Electron Displacement Effects in Covalent Compounds:

1. Inductive Effect
2. Hyperconjugation Effect
3. Electromeric Effect
4. Resonance Effect (Mesomeric Effect)

Inductive Effect:

- Partial shifting of $\sigma$ electron towards more $\pi$-atom of $\sigma$ bond
- Partial charges are developed

$$\begin{align*}
\text{EN of } X > \text{EN of } C \\
\rightarrow \text{Electron withdrawing group (}-I\text{ group)}
\end{align*}$$

$$\begin{align*}
\text{EN of } Y < \text{EN of } C \\
\rightarrow \text{Electron donating group (}+I\text{ group)}
\end{align*}$$

- It travels $\sigma$ decreases with distance.

Which is more stable?

- a) $\text{F-CH}_2\text{-COO}^-$
- b) $\text{Cl-CH}_2\text{-COO}^-$
- c) $\text{Br-CH}_2\text{-COO}^-$
- d) $\text{I-CH}_2\text{-COO}^-$

- I group order: $F > Cl > Br > I$
- Stability: $a > b > c > d$

Teacher's Signature
- I group order:

\[ \text{F} > \text{N} \rightarrow \text{H} > \text{N} \rightarrow \text{R} > \text{N} \rightarrow \text{N} \rightarrow \text{H} > \text{NO}_2 > -\text{C}=\text{N}- \]

\[ \text{F} > \text{R} > \text{H} \]

\[ \text{C} - \text{H} > -\text{C} - \text{R} > -\text{C} - \text{OH} > \text{F} > \text{Cl} > \text{Br} > \text{I} \]

\[ -\text{O} = \text{R} > -\text{O} - \text{H} > -\text{C} = \text{CH} > -\text{NH}_2 \]

\[ \text{CH} = \text{CH}_2 > \text{H} \]

1. Which is more stable?
   a) \( \text{NO}_2 \rightarrow \text{CH}_2 \rightarrow \text{C} = \text{O} - \)
   b) \( \text{CH}_3 \rightarrow \text{CH} \rightarrow \text{C} = \text{O} - \)
   c) \( \text{F} \rightarrow \text{CH}_2 \rightarrow \text{C} = \text{O} - \)

2. Acidic Order:

\[ \text{HA} = \text{H}^+ + \text{A}^- \]

Which is more acidic?

a) \( \text{CH}_3 \rightarrow \text{C} = \text{O} - \text{H} \)
   \[ \text{b} > \text{c} > \text{a} \]

b) \( \text{CH}_2 \rightarrow \text{C} = \text{O} - \text{H} \)
   \[ \text{More } -\text{I effect} \]
   \[ \Rightarrow \text{More acidic nature} \]

c) \( \text{CH}_2 \rightarrow \text{CH}_2 \rightarrow \text{C} = \text{O} - \text{H} \)
$+I$ effect $\rightarrow$ Electron donating group

$\text{CH}_2^- > \text{NH}_2^- > \text{O}^- > \text{COO}^- > -\text{C} - \text{CH}_3 > -\text{C} - \text{CH}_2^-$

- $\text{C} - \text{CH}_3 > -\text{CH}_3$

Arrange in order of Acidic strength

1. $\text{CH}_3 - \text{C} - \text{OH}$
2. $\text{CH}_3 - \text{C} - \text{OH}$
3. $\text{CH}_3 - \text{CH}_2 - \text{OH}$
4. $\text{CH}_3 - \text{OH}$

Order: $d > c > b > a$

More $+I$ effect $\Rightarrow$
Lesser Acidic Nature $\Rightarrow$
Basic nature

Arrange in order of acidic strength:

1. $\text{CH}_3 - \text{CH}_2 - \text{COOH}^+$
2. $\text{CH}_3 - \text{COOH}^+$
3. $\text{CH}_3 - \text{CH}_2 - \text{COOH}^+$

Order: $3 > 2 > 1$
1. Resonance Structures

- Shifting of π-electron pair within the compound
- Resonating structures are hypothetical and intramolecular phenomenon.
- Combination of resonating structure is hybrid structure.

1. \[ \text{CH}_2 = \text{CH} - \text{CH}_2^+ \quad \text{or} \quad \text{CH}_2^+ - \text{CH} = \text{CH}_2 \]

2. \[ \text{CH}_2 = \text{CH} - \text{CH}_2^- \quad \text{or} \quad \text{CH}_2^- - \text{CH} = \text{CH}_2 \]

3. [Diagram showing structures and arrows indicating resonance]
→ Conditions for Resonance →

1. Conjugation \( \pi \rightarrow \sigma \rightarrow + \)
   \( \pi \rightarrow \sigma \rightarrow \text{Lup.} \)
   \( \pi \rightarrow \sigma \rightarrow \cdot \)
   \( \pi \rightarrow \sigma \rightarrow \pi \)
   \( \cdot \rightarrow \sigma \rightarrow + \)

# Conjugate position of the molecules:

1. \( \pi \rightarrow \sigma = + \)

\[ \text{CH}_2 = \text{CH} - \text{CH}_2^+ \quad \text{CH}_2^+ - \text{CH} = \text{CH}_2 \]

\[ \text{CH}_2 = \text{CH} = \text{CH}_2 \]

* 

Hybrid
b) $\pi \rightarrow \sigma^*$

a) $\text{CH}_2 = \text{CH} \rightarrow \text{CH}_2^\text{-} \text{CH} = \text{CH}_2^\text{-}$

b) $\text{N}^\text{-} \rightarrow \text{N}^\text{+}$

c) $\text{CH}_2 = \text{CH} \rightarrow \text{NH}_2^\text{-} \rightarrow \text{CH}_2^\text{-} \text{CH} = \text{NH}_2^\text{-}$

d) $\text{CH}_2 = \text{CH} \rightarrow \text{OH} \rightarrow \text{CH}_2^\text{-} \text{CH} = \text{OH}^\text{+}$

Note: The total charge on all resonance structures must be equal. Position of atom must not be changed.
$\pi-\sigma^* \cdot$ (free radical)

\[ \text{Heterolytic fission} \quad A \rightarrow B \rightarrow A^+ + B^- \quad [\text{E.N. of } B > \text{E.N. of } A] \]

\[ \text{Homolytic fission} \quad A \rightarrow A^* + A^* \quad [\text{E.-deficient species}] \]

**Free radical**

1. $\text{CH}_2 = \text{CH} \rightarrow \text{CH}_2 \quad \rightarrow \quad \text{CH}_2 = \text{CH} = \text{CH}_2$

   \[ \text{full process} = \text{H} \rightarrow \text{O} \quad \text{homolytic fission} \]

   $\text{CH}_2 = \text{CH} \rightarrow \text{CH}^* \quad \rightarrow \quad \text{CH}_2 = \text{CH}^* \quad (\text{Unstable})$

   \[ \downarrow \]

   $\text{CH}_2 = \text{CH} \rightarrow \text{CH}_2$

2. \[ \text{Diagram} \]
\[ (d) \quad \Pi - \sigma - \Pi \]

\[ \rightarrow \quad \text{CH}_2=\text{CH} - \text{CH}=\text{O} \quad \leftarrow \quad \text{CH}_2=\text{CH}-\text{CH}^+ - \text{O}^\text{=} \]

\[ \quad \overset{\delta^+}{\text{CH}_2 - \text{CH} = \text{CH} - \text{O}} \]

\[ \overset{\delta^+}{\text{CH}_2=\text{CH}=\text{CH} = \text{O}^\text{=} \quad \text{CH}_2 - \text{CH} = \text{CH} - \text{O}} \]
\[ \text{lp} \circ \text{ (P)/ vacant orbital} \]

\[ \text{CH}_2 - \text{NH} \rightarrow \text{CH}_2 \]

\[ \text{CH}_3 - \text{NH} \rightarrow \text{CH}_2 \]

\[ \text{CH}_3 - \text{O} \rightarrow \text{C}_2 \]

\[ \text{CN}_2 \rightarrow \text{CH}_2 \]

\[ \text{CH}_3 - \text{O} \rightarrow \text{CH}_2 \]

\[ \text{CH}_2 - \text{CH} = \text{CH} \rightarrow \text{O} - \text{H} \]

\[ \text{CH}_2 \text{C} - \text{CH} = \text{O} - \text{H} \]

\[ \text{CH}_2 = \text{CH} - \text{OH} - \text{CH}_3 \]

\[ \text{CH}_2 = \text{CH} = \text{CH} - \text{OH} - \text{CH}_3 \]
Stability of Resonance Structure

Rules for Stability

1. More no. of covalent bonds makes structures stable.
2. Neutral species are more stable than charged species.
3. Negative charge on more EN atom = more stability.
4. Two like charges must be separated far for being stable.

Practice problems

1. \( \text{CH}_3\text{-} \text{O} \overset{\Delta}{=} \text{CH}_2^+ \leftrightarrow \text{CH}_3\text{-}O^+ = \text{CH}_2 \)

   (a) \hspace{2cm} (b)

   \( a \) is more stable than \( b \) due to more no. of covalent bond (why?)

   Due to bond formation, more energy will be released hence stable.

2. \( \text{CH}_2 = \text{CH} \overset{\Delta}{=} \text{NH}_2 \leftrightarrow \text{CH}_2^\ominus + \text{CH} = \text{NH}_2^+ \)

   (a) \hspace{2cm} (b)

   \( b \) is less stable than \( a \) because neutral species are more stable than charged species.

3. \( \text{CH}_2 = \text{CH} \overset{\Delta}{=} \text{CH}_2 \leftrightarrow \text{CH}_2^\ominus \overset{\Delta}{=} \text{CH} = 0 \)

   (a) \hspace{2cm} (b)

   \( a \) is more stable than \( b \) because negative change is on the more EN atom.
(i) Arrange in the order of stability:

\[ \xrightarrow{a > b > c} \]

(ii) a) \( H - C^+ - O^+ \) b) \( H - C = O^- \) c) \( H - C^+ - O^- \) d) \( H - C^+ - O^- \)

\[ \xrightarrow{a > b > c > d} \]

(iii) a) \( CH_2 = N^+ = N^- \) b) \( CH_2^+ \) c) \( CH_2^- \) d) \( CH_2^- \)

\[ \xrightarrow{a > c > b > d} \]

(iv) a) \( CH_2 = CH - NH \) b) \( CH_2 - CH^+ - NH \)

\[ \xrightarrow{a > c > b} \]
(a) \[ \text{CH}_2 = \text{CH} - \text{NH}_3 \]

(b) \[ \text{CH}_2 - \text{CH} = \text{NH}_3 \]

\[ \rightarrow \quad a > b \; \text{because } b \text{ doesn't exist as Nitrogen can never be pentavalent.} \]

8. Which of the following is least stable?

\[ \begin{align*}
\text{a)} & \quad \text{\(O^- = N^+ = O\)} \\
\text{b)} & \quad \text{\(O^- = N^+ = O\)} \\
\text{c)} & \quad \text{\(O^- = N^+ = O\)} \\
\text{d)} & \quad \text{\(O^- = N^+ = O\)}
\end{align*} \]

\[ \rightarrow \quad \text{Because Nitrogen can never be pentavalent,} \]

9. Which of the following is least stable?

\[ \begin{align*}
\text{a)} & \quad \text{\(N = O\)} \\
\text{b)} & \quad \text{\(N = O\)} \\
\text{c)} & \quad \text{\(N = O\)} \\
\text{d)} & \quad \text{\(N = O\)}
\end{align*} \]

\[ \rightarrow \quad \text{Two closely like charge makes structure unstable, vice versa} \]

* (Which is more stable?)

\[ \begin{align*}
\text{a)} & \quad \text{\(N = O\)} \\
\text{b)} & \quad \text{\(N = O\)} \\
\end{align*} \]
**Meromeric Effect:**

It is defined as the movement of \( \pi \) e\(^-\) towards or away from a substituent group.

\[
\text{CH}_2=\text{CH}-\text{CH}-\text{CH}_2\xrightarrow{\text{OH}} \text{I} \quad \text{e}^- \text{ donate through resonance.}
\]

\[
\text{CH}_2=\text{CH}-\text{CH}-\text{CH}_2\xrightarrow{\text{N}} \quad \text{e}^- \text{ withdraw through resonance (-N effect)}
\]

→ All resonance effects are not meromeric effects but all meromeric effects are called meromeric resonance effects.

**Positive Meromeric effect (+M effect):** (\( \delta^+ \) / -ve charge)

\[\text{NH}_2\]

↑↑ Positive Meromeric effect in Aniline ↑↑

* In this effect, the transfer of e\(^-\) is away from an atom or substituted group attached to the conjugated system. This e\(^-\) displacement makes certain position in the molecule of high e\(^-\) density.

* \[\text{GF} \quad \text{+M effect (all halogens); but e- density ↑} \quad \text{as} \quad [-I > +N}\]

* \[\text{I} \quad \text{+M effect}\]
"Ring se direct joda atom π bond se apane se jyada F-N atom se attached ho to ← M-effect."

# Negative Mesomeric Effect

→ Negative mesomeric effect in Nitrobenzene

\[ \text{C}_6\text{H}_5\text{NO}_2 \]

→ M-effect

\[ \text{C}_6\text{H}_5\text{CH}_3 \]

→ M-effect

\[ \text{C}_6\text{H}_5\text{OH} \]

→ In +M-effect \(\rightarrow\) e- density increases specially in ortho and para positions.

⇒ In -M-effect \(\rightarrow\) e- density decreases specially in ortho and para positions.

8) Arrange in the order of decreasing e- density in the following benzene ring.

a) \[ \text{C}_6\text{H}_5\text{OH} \]

b) \[ \text{C}_6\text{H}_5\text{NO}_2 \]

c) \[ \text{C}_6\text{H}_5\text{CH}_3 \]

⇒ Order: \(a > c > b\)

Note: *Mesomeric effect always dominates over inductive effect except in halogens.*
$\text{F-benzene has more e- density than CCl-benzene.}$

$\text{Less charge - more stable} \uparrow$

**Q.1** Arrange in the order of increasing e- density:

- $\text{a) } + M \text{ OH}$
- $\text{b) } - I \text{ Cl}$
- $\text{c) } + I \text{ CH}_3$
- $\text{d) } - I \text{ NO}_2$

Order: $d < b < c < a$

$\rightarrow$ **Order of $-M$ effect:**

$\text{--CH}_2^+ > -\text{NO}_2 > -\text{C} = \text{N}$

$\text{--} -\text{C-OH} > -\text{C-R} > -\text{C-OH}$

$\rightarrow$ **Order of $+M$ effect:**

$\text{--CH}_2 > -\text{NH} > -\text{O} > -\text{NH}_2 > -\text{NH}_2 > -\text{NR}_2 > -\text{OH} > -\text{O-R} > -\text{NH}_2 > -\text{CH}_3 > \text{OCOR}$

**Q.2** Arrange in the order of acidic strength:

- $\text{a) } + \text{OH}$
- $\text{b) } - \text{OH}$
- $\text{c) } + \text{CH}_3$
- $\text{d) } - \text{ C-M}$
- $\text{e) } - \text{ I/ C-O}$

$\text{No effect}$

Unstable

Order: $c > d > a > b$
b) i) \( \text{OH} \)
   C\(_2\)

ii) \( \text{OH} \)
   \( \text{CH}_3 \)

iii) \( \text{OH} \)
   \( \text{NO}_2 \)

iv) \( \text{OH} \)
   \( \text{OCH}_3 \)

Order - (iii) > (i) > (ii) > (iv)

C) (i) \( \text{OH} + M \)
   \( \text{C} \)

(ii) \( \text{OH} + M \)
   \( \text{C} \)

(iii) \( \text{C} \)
   \( \text{I} \)

(iv) \( \text{C} \)
   \( \text{I} \)

Order - (iii) > (iv) > (ii) > (i)
Hyperconjugation = (no bond resonance)

More hyperconjugation → More stable compound

It governs the stability of carbocation, free radical and alkene.

Relocalization of conjugated (C-H) sigma electron with π-bond or positive charge or free radical is called hyperconjugation.

Conditions for hyperconjugation:

1. Compounds should have at least sp² hybrid carbon of either alkene, alkyl carbocation or alkyl free radical.
2. α-carbon near sp² hybrid carbon should have atleast one hydrogen.

\[
\begin{align*}
\text{CH}_3 & \to \text{CH}_2 \\
\alpha-C & \to H - C - CH_2 \\
3\alpha-H & \to H \\
\end{align*}
\]

Note:

No. of no bond ρ-es = No. of sp² carbon
1) How many hyperconjugating structures are possible of
\[ \text{CH}_3 - \text{CH} - \text{CH}_3 \]
\[ \text{CH}_3 - \text{CH} - \text{CH}_3 \]
\[ \text{CH}_3 - \text{CH} - \text{CH}_3 \]
\[ \text{Total no. of } \alpha - \text{H} = 6 \]
\[ \therefore \text{No. of hyperconjugating structures} = 6 \text{ and} \]

2) How many hyperconjugating structures are possible of
\[ \text{CH}_3 - \text{CH} - \text{CH}_3 \]
\[ \text{CH}_3 - \text{CH} - \text{CH}_3 \]
\[ \text{Total no. of } \alpha - \text{H} = 2 \alpha - \text{H} \]
\[ \therefore \text{No. of hyperconjugating structures} = 9 \]

3) Find the no. of contributing structures of
\[ \text{CH}_3 - \text{CH} - \text{CH}_3 \]
\[ \text{Total no. of } \alpha - \text{Hydrogen} = 3 + 2 + 1 = 6 \alpha - \text{H} \]
\[ \therefore \text{No. of Contributing structures} = 6 \]

4) Arrange in the order of stability:
\[ \text{CH}_3, \text{CH}_3 - \text{CH}_2, \text{CH}_3 - \text{CH} - \text{CH}_3, \text{CH}_3 - \text{CH} - \text{CH}_3 \]
\[ \text{More hyperconjugating structures } \Rightarrow \text{More stable} \]
\[ \therefore \text{Order} - \text{CH}_3 > \text{CH}_3 - \text{CH}_2 > \text{CH}_3 - \text{CH} - \text{CH}_3 > \text{CH}_3 - \text{CH} - \text{CH}_3 > \text{CH}_3 - \text{CH} - \text{CH}_3 > \text{CH}_3 - \text{CH} - \text{CH}_3 \]
#. Hyperconjugation in free radicals:

\[
\begin{align*}
\text{CH}_3 - \text{CH}_2 & \quad \text{(hyperconjugating structures)}
\hline
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H} \\
\end{align*}
\]

1. No. of \( \alpha - H = 3 \)

2. No. of hyperconjugating structures = 3
Arrange in the order of stability:

\[ \text{CH}_3 \quad \text{CH}_3-\text{CH}_2 \quad \text{CH}_3-\text{CH} \quad \text{CH}_3-\text{C} \quad \text{CH}_3 \]

\[ 0 \alpha-\text{H} \quad 3 \alpha-\text{H} \quad 6 \alpha-\text{H} \quad 9 \alpha-\text{H} \]

\( \text{Order} = \text{IV} > \text{III} > \text{II} > \text{I} \)

* Hyperconjugation in Alkene *

Hyperconjugation structures of \( \text{CH}_2=\text{CH}=\text{CH}_2 \)

\[ \begin{align*}
\text{H} & \quad \text{H}^+ \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H}^+ \\
\text{H} & \quad \text{H} \\
\text{H} & \quad \text{H}^+ \\
\text{H} & \quad \text{H} \\
\end{align*} \]

No. of \( \alpha-\text{H} = 8 \) = No. of hyperconjugating structure

Arrange in the order of stability:

\[ \begin{align*}
a) & \quad \text{C} = \text{C} - \text{CH}_3 \\
b) & \quad \text{C} = \text{C} - \text{CH}_3 \\
c) & \quad \text{CH}_3 - \text{CH}_3 \\
d) & \quad \text{CH}_3 - \text{CH}_3 \\
\end{align*} \]

\[ 0 \alpha-\text{H} \quad 3 \alpha-\text{H} \quad 6 \alpha-\text{H} \quad 9 \alpha-\text{H} \]

\( \text{Order} = \text{I} > \text{III} > \text{II} > \text{V} \)
# Arrange in the order of stability:

\[
\begin{align*}
\text{H} & \quad \text{C} = \text{C}-\text{CH}_3 & \text{C} = \text{C}-\text{CH}_3 & \text{C} = \text{C}-\text{CH}_3 \\
\text{H} & \quad \text{CH}_3 & \text{H} & \text{CH}_3 & \text{H} & \text{CH}_3 & \text{H}
\end{align*}
\]

(a) (b) (c)

\[\Rightarrow \alpha - \text{H} \text{ are equal in all structures.}\]

\[\rightarrow \text{h and c are geometrical isomers.}\]

\[C > b \quad \text{[trans > cis]}\]

\[\rightarrow \text{But, a is more stable than both b and c due to more } \alpha - \text{H on a single carbon.}\]

Hence, stability order: \[a > c > b\]

# Why iso-butene is more stable than trans-but-2-ene

\[\begin{align*}
\text{CH}_3 & \quad \text{H} \quad \text{CH}_3 \\
\text{CH}_3 & \quad \text{H} & \text{(CH}_2\text{)} - \text{(F effect)} \\
\rightarrow \quad \text{CH}_2 - \text{CH} & \quad \text{CH}_3
\end{align*}\]

* The group in dotted line is an electron withdrawing group, thus charge disperses in whole structure hence become stable

\[\rightarrow \text{trans-but-2-ene} - \text{CH}_3 - \text{CH} = \text{CH} - \text{CH}_3 \quad \rightarrow \text{CH}_2 = \text{CH} - \text{CH}_2\]

* The group in dotted line is an electron donating group which increases e density, hence becomes unstable.
Aromaticity

Aromatic compounds are specialized cyclic compounds which are known for their distinct smell (aroma - fragrance). This group is called arenes.

Characteristics for being aromatic:

1. Planarity (2-D) [sp² carbon]
2. Conjugated system (de-localization of tetrahedral bonding)
3. Cyclic
4. Presence of \((4n+2)\pi e^-\) in the ring, where \(n = 0, 1, 2, 3, \ldots\)

This is often referred to as Hückel's rule.

\[\pi e^-\] are loosely bonded electrons, \(\pi^+\) are also \(\pi e^-\).

- Benzene
- Cyclopentadienyl anion
- Cycloheptatrienyl cation
- Naphthalene \((n=2, 10\pi e^-)\)
# Anti-Aromatic Compounds

- Cyclic
- Planer
- Congugated System
- $\Pi e^\pi$ should present in the ring. Where $n = 1, 2, 3, \ldots$

- Highly Unstable

Cyclobutadiene

$\pi(4 \rightarrow 4\pi e^-)$

# Non-Aromatic Compounds

Compounds which are neither aromatic nor anti-aromatic.

1. \[ \text{Diagram of a non-aromatic compound} \]
2. \[ \text{Diagram of another non-aromatic compound} \]

- Stability Order of Compounds
  
  Aromatic $>\text{Non-aromatic} >\text{Anti-Aromatic}$
Identify the following as aromatic/anti-aromatic or non-aromatic:

1. \( n = 1 \Rightarrow 6\pi e^- \)
   - Aromatic Compound (cyclic, planar, conjugated, \( 4\pi + 2\pi e^- \))

2. \( n = 1 \Rightarrow 6\pi e^- \)
   - Aromatic Compound (cyclic, conjugated, planar, \( 4\pi + 2\pi e^- \))

3. Cyclic
   - Conguration
   - Non-aromatic

4. \( n = 1 \Rightarrow 4\pi e^- \)
   - Cyclic, planar, conjugated, \( 4\pi e^- \)
   - (Anti-aromatic)

5. \( n = 1 \Rightarrow 4\pi e^- \)
   - Cyclic, planar, conjugated, \( 4\pi e^- \)
   - Anti-aromatic

6. \( n = 1 \Rightarrow 8\pi e^- \)
   - Cyclic, planar, conjugated (\( 4\pi + 2\pi e^- \))
   - Aromatic Compound
Those $\pi$-e- are counted which take part in conjugation.

7) **Anthracene**
- Cyclic, planar, conjugated, $4n+2\pi e^-$
- $n=3 \Rightarrow 14\pi e^-$
- Aromatic

8) **Phenanthrene**
- Cyclic, planar, conjugated, $(4n+2)\pi e^-$
- $n=3$, $10\pi e^-$
- (Aromatic)

9) **Non-conjugated**
- Cyclic, non-conjugated, non-aromatic

10) **Cyclic, conjugated, planar**
- $m=3 \Rightarrow 6\pi e^-$, $9n\pi e^-$

11) **Aromatic**
- Cyclic, non-conjugated, non-aromatic

12) **Cyclic, conjugated, planar**
- $(4n+2)\pi e^-$
- $n=1 \Rightarrow 6\pi e^-$
- (Furan) Aromatic

13) **Cyclic, conjugated, planar**
- $(4n+2)\pi e^-$
- $m=1 \Rightarrow 6\pi e^-$
10. Cyclic, conjugated, planar \((4n+2)\pi e^-\)

\[(\text{Thiophene})\]

Aromatic

15. Cyclic, conjugated, planar \((4n+2)\pi e^-\)

\[(\text{Pyridine})\]

Aromatic

**Question:** Why is pyridine a better base than pyrrole?

One who donates e\(^-\) is a better base. Pyrrole's lone pair on N is trapped in delocalization, but pyridine NO can donate it, because it doesn't take part in conjugation. That is why pyridine is a better base than pyrrole.

16. Cyclic, non-conjugated \((4\pi\sigma+2)\pi e^-\)

\[(\text{Non-aromatic})\]

Conjugation \((4n\pi\sigma+2)\pi e^-\)

17. Cyclic, conjugated \((4n+2)\pi e^-\)

Aromatic

18. Cyclic, conjugated \((4n+2)\pi e^-\), planar

Aromatic
Special Cases:

1. Biphenyl

→ There are planer until and unless a substituent attack on ortho-position.

→ Check conjugation $\pi$ and $\pi^*$ in each ring.

→ Combination of each aromatic compound comes out to be aromatic.

Guess which of the following is most stable?

a) 

b)

c) 

d) 

→ Cyclic

→ Non-conjugated

→ Non-aromatic
Some Important points about Anti-Aromatic

(i) Dimerisation

\[
\text{[I]} + \text{I} \rightarrow \text{[I][I]}
\]

Anti-aromatic \quad \text{Non-Aromatic}

(ii) Reaction with active metals

\[
\text{[I]} \xrightarrow{\text{Homolysis}} \text{[I]_3} + 2\text{Na} \quad \text{other} \quad \text{[I]_3} + 2\text{Na}^+
\]

Anti-aromatic \quad \text{Aromatic}

(iii) \[
\text{[I]} + 2\text{Fe}^{3+} \rightarrow 2\text{Fe}^{2+} + \text{[I]}^{\text{II}}
\]

Anti-aromatic \quad \text{Aromatic}

# Important reaction

\[
\text{R-Cl} \xrightarrow{\text{R-Br}} \text{R}^+ + \text{AgCl} \quad \text{R-Br} \xrightarrow{\text{Ag}} \text{R}^+ + \text{AgBr}
\]

“Alkyl group loses halogens in the presence of silver”

To Que: Which of the following reaction takes place?

(a) \[
\text{[I]} + \text{Ag} \rightarrow \text{AgI} + \text{[I]}
\]

(b) \[
\text{Br} + \text{Ag} \rightarrow \text{AgBr} + \text{[I]}
\]

(c) \[
\text{[I]} + \text{Ag} \rightarrow \text{AgI} + \text{[I]}
\]
Reaction Intermediates

→ Reaction intermediates are generated by the breaking of covalent bond of the substrate. They are short-lived species (half-life $\geq 10^{-6}$ sec) and are highly reactive.

→ Few important types of reaction intermediates

1. Carbocation
2. Carbanion
3. Free Radical
4. Carbenes, Nitrenes, Benzynes

17. Carbocations

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

→ $\text{CH}_3^+$ Methyl carbocation
→ $\text{CH}_2^+\text{CH}_3$ Ethyl carbocation
→ $\text{CH}_3\cdot\text{CH}_2\cdot\text{CH}_3^+$ Propyl carbocation
→ $\text{CH}_2=\text{CH}^+\cdot\text{CH}_2$ Allyl carbocation
→ $\text{CH}_2=\cdot\text{CH}^+$ Vinyl carbocation
# Characteristics of Carbo-cation —

i) It has a positive charge on carbon.
ii) It has only 6 e- in the outermost shell. It has an incomplete octet. It is a electrophile (e- lover).
iii) Carbo-cations are sp² hybridized. They are planar with empty p-orbitals.

> Stability of Carbo-cations —

\[
\begin{align*}
CH_3 & \rightarrow C^+ > CH_3CH_3 & \rightarrow C^+ > CH_3CH_3 & \rightarrow C^+ > CH_3CH_3 \\
& \text{CH}_3 & \text{H} & \text{H} & \text{H} \\
& \text{CH}_3 & \text{H} & \text{H} & \text{H} \\
& 9\alpha-H & 6\alpha-H & 3\alpha-H & \alpha-H
\end{align*}
\]

On the basis of Hyper conjugation & Inductive effect.

i) More resonating structure — More stable

9) 3) \( CH_3 \rightarrow CH_2 \rightarrow CH_3 \) < \( CH_3 \rightarrow CH \rightarrow CH_3 \)

Hyperconjugation

9) 4) \( \text{CH}_3 - \text{CH} = \text{CH}_2 \rightarrow \text{CH}_3 - \text{CH}_2 \rightarrow \text{CH}_2 \rightarrow 3\alpha-H \)

Hyperconjugation

Resonance effect

*E effect
Q5) a) D compared to benzene it is electron rich. b) Resonance

CH₂ - CH = CH₂  >  CH₂ = CH - CH₃

Resonance

Hyperconjugation

Inductive effect

Stability Order of Carbocation

(R) > (Ph₃)C⁺ > (Ph₂)C⁺ > Ph⁺ > (CH₃)₂C⁺ > CH₃⁺

CH₂ - CH = CH₂  >  (CH₃)₂C⁺  >  CH₃CH₂ > CH₃⁺

Que.  a) CH₂ - CH = CH₂  >  CH₃ - C - CH₃  >  CH₃ - C - CH₃

3°+group

Diagram:  a) carboxyclic

Order - (iii) > (i) > (ii)

Que. b) CH₂ - CH = CH₂  >  CH₃CH₂ = CH₂

(i)  (ii)

Diagram:  (c) "+" symbol

Order - (iii) > (i) > (ii)

Que. c) (R)  (R)

Diagram:  (c) "+" symbol

Order - a > c > b > d
LEARN! LEARN! LEARN!

- Learn there exceptionally highly stable carbocations:

\[
\begin{align*}
\text{cyclopropyl} & > \text{cyclobutyl} > \text{cyclopentyl} + \text{CH}_2 \\
\end{align*}
\]

**Ques.** \( \text{CH}_3 \to \text{CH}_2 \to \text{CH}_2 = \text{CH} \to \text{CH} = \text{C} \)

- (a) 3α-H
- (b) 2α-H
- (c) 1α-H

**Self Effect**

- Conclusion - The charge on the bond makes the compound unstable.

**Ques.**

\[
\begin{align*}
\text{(a)} & \quad \text{CH}_2^+ \quad \text{CH}_2^+ \\
\text{(b)} & \quad \text{CH}_2^+ \quad \text{CH}_2^+ \\
\text{(c)} & \quad \text{CH}_2^+ \quad \text{CH}_2^+ \\
\text{(d)} & \quad \text{CH}_2^+ \quad \text{CH}_2^+ \\
\end{align*}
\]

- Conclusion - The order is:

\[
\text{(c)} > \text{a} > \text{d} > \text{b}
\]

**Ques.**

\[
\begin{align*}
\text{(a)} & \quad \text{CH}_2^+ \quad \text{CH}_2^+ \\
\text{(b)} & \quad \text{CH}_2^+ \quad \text{CH}_2^+ \\
\text{(c)} & \quad \text{CH}_2^+ \quad \text{CH}_2^+ \\
\text{(d)} & \quad \text{CH}_2^+ \quad \text{CH}_2^+ \\
\end{align*}
\]

- Order - \( a > b > c > d \)

- Conclusion - \( +\text{M} \) effect than \( \text{OH} \) group.
Question 1:

Order: $\alpha > b > a > c$

Conclusion:

1. Mesomeric effect doesn't take place at meta-
2. Mesomeric effect doesn't depend upon distance, but $\pi$-effect does.

Thus, $(a > c)$

Question 2:

However, Hyperconjugation $> \pi$-effect

$a > b > c$
8. Carbon free radicals

These are odd e− species in which carbon atom bears the odd e−.

- $\text{CH}_3$ - Methyl free radical
- $\text{CH}_2\text{CH}_2$ - Ethyl free radical
- $\text{CH}_2\text{CH}_2\text{CH}_2$ - Propyl free radical
- $\text{CH}_2\text{CH} = \text{CH}_2$ - Allyl free radical
- $\text{CH}_3\text{CH} = \text{CH}_3$ - Iso-propyl free radical

Characteristics of Carbon free radical:

(i) There are lone e− in the outermost shell of Carbon.
(ii) Free radicals are electrophile.
(iii) Alkyl free radicals are $\text{sp}^2$ hybridized.
(iv) They are paramagnetic in nature.
(v) Free radicals react with itself to become neutral

$$\text{Cl} + \text{Cl} \rightarrow \text{Cl}_2$$

$$\text{H} + \text{H} \rightarrow \text{H}_2$$

(vi) They are formed by excess heat ($<500^\circ\text{C}$), electricity, light, peroxide, radicals - (HELPR)
Stability of free radicals

1. \( CH_3 \rightarrow CH_2 \rightarrow CH \rightarrow CH_3 + CH_2 \rightarrow CH_3 \)
   
   \( \text{H, I} \) \( \text{6-} \) \( \text{3-} \) \( \text{0-} \)
   
   \( CH_3 \) \( (\text{H, I}) \) \( (\text{H, I}) \)
   
   \( \text{9-} \)

2. \( CH_2 \rightarrow CH = CH_2 \rightarrow CH_3 \)
   
   \( a \) \( (R, H) \) \( b \) \( (H, I) \) \( c \)
   
   \( \omega - \) \( \text{3-} \) \( \text{0-} \)

LEARN \! LEARN \!

Stability series of carbon-free radical

\( (C_6H_5)_3C^+ > (C_6H_5)_2CH > (C_6H_5)CH_2CH > CH_2 = CH = CH_2 > (CH_3)_3C^+ > (CH_3)_2CH > CH_3 - CH_2CH_3 \)

(a) Arranged in the order of stability

\[ [I] \]

\[ \begin{align*}
(a) & \quad \begin{array}{c}
\text{(a)} \\
\text{(b)} \\
\text{(c)}
\end{array} \\
(b) & \quad \begin{array}{c}
\text{(a)} \\
\text{(b)} \\
\text{(c)}
\end{array}
\end{align*} \]

Order: \( b > c > a \)

\[ [II] \]

\[ \begin{align*}
(a) & \quad \begin{array}{c}
\text{(a)} \\
\text{(b)} \\
\text{(c)}
\end{array} \\
(b) & \quad \begin{array}{c}
\text{(a)} \\
\text{(b)} \\
\text{(c)}
\end{array}
\end{align*} \]

Order: \( d > c > a > b \)
Carboxoniums

Anion of Carbon is known as Carboanion. It carries 3 - b.p. and 1 - l.p. thus making the carbon atom negatively charged.

- \( \text{CH}_2 - \text{CH} = \text{CH}_2 \rightarrow \text{Allyl Carboanion} \)
- \( \text{CH}_3 - \text{CH}_2 \rightarrow \text{ethyl} \)

**Characteristics:**

1. It has 8 electrons in valence shell.
2. It behaves as nucleophile (nucleus lover).
3. Hybridisation - \( 2p^3 \)
   Shape - pyramidal

IV. It is diamagnetic in nature as all e- are paired.
Stability of Carbanions -

I. \( \text{CH}_3 \overset{+}{\text{C}} \text{=CH}_3 < \text{CH}_3 \overset{+}{\text{C}} \text{=CH}_2 < \text{CH}_3 \overset{+}{\text{C}} \text{=CH} < \text{CH}_3 \overset{+}{\text{C}} \text{=CH}_2 < \text{CH}_3 \)

II. \( \text{CH}_2 \overset{+}{\text{C}} \text{=CH} = \text{CH}_2 \quad \text{CH}_3 \overset{+}{\text{C}} \text{=CH} = \text{CH}_3 \quad \text{CH}_3 \overset{+}{\text{C}} \text{=CH} = \text{CH}_2 \)

(a) \quad (b) \quad (c)

Order - \( a > c > b \)

III. \( \text{CH}_3 \overset{+}{\text{C}} \text{=CH}_2 < \text{CH}_2 = \text{CH}^- < \text{CH} \equiv \text{C}^- \)

(a) \( \text{SP}^3 (25\%) \) \quad (b) \( \text{SP}^2 (33\%) \) \quad (c) \( \text{SP} (50\%) \)

\( \% \) S Character \( \propto E \cdot N \)

\( \therefore \) Order = \( c > b > a \)

Stability Series for Carbanions -

\( (\text{C}_6\text{H}_5)_3 \overset{+}{\text{C}} > (\text{C}_6\text{H}_5)_2 \text{CH} > \text{C}_6\text{H}_5 \text{CH}_2 \)

\( \text{CH}_2 \overset{+}{\text{C}} \text{=CH} = \text{CH}_2 \quad \text{CH}_3 \overset{+}{\text{C}} \text{=CH} = \text{CH}_2 \quad \text{CH}_3 \overset{+}{\text{C}} \text{=CH} = \text{CH}_2 \quad \text{CH}_3 \overset{+}{\text{C}} \text{=CH} = \text{CH}_2 \)

\( \text{CH}_3 \overset{+}{\text{C}} \text{=CH} = \text{CH}_2 \quad \text{CH}_3 \overset{+}{\text{C}} \text{=CH} = \text{CH}_2 \quad \text{CH}_3 \overset{+}{\text{C}} \text{=CH} = \text{CH}_2 \)

Order - \( b > a > c \)
Order - b > c > g > a > f > e > d
Carbene \( \{ \gamma - \overset{\cdot}{C} - \alpha \} \)

**Characteristics:**
- It has 6 e- neutral specie.
- It behaves as electrophile.
- It is e- deficient specie.
- It is highly unstable.

\[ \overset{\cdot}{:}CH_2 \rightarrow \overset{\cdot}{Methyl} \text{Carbene (Methylene)} \]

\[ \overset{\cdot}{:}CCl_2 \rightarrow \overset{\cdot}{Dichloro} \text{Carbene} \]

\[ \overset{\cdot}{:}C_6H_5 - \overset{\cdot}{C} - H \rightarrow \overset{\cdot}{Phenyl} \text{Carbene} \]

**Singlet Carbene**
- \( \Box CH_2 / 12CH_2 \)
- They are \( sp^2 \) hybridized
- Carbon remains in its ground state

**Triplet Carbene**
- \( \Box CH_2 / [\Box CH_2 \Box CH_2 \Box CH_2] \)
- They are \( sp^2 \) hybridized
- Carbon remains in exited state

- It has \( 2 \beta \) and \( 2 \varepsilon \) in each p-orbital
- 1 Vacant orbital
- \( \overset{\cdot}{\text{It is bent shaped or V-shaped}} \)
- \( \overset{\cdot}{\text{It has linear structure}} \)
- \( \overset{\cdot}{\text{It is diamagnetic}} \)
- \( \overset{\cdot}{\text{It is paramagnetic}} \)
At violates Hund's rule. At follows Hund's rule.

Spin state: \[ 2 \uparrow 2 \downarrow \uparrow \downarrow \uparrow \downarrow \]

\[ 2 \frac{1}{2} - \frac{1}{2} + 1 \]

\[ 2 \times 0 + 1 \]

\[ -1 \]

\[ 3 \]

Which one is more stable?

a) Singlet methylene, triplet methylene

Solution

Triplet methylene is more stable.

Here, repulsion is less, hence stable.

Stability of Carbene

(a) \[ \begin{array}{c} \text{T} \text{CCl}_2 \\ \text{Triplet} \end{array} \] \[ \begin{array}{c} \text{C} \text{Cl}_2 \\ \text{Singlet} \end{array} \]

Here, repulsion is more, hence unstable.

(b) \[ \begin{array}{c} \text{T} \text{CBr}_2 \\ \text{Triplet} \end{array} \] \[ \begin{array}{c} \text{CBr}_2 \\ \text{Singlet} \end{array} \]

Partial back bonding.
Triplets carbene are also known as diradical.

### Formation of Carbene—I (It is not a product)

1. $\text{CHCl}_3 + \text{KOH} \rightarrow$

\[
\begin{align*}
\text{Cl}^- & \rightarrow \text{C}^+ + \text{H}^+ \ + \text{OH}^- \rightarrow \text{Cl}^- \ + \text{C}^- \\
\text{Cl}^- & \rightarrow \text{KCl} \\
\text{Cl}^- \rightarrow \text{C}^- \ (\text{Singlet carbene})
\end{align*}
\]

2. $\text{CHF}_2\text{Cl} + \text{OH}^- \rightarrow \text{CHClO}$

\[
\begin{align*}
\text{F}^- & \rightarrow \text{Cl}^- \ + \text{Cl}^+ \ + \text{OH}^- \rightarrow \text{F}^- \ + \text{H}_2\text{O} \\
\text{Cl}^- & \rightarrow \text{F}^- \ + \text{C}^- \ + \text{K}^+ \\
\text{F}^- & \rightarrow \text{Cl}^- \ + \text{C}^- \ (\text{Difluoro singlet carbene})
\end{align*}
\]

3. $\text{CH}_2\text{Br}_2 \rightarrow$

\[
\begin{align*}
\text{I}^- & \rightarrow \text{C}^- \ + \text{H}^+ \ + \text{OH}^- \rightarrow \text{I}^- \ + \text{H}_2\text{O} \\
\text{Br}^- & \rightarrow \text{I}^- \ + \text{C}^- \ + \text{K}^+
\end{align*}
\]
Pyrolysis/Photolysis of Diazomethane (\( \text{CH}_2\text{N}_2 \))

\[
\text{CH}_2 = \text{N} = \text{N} \xrightarrow{\Delta, \text{hv}} \text{N}_2 \uparrow + \cdot \text{CH}_2
\]

# Rearrangement of Carboxation

→ It wants to gain stability.

→ Stable carboxations can be formed by these shifts

(i) Hydride Shift (\( \text{H}^- \))

(ii) Alkyl Shift (\( \text{CH}_3^- \))

(iii) Pheny Group Shift (\( \text{Ph}^- \))

- Some examples –

1. \( \text{CH}_3 - \text{CH}_2 - \text{CH}_2 \xrightarrow{[1,2]} \text{H}^- \)  
   \( \text{CH}_3 - \text{CH}^+ - \text{CH}_2 \)
   
   → 1° carboxation (less stable) → 2° carboxation (more stable)

2. \( \text{CH}_3 - \text{C} - \text{CH}_2 \xrightarrow{[1,2]} \text{CH}_3 - \text{C}^+ - \text{CH}_2 - \text{CH}_2 \)
   
   → 1° carboxation (more stable) → 2° carboxation (less stable) → 3° carboxation (more stable)

3. \( \text{Ph} - \text{C} - \text{CH} \xrightarrow{[1,2]} \text{Ph}^- \)  
   \( \text{Ph} - \text{C}^+ - \text{CH} - \text{Ph} \)
   
   → Does stable → More stable
Migratory Aptitude:

- More e⁻ density
- More e⁻ donating group

Order: \( H^+ > Ph^+ > 3°alkyl > 2°alkyl > 1°alkyl > CH_3 \)


Arrange in the order of migratory aptitude:

\[ \begin{align*}
(a) & \quad \text{O} \\
(b) & \quad \text{O} \\
(c) & \quad \text{NO}_2 \\
\end{align*} \]

\[ \text{Order} = b > a > c \]

Question:

\[ \text{CH}_3 - C - \text{CH}_2 - C_H \text{[shift]} \rightarrow \text{CH}_3 - C - \text{CH}_3 \]

More stable

5)

\[ \text{CH}_3 - \text{C} - \text{C}_H \text{[shift]} \rightarrow \text{CH}_3 - \text{C} - \text{CH}_3 \]

More stable

Note: Shifting continues until the carbocation becomes most stable. (It wants stability in each step.)
Extended Shifting:

6) \[ \text{CH}_3 - \text{CH} - \text{CH}_2 - \text{CH}_2^+ \xrightarrow{\text{shift}} \text{CH}_3 - \text{CH} - \text{CH} - \text{CH}_3 \]

\[ \text{CH}_3 - \quad \text{C}^+ - \text{CH}_2 - \text{CH}_3 \]

\[ \text{CH}_3 - \quad \text{CH}_3 \]

4) \[ \text{CH}_3 - \text{CH} - \text{CH} - \text{CH}_2 - \text{CH}_2^+ \xrightarrow{1/2 \text{H}^-} \text{CH}_3 - \text{CH} - \text{CH} - \text{CH} - \text{CH}_3 \]

\[ \text{CH}_3 - \quad \text{CH}_3 \]

Extended Shifting:

\[ \text{CH}_3 - \text{CH} - \text{C}^+ - \text{CH}_2 - \text{CH}_3 \]

\[ \text{CH}_3 - \quad \text{CH}_3 \]

Most stable than any formed in each step.
(B) $\text{CH}_3 - \text{C}^+ - \text{CH}_2 - \text{CH}_3$

More stable due to more migratory aptitude.

(A) Only formed when it is rate-determining step (RDS) as in case of back-bonding.

(B) $\text{CH}_3 - \text{C}^+ - \text{CH}_2 - \text{CH}_3$

More stable

In most cases, (B) forms as carbocation wants more stability.

back-bonding $\text{C}^+\text{OCH}_3$

(As backbonding takes place first)

(B) $\text{OCH}_3 - \text{C}^+ - \text{CH}_2 - \text{CH}_3$

3° benzylic + Back bonding (93%)

+ Resonance (7%)
2° + Resonance stabilized

5α-H

No restable

5α-H

One of the (most stable.)