

GOC

Basics:- Sarak hel electron density ka hai.

Electron density $\propto \frac{1}{\text{Size}}$

E.g:- Size:- C > N > O > F

Electron density:- $C^\ominus < N^\ominus < O^\ominus < F^\ominus$

Electron density $\propto (-\text{ve}) \text{ charge} \propto \frac{1}{(+\text{ve}) \text{ charge}}$

E.g:- Electron density:- $A^{3-} > A^{2-} > A^- > A > A^+ > A^{2+}$

Inductive Effect

- Operate to sigma bond.
- Partial charge development.
- Distance dependent effect.
- Can be neglected after 3rd C-atom.

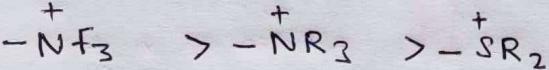
Power of Inductive effect

$+I$ Power :- (e⁻ donating grp)

$-CH_2^\ominus > -NH^\ominus > -O^\ominus > -COO^\ominus > 3^\circ R > 2^\circ R > 1^\circ R > -Me$

$-T > -D > -H \rightarrow$ No inductive (zero)

$\Rightarrow -I$ group :- (e⁻ withdrawing grp)



Na Farhan Na Ritik Shahrukh

$-NH_3^+ > -NO_2 > SO_3H > -CN >$

Na Hiresh Na Omprati Salman Cyana

$-CHO > -COOH > -F > -Cl > -Br >$
Ali Ki Carme Father Collector Beta

$-I > -OR > -OH > -C\equiv CH >$
Inspector aur Alcohol ki Mumkin Alkyne

$-NH_2 & NR_2 > -Benz > Ene > H$
nahi hai Benzene ene hai

Applications

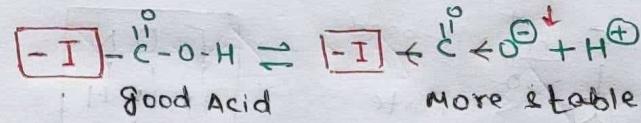
① To compare Acidic strength of Aliphatic carboxylic Acid

without Benzene ring

(openchain
cycloalkane)

OP Point:-

$$A \cdot S \propto [H^+] \propto K_a \propto \frac{1}{pH} \propto \frac{1}{pK_a}$$



$$A \cdot S \propto I \propto \frac{1}{+I}$$

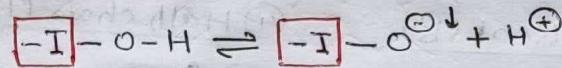
-I stabilizes anion
+I destabilizes anion

$$D > N > P$$

Distance Number Powers

DNP Trick
DO NOT PLAY

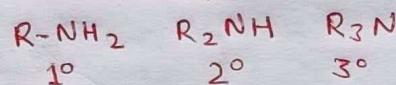
To compare A.S of Alcohols



$$A \cdot S \propto I \propto \frac{1}{-I} \rightarrow \text{Same as carboxylic acid.}$$

To compare Basic strength of Amines

$$B \cdot S \propto I \propto \frac{1}{-I}$$



In gas phase:- $3^\circ > 2^\circ > 1^\circ$

In aqueous medium:- R=me ($2^\circ > 1^\circ > 3^\circ$)

R=Et ($2^\circ > 3^\circ > 1^\circ$)

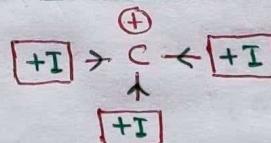
onwards $\rightarrow R = Prop, but ... etc$

Always $[3^\circ > 2^\circ > 1^\circ]$

According to solvation:- $[1^\circ > 2^\circ > 3^\circ]$

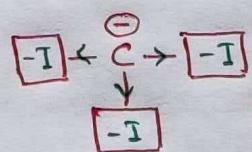
According to $+I$ effect:- $[3^\circ > 2^\circ > 1^\circ]$

To compare stability of carbocations



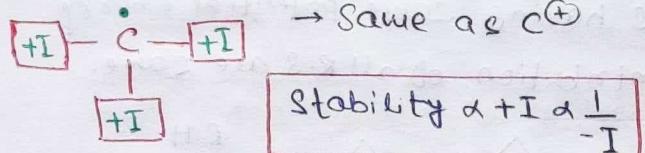
$$\text{Stability} \propto +I \propto \frac{1}{-I}$$

To compare stability of carboanions



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

⑥ To compare stability of free radicals



Hyperconjugation: $[C^+, C^{\cdot}, C=C]$

→ Baker-Nathan effect
or
No bond resonance

* Condition for exhibition of hyperconj.

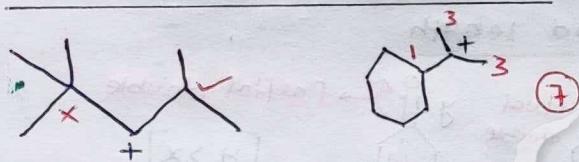
① $\alpha-C \rightarrow sp^3$

② $\alpha-H$

→ Total no. of hyperconjugative structures (Involving C-H bond breaking) = no. of $\alpha-H$

→ Total no. of Hyperconjugative structures = no. of ($\alpha-H + 1$)

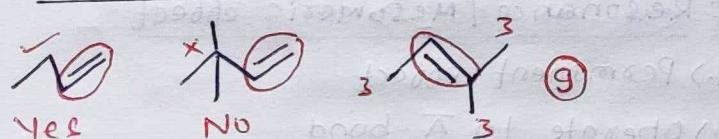
① Carbocation ($\sigma +$ vacant P)



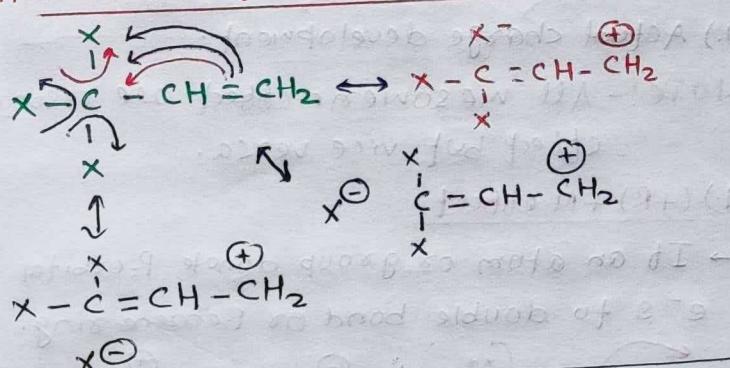
② Free radical ($\sigma +$ half-filled P)



③ Alkenes ($\sigma + \pi^*$ overlapping)



Reverse hyperconjugation (-H)

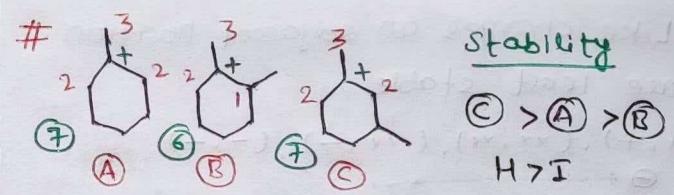


Application of Hyperconjugation

→ To compare stability of $C^+, C^{\cdot}, C=C$.

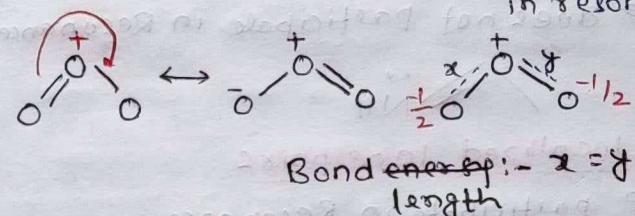
Stability \propto no. of $\alpha-H$

Priority
 $H > C > I$



RESONANCE

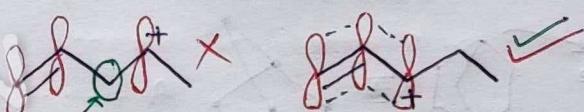
- Resonating str. are hypothetical.
- Resonance hybrid → Actual structure (Most stable)
- πe^- movement, atom can not move in resonance.



Type of conjugation

Condition for exhibition of Resonance

- Comp. must be planar
- Conjugation system p^3 parallel position of P-orbitals.

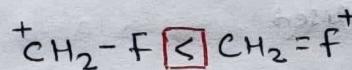


Stability of Resonating structure

- Neutral R.S. > Charged R.S.

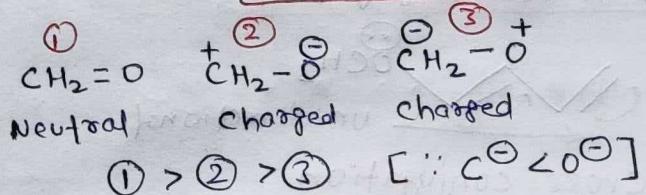


- Stability \propto no. of π -bonds



- Stability of R.S. & stability of charge

Priority: $-ve > +ve$

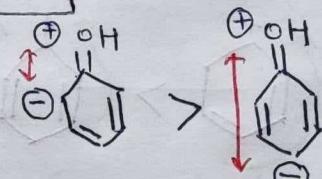


L to R: - $E \cdot N$ $C^- < N^- < O^- < F^-$

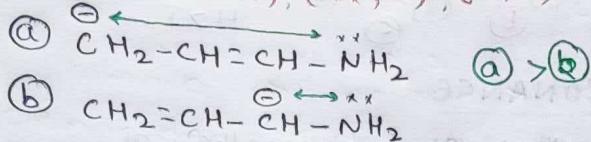
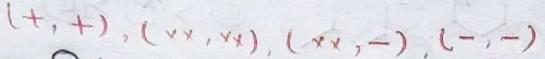
T to B: - Size $F^- < Cl^- < Br^- < I^-$

- Charge separating R.S. are less stable

+ & - do not do it
Kam stable



⑤ Like charges on adjacent position are least stable.



[Paar Paar least stable
door door More stable]

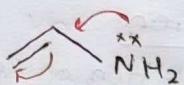
Localized lone pairs

↳ L.P. does not participate in Resonance.



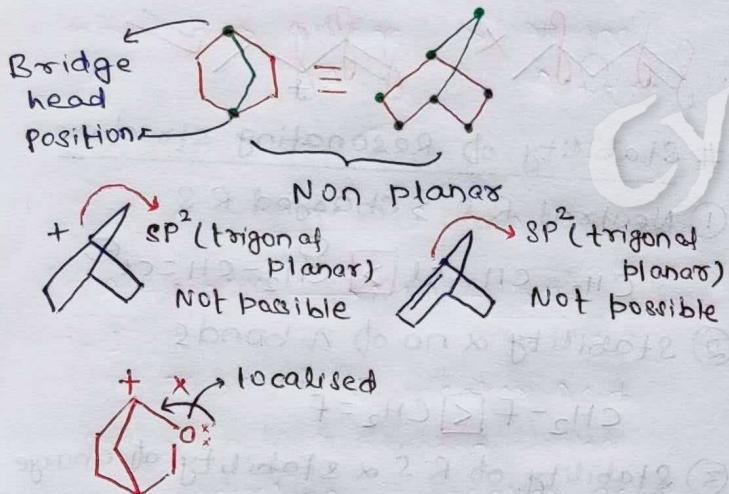
Delocalized lone pairs

↳ L.P. participate in Resonance.

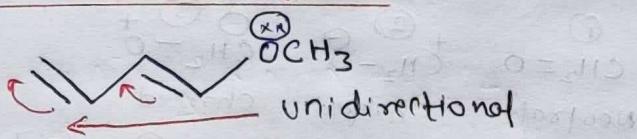


Bredt's Rule

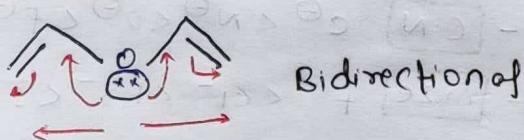
SP^2 hybrid \Rightarrow Not possible at bridge head position.



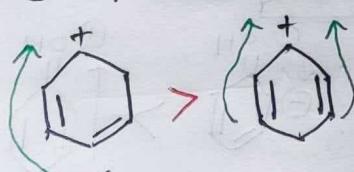
Extended conjugation



Cross conjugation



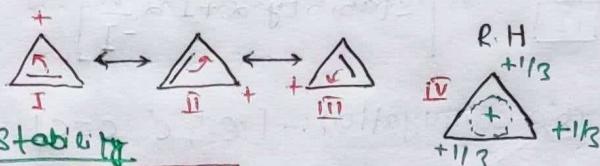
Q → Compare?



Equivalent Resonance (same stability)

1.) R.S having same potential energy

2.) Contribution of all R.S are same.

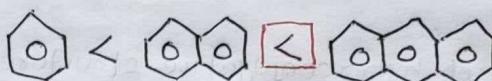


IV > I = II = III

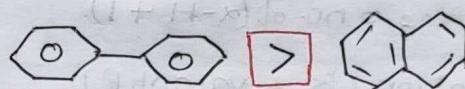
Fries Rule

↳ For Resonating structure of Benzoid compound.

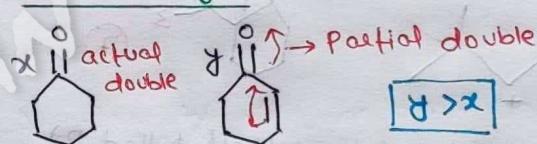
① Stability \propto no. of benzoid rings



② Two separated benzoid rings are more stable than two fused benzoid rings.



Bond length



Relo(X) Reso(V)

B.E: - \equiv > = > \approx - \approx Partial double bond

B.L! - \equiv < = < \approx -

Resonance / Mesomeric effect

1.) Permanent effect

2.) Operate to π -bond.

3.) Distance independent effect.

4.) Actual charge development.

NOTE:- All mesomeric effect are resonance effect but vice versa.

(i) (+R) + M effect

↳ If an atom or group donate P-orbital e⁻s to double bond or Benzene ring.



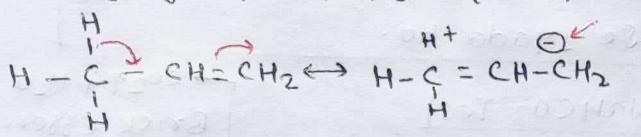
L.P. \rightarrow R.P.

R.P. \rightarrow L.P.

+M group

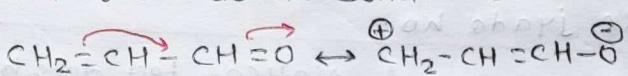
① L.P. on 1st atom connected to alkene or benzene. $\text{CH}_2 = \text{CH}-\overset{\times}{\text{A}}$

② Alkyl group $\rightarrow +M$ due to $+H$



(2) (-R)-M effect

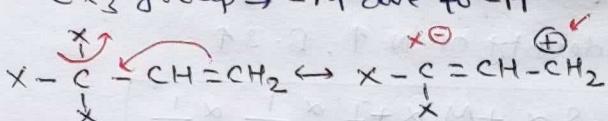
↳ If an atom or group withdraws p-orbital e- from double bond or Benzene ring.



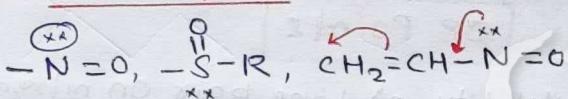
-M group

① π-bond on 1st atom connected to alkene or benzene. $\text{CH}_2 = \text{CH}-\text{A}=\text{B}$

② $-\text{CX}_3$ group $\rightarrow -M$ due to $-H$



+M & -M both



Comparison power of +M group

* +M power & extent of overlapping

comparable size
or
size difference

Extent \uparrow

\rightarrow size: $\text{C} > \text{N} > \text{O}$

+M power $\rightarrow -\text{NH}_2 > -\text{OH}$

Priority: $e\text{-density} > \text{size}$

+M power $\rightarrow -\overset{\ominus}{\text{NH}} > -\overset{\ominus}{\text{O}} > -\text{NH}_2 > -\text{OH}$

* OP Points:-

① M-effect doesn't act on meta-position e-density in Ring $\rightarrow +M > -M$

② Effects

① $M > H > I$ (In general)

② $+M > -I$ ($-\text{NH}_2, -\overset{\ominus}{\text{OH}}, -\overset{\ominus}{\text{OR}}, -\text{NH}-\overset{\oplus}{\text{C}}-\text{CH}_3, -\overset{\ominus}{\text{O}}-\overset{\oplus}{\text{C}}-\text{CH}_3$)

③ $-I > -H$ ($-\text{CX}_3$) $\left[\begin{array}{l} -I \text{ power} - f > o > Br > I \\ +M \text{ power} - \end{array} \right]$

④ $-I > +M$ ($-X$) $\left[\begin{array}{l} +M \text{ power} - \\ \text{withdraw power} \end{array} \right]$

Halogenes \rightarrow EN elements $\left[\begin{array}{l} -F < -Cl < -Br < -I \\ \hookrightarrow \text{Jyada kheechenge, kaw denge.} \end{array} \right]$

⑤ $+M$ due to L.P. $> +M$ due to internal conju.

$\left[\begin{array}{l} \text{e-} \rightarrow \text{C}^P \\ -\text{NH}_2 > -\text{NH}-\overset{\oplus}{\text{C}}-\text{CH}_3, -\overset{\ominus}{\text{OH}} > -\overset{\ominus}{\text{O}}-\overset{\oplus}{\text{C}}-\text{CH}_3 \end{array} \right]$

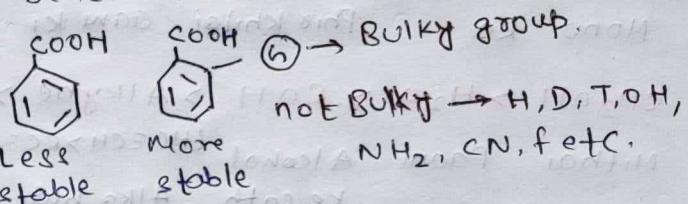
attractive donation effective donation

⑥ $+M$ due to L.P. $> +M$ due to $+H$

$\left[\begin{array}{l} \text{e-} \\ -\overset{\ominus}{\text{OH}} > -\text{CH}_3 \end{array} \right]$

Ortho-effect

↳ Acidic strength of ortho-substituted benzoic acid \uparrow due to ortho effect.



↳ It is an example of S.I.R effect.

steric inhibition in resonance
OP point:-

① size of R \uparrow , A.S \uparrow [Priority:-
Nat R $>$ size of R]

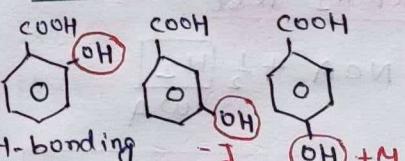
Application of M-effect

① To compare Acidic strength

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

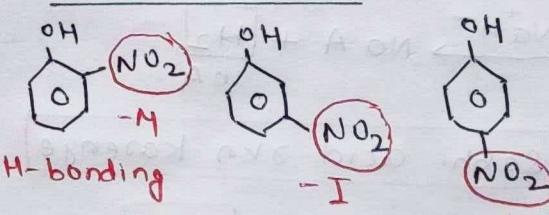
② Hydrogen bonding may \uparrow or \downarrow A.S

① In carboxylic Acid



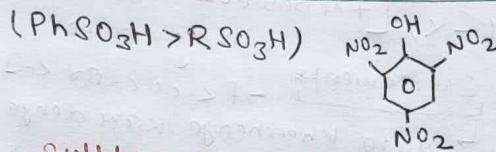
$O > M > P$

② In nitro phenol

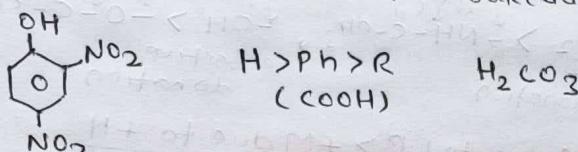


$P > O > M$

Acidic strength in different family



Sulphonate
Salman ne
Sulphonic acid
Picric acid
Pikkiya
Sakeera ko



dinitrophenol > carboxylic acid > carbonic acid
din me aur car he car me

($\text{P} > \text{O} > \text{N}$)
Mono nitrophenol > Phenol > ammonium

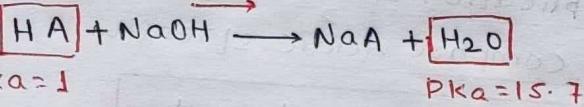
Mono ko Phir khilai aam ki

$\text{CH}_3\text{OH} > \text{H}_2\text{O} > \text{ROH} > \text{Alkyne} >$
Mithai Paani Alcohol ($\text{HC}\equiv\text{CH} > \text{RC}\equiv\text{CH}$)
ke leath Alka boli

NH_3 ($\text{C}=\text{C}$) ($\text{C}-\text{C}$)
Ammonia > Alkene > Alkane
A A A

Application of A.S in diff. family

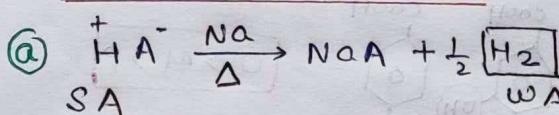
SA forward skn \rightarrow IWA



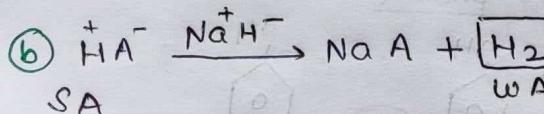
$\text{PK}_{\text{a}} \uparrow$, $\text{IC}_{\text{a}} \downarrow$, weaker Acid

Note! - Rxn will proceed in the production of weaker acid.

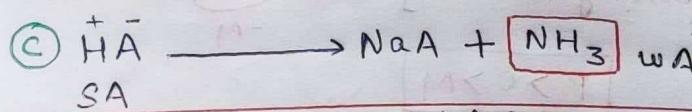
① Na, NaH, NaNH_2 Test



Na/Δ sabhi acid rxn karenge

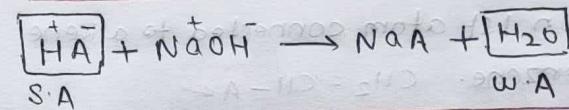


NaH sabhi acid rxn karenge



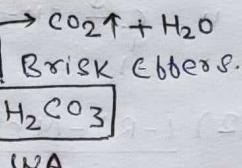
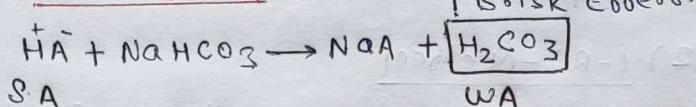
NH_3 , Aise acid jinki A.S NH_3 se jyada ho.

② NaOH Test



NaOH, Aise acid jinki A.S. H_2O
se jyada ho.

③ NaHCO_3 Test

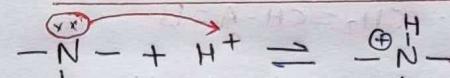


NaHCO_3 , Aise acid jinki A.S. H_2CO_3
se jyada ho

→ P-nitro phenol, NaHCO_3 test details.

Application of M-effect

→ To compare Basic strength

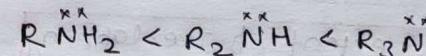


e^\ominus density on 'N' ↑, B. S ↑

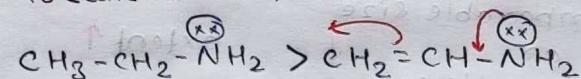
$$\text{B. S} \propto +M \propto +I \propto \frac{1}{-M} \propto \frac{1}{-I}$$

OP Points

① Availability of Lone pair on nitrogen, more will be the basicity.



② Localised LP > Delocalised LP.



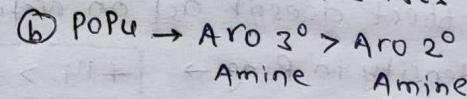
③ Organic Nitrogenous bases

Guanidine > Amidine > Amines >
Imines > Amides > cyanides.

Steric Effect

① SIR @ ortho, o-Subs. Benzoic Acid

A.S ↑ee



B.S ↑ee

② SIP

A \approx 1° amine

B.S Jee

Aromaticity

- ① Cyclic
- ② Planar (sp^2)
- ③ Conjugation ($L_A = B - C^{+} / \square \times 10^{-1}$)
- ④ Hückel's Rule

In me se koi v baal
ho jaye toh
Non-aromatic

$$(4n+2)\pi e^-$$

$$n=0 \rightarrow 2\pi e^-$$

$$n=1 \rightarrow 6\pi e^-$$

$$n=2 \rightarrow 10\pi e^-$$

Aromatic (A)

$$4n\pi e^-$$

$$n=1 \rightarrow 4\pi e^-$$

$$n=2 \rightarrow 8\pi e^-$$

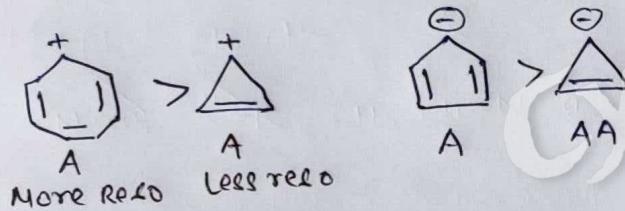
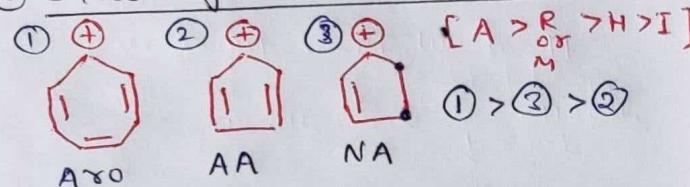
$$n=3 \rightarrow 12\pi e^-$$

Anti-Aromatic (AA)

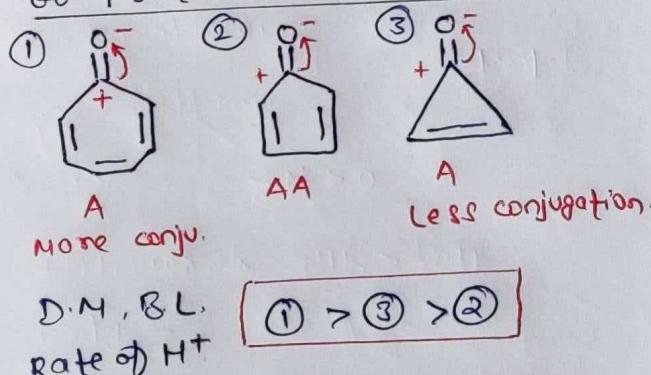
Stability :- A > NA > AA

Application of Aromaticity

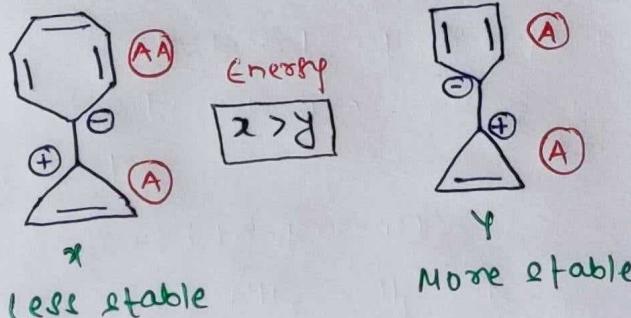
① Stability of Intermediates



② Dipole Moment, Bond length & rate of protonation

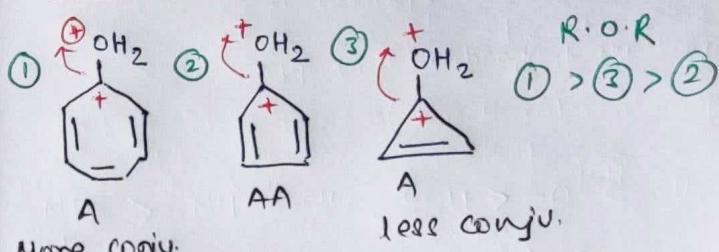


③ Rotational Energy barrier



④ Reactivity with HX & H_2SO_4

$R-O-R \propto$ stability of R^+



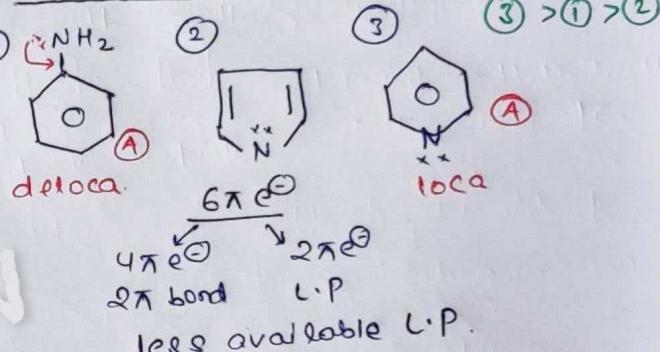
⑤ Reactivity towards $AgNO_3$ & $SbCl_5$

$R-O-R \propto$ stability of R^+

$$R-O-R \rightarrow A > AA$$

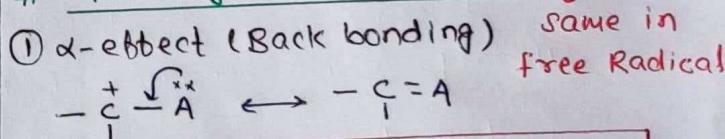
⑥ Acidic strength $\rightarrow A > AA$

⑦ Basic strength



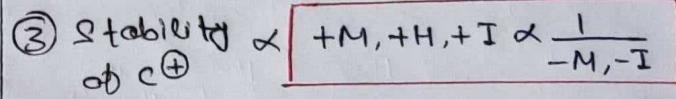
Stability of Intermediates

Stability of carbocations

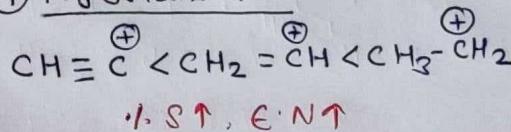


Size diff b/w C & A \downarrow , stability \uparrow

② Priority :- $BFS > Azo > M > H > I$



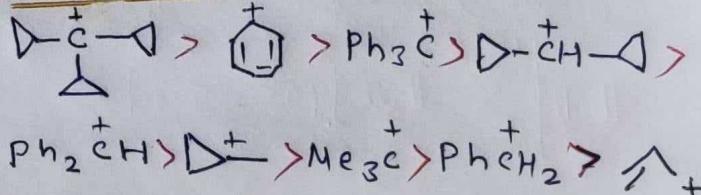
④ Hybridisation :-



E.N element por '+ve' less stable

⑤ Stability of Ring $\rightarrow 3 > 2 > 1$

OP Point:-



* Properties of carbocations

↳ Both in localised & delocalised

① SP^2

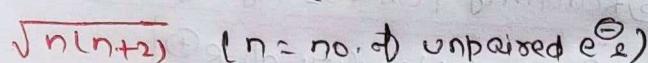
② Trigonal planar

③ Vacant orbital

④ Lewis acid

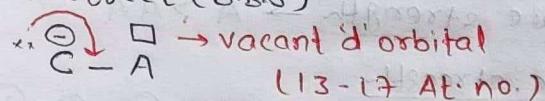
⑤ Diamagnetic

⑥ Magnetic moment ($M.M = 0$)



Stability of carbanion

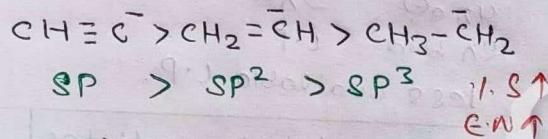
① α -effect (B.B.S)



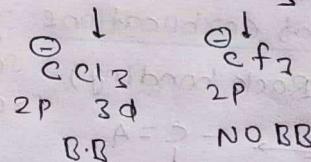
② Priority:- $RR_8 > AR_9 > M > H > I$

③ stability $\propto \frac{1}{\alpha C^-}$

④ Hybridisation



⑤ A.S of $CHCl_3 > CHF_3$



⑥ stability $\rightarrow 3R_{90} > 2R_{90} > 1R_{90}$

Properties of carbanions

localised

SP^3

Trigonal pyramidal

Lewis base

Diamagnetic

$M.M = 0$

Delocalised

SP^2

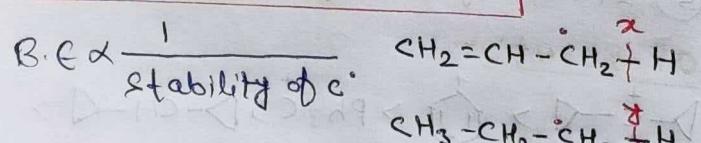
Trigonal planar

Lewis base

Diamagnetic

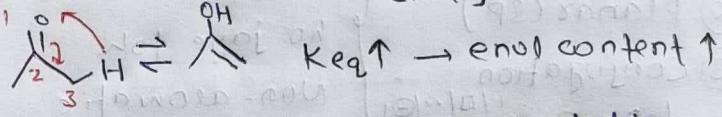
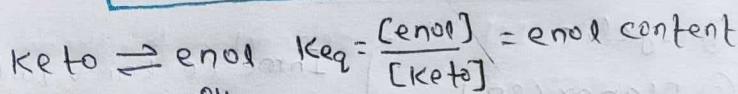
$M.M = 0$

* Comparison of Bond Energy



B.E $\alpha < \gamma$

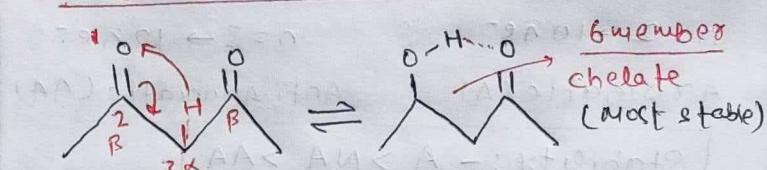
ENOL content



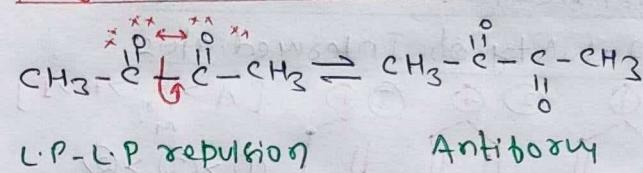
generally keto form more stable than enol.

stability of enol of $ArO, ReLO, H$ -bonding alkene stable

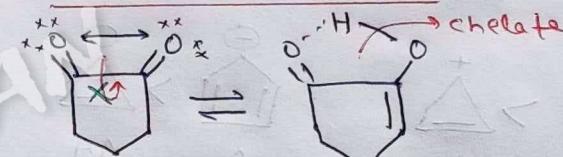
① Acyclic beta diketones



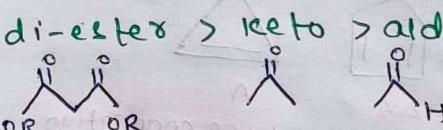
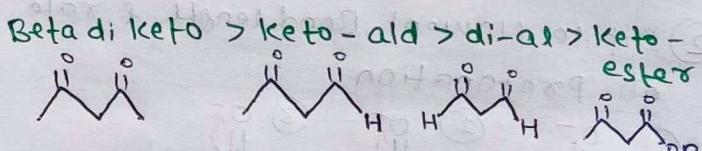
② Acyclic alpha diketones



③ Cyclic alpha diketones



enol content order



Di > Mono
Ket > Ald > ester

Electrophile

• Electron loving species

• Having or not having vacant orbital

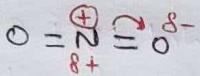
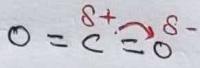
Case I - Having vacant orbital

① Vacant S & P $\rightarrow H^+, CH_3^+, BH_3$ etc.

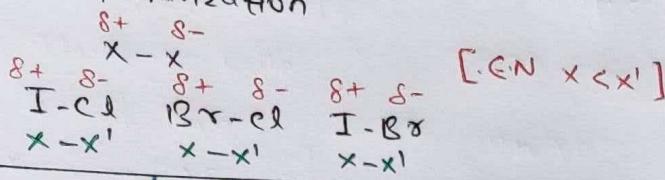
② Vacant d $\rightarrow TiCl_3, SO_3, FeCl_3, SbCl_5$ etc.

Case II → Not having vacant orbital

① π -polarization



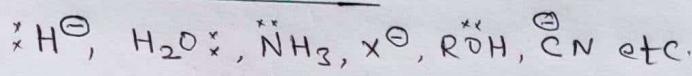
② σ -polarization



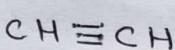
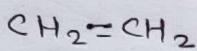
Nucleophile \rightarrow Nucleus loving

- Electron rich (L.P. wale) & Precise species (Bina L.P.)
- Having or not having L.P.

Case I - Having L.P.



Case II - No having L.P. (due to π -bondes)

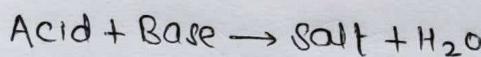


OP Points :-

$\text{NH}_4^+, \text{H}_3\text{O}^+, \text{BH}_4^-$ neither electrophile nor nucleophile

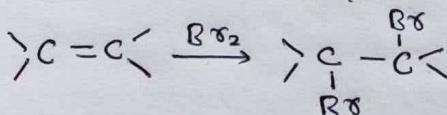
Types of Reaction

① Acid - Base Reactions

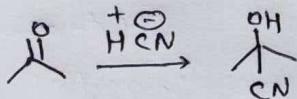


② Addition Reactions

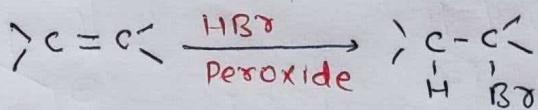
① Electrophilic addition rxn (EAR)



② Nucleophilic addition rxn (NAR)

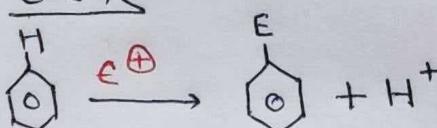


③ Free radical addition rxn (FRAR)

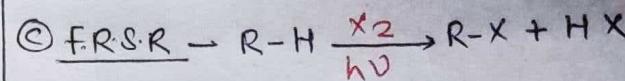
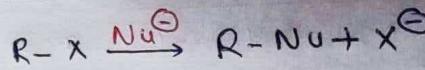


④ Substitution Reactions

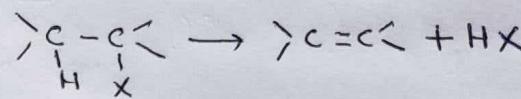
⑤ E.S.R



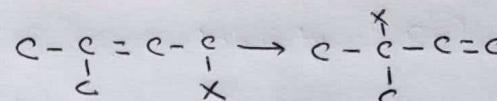
⑥ N.S.R



⑧ Elimination Reactions (E_1, E_2, E_b, E_i)

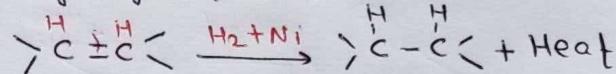


⑨ Rearrangement Reactions



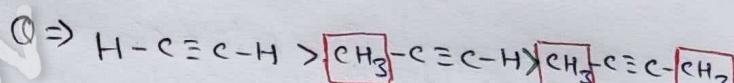
Heat of Hydrogenation (HOH)

↳ The amount of energy released during hydrogenation rxn.



- HOH & no. of π -bonds

• R-O-R & Reactivity & H.O.H \rightarrow Alkyne $>$ Alkene



★ OP Points

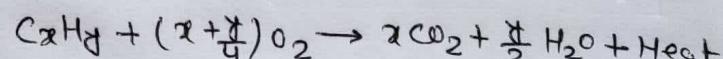
$$\text{HOH} \propto \frac{1}{\text{S.H}}$$

- HOH & no. of π -bonds

• HOH $\propto \frac{1}{\text{stability}}$ (If π -bonds are same)
stability \propto resonance \propto no. of α -H

Heat of combustion (HOC)

↳ The amount of energy released during combustion rxn.



$$\Delta H_{\text{HOC}} = -\text{ve}$$

$$< 0$$

★ OP Point

- HOC \propto no. of C-atoms

• HOC $\propto \frac{1}{\text{stability}}$

- stability of alkene \propto no. of α -H

- stability of alkene \propto Branching

- stability of cycloalkene $\rightarrow 6 > 5 > 4$

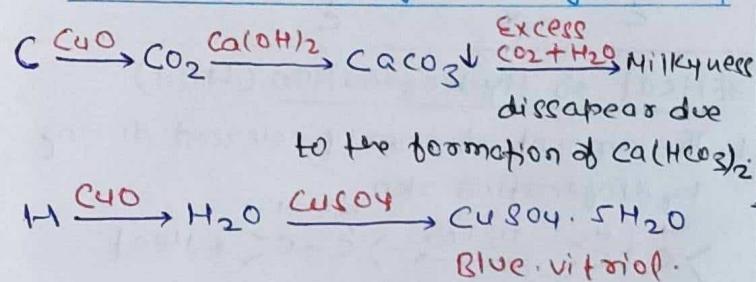
Resonance Energy

- ↪ Potential diff. b/w Resonance hybrid & most stable Resonating structure
- ↪ R.E is always negative
- ↪ R.E can be calculated by HOMO data.

$$R.E = x - y \quad (x < y)$$

stability
R.H > R.S
Energy \rightarrow R.H < R.S

Qualitative analysis of organic comp.

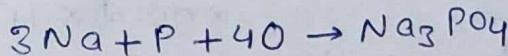
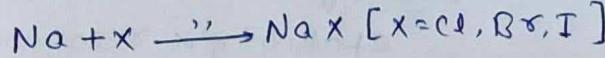
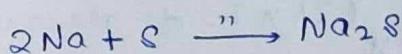
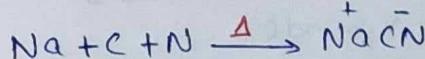


Lassaigne's Test

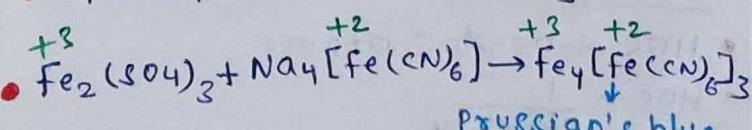
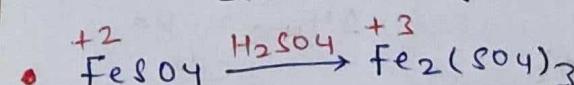
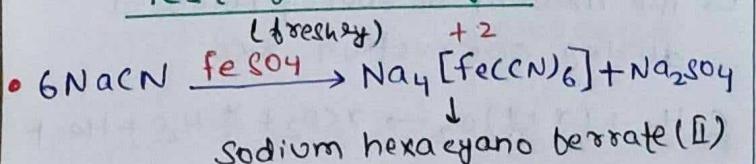
- ↪ Phosphorous, Sulphur, halogenes & Nitrogen are detected by this test.

Pankaj $\xleftarrow{\text{P, S, N, X}}$ Six Nickel holiday pair

Covalent → Ionic comp.



Test for Nitrogen



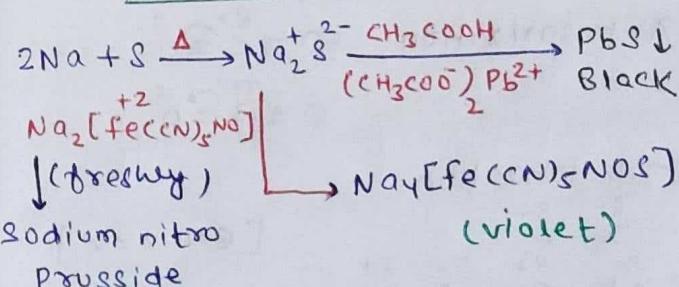
Ferric ferrocyanide

or

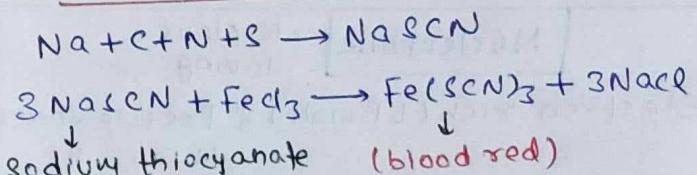
Iron(II) hexacyanoferrate (II)

- ↪ This test fails in case of diazo comp (-N=N), also hydrazone. (NH₂-NH₂).

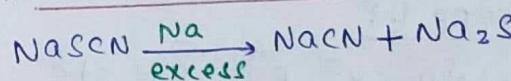
Test of Sulphur



If N & S present



If Na in excess

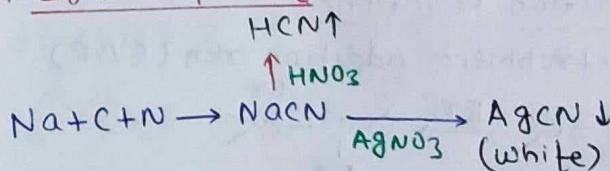


Test for Halogens

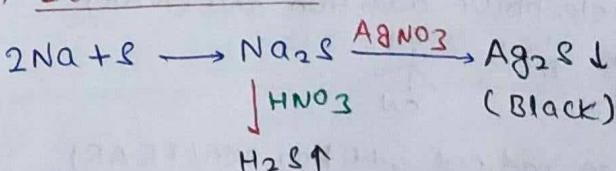


NaCl	NaBr	NaI
HNO ₃ AgNO ₃	HNO ₃ AgNO ₃	HNO ₃ AgNO ₃
AgCl ↓ (white) + NaNO ₃ NH ₄ OH [Ag(NH ₃) ₂]Cl soluble	AgBr ↓ (Pale Yellow) [Ag(NH ₃) ₂]Br partial soluble	AgI ↓ (Yellow) Insoluble

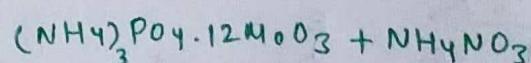
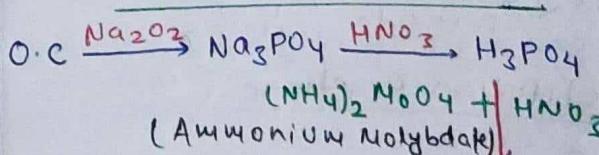
If N is present



If S is present



Test for Phosphorous



Ammonium phosphomolybdate
(canary yellow)

Quantitative Analysis

Estimation of carbon & hydrogen

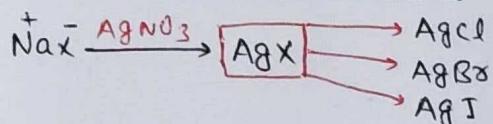
↳ By Liebig's combustion method.

$$\% \text{C} = \frac{12}{44} \times \frac{W_1}{W} \times 100 \quad W_1 \rightarrow \text{wt. of CO}_2$$

$W_2 \rightarrow \text{wt. of H}_2\text{O}$

$$\% \text{H} = \frac{2}{18} \times \frac{W_2}{W} \times 100 \quad W \rightarrow \text{wt. of O.C.}$$

Estimation of Halogens → Carius Method



$$\% \text{Cl} = \frac{35.5}{143.5} \times \frac{W_1}{W} \times 100 \quad W_1 = \text{wt. of AgCl prod.}$$

$$\% \text{Br} = \frac{80}{188} \times \frac{W_2}{W} \times 100 \quad W_2 = " \text{ " AgBr } "$$

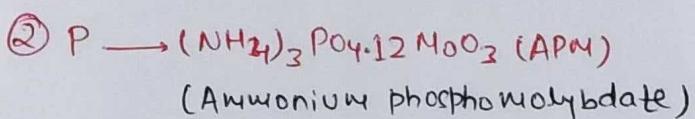
$$\% \text{I} = \frac{127}{235} \times \frac{W_3}{W} \times 100 \quad W_3 = " \text{ " AgI } "$$

$W_1 = \text{wt. of BaSO}_4 \text{ formed}$

Estimation of Phosphorus



$$\% \text{P} = \frac{62}{622} \times \frac{W_1}{W} \times 100 \quad W_1 = \text{wt. of Mg}_2\text{P}_2\text{O}_7 \text{ produced.}$$



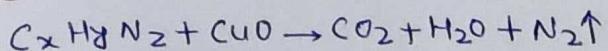
$$\% \text{P} = \frac{31}{1877} \times \frac{W_1}{W} \times 100 \quad W_1 = \text{wt. of APM formed.}$$

Estimation of Nitrogen

① Duma's Method

② Kjeldahl's Method

A) Duma's Method



Volume (V_2) = ?

$$\frac{(\text{P} - \text{P}_1) V_1}{T_1} = \frac{P_2 V_2}{T_2} \quad P \rightarrow \text{Press. of moist gas}$$

$P_1 \rightarrow \text{Aq. tension}$

$V_1 = \text{vol. of gas at T}_1\text{K}$

$T_1 = \text{temp in } ^\circ\text{K}$

$\text{P}_2 = 1 \text{ atm or } 760 \text{ mm of Hg}$

$V_2 = \text{Volume at STP (in ml)}$

$T_2 = 273 \text{ K}$

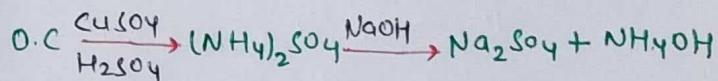
$$\% \text{N} = \frac{28}{224} \times \frac{V_2(\text{ml})}{W(\text{gm})} \cdot 100$$

B) Kjeldahl's Method

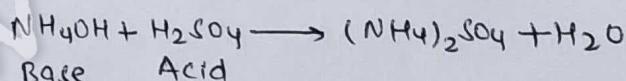
↳ In this method, nitrogen present in the organic comp. is converted into NH_3 .

↳ Not applicable to comp. containing nitro (-NO₂), Nitroso (NO), azo group (-N=N-), azoxy comp. (-N=N-) & nitrogen present in the ring (Pyridine

O_2N), quinoline O_2N_2 , bcz, nitrogen present in these comp. is not quantitatively converted into ammonium sulphate.



Acid-base Rxn



No. of gm. eq. of NH_4OH = No. of gm. eq. of H_2SO_4 .

$$\text{gm.eq} = N \times V$$

$$\text{gm.eq} = M \times n_f \times V$$

M = molality of H_2SO_4

V = Vol. in ml of H_2SO_4

$$n.f(\text{H}_2\text{SO}_4) = 2$$

$$\% \text{N} = \frac{1.4}{W} \times N \times V(\text{ml}) \cdot 100$$

N = normality of H_2SO_4 .

V = volume of H_2SO_4 in ml.

W = wt. of O.C in gm.

$$N = M \times n_f$$

$$M = \text{molality of H}_2\text{SO}_4$$

$$n.f(\text{H}_2\text{SO}_4) = 2$$