

Inductive
 $A.S \propto -I \propto K_a \propto P K_b$
 $A.S \propto +I \propto P K_a \propto K_b$

$D > N > P$
 $HF_3 > HCl_3 > NH_3 > NO_2 > ...$
 $I > Cl > OH > ...$

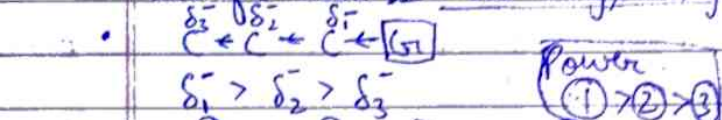
Basic Concepts of Organic Chemistry

Organic compounds are formed by covalent bonds.
 Different factors that influence organic reactions are:
 (1) Inductive Effect (2) Electromeric effect (3) Resonance (4) Hyperconjugation

Inductive Effect: - The polarization of a σ bond due to electron withdrawing or e^- donating effect of adjacent group.

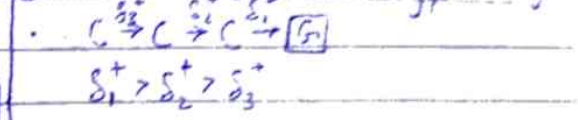
- Partial charge development.
- Can be neglected after 3rd atom.
- Distance dependent.

+ I
 If the substituent attached at the end of C-chain is e^- donating/releasing.



- ① $-CH_3 > -NH_2 > -O^- > -COO^-$
- ② $3^\circ > 2^\circ > 1^\circ > -CH_3$
 $-CMe_3 > CHMe_2 > CH_3CH_2$
- ③ $T > D > H$ ④ $SiH_3 > CH_3$

- I
 If substituent attached to the end of C-chain is e^- withdrawing/accepting.



- $-NO_2 > -CN > -COOH > -F > -Cl > -Br > -I > -H$

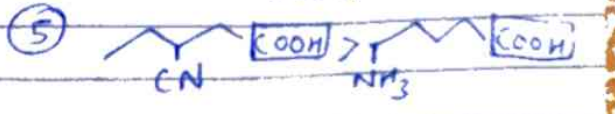
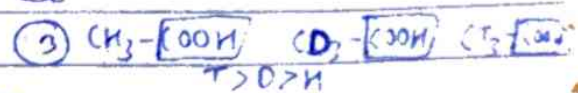
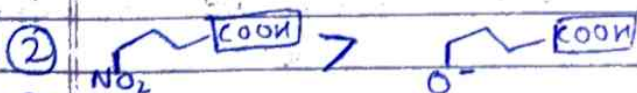
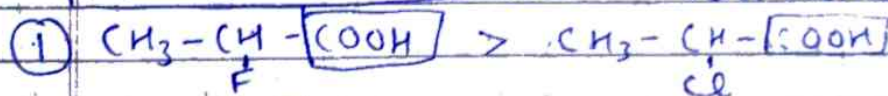
Application of Inductive
 → To determine acidic strength.

PRIORITY $D > N > P$
 Distance > No. > Power

$A.S \propto -I \propto \frac{1}{+I}$

Due to -I, stability increases as EWG stabilizes COO^- while EDG destabilizes COO^- .

$A.S \uparrow K_a \uparrow P K_a \downarrow P K_b \uparrow K_b \downarrow$

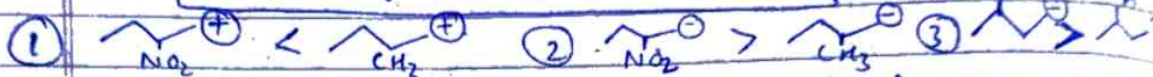


→ To determine stability of carbocation and carbanion

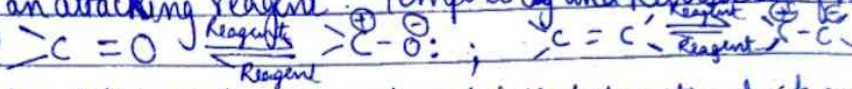
$$\text{Stability of Carbocation} \propto +I \propto \frac{1}{-I}$$



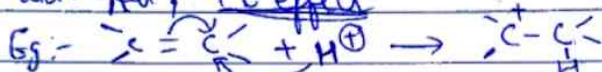
$$\text{Stability of Carbanion} \propto -I \propto \frac{1}{+I}$$



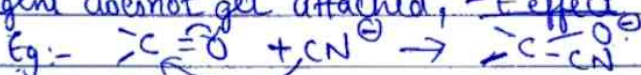
• Electromeric Effect:- It is an intramolecular movement of e^- s from a pi bond to another atom in the molecule in the presence of an attacking reagent. Temporarily and Reversible. [After removal of reagent]



✓ → If $\pi-e^-$ s of multiple bond are transferred to that atom to which reagent gets attached, +E effect

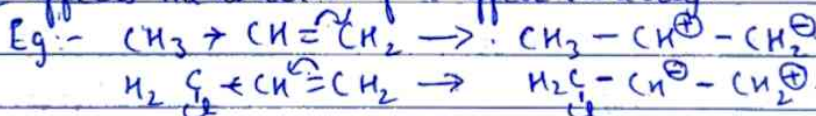


✓ → If $\pi-e^-$ s of multiple bond are transferred to the atom to which attacking reagent does not get attached, -E effect



✓ → In general, Unsaturated system shows +E effect with electrophile and -E effect with nucleophiles.

✓ → If a grp attached to multiple bonded C atom having +I or -I effect, it affects the direction of E effect directly.



• Resonance or Mesomeric Effect

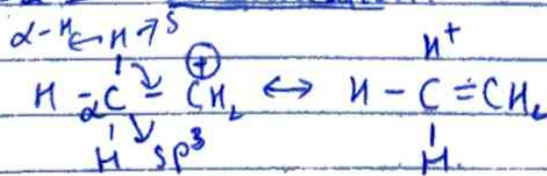
No bond Resonance

★ Hyperconjugation:- Delocalisation of e^- s with the participation of bonds of primarily σ character through $\sigma-\pi$ or $\sigma-p$ orbitals.

→ Similar to resonance but extended to σ bonds (Baker Nathan effect)

→ Since, there is no bond b/w Carbon and H atom in these structures, so also known as No bond Resonance.

• Case 1:- In carbocation



No. of Hyperconjugative structures = No. of $\alpha-H$.

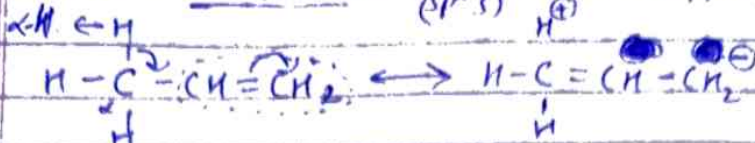
$\sigma-p$ overlapping = $sp^3 s$

Priority: Hyperconjugation > Inductive

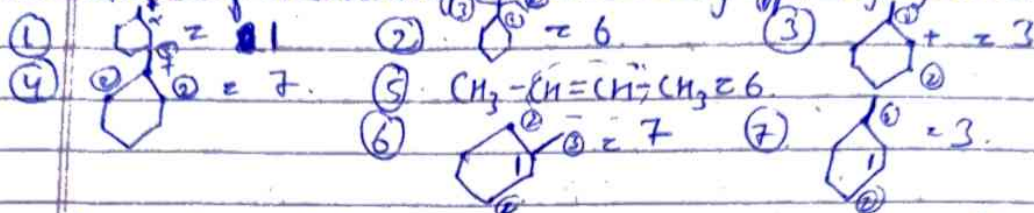
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Case 2:- In Alkenes ($\sigma - \pi^*$ overlapping)



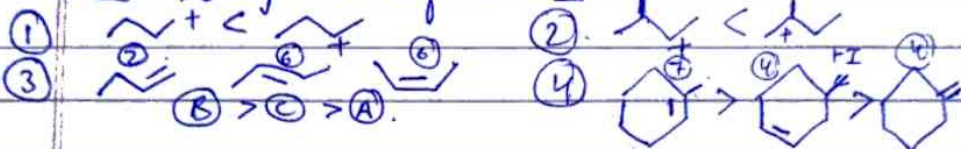
① Total no. of contributing Struct. showing hyperconjugation



* Application of Hyperconjugation:-

• To compare stability of Carbocation & alkenes

[Stability & No. of α -H]



$\text{H} > \text{I}$

Trans > Cis

* Significance of Hyperconjugation effect

- Directive influence of alkyl groups :- o, p - directing
- Shortening of C-C adjacent to multiple bonds
- Relative stabilities of alkenes
- Stability of carbocations and free radicals

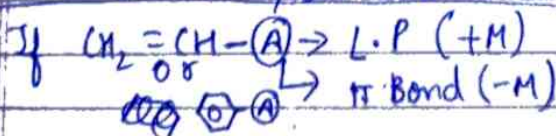
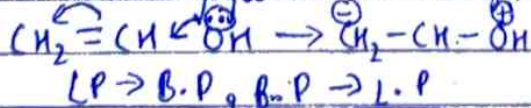
* Resonance or Mesomeric effect :- Polarity created b/w atoms of a conjugated system via e^- transfer or π bond transfer

→ Operate to π bond → Distance independent → Actual charge development

✓ → Conjugation:- $\text{A}^{\oplus}-\text{B}=\text{C}, \text{A}-\text{B}=\text{C}^{\oplus}, \text{A}^{\oplus}-\text{B}=\text{C}^{\oplus}, \text{A}-\text{B}=\text{C}^{\oplus}$
 $\text{A}=\text{B}-\text{C}=\text{D}$

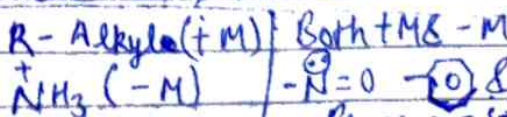
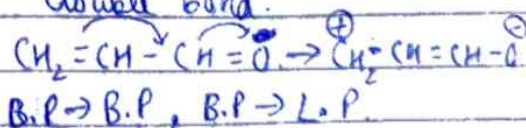
* $+M$

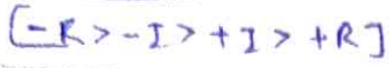
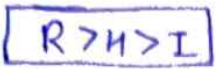
• Groups which donate e^- to double bond or to a conjugated or aromatic system



$-M$

• Groups which withdraw e^- from double bond





More Resonating structures \uparrow , Stability \uparrow
 Resonance hybrid Stable \uparrow No.
 delocalisation lower the energy

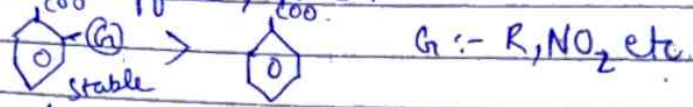
Application of Mesomeric Effect

To determine Acidic Strength of Aromatic Carboxylic acid.

$[A.S \propto -M \& -I \propto \frac{1}{+M \& +I}]$

Imp points

- ① M effect doesnot operate on meta position
- ② $+M > -I$ ($-OH, -OCH_3, -NH_2, F$)
- ③ $-I > +M$ ($-Cl, Br, I$)
- ④ $+M$ of L.P $> +M$ of Alkyl ($-OH > -CH_3$)
- ⑤ Ortho effect (S.I.R) Steric Inhibition in Resonance
 Due to Ortho effect, A.S \uparrow



Q Compare Acidic Strength

① ① > ②

② ① > ②

③ ① > ②

④ ① > ②

⑤ ② > ①

⑥ ② > ①

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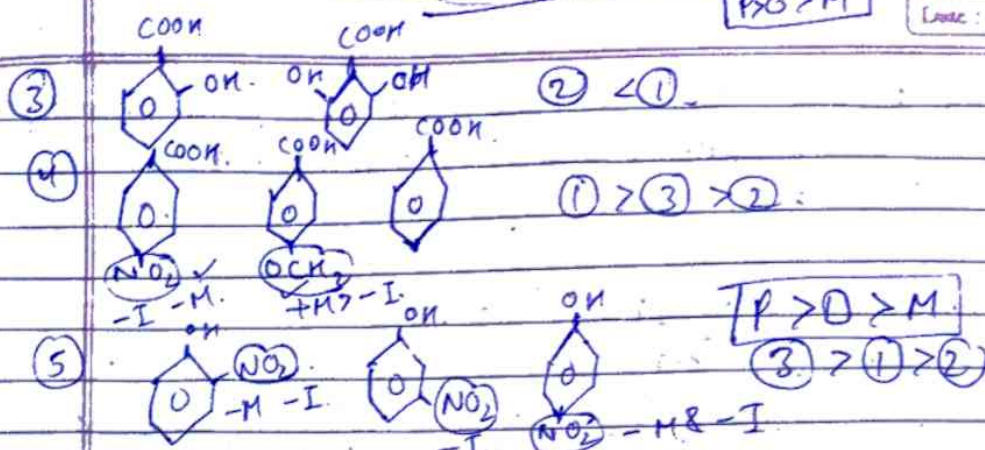
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If Phenol derivative
No ortho effect

$P > O > M$

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- M effect :- Eg:- $>C=O$, $-CHO$, $-COOR$, $-CN$, $-NO_2$
- +M effect :- Eg:- $-OH$, $-OR$, $-SH$, $-SR$, $-NH_2$, $-NHR$, $-Cl$, $-Br$, $-I$

* Reagent types :- ① Electrophiles ② Nucleophiles.

Electrophiles (e^- -loving) :- Electron deficient species and tend to attack the substrate at a site of high e^- density.

Incomplete octet

→ Maybe neutral (Lewis acids such as BF_3 , $AlCl_3$, $ZnCl_2$) & Carbenes (CCl_2) or +vely charged species.

Eg:- Cl^+ , Br^+ , NO_2^+ , NO^+ , H^+ , $CH_3-C(=O)$ (+vely charged)
 CO_2 , SO_3 , CCl_4 , $AlCl_3$, BF_3 (neutral)

Nucleophiles (e^- -hating) :- They are e^- -rich species, maybe neutral having non-bonding lone pair of e^- s or negatively charged.

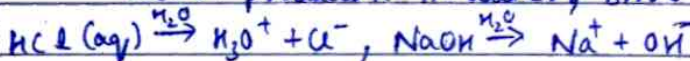
Complete octet

→ Tend to attack e^- deficient species.

Eg:- Cl^- , Br^- , OH^- , CN^- , SH^- , NH_2^- , OCN^- (-vely charged)
 H_2O , $R-O-H$, NH_3 , $R-NH_2$, R_2O , Me_2S (neutral)

* Arrhenius Theory :- He stated that ionic compounds dissociate when dissolved in water and can become free ions acting as individual entities in solution.

ACID: produces H^+ in water, BASE: produces OH^- in water.



Arrhenius acid & base neutralises each other to produce salt and water.

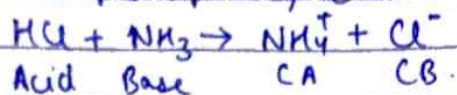


Arrhenius theory requires reactions to take place in solution (aqueous).

* Bronsted-Lowry Theory :- His approach was not limited to aqueous solution but for all protons (H^+) containing species. He defined acid and bases as donor and acceptor of proton respectively.

ACID :- Donate proton, BASE - Accept proton.

- Acid transfer its proton to medium or base and rxn occurs. The product of rxn is ^{of conjugate base} formed.
- When base accepts a proton, it becomes conjugate acid.



- For acidic rxn, $\text{HA} + \text{H}_2\text{O} \rightleftharpoons \text{A}^- + \text{H}_3\text{O}^+$

$$K_a = \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}][\text{H}_2\text{O}]}$$

as water is solvent

$$= \frac{[\text{A}^-][\text{H}_3\text{O}^+]}{[\text{HA}]}$$

$$K_a \propto \text{Acidic strength}$$

$$pK_a \propto \frac{1}{\text{A.S.}}$$

$$pK_a = -\log K_a$$

- For Basic rxn, $\text{B} + \text{H}_2\text{O} \rightleftharpoons \text{BH} + \text{OH}^-$

$$K_b = \frac{[\text{BH}][\text{OH}^-]}{[\text{B}]}$$

$$K_b \propto \text{B.S.}$$

$$K_b \propto \frac{1}{\text{B.S.}}$$

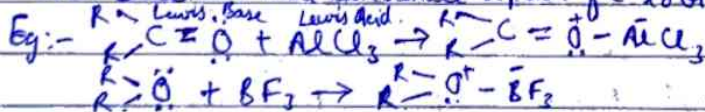
$$pK_b = -\log K_b$$

* Lewis Theory:-

- Arrhenius theory didnot support acid-base behaviour in non-aqueous system.
- Bronsted & Lowry theory excluded non-protonated system.
- Lewis suggested theory that explained all kinds of acids & bases.

ACID: e^- deficient substances that can accept a pair of e^- from another substance to form an adduct.

BASE: e^- rich substance that can donate a pair of e^- to other substance to form an adduct.



Lewis Acid:- Eg:- H^+ , BF_3 , ZnCl_2 , AlCl_3 , FeCl_3 , SnCl_4 etc.

Lewis Base:- H_2O , R-OH , R-O^- , R-OH , RCH_2O^- , R_3N , R_2S etc.

* Hard and Soft Acids & Bases