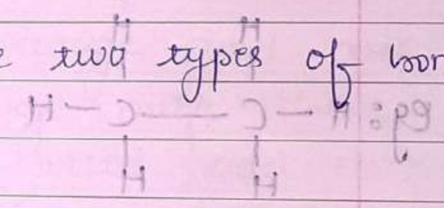
GOC (GENERAL ORGANIC CHEM.):

* **Bond Cleavage:**

Heterolytic cleavage	Homolytic cleavage
↓	↓
ions are formed	free radicals are form
↳ C^+ = carbocation (carbonium)	$\dot{C}H_3$
↳ C^- = carbanion	(C-free radical)

- during chemical reaction there are two types of bond cleavage are formed: ← homolytic cleavage

eg:


→ 1) Heterolytic cleavage:
- in this process of bond breakage, electron pair is moved towards one of the atom with more electronegativity.

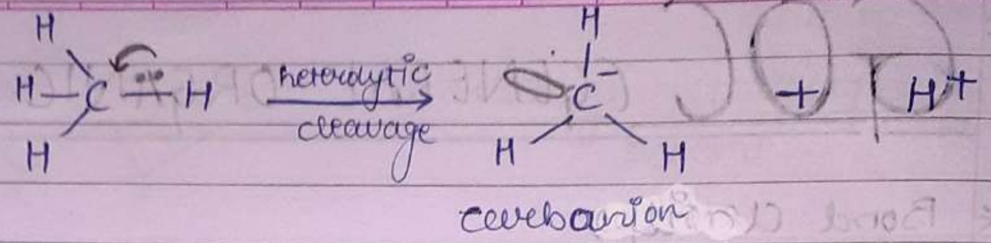
- due to unequal distribution of electrons ions are formed.

eg: $HCl \longrightarrow H^+ \; Cl^-$ $\qquad$ $CH_3Cl \longrightarrow CH_3^+ \; Cl^-$

CH_3^+ → methyl carbocation (Reaction intermediate)

Cl^- → Chloride

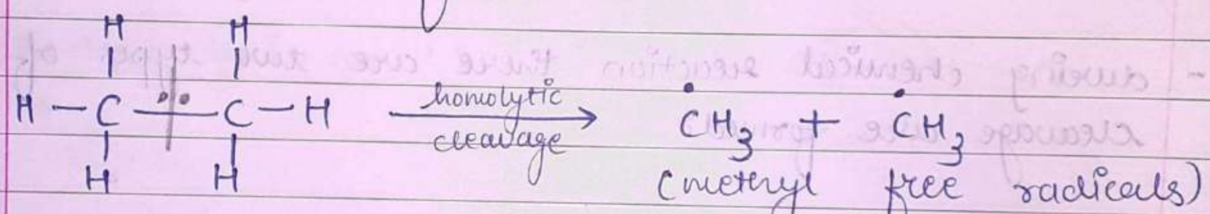
- in this type of cleavage we also get carbon atoms which are positively (+ve) called CARBOCATION and negatively (-ve) called CARBANION. (charged) eg: CH_4 or



→ II) Homolytic cleavage:
- after bond breakage when electrons are distributed equally among reactants.

- the intermediate species during homolytic cleavage are called free radicals.

eg:



* Reaction intermediate:

1.) CARBOCATION:
- formed due to heterolytic cleavage.
- positively charged. (+ve) carbon atom
- due to electron-deficiency, they act as an **electrophile** and always attack over electron-rich site.
- they have incomplete octate. as they have 6-electrons in valence shell hence are called OCTATE-DEFICIENT species,
- Sp^2 hybridised. (trigonal planner shape)

2.) CARBANION:

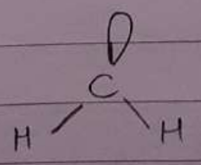
- formed due to heterolytic cleavage.
- negatively charged (C-ve) carbon atom.
- total 8 electrons are available in their valence shell (6 bonded e^- + $2e^-$ (LP))
- sp^3 hybridised. and due to presence of non-bonded electrons they act as a NUCLEOPHILE.
- tetrahedral shape.

* Free radicals:

- formed due to homolytic cleavage and are neutral species with no charge over them.
- have an unpaired electron called odd electron.
- total 7 valence electrons (6 bonded + 1 radical)
- sp^2 hybridised.
- have incomplete octate and are called electron deficient species.

* Carbene:

- are electron deficient neutral species where unpaired electron are present over carbon atom. (2 non-bonded electrons).
- behaves as an electrophile.
- total six electrons are available in valence shell.
- 4 electrons are bonded and 2 are non-bonded electrons.
- sp^2 hybridised.



(CH_2)

* Difference between electrophile and nucleophile:

ELECTROPHILE	NUCLEOPHILE
- accept electron pair.	- supplies electron pair.
- electron deficient.	- electron rich.
- attack points at high electron density.	- attacks point of low electron density
- lewis acid	- lewis base
- possess empty orbital to receive electron pair.	- possess an electron pair which is loosely held and can be supplied easily.
- usually positively charged species.	- usually negatively charged species.
- forms an extra bond with nucleophile.	- increase its covalency by one unit.

* Electron displacement effect:

- Permanent effect
  - Inductive effect (I effect)
  - Resonance effect or Mesomeric effect
  - Hyperconjugation effect (H - effect)
- Temporary effect
  - Electromeric effect

* 1.) Inductive effect [I-effect]:

- permanent effect with polarisation of a molecule due to displacement of 'σ' electron towards more electronegative element.
- it is not related to any kind of 'π-bond' participation
- it is a $\boxed{\text{weak effect}}$ due to 'σ' bond presence.
- inductive effect decreases on increasing distance from electronegative atom.
- it is negligible after counting three atoms from 3 electronegative atoms.
- this effect is relative effect and it depends upon the attached group.
- Hydrogen is used as reference in studying I-effect
- I-effect of hydrogen is zero.

$$\overset{}{CH_3} - \overset{+\delta\delta\delta}{CH_2} - \overset{+\delta\delta}{CH_2} - \overset{+\delta}{CH_2} - \overset{-\delta}{F} \rightarrow -I \text{ group.}$$

- 2 possible groups:

A.) Electron donating group (+I group): $CH_3 \rightarrow +I$
- more electron donating as compared to hydrogen

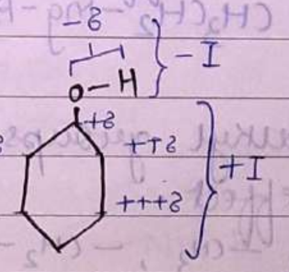
B.) Electron withdrawing group (−I group): $F \rightarrow -I$
- more electron withdrawing as compared to hydrogen

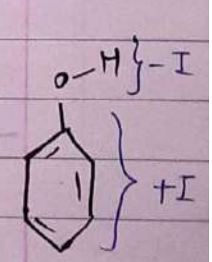
Q:1 Find +I / −I group:-

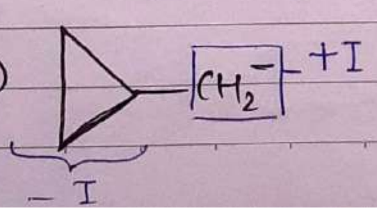
(A) $\overset{++\delta}{CH_3}\ \overset{+\delta}{CH_2}\ \overset{-\delta}{Cl}$

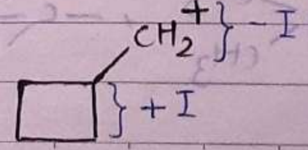
$\rightarrow +I \Rightarrow CH_3CH_2$

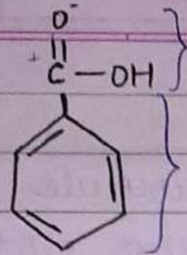
$-I \Rightarrow Cl$

(B)


(C)


(D)


(E)


(F) 

(G) $\underbrace{CH_3 -}_{+I} \underbrace{\overset{sp}{C} \equiv CH}_{-I}$

(%S ↑ electronegativity ↑)

(H) $\underbrace{CH_3 - CH}_{+I} = \underbrace{\overset{sp^2}{C}H_2}_{-I}$ (%S) ↑

(I) $\underbrace{CH_2 = CH}_{+I} - \underbrace{C \equiv CH}_{-I}$

(J) $\underbrace{CH_3 - CH_2}_{+I} - \underbrace{NO_2}_{-I}$

(K) $\underbrace{CH_3 - C \equiv C}_{+I} - \underbrace{CN}_{-I}$

*** NOTE:**
- while identifying +I or -I effect in a compound than consider the complete group, not just an atom.

+I effect group	-I effect group
- negatively charged species (ANION) are included. [eg: $-CH_2^-$, $-O^-$]	- positively charged species (CATION) are included. [eg: $-CH_2^+$, $-NH_3^+$]
- if any metal attached to the main chain then it shows +I effect always. [eg: $CH_3CH_2-Mg-Br$]	- all halogens show -I effect always. [eg: F^-, Cl^-, Br^-, I^-] [eg: CH_3-CH_2-I]
- all alkyl groups show +I effect. [eg: $-CH_3$, $-CH_2-CH_3$] [$-CH(CH_3)_2$, $-C(CH_3)_3$]	- group of electronegative atoms show -I effect. [eg: $-NO_2$, $-\overset{O}{\overset{\Vert}{C}}-OH$, $-CF_3$]

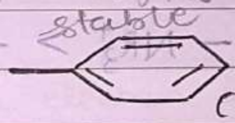
Mg-Br ⇒ Grignyar reagent

$-O^+<^H_H$

⟹ Comparison of −I / +I group:

★⟹ A.) −I group:

- $-F > Cl > Br > I$
- $-C\equiv N > -C\equiv CH$
- $-OH > -C\equiv CH$
- $-C\equiv CH > -CH=CH_2$
- $-NO_2 > -C\equiv N$
-  >

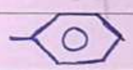
Q:2 $-NO_2$ (A) ; $-CHO$ (B) ; $-F$ (C) ;  (D) Arrange.

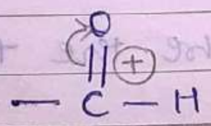
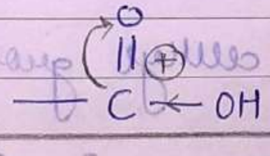
→ a > b > c > d

Overall order of −I effect in different group:

$-N^+F_3 > -N^+R_3 > -N^+H_3 > -NO_2 > -CN$

$> -\overset{O}{\overset{||}{C}}-H > -\overset{O}{\overset{||}{C}}-R > -\overset{O}{\overset{||}{C}}-OH > -F > -Cl > -Br$

$> -I > -OR > OH > -C\equiv CH > -NH_2 >$  $> -CH=CH_2 > -H$

> ★ NOTE:
> - CHO show more −I effect as compared to −COOH, as in −COOH group −OH reduces charge on carbon atom of carbonyl groups.
>
>  more (directly) 

Q:3 Arrange:  (A) ; $-SO_3H$ (B) ; $-NH^+R$ (C) ; $-F$ (D) ; $-CH_2$ (E)

⟶ c > b > d > a > e

*** NOTE:**

- substituted heteroatom (N, O, S) are more electronegative as compared to less substituted due to availability of bulky groups and bond angle.

$-OR > -OH \quad -N^+R_3 > -NH_3^+ \quad -NF_3^+ > NR_3^+$

$-NR_3^+ > -NHR > -NH_2$

*** NOTE:**

- sp hybrid carbon atom is more electronegative as compared to sp^3 hybrid Nitrogen atom

$-C\equiv CH > -NH_2$

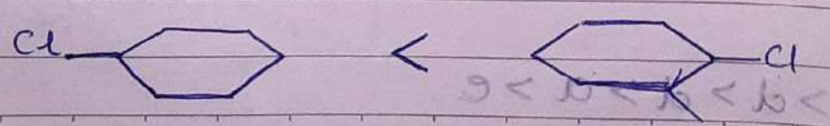
★ ⟹ B.) +I group:

Q:4 Compare different +I groups:

⟶ $-CH_3 < -CH_2-CH_3 < -\underset{}{\overset{CH_3}{\overset{|}{C}}}H-CH_3 < -\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$

- larger the alkyl group more will be the +I effect

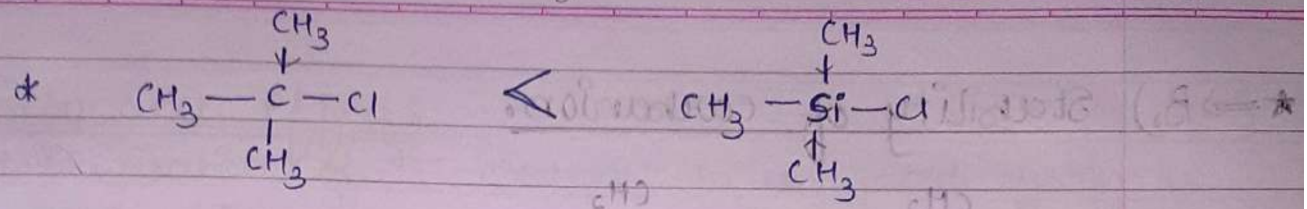
* $CH_3CH_2CH_2CH_2F < CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3$

* 

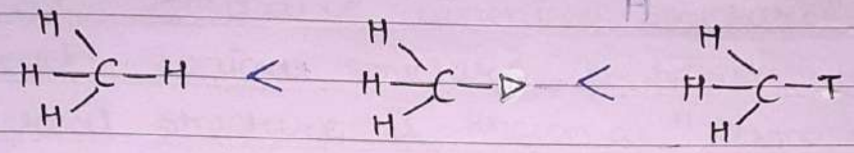
→ Jitna charge distributed utna I-effect

to +I grp → charge dis ↑ +I ↓

−I grp → charge dis ↑ −I ↑



eg: $-CH_2^- > -NH^- > -O^-$



(ISOTOPES) (OF Hydrogen)

⟹ heavier isotopes have more electron density hence, they will show more +I effect.

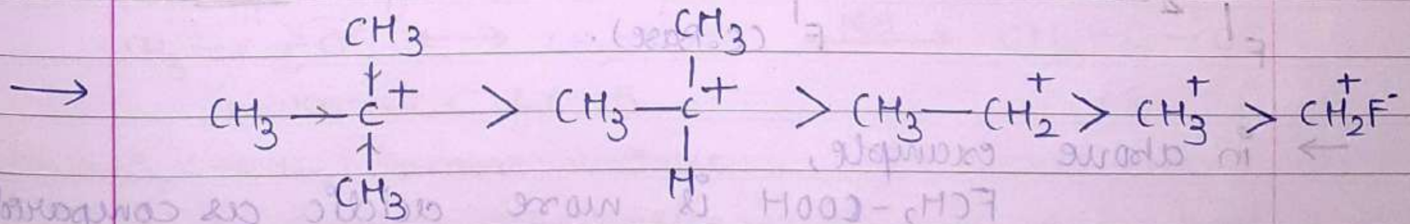
- overall order of +I effect in different groups:

$-CH_2^- > -NH^- > -O^- > -\overset{O}{\overset{||}{C}}-O^- > -C(CH_3)_2-CH_3 > -CH(CH_3)-CH_3$ (distance)

$> -CH_2-CH_3 > -CH_3 > -T > -D > -H$

⟹ Application of I-effect:

★⟹ A.) Stability of carbocation:



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

- equal distribution of charge leads to more stability of ion.

★⟹ B.) Stability of carbanion:

⟶ $CH_3-\underset{CH_3}{\overset{CH_3}{C^-}} < CH_3-\underset{H}{\overset{CH_3}{C^-}} < CH_3-CH_2^- < CH_3^-$

eg: $CH_3-CH_2-\underset{F}{CH}-CH_2^- > CH_3-\underset{F}{CH}-CH_2-CH_2^- > \underset{F}{CH_2}-CH_2-CH_2-CH_2^-$

(distance ↓ charge ↑ −I ↑)

★⟹ C.) Determine Acidity:

Strength of Acid ∝ Stability of conjugated base ∝ $\frac{-I \text{ effect}}{+I \text{ effect}}$

eg: $CH_3COOH \rightleftharpoons CH_3COO^- + H^+$ <u>case-1</u>
(C Base)

$\underset{F}{CH_2}COOH \rightleftharpoons \underset{F}{CH_2}-COO^- + H^+$ <u>case-2</u>
(C. Base).

→ in above example,
FCH_2-COOH is more acidic as compared to CH_3COOH as FCH_2-COO^- (conjugated base) is more stable as compared to CH_3COO^-.

eg:- $CH_3-CH_2-\underset{F}{CH}-COOH$ > $CH_3-\underset{F}{CH}-CH_2-COOH$
|←dist→| |←dist→|

$HCOOH > CH_3COOH$