Page#3

HOMOLYTIC BOND FISSION HOMOLYSIS

The bond cleavage in which each bonded atom gets their own contribution

$$\begin{array}{ccc}
A - B \longrightarrow A^{\circ} + B^{\circ} \\
\text{or} & \downarrow \\
A & B
\end{array}$$
Free Radical

- Cleavage takes place due to
 - HELP (H = Heat, E = Electricity, L = light, P = Peroxide)
- Favoured when E.N. difference is less or zero.
- Cleavage favoured in non polar solvent.

HETROLYTIC BOND FISSION

$$C = A \xrightarrow{C} C + A \xrightarrow{\Phi} (C \text{ is more electronegative})$$

$$C = A \xrightarrow{C} C + A \xrightarrow{\Phi} (A \text{ is more electronegative})$$

$$C = A \xrightarrow{C} C + A \xrightarrow{\Phi} (C \text{ is more electronegative})$$

$$C = A \xrightarrow{C} C + A \xrightarrow{\Phi} (C \text{ is more electronegative})$$

$$C = A \xrightarrow{C} C + A \xrightarrow{\Phi} (C \text{ is more electronegative})$$

$$C = A \xrightarrow{C} C + A \xrightarrow{\Phi} (C \text{ is more electronegative})$$

$$C = A \xrightarrow{C} C + A \xrightarrow{\Phi} (C \text{ is more electronegative})$$

$$C = A \xrightarrow{C} C + A \xrightarrow{\Phi} (C \text{ is more electronegative})$$

(Carbocation or carbonium ion)

- It is formed when the electronegativity difference between the bonded atom is more
- formation is favoured by polar solvent

+ve charge of the solvent attracts the -ve pole of compound and the

-ve pole of the solvent attracts +ve

pole of compound and the bond breaks.

INTERMEDIATES OF ORGANIC COMPOUNDS

	Fre	e Radical	Carbocation	OLYMP Carbanion
(1)	Lone pair	Ourturing po	tent@l through	education
(2)	Bond pair	3	3	3
(3)	Unpaired e⁻	1	×	×
(4)	Bond Angle	120°	120°	1070
(5)	Hybridisation	sp ²	sp ²	sp³
(6)	Shape	Trigonal planer	Trigonal planer	Pyramidal
(7)	Magnetic property	Para magnetic	Diamagnetic	Dia magnetic)
(8)	Stability order	$3^{\circ} > 2^{\circ} > 1^{\circ}$	$3^{\circ} > 2^{\circ} > 1^{\circ}$	1° > 2° > 3°
	(As per inductive			
	effect)			
(9)	e- rich/deficient/poor	ED(Deficient)	ED	ER(Rich)
(10)	Reactivity order	$1^{\circ} > 2^{\circ} > 3^{\circ}$	$1^{\circ} > 2^{\circ} > 3^{\circ}$	3° > 2° > 1°
(11)	+I/-I (stablized)	+I	+I	-I

394 - Rajeev Gandhi Nagar Kota, Ph. No. 0744-2209671, 93141-87482, 93527-21564 IVRS No. 0744-2439051, 0744-2439052, 0744-2439053, www.motioniitjee.com, email-hr.motioniitjee@gmail.com



Page#4

GOC

ELECTRONIC DISPLACEMENT EFFECT

The displacement of electrons with in the same molecule is known as electronic displacement. These effects affect the stability of a species or compound and it also affect the acidic & basic strength.

Electronic Displacement Effect is divided into two parts:-

- (1) Permanent effect
- (2) Temporary effect
- (1) Permanent effect
 - (i) Inductive effect
 - (ii) Mesomeric (resonance) effect
 - (iii) Hyperconjugation
- (2) Temporary effect:
 - (i) Electromeric effect
 - (ii) Inductomeric effect
- (i) Inductive effect:

It is an effect in which permament polarisation arises due to partial displacement of σ -electrons along carbon chain or partial displacement of sigma-bonded electron toward more electronegative atom in carbon chain.

$$+\delta_3 +\delta_2 +\delta_1 -\delta$$

 $C \rightarrow C \rightarrow C \rightarrow CI$

Magnitude of partial positive charge

$$+\delta_1>+\delta_2>+\delta_3=\delta^-$$
 (net charge remain constant in a molecule having inductive effect)

Inductive effect

It is a permament effect

if X i.e more electronegative

(After carbon No. 3 the effect disappears)

$$C \xrightarrow{\delta\delta\delta+} C \xrightarrow{\delta\delta+} C \xrightarrow{\delta-} C \xrightarrow{\delta+} (+ \text{ I effect of Y})$$

*
$$H = \stackrel{\downarrow}{N} = H$$
 $+ \stackrel{\downarrow}{N} = H$ $+ \stackrel{\downarrow}{N} = H$

- * $O^- < O < O^+$ (-I effect order)
- It is a permament effect
- It is caused due to electronegative difference.
- It operates via σ bonded electron.
- It is distance dependent effect.



GOC

Page#5

As distance increases, its effect decreases.

- It can be negalected after third carbon.
- It is a destablising effect.
- It is divided into 2 parts. (On the basis of electronegativity w.r.t. hydrogen atom)
 - (1) +I effect
 - (2) I effect

If any atom or group having electronegativity greater than that of hydrogen. than it is considered as – I effect and vice-versa.

+I effect – I effect

- (i) e- releasing group (i) e- accepting group
- (ii) EN less than H (ii) EN greater than H
- (iii) Those group which are (iii) Those group showing –I effect showing + I effect, disperses disperses + ve charge on the C-chain partial ve charge on the C-chain

Eg.
$$CH_3 - CH_2 - CI (-I \text{ of } CI)$$

Eg.
$$CH_3 - CH = CH_2(-I \text{ of } -CH = CH_2 \& +I \text{ of } -CH_3)$$

Eg.
$$CH_3 - CH_2 - C \equiv CH (-I \text{ of } -C \equiv CH \& + I \text{ of } -CH_2 - CH_3)$$

Eg.
$$CH_2 = CH \longrightarrow (-I \text{ of } -ph)$$

Order of -I effect showing group:

$$- \text{NF}_{3} > - \text{NR}_{3} > - \text{NH}_{3} > - \text{NO}_{2} > - \text{CN} > - \text{C-H} > - \text{C-R} > - \text{C-OH} > - \text{F} > - \text{CI} > - \text{Br} > - \text{I}$$

$$(-\text{I order}) - \text{C} = \text{CH} > - \text{CH} = \text{CH}_{2}$$

$$- \text{CH} = \text{CH}_{2} < \text{CH} > - \text{CH} = \text{CH}_{2}$$

Order of + I effect showing group potential through education

$$-\stackrel{\scriptsize \bigcirc}{\mathrm{CH}_{2}}>-\stackrel{\scriptsize \bigcirc}{\mathrm{NH}}>-\stackrel{\scriptsize \bigcirc}{\mathrm{O}}>-\mathrm{CMe_{3}}>-\mathrm{CHMe_{2}}>-\mathrm{CH_{2}Me}>\mathrm{CT_{3}}>\mathrm{CD_{3}}>\mathrm{CH_{3}}>\mathrm{T}>\mathrm{D}>\mathrm{H}$$

Bond Strength: $CT_3 > CD_3 > CH_3$ (+ I of T > D > H)

Q. Why carbon - hydrogen bond is longer than C - T bond

Ans. As the mass increases, vibration decreases as a result of which the heavier isotope will be more closer to the C-atom for a longer time. There for C – T bond is stronger C – T > C – D > C – H Which implies that C – H bond has longest bond

APPLICATION OF INDUCTIVE EFFECT

To compare the stability of intermediates.

Intermediates

These are reals reparable species having measurable stability formed during coversion of reactant to product. (After bond cleavage and before bond formation).

6 types of intermediates:

(i) Free radical

(ii) Carbocation (iii) Carbanion

(iv) Carbene

(v) Nitrene

(vi) Benzyne

They are formed by homolytical and heterolytical cleavage.

MESOMERIC EFFECT (RESONANCE EFFECT)

Mesomeric effect is valid only for conjugated system.

Types

1 + M effect (+R)

2 - M Effect (-R)

Consider the following conjugated system

$$H_2C = CH - CH = CH - Y \longleftrightarrow \overline{C}H_2 - CH = CH - CH = Y + CH = Y +$$

(+M effect of y)

Consider another conjugated system

$$C = C - C = C - N = 0 \longleftrightarrow C^{+} - C = C - C = N$$

(- M effect of NO₂)

MESOMERIC EFFECT IN PHENOL (+ M EFFECT)

+M effect in aniline

if more of e^- towards ring \Rightarrow (+M effect)

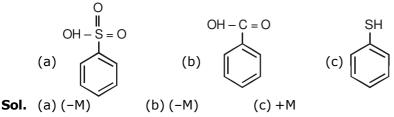
- This effect increases the electron density over benzene ring.
- -M effect in Benzaldehyde



Page#7

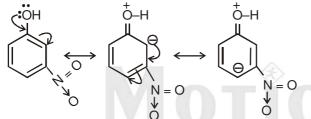
$$H-C=O H-C-O H-C-O H-C=O H-C=$$

Ex.23 Idenfity the compound showing +M or -M seperately



- * +M group increases electron density of ring while M decreases the electron density of benzene ring.
- * if NO₂ is present on the ortho or para position then along with its –I effect, It will also show –M effect.

* Above comound have +M of -OH and -M of NO₂ group.



as we can easily see that $-NO_2$ at meta position is not attracting e-density towards it self and that's why it will not show -M effect at m-position

RESONANCE

Delocalisation of π -electrons in conjugation is known as resonance.

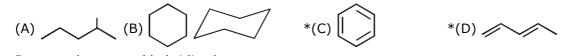
$$(\text{resonating structures}) \equiv (\text{Resonance hybrid})$$





CONDITION FOR SHOWING RESONANCE

- 1. Molecule should be planer, nearly planer or a part of it is planar
- Q.1 Which are planer



Becouse they are sp² hybridised.

Q.2 Molecule should posses conjugated system.

Conjugated system:-

Continous unhybridised p-orbital parallel to each-other.

Types of conjugated system:-

- (1) π -bond aternate to π -bond $CH_2 = CH CH = CH_2$
- (2) π -bond alternate to + charge $CH_2 = CH CH_2^+$

Eg.
$$CH_2 = CH - CH = CH_2$$
 $CH_2 - CH = CH - CH_2$
 $CH_2 - CH = CH - CH_2$

Eg.
$$CH_2 = CH - CH_2$$

$$CH_2 - CH = CH_2 = \begin{bmatrix} \delta^- \\ CH_2 - CH_2 \end{bmatrix}$$

GOC

Eg.
$$CH_2 = CH - CH_2$$

$$CH_2 - CH = CH_2$$

$$CH_2 - CH = CH_2$$

$$CH_2 - CH = CH_2$$

(4)
$$CH_2 = CH - NH_2 \iff CH_2 - CH = NH_2$$

(5)
$$\overrightarrow{CH_2} = \overrightarrow{CH} - \overrightarrow{CH_2}$$
 \longleftrightarrow

(6)
$$CH_2 = CH - BH_2$$
 $B \leftarrow H$

- (2) Resonance takes place due to delocalization of πe^- .
 - (a) //

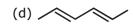
Resonance

(b)

Resonance absent



Resonance



Resonance

(3) Position of the atoms remains the same, only delocalization of πe^- takes place.

(4) Bond pair get converted into lone pair and l.p. get converted into b.p.

$$\overrightarrow{CH_3} = \overrightarrow{C} \cdot \overrightarrow{NH_2} \longleftrightarrow \overrightarrow{CH_2} - \overrightarrow{C} = \overrightarrow{NH_2}$$

(5) In Resonance No. of unpaired e⁻ remains the same

$$CH_2 = CH - CH = CH_2 \longleftrightarrow CH_2 - CH = CH - CH_2$$

(They are not resonating structure)

Resonating structure:

- (1) Hypothetical strtucture exist on paper
- (2) The energy difference b/w different resonating structure is very small.

- (3) All R. S. contribute twoards the formation of resonance hybrid (Their contribution may different)
- (4) A single R. S. Can't explain each & every property of that particular compound

Draw the resonating structures: -

$$Q.1 \qquad \overbrace{\mathsf{CH}_2 = \mathsf{CH} - \mathsf{CH} = \mathsf{CH}}^{\bullet} - \underbrace{\mathsf{CH}_2}_{\bullet} - \mathsf{CH} = \mathsf{CH} - \mathsf{CH} = \underbrace{\mathsf{NH}_2}_{\bullet}$$

Resonance hybrid: -

It is a real structure which explain all the properties of a compound, formed by the contribution of different R. S. Pt has got maximum stability as compared R. S.

Resonance Energy: -

It is the diffrence b/w theoriticle value of H.O.H & experimental value.

Or

It is the difference b/w more stable R.S. & R. H.

- * More the resonance energy, more stable will be the molecule.
- * Cyclohexane is thermodynamically more stable than benzene, even though resonance energy of benzene is more.
- * Resoance energy is a absolute term.

CONTRIBUTION OF DIFFERENT R. S. TOWARDS RESOANCE HYBRID

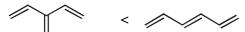
- (1) Non-polar R. S. contribute more than polar R. S. (a) $CH_2 = CH CH = CH_2$ (b) $^+CH_2 CH = CH CH_2^{\ominus}$ (c) $^{\ominus}CH_2 CH = CH CH_2^{+}$ a > b = c stability
- (2) Polar R. S. With complete octet will contribute more as compared with the one with incomplete octet $CH_3 CH^+ OCH_3 \longleftrightarrow CH_3 CH = :O^+ CH_3$ Incomplete octet Complete octet
- (3) In polar R. S. The -ve charge should be on more electro ve atom & +ve charge should be more electro + ve atom

(a)
$${}^{\odot}_{\text{CH}_2}$$
 - C - CH₃ \longleftrightarrow CH₂ = C - CH₃

(b)
$$\overset{\oplus}{\operatorname{CH}}_2 \overset{\bullet}{-} \overset{\ominus}{\operatorname{C}} - \overset{\ominus}{\operatorname{CH}}_3 \longleftrightarrow \overset{\ominus}{\operatorname{CH}}_2 = \overset{\ominus}{\operatorname{C}} - \overset{\ominus}{\operatorname{CH}}_3$$



- (4)Compound with more covalent bond will contribute more
- (5) Unlike charges should be closer to each other whereas like charges should be isotated.
- (6)Extended conjugation contribute more than cross conjugation.



Cross conjugation < Extended conjugation



(Extended) (cross)

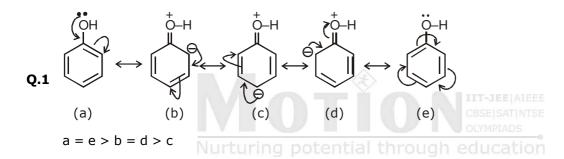
Fries Rule:-

Compound with more benzenoid structure are more stable as their Resonance energy is greater than those in which lesser no. of benzenoid structure are present.

R. E. is
$$\longleftrightarrow$$
 $<$

If double bond is participating in resonance then it will aquire partial single bond character as a result of which bond length increase & bond strength decreases.

If a single bond is involved in resonance then it will aquire partial doulbe bond character. As a result of which bond length decreases & bond strength increase.



Q.2 (a)
$$CH_2 = N = N$$

(b)
$$\overset{\odot}{CH_2} \overset{\oplus}{\sim} \overset{\cdots}{N} \overset{\cdots}{\equiv} \overset{\cdots}{N}$$

(c)
$${}^{\oplus}CH_2 - \overset{\bullet}{N} = \overset{\bullet}{\overset{\bullet}{N}}$$
 (incomplete)

(c)
$${}^{\oplus}CH_2 - \overset{\dots}{N} = \overset{\dots}{\overset{N}{\overset{}{\circ}}} (incomplete)$$
 (d) ${}^{\ominus}CH_2 - \overset{\dots}{\overset{}{\overset{}{\overset{}{\circ}}}} = \overset{\dots}{\overset{\overset{}{\overset{}{\overset{}{\circ}}}}} (incomplete)$

Page # 12 GOC

Q.4 (a)
$$(H_2) = CH$$
 $(H_2) = CH$ (b) $(H_2) - CH = F^+$ a > b (stability)

Note:—When lone pair as well as double bond as present in some atom. Then only π bond will participating resonance. Where as lone pair remains sp² hybridises orbital.

When an atom two and more then two known a lone pair of e- will participet. Then only one lone pair remins sp² hybridised.

HYPER CONJUGATION

Permanent polarisation caused by displacement of σ -electrons into π -molecular orbital is known as hyperconjugation

Hyper conjugation is called No bond Resonance

- More α C H bond, more will be the no bond resonating structure (Hyper conjugation)
- More α (C H) bond, more will be the stability of free radical.

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

$$9 \propto (C-H) \quad 6 \propto (C-H) \quad 3 \propto (C-H) \quad 0$$

$$Nurturin Stability order$$

Properties of Free Radical

- 1. It is a neutral species.
- 2. It has one upaired electron that's why paramagnetic in nature.

Structure:

 $\dot{c}_{H_2} \rightarrow \text{methyl free Radical}$

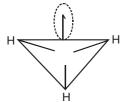
 ${}^{\bullet}_{\text{CH}_3\text{CH}_2} \rightarrow \text{ethyl free radical}$



Page # 13

3. its hydridisation is sp² and triangular planer shape.

Note: unpaired electron is not counted while calculating the hybridisation state.



(unpaired electron stay perpendicular to the plane)

Stability of free Radical:

Its stability can be determined with the help of hyperconjugation as well as Resonance effect

ALLYLIC FREE RADICAL

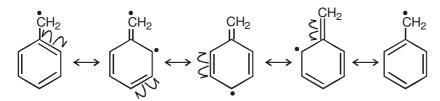
$$CH_2 = CH - CH_2 \longleftrightarrow CH_2 - CH = CH_2$$
(Homolysis)

(Free Radical is on next carbon to doubly bonded carbon atoms)

Effect of Resonance > Hyper conjugation

$$\overset{\bullet}{C}H_2 - CH = CH_2 > (CH_3)_3 \overset{\bullet}{C}$$
(stability)

BENZYLIC FREE RADICAL



(4 Resonating structure)

* More Resonating structure, more will be the stability of the free Radical.



No. of Resonating structure = 7

No. of Resonating structure = 10



Stability Order:

$$\mathsf{ph}_3\: \mathsf{C} > \mathsf{ph}_2\: \mathsf{C}\: \mathsf{H} > \mathsf{ph}\: \mathsf{C}\: \mathsf{H}_2 > \mathsf{C}\: \mathsf{H}_2 = \mathsf{C}\: \mathsf{H} - \: \mathsf{C}\: \mathsf{H}_2 > (\mathsf{C}\: \mathsf{H}_3)_3\: \mathsf{C} > (\mathsf{C}\: \mathsf{H}_3)_2\: \mathsf{C}\: \mathsf{H} > \mathsf{C}\: \mathsf{H}_3 - \mathsf{C}\: \mathsf{H}_2 > \mathsf{C}\: \mathsf{H}_3$$

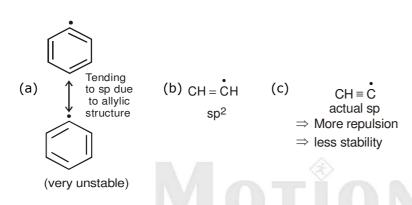
- **Ex.1** Compare the stability of the following free Radical.
 - (a) $CH_3 \dot{C}H_2$ (b) $CH_2 = \dot{C}H$ (c) $CH = \dot{C}H$
- **Sol.** (a) $CH_3 CH_2$ will be most stable due to hyper conjugation

between
$$CH_2 = CH$$
 and $CH = C$

- \Rightarrow more s-character
- ⇒ more electronegative
- ⇒ e⁻ density maximum
- ⇒ more repulsion
- \Rightarrow less stable

Ans. a > b > c

- More repulsion, less stability
- **Ex.2** Compare the stability of the following free Radicals



(Therefore this resonating structure is not possible)

Sol. b > a > c

Ex.3 (a)
$$CH_3 - \dot{C}H - CH_3$$
 (b) $CH_3 - \dot{C}H_2 - CH_3$ (c) $CH_3 - \dot{C}H_3$ (d) $\dot{C}H_4$ | CH_3

Compare the C-H bond energy of the above compounds.

Sol. After forming free radical from the compound

GOC

Page #15

- (3°) (a)
- (2°) (b)
- (1°) (c)
- methyl free radical

(d)

(most stable)

 \downarrow

therefore will have more

tendency to come in this form

 \downarrow

And C - H bond will break very readily

- \Rightarrow bond energies will be very less.
- a < b < c < d < (bond energies order)
- * Bond length ∝ stability of free Radical
- **Ex.4** Compare the potential energy of the following compounds (above compounds)
- **Sol.** If compound after being in free Radical form is very stable (i.e., less energy) it mean it would have possessed more energy initially i.e. it potential energy will be most

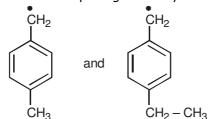
- * Potential energy ∝ stability of free Radical
- $\mbox{\bf Ex.5}$ Compare the bond energies of C H bond

(at a, b, c, d, e and f position)

$$e > b > a > f > c = d$$

Stability order of free Radical that might be formed after removal of H (Homolytically) from the given carbon.

- \Rightarrow e < b < a < f < c = d
 - (C H bond energies)
- In the above compound while comparing 2° benzylic allylic stability at two given position



while drawing the resonating structure of the

Motion (assistatives converged by Nurturing potential through education



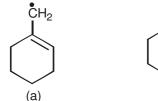
$$\begin{array}{c}
\stackrel{\bullet}{\text{CH}_2} \\
\stackrel{\bullet}{\text{CH}_2} \\
\stackrel{\bullet}{\text{CH}_3} \\
\stackrel{\bullet}{\text{CH}_3} \\
\stackrel{\bullet}{\text{CH}_3} \\
\stackrel{\bullet}{\text{H-C-H}_2} \\
\stackrel$$

(Here inspite of Resonace three $\alpha(C-H)$ bond are available for no bond Resonance.

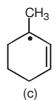
 \Rightarrow Therefore extra stable than which have only two α (C – H) bond for Hyper conjugation. CH_2CH_3

Therefore 2° benzylic allylic corresponding to structure (a) is more stable than that of structure (b)

Ex.6 Compare the stability of the following free Radical



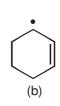




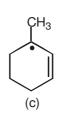
$$CH_2 = CH - CH_2$$

(d)

Sol. CH₂



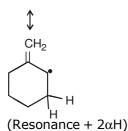
 2° allylic + $2\alpha H$



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

(d)

(c) 3° allylic + 5αH • CH₂ – CH = CH₂ (only resonance)



1º allylic

(d)

O T O SESSISATINTSE
OLYMPIADS

Nurturang pcxbxa dhrough education

For 7 Commons the metantial energy of

Ex.7 Compare the potential energy of $CH_3 - CH_3$, $CH_2 = CH_2$

Sol. After making free Radical of the above compounds

$$CH_3 - \dot{C}H_2$$
 $CH \equiv \dot{C}$ $CH \equiv \dot{C}$ (least stable)

GOC

$$CH_3 - CH_2 > CH_2 = CH > CH \equiv C$$
(a) (b) (c)
 $a > b > c$

CARBOCATION

$$\overset{^{+}}{\mathsf{C}}\mathsf{H}_{3} \to \mathsf{Carbonioum}$$
 ion

$$CH_3 - \overset{+}{C}H_2 \rightarrow Methyl carbonium ion$$

$$CH_3 - CH - \overset{\scriptscriptstyle +}{C}H_2 \rightarrow Isopropyl carbonium ion$$
 | CH_3

Properties of Carbocation:

- 1. it is positivly charged species
- **2.** it has sixtet of electrons i.e. diamanetic
- **3.** it is formed by heterolysis
- 4. it is generally formed due to polar solvent

Structure:

(sp²) Triangular planer

Stability:

Its stability can be determined with the help of Inductive effect, Hyper conjugation and Resonance effect.

Stability of Carbocation:

$$\overset{\scriptscriptstyle{+}}{\mathsf{C}}\mathsf{H}_{3},\quad \mathsf{C}\mathsf{H}_{3} \xrightarrow{} \overset{\scriptscriptstyle{+}}{\mathsf{C}}\mathsf{H}_{2} \ \ \, \text{(+ I effect)}$$

$$charge \propto \frac{1}{Stability}$$

$$\overset{+}{\text{CH}_3}$$
, < $\overset{+}{\text{CH}_3} \rightarrow \overset{+}{\text{CH}_2}$ (stability order)

Stability of carbocation can also be determined by Hyper conjugation (no bond Resonance)

$$\begin{array}{ccc} H & & H^+ \\ & | & \\ H - C - CH_2 & \longleftrightarrow & H - C = CH_2 \\ & | & | & \\ H & & H \end{array}$$

 9α C - H bond 6α C - H bond 3α C - H bond



ALLYLIC CARBOCATION

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

allylic carbocation

Actual Resonance

BENZYLIC CARBOCATION

$$\overset{+}{\text{CH}_2} \longleftrightarrow \overset{\text{CH}_2}{\text{CH}_2} \longleftrightarrow \overset{\text{CH}_2}{\text{CH}_2}$$

ph₂ CH → 7 Resonating strucutre

 $ph_3 \stackrel{^{\scriptscriptstyle T}}{C} \rightarrow 10$ Resonating strucutre

$$ph_3 \overset{+}{C} > ph_2 \overset{+}{C}H > (CH_3)_3 \overset{+}{C} > ph \overset{+}{C}H_2$$

Ex.8 Compare the stability of th following carbocation

(a)
$$CH_3 - CH_2$$
 (b) $CH_2 = CH_2$ (c) $CH_3 - CH_2$

- ⇒ more electronegativity
- ⇒ +ve charge on more electronegative element is symbol of unstability.

Ex.9 Compare the stability of the following compounds

(a)
$$\overset{+}{C}H_2 - CF_3$$

(b)
$$\overset{+}{C}H_2 - CCI_3$$
 (c) $\overset{+}{C}H_2 - CBr_3$

(c)
$$\overset{+}{C}H_{2} - CBr_{3}$$

Sol. d > c > b > a

F being most electron attracting group decreases the e- density from positively charged C-atom and decreases the charge density and makes the carbo cation less stable.

Compare the stability of the following carbocation: Ex.10

(a)
$$\overset{+}{C}H_2 - F$$

(b)
$$\overset{+}{C}H_2 - CI$$

(b)
$${}_{CH_{2}-Cl}^{+}$$
 (c) ${}_{CH_{2}Br}^{+}$ (d) ${}_{CH_{2}-l}^{+}$

Sol. due to greater size of Iodine, its L.P. will not be available for coordinate bond. Therefore L.P. would not stabilize corbocation.

In case of F due to its small size its lone pair can be easily coordinated to $\frac{\Phi}{C}$ making it most stable

$$a > b > c > d$$
 (Stability)

By coordination the carbocation completes its octet and structure having complete octet of its atom is supposed to be most stable.

(Each atom has its full octet)

*
$$\overset{\bigcirc}{\nearrow} \overset{\bigcirc}{\overset{\bigcirc}{\overset{\frown}{C}}} \overset{\circ}{\overset{\frown}{\overset{\frown}{A}}} > ph_3\overset{\bigcirc}{\overset{\frown}{\overset{\frown}{\overset{\frown}{C}}}}$$
(stability)



GOC

Page # 19

Note: In Rasonating Structure of $ph_3\overset{+}{C}$, at least one C gets sixtet of e^- and hence less stable than coordinated compound.

- Compare the stabilities of the following corbocation Ex.11
 - (a) CH₂NH₂
- (b) CH₂ OH

Sol. N, O, F belongs to same period

- In period Electronegativity of the atom is deciding factor
- \Rightarrow F being most electronegative, holds its e-pair very firmly.
- Its L.P. will not be easily available for coordination.
- Stability by it will be minimum.

- Ex.12 Compare the following corbocation in order of their stability.
 - (a) CH₂ CI
- (b) CH₂ OH
- **Sol.** If periods of atoms which have to donate their electrons for coordination (for stability) is different then atomic size will be deciding factor. The atom whose size is greater will be unable to make it e- pair available for coordination.

Ex.13 Compare the stability of the following compounds

(a)
$$CH_3 \rightarrow CH_2 = \overset{\dagger}{C}H_2$$

(a)
$$CH_3 \rightarrow CH_2 = \overset{+}{C}H_2$$
 (b) $CH_2 = CH - \overset{+}{C}H_2$ (allylic) (c) $CH = \overset{+}{C} - \overset{+}{C}H_2$ (d) $ph \leftarrow CH_2 - \overset{+}{C}H_2$

Sol ⇒ more s-character

- \Rightarrow more e.n.
- ⇒ attracts e
- \Rightarrow reduces, stability

CARBANION

- it is a -ve charged species
- 2. it has octet of electrons.
- 3. diamagnetic

Strucutre:

- if -ve charge is in Resonance then the hybridisation of carbanion is sp2 (Triangular planer shape)
- If -ve charge is not in Resonance then the hybridisation of carbanion is sp3 (pyramidal)

Stability:

Its stability can be determined with the help of

- (1) Inductive effect
- (2) Resonance effect

Ex.14

$$\Theta$$
 Θ CH_3 , CH_3CH_2 (a) (b) $A > b$ (stability)

Stability of the carbanion is as follows



Ex.15 Compare the stability of the following carbacation

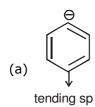


(c)
$$CH_2 = \overset{+}{C}H$$

tending to sp

Sol. c > a > b

Ex.16 Compare the stability of the following carbanion



(b) –ve change is attracted sp (c) CH₂ = CH hybridised corbon hybridised carbon (most electronegative)

⇒ become more stable

Sol. b > a > c

Compare the stability of the following carbanion

(a)
$$_{\text{CH}_2-\text{CF}_3}^{\Theta}$$
 (b) $_{\text{CH}_2-\text{CCI}_3}^{\Theta}$ (c) $_{\text{CH}_2-\text{CBr}_3}^{\Theta}$

(b)
$$\Theta_{CH_2-CCl_3}$$

(c)
$$\Theta_{CH_2-CBr_3}$$

Sol. a > b > c

Arrange the following anion order of their stability Ex.18

- (c) F-
- (d) I- (maximum size)

⇒ maximum dispersion –ve charge

⇒ max stability

Sol. d > b > a > c

Ex.19 Compare the stability of the following

- (a) CH₃
- (b) NH₂
- (c) OH
- (d) F-

Sol. Same period element (C, N, O, F)

 \Rightarrow Stability \propto E.N. of the atom

Compare the acidic strength Ex.20

- (b) HF
- (C) HBr
- (D) HI

Sol. Acidic strength ∝ stability of the anion formed (conjugate base)

as we know $I^- > Br^- > Cl^- > F$

 \Rightarrow H I > HBr > HCl > HF

Compare the Acidic strength of the following

- (b) pH₃
- (c) AsH₃
- (d) SbH₃
- (e) BiH₃

Sol. Anion formed from there acids

 $\overline{NH}_2 < \overline{PH}_2 < \overline{AsH}_2 < \overline{SbH}_2 < \overline{BiH}_2$ (Stability)

 \Rightarrow acidic strength e > d > c > b > a



GOC

Page # 21

- Compare the acidic strength of the following comounds Ex.22 CH₄, NH₃, H₂O, HF
- **Sol.** The conjugate base of the given acid is as follows

$$\overline{\mathrm{CH}}_{3},\overline{\mathrm{NH}}_{2},\overline{\mathrm{OH}},\overline{\mathrm{F}}$$

we have already proved that

$$\begin{array}{ll} F^- > OH^- > \stackrel{\longleftarrow}{N}H_2 > CH_3 \ \ (Stability) \\ HF > H_2O > NH_3 > CH_4 \ \ (acidic strength) \end{array}$$

- Ex.24 Compare the stability of the following carbanion.

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

- **Sol.** d > c > b > a
- +M or -M is not distance dependent
- Ex.25 compare the stability of the following carbocation

(a)
$$\overset{\overset{\leftarrow}{\mathsf{C}}\mathsf{H}_2}{\overset{\leftarrow}{\mathsf{H}_2}}$$
 (b) $\overset{\overset{\leftarrow}{\mathsf{C}}\mathsf{H}_2}{\overset{\leftarrow}{\mathsf{N}}\mathsf{N}_2}$ (c) $\overset{\overset{\leftarrow}{\mathsf{C}}\mathsf{H}_2}{\overset{\leftarrow}{\mathsf{N}}\mathsf{N}_2}$ (d) $\overset{\overset{\leftarrow}{\mathsf{C}}\mathsf{H}_2}{\overset{\mathsf{N}}{\mathsf{N}}_2}$ (-M, -I)

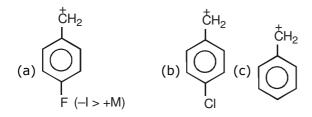
Sol. a > b > c > d

Ex.26 Compare the stability of the following carbocation.

Page # 22

GOC

Ex.27 Compare the stability of the following carbocation



Sol. c > a > b

Ex.28 Compare order of dehydration of the following alcohols :

OH OH
$$C - C - C$$
 $C - C - C - C$ $C - C - C - C$

Sol. After formation of carbocation

Since 3° carbocation is most stable therefore it will show greatest tendency to lose water as after lose of water it comes in stable form.

TYPES OF REAGENT

- **1. Electrophilic reagent**: All electron deficient atom or group of atoms is known as Electrophilic reagent, the electrophile attacks at the electron rich centre.
 - (a) all positively charged species are electrophile

H⁺, NO₂⁺, Br⁺, Cl⁺, etc.

- (b) The compound in which the octet of central atom is not complete BF₃, AlCl₃, ZnCl₂, etc.
- (c) all the compound in which the central atom can expand its octetSATINTSE $SnCl_4$, $SiCl_4$, etc.
- (d) all polarising functional group are electrophile as well as nuelophile

$$C = 0$$
, $-C = N$, etc.

Nucleophile:

All electron rich compounds are nucleophile and attack at the electron deficient centre.

(a) all negatively charged species

$$H^-$$
, CI^- , NO_2^- , Br^- , CH_3^- etc.

(b) the compound in which the central atom has lone pair of electron.



Page # 23

(c) all organometallic compounds are nucleophile

(d) The compound having
$$\pi$$
 e⁻ density, $CH_2 = CH_2$, \bigcirc etc.

Nucleophilicity:

The power of nucleophile is known as nucleophilicity.

⇒ The nucleophilicity of negative charge is greater than the nucleophilicity of lone pair

$$\overline{O}H > H_2O$$

$$CH_3\overline{O} > CH_3OH$$

⇒ If lone pair or –ve charge is present on the different atom then less electronegativity, more will be the nucleophilicity.

$$CH_3^-$$
, NH_2^- , OH^- , F^-

Nucleophilicity $CH_3^- > NH_2^- > OH^- > F^-$

- \Rightarrow NH₃ < PH₃ < AsH₃ < SbH₃ < BiH₃ (Nucleophilicity)
- \Rightarrow If -ve charge or lone pair of electron is present on the same atom then the less stable -ve charge will be the better nucleophile

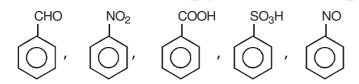
$$CH_3O^- > OH^- > CH_3COO^-$$
 (nucleophilicity)

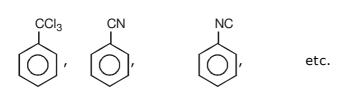
ACTIVATOR & DEACTIVATOR

The groups in benzene which show +M effect or +I effect Increases the electron density on benzene it means they activate the ring towards electrophile and known as activator.

$$NH_2$$
 — OH $COO^ O^ O^$

The groups which shows -M or -I effect (resultant) decreases the e-density from benzene ring. It means they deactivate the ring towards electrophile





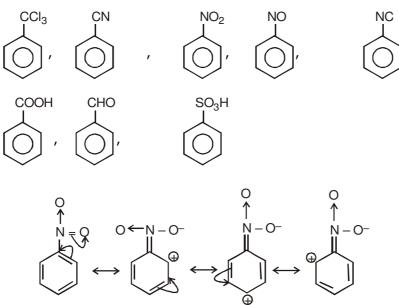


ORTHO PARA & META DIRECTOR

The groups which shows +I (resultant) or +M effect then negative charge is developed at the ortho & para position. Therefore electrophile attack at the ortho & para position and the groups are known as OP director.

$$\bigoplus_{+\mathsf{M}\;\mathsf{Effect}}^{\mathsf{G}^+}\longleftrightarrow\bigoplus_{\mathsf{P}}^{\mathsf{G}^+}\longleftrightarrow\bigoplus_{\mathsf{P}}^{\mathsf{G}^+}$$

The groups which shows -M effect or - I effect (resultant) then +ve charge is developed at the ortho & para position this means electron density is minimum at the ortho & para positions and electronphile will attack at the meta position the groups are known as meta director.



HEAT OF HYDROGENATION(H.O.H)

It is the amount of energy realeased when one mole of H_{2} is added to any unsaturated system.

$$CH_2 = CH_2 + H_2 \rightarrow CH_3 - CH_3 + energy$$

HOH is exothermic process $\Delta H = -ve$

*HOH \propto No. of π -bonds in compound

If no. of π -bonds is same then

*HOH
$$\propto \frac{1}{\text{stability of compound}}$$

.. In case of alkene

** HOH
$$\alpha$$
 $\frac{1}{\text{stability of compound}}$ α $\frac{1}{\text{No.of } \alpha \text{ H}}$



Page # 25

Ex.

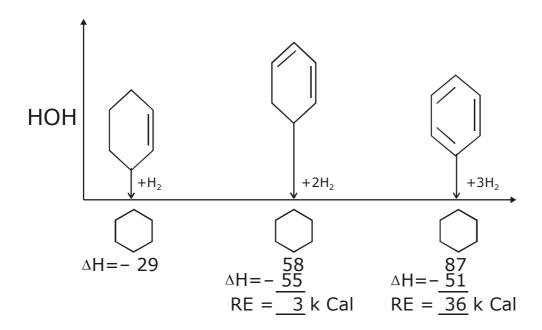
$$a \longrightarrow + H_2 \longrightarrow + 29 \text{ kcal}$$

$$b \longrightarrow + 2 H_2 \longrightarrow + 58 \text{ kcal} \Longrightarrow 55 \text{ kcal}$$

$$c \longrightarrow + 3 H_2 \longrightarrow + 87 \text{ k cal} \Longrightarrow 51 \text{ k cal}$$

$$(expected) \longrightarrow (actual)$$

b > c > a Energy



Some examples of Arromatic(A), Non-arromatic(NA) and Anti-arromatic(AA)



(A)



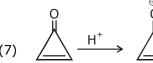
(AA)







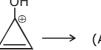














(8)
$$\stackrel{\text{Br}}{ } \stackrel{\overset{\oplus}{\text{AgNO}_3/\Delta}} \longrightarrow \stackrel{\overset{\oplus}{\text{AgNO}_3/\Delta}} \longrightarrow (A)$$

$$(9) \quad \boxed{ } \longrightarrow (A) \longrightarrow (2\pi e)$$

(10)
$$\longrightarrow$$
 (A) \longrightarrow (6 π e)

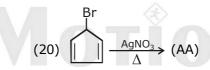
$$(11) \quad \boxed{ } \longrightarrow (NA)$$

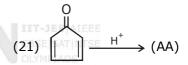
$$(12) \quad \bigcirc \longrightarrow (NA)$$

(13)
$$\longrightarrow$$
 (AA) \longrightarrow (4 π e)

$$(16) \quad \stackrel{\mathsf{H}^+}{ }) \qquad (A)$$

$$(18) \quad \stackrel{\mathsf{H}}{\underbrace{\hspace{1cm}}} \stackrel{\mathsf{H}}{\underbrace{\hspace{1cm}}} \stackrel{\mathsf{H}}{\underbrace{\hspace{1cm}}} \stackrel{\ominus}{\underbrace{\hspace{1cm}}} (\mathsf{AA})$$





(22) (AA)

$$(27) \qquad (NA)$$