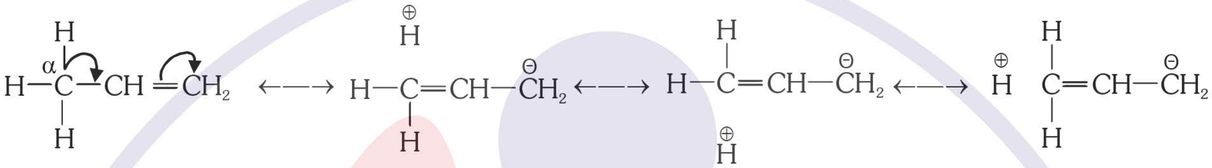


all are called as hyperconjugating structures or canonical structures.

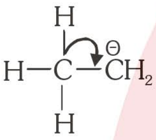
2. If there is C–H σ bond and free e^- are in conjugation then there will be H-effect.
Carbon, which is attached to C having unpaired e^-, is called as α–C and H which are attached to α-C are called as α-H.



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 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 ∝ No. of canonical structures ∝ No. of α H.

Example : Give stability order for :-

(i)

$CH_3-\overset{\displaystyle CH_3}{\underset{\displaystyle CH_3}{C^*}} > CH_3-\underset{\displaystyle CH_3}{\overset{*}{C}H} > CH_3-\overset{*}{C}H_2 > \overset{*}{C}H_3$ **(* = +/·)**

9 α-H 6 α-H 3 α-H Zero α-H

Maximum stable

(ii)

(* = +/·)

7 α-H 4 α-H 1 α-H

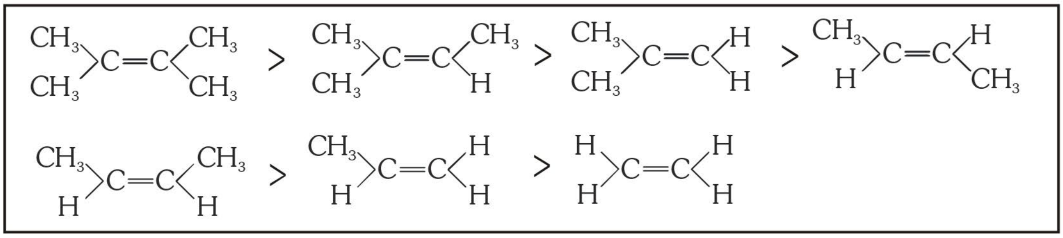
Maximum stable

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

3 α-H Zero α-H

more stable

(iv) Stability order of alkenes will be



GOLDEN KEY POINTS

- **Heat of hydrogenation :**

$R—CH{=}CH_2 + H_2 \longrightarrow R—CH_2—CH_3 + \Delta H$ (Heat of hydrogenation)

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

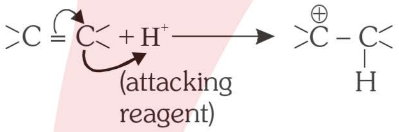
(If alkene is more reactive towards hydrogen then it will evolve more ΔH)

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

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.

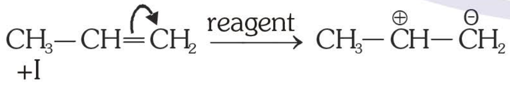
(i) **Positive Eelctromeric Effect (+ E effect) :** In this effect the π -electrons of the multiple bond are transferred to that atom to which the reagent gets attached. For example :

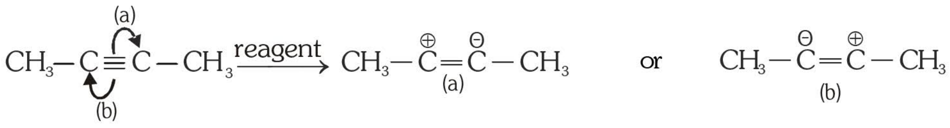


(ii) **Negative Electromeric Effect (-E effect) :** In this effect the π- electrons of the multiple bond are transferred to that atom, to which the attacking reagent does not get attached. For example.

Shifting of π electrons :

(i) 
$CH_2{=}CH_2 \xrightarrow{\text{reagent}} \overset{\oplus}{C}H_2-\overset{\ominus}{C}H_2$

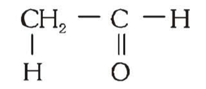
(ii) 
$\underset{+I}{CH_3}-CH{=}CH_2 \xrightarrow{\text{reagent}} CH_3-\overset{\oplus}{C}H-\overset{\ominus}{C}H_2$

(iii) 
$CH_3-C\equiv C-CH_3 \xrightarrow{\text{reagent}} CH_3-\overset{\oplus}{C}=\overset{\ominus}{C}-CH_3$ (a) or $CH_3-\overset{\ominus}{C}=\overset{\oplus}{C}-CH_3$ (b)

(iv) 
$\underset{-I}{CCl_3}-CH{=}CH_2 \xrightarrow{\text{reagent}} CCl_3-\overset{\ominus}{C}H-\overset{\oplus}{C}H_2$

3.5 TAUTOMERISM OR DESMOTROPISM

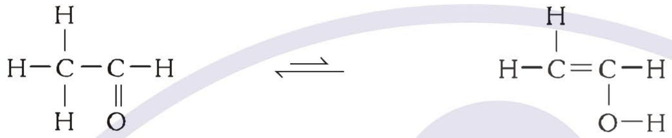
- Tautomers have same molecular formula but different structural formula due to migration of active hydrogen from one polyvalent atom to another polyvalent atom. This pnenomena is known as tautomerism.
- Desmotropism means bond turning. [Desmos = Bond ; Tropos = Turn]



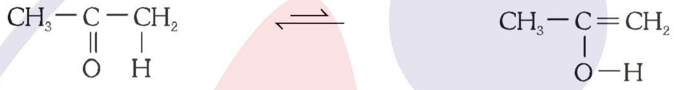
$\underset{H}{\underset{\vert}{CH_2}}-\underset{O}{\underset{\Vert}{C}}-H$

α–Hydrogen or active H

α–H of carbonyl compound is active H

Ex. 

$$H-\underset{H}{\underset{\vert}{\overset{H}{\overset{\vert}{C}}}}-\underset{O}{\underset{\Vert}{C}}-H \rightleftharpoons H-\overset{H}{\overset{\vert}{C}}=\underset{O-H}{\underset{\vert}{C}}-H$$

Ex. 

$$CH_3-\underset{O}{\underset{\Vert}{C}}-\underset{H}{\underset{\vert}{CH_2}} \rightleftharpoons CH_3-\underset{O-H}{\underset{\vert}{C}}=CH_2$$

keto

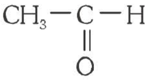
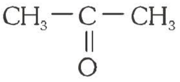
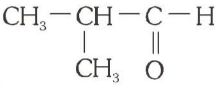
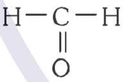
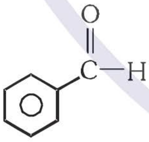
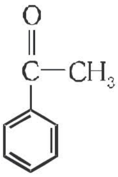
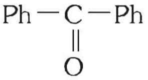
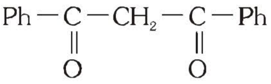
ene + ol = enol

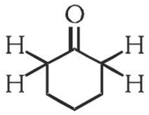
Note : **(1)** Tautomers exist in dynamic equilibrium.

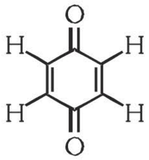
(2) By shifting of H–atom, π bond also changes its position.

(I) Condition for Tautomerism :

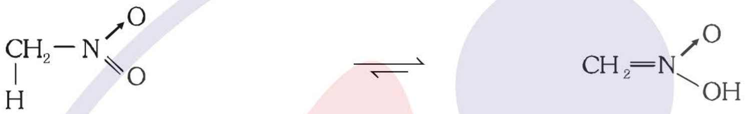
(a) For carbonyl compounds :- Carbonyl compounds having at least one active-H (α–H) show tautomerism

(i)	 $CH_3-\underset{O}{\underset{\Vert}{C}}-H$	3 α H,	shows tautomerism.
(ii)	 $CH_3-\underset{O}{\underset{\Vert}{C}}-CH_3$	6 α H,	shows tautomerism
(iii)	 $CH_3-\underset{CH_3}{\underset{\vert}{CH}}-\underset{O}{\underset{\Vert}{C}}-H$	1 α H,	shows tautomerism
(iv)	 $H-\underset{O}{\underset{\Vert}{C}}-H$	No α H,	No tautomerism
(v)		No α H,	No Tautomerism
(vi)	 (Acetophenone)	3 α H,	shows tautomerism (Acetophenone)
(vii)	 $Ph-\underset{O}{\underset{\Vert}{C}}-Ph$ (Benzophenone)	No α H,	No tautomerism (Benzophenone)
(viii)	 $Ph-\underset{O}{\underset{\Vert}{C}}-CH_2-\underset{O}{\underset{\Vert}{C}}-Ph$	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



Nitro form

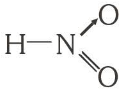
Acinitro form

(acidic form so soluble in base)

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

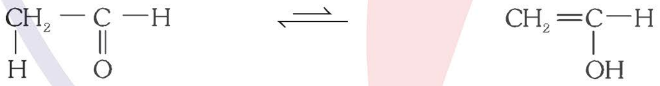
$H—C\equiv N \rightleftharpoons C\equiv N—H$

Active H

(d)  and H—O—N=O are tautomers.

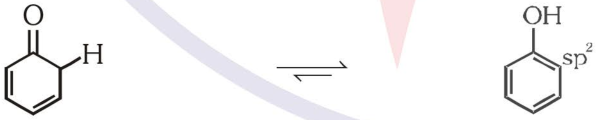
Note : Nitro compounds with at least one α–H are soluble in NaOH.

(II) Enol Content :

1. 

$$CH_3-\overset{\displaystyle O}{\overset{\|}{C}}-H \rightleftharpoons CH_2=\underset{\displaystyle OH}{\underset{|}{C}}-H$$

"keto" (≈ 99%) "enol" (≈ 1%)

2. 

"keto" (≈ 1%) "enol" (stable by resonance and aromatic nature) (≈ 99%)

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.