# TOPIC : GOC-I & II EXERCISE # 1 PART - I (GOC-I)

#### SECTION (A)

- **1.** As per the definition.
- **2.** As per the definition.
- 4. -C- shows -I effect, so correct direction of I effect is  $CH_3 \rightarrow C \leftarrow CH_2 \leftarrow CH_3$
- 6. Order of  $+I = (CH_3)_3 C > (CH_3)_2 CH > CH_3 CH_2 > CH_3$ .
- **8.**  $-NO_2 > -CN > -CI > -NH_2$ .
- **10.** Dipole moment increases with electron withdrawing nature (-I) of groups.

#### SECTION (B)

- 1. This is fact.
- 2. This is fact.
- 3. Due to presence of conjugated system.
- 5. (1)  $CH_3 CH = CH CH_3$  only hyper conjugation

(2) 
$$H_2C = CH^{-} HC = CH_2 \longleftrightarrow CH_2 - CH = CH - CH_2$$
  
(3)  $CH_2 = CH^{-} - CH = CH^{-} CH = CH_2 \longleftrightarrow CH_2 - CH = CH - CH = CH - H_2C$   
(4)  $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$   $(4)$ 

- **6.**  $CH_2 = CH N \overset{+}{\swarrow} \overset{-}{\bigcirc} \overset{-}{\longleftrightarrow} CH_2 CH = N \overset{-}{\swarrow} \overset{-}{\bigcirc} \overset{-}{\bigcirc}$
- **8.** 7 including the given structure in which every C will recieve a positive charge.
- **10.** a is least stable since charge separation is done and +ve charge is towards –m group. d is most stable due to no charge separation and more linearly conjugation.
- **11.** Lone pair present on nitrogen repel the negative charge.

#### SECTION (D)

- 3. Hyperconjugation  $CH_3 > CH_3CH_2 > (CH_3)_2CH > (CH_3)_3C$
- 4. For showing hyperconjugation their must be minimum of 1  $\alpha$ -hydrogen atom to sp<sup>2</sup> hybridized carbon in Which is only possible in toulene.
- **5.** Species which has more  $\alpha$ –H, shows maximum hyperconjugation.
- **6.** Those species which has no  $\alpha$ –H, not show hyperconjugation.
- **9.** Hyperconjugation.
- **10.** Heat of hydrogenation  $\propto \frac{1}{1}$

stability of alkene

(III & IV have both resonance and hyperconjugation where as I and II have only hyperconjugation.)

#### SECTION (E)

6. Here the lone pair present over nitrogen atom is involved in conjugation thus is sp<sup>2</sup> hybrdized.

9.

contain 10  $\pi$  electrons. Azulene is a dipolar ion and has both rings aromatic in its ionic form.

# PART - II (GOC-II)

#### SECTION (F)

- 2. More electronegative atom release H<sup>+</sup> ion easily.
- **3.** The geometry of a methyl carbocation and methyl carbanion is likely to be respectively planar & tetrahedral
- 4. Combine effect of + I effect and hyperconjugation.
- 8. Carbocation stability is depends upon +I effect and hyperconjugation.
- **9.** Allyl carbocation  $(H_2C=CH-CH_2)$  is more stable than propyl carbocation due to resonance.
- **11.** Aromatic carbocation is more stable than resonance stabilised carbocation and generally simple carbocation is less stable than resonance stabilised carbocation.
- **12.** Cyclopropylmethyl is more stable.

#### SECTION (G)

**7.** (i) > (ii) > (iii) > (iv)



destabilising factor for carbanion [+M > +I]

# SECTION (H)





9  $\sigma$  bonds; 1  $\pi$  bonds and 2 lonepairs.

7. 
$$C = CH - C - CH_{3}$$

#### SECTION (I)

1.  $K_a \propto$  stability of conjugate base

 $\propto$  (–I, –m groups).

- 5.  $CH_3-CH_2-CH_2$  COOH >  $CH_3CH_2COOH$  >  $CH_2=CH_COOH$  > HC=C-COOH. (order of pKa)
- 6.  $K_a \text{ order } : (1) > (2) > (3) > (4)$
- 8.  $PhSO_3H > PhCO_2H > PhOH > PhCH_2OH.$
- **11.** I effect depends upon distance.
- **12.** + I effect increases, acidic strength of alcohol decreases. So, order is  $CH_3OH > CH_3CH_2OH > (CH_3)_2CHCH_2OH > (CH_3)_3COH$
- **13.** Due to ortho effect ortho substituted benzoic acid is stronger acid than its other isomers as well as benzoic acid.
- **14.**  $K_a \propto$  stability of conjugate base

 $\propto$  (–I, –m groups).

In the (iii) option ortho effect operates thus acidic nature increases

- **15.** Acid which has more than one –COOH groups.
- **20.** On the basis of stability of conjugate base due to electronic effects.
- **21.** Acidic strength is directly related to stability of conjugate base.
- **23.** The acidity of phenols increases strongly due to -I, -m group on their ortho and para positions. But para substituted phenol is more acidic than ortho substituted due to intramolecular hydrogen bonding in the ortho substituted phenol.



## SECTION (J)

- 1. This is fact.
- 4.  $(CH_3)_3N > (CH_3)_2NH > CH_3NH_2 > NH_3$ In gas phase only I effect (electronic effect) operates.

- 5.  $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$ 
  - In aqueous phase both I effect & sterric Hindrence (Due to solvation of conjugate acid) operates.
- 6.  $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$ In aqueous phase both I effect & sterric Hindrence (Due to solvation of conjugate acid) operates.
- 7. Basicity is inversely related to stability of anions.
- **8.** –I effect increases, basic strength decreases.
- 10. Guanidine is strongest nitrogeneous base.
- **12.** (3) > (1) > (4) > (2)



**16.** (1) Anionic bases are stronger than neutral bases and ( $2^\circ$  Amine >  $1^\circ$  Amine >  $3^\circ$  Amine >  $NH_3$ )

17.

It does not have any lone pair of electrons to donate to  $H^{\Theta}$  ion.

- **18.** Only in (4) the  $\ell$ .p of N atom is not involved in resonance with benzene ring.
- **20.** III > II > I

The basicity order is inversaly related to delocalisation of lone pair.



The lone pair at N is not delocalized in the ring.

# EXERCISE # 2 PART - I <u>PART - I (GOC-I)</u>

1. Correct respesentation for incorrect representations given :

$$R \Rightarrow \bigcup_{C-H} S \Rightarrow CH_{3}CH_{2} \checkmark MgBr$$

- **2.**  $-\overset{+}{\mathsf{N}}(\mathsf{CH}_3)_3 > -\overset{+}{\mathsf{N}}\mathsf{H}_3 > -\overset{+}{\mathsf{S}}(\mathsf{CH}_3)_2 > -\mathsf{F}.$
- **5.** As per the definitions.
- 7. More electronegative atom having –ve charge and more electropositive having +ve charge.

8. Maximum charge separation stability increases



Then ans is (4)

- **9.** NO<sub>2</sub>,CN,SO<sub>3</sub>H having only –m (mesomeric) effect.
- 10.  $-CHO \longrightarrow -I; -m$  $-NO_2 \longrightarrow -I; -m$  $-CI \longrightarrow -I; +m$  $-CH_3 \longrightarrow +I;$  hyperconjugation.
- **11.** No  $\alpha$  hydrogen is present in any other option.
- **12.** (i) Only inductive (ii) hyperconjugation (iii) Inductive, mesomeric and hyperconjugative. (iv) resonance and hyperconjugation
- **15.**  $\alpha$ -D or  $\alpha$  H will show hyperconjugation.
- **16.** Stability  $\propto$  Number of hyperconjugative H-atoms.
- 18. This is fact.
- **19.** C–C bond length  $\infty$  No. of hyperconjugative structure.
- **22.**  $C^1 C^2$  is shorter because it is double bond in two of three resonance strucutre ;  $C_2 C_3$  is a single bond in two of three resonance strucutres.
- 23. The + m order is

$$-\ddot{N}H_{2} > -\ddot{N}R_{2} (SIR) > -\ddot{N}H - C - R | O (cross conjugation) | (cross conjugation) | O (cross conjugation)$$

**25.** Aromatic species are



- 26. I = Aromatic II = Aromatic III = Nonaromatic
- **28.**  $H_3C-CH-CH=CH_2$  in this  $\sigma$ -p orverlapping occurs due to hyperconjugation and  $p\pi$ - $p\pi$  overlap occur due to resonance.

# PART - II (GOC-II)

- **29.** Free radical is a paramagnetic in nature.
- **31.** (1) Have not stabilization effect
  - (2) Only stabilized by resonance.
  - (3) Only stabilized by hyperconjugation.
  - (4) Stabilized by resonance and hyperconjugation.

#### SECTION (B)

**39.** On heterolysis of propane carbocation and carbanion is formed.



## SECTION (C)

42. sp<sup>3</sup>  $\alpha$ -H absent.



Total number of enolizable H-atoms = 6

## SECTION (D)

- **54.** On the basis of electronic effect and hydrogen bonding.
- 55. Carbanion at position 'P' will be stabilised by both oxygens.





Acidic order is I > II . due to the presence of ortho effect on – COOH group

- 64. More acidic easily ionized. Acidic order : (3) > (4) > (2) > (1).
- 67. Acidic strength  $\propto$  –I effect CH<sub>3</sub> CHFCOOH > CH<sub>3</sub>CH(CI)COOH > FCH<sub>2</sub>CH<sub>2</sub>COOH > (CI)CH<sub>2</sub>CH<sub>2</sub>COOH
- **69.**  $H_3N^{\oplus}$  (CH<sub>2</sub>)<sub>2</sub> COOH has strongest acid due to strong –I effect of – $NH_3$ .
- **70.** I effect depends upon distance.
- 71.  $K_a$  order is : I < II < III Hence,  $pK_a$  order is : III < II < I
- 74. Salicylic acid is more acidic than p-hydroxy benzoic acid.
- 75. On the basis of stability of conjugate base due to electronegativity.
- **76.** The stronger acid displaces the weaker acid from the salt of weaker acid.

# SECTION (E)

77 
$$\begin{array}{c} \mathsf{CH}_{3} - \overset{\mathsf{NH}}{\mathsf{C}} - \mathsf{NH}_{2} \xrightarrow{\mathsf{H}} \mathsf{CH}_{3} - \overset{\mathsf{C}}{\mathsf{C}} \xrightarrow{\mathsf{NH}_{2}} \overset{\mathsf{H}}{\mathsf{NH}_{2}} \overset{\mathsf{CH}_{3}}{\longleftrightarrow} \mathsf{CH}_{3} - \overset{\mathsf{NH}_{2}}{\mathsf{C}} \xrightarrow{\mathsf{C}} \mathsf{H}_{3} \xrightarrow{\mathsf{C}} \mathsf{CH}_{3} - \overset{\mathsf{NH}_{2}}{\mathsf{C}} \overset{\mathsf{H}}{\mathsf{NH}_{2}} \overset{\mathsf{H}}{\longleftrightarrow} \mathsf{CH}_{3} - \overset{\mathsf{C}}{\mathsf{C}} = \overset{\mathsf{NH}_{2}}{\mathsf{NH}_{2}} \overset{\mathsf{H}}{\underset{\mathsf{II}}} \xrightarrow{\mathsf{C}} \mathsf{CH}_{3} - \overset{\mathsf{C}}{\mathsf{C}} = \overset{\mathsf{NH}_{2}}{\mathsf{NH}_{2}} \overset{\mathsf{H}}{\underset{\mathsf{II}}} \overset{\mathsf{C}}{\mathsf{C}} \overset{\mathsf{H}}{\underset{\mathsf{II}}} \overset{\mathsf{H}}{\underset{\mathsf{N}}} \xrightarrow{\mathsf{C}} \mathsf{CH}_{3} - \overset{\mathsf{C}}{\mathsf{C}} = \overset{\mathsf{NH}_{2}}{\mathsf{NH}_{2}} \overset{\mathsf{H}}{\underset{\mathsf{II}}} \overset{\mathsf{C}}{\mathsf{C}} \overset{\mathsf{H}}{\underset{\mathsf{II}}} \overset{\mathsf{C}}{\mathsf{C}} \overset{\mathsf{H}}{\underset{\mathsf{II}}} \overset{\mathsf{C}}{\mathsf{C}} \overset{\mathsf{C}}{\mathsf{C}} \overset{\mathsf{C}}{\underset{\mathsf{II}}} \overset{\mathsf{C}}{\mathsf{C}} \overset{\mathsf{C}}{\underset{\mathsf{II}}} \overset{\mathsf{C}}{\mathsf{C}} \overset{\mathsf{C}}{\underset{\mathsf{II}}} \overset{\mathsf{C}}{\mathsf{C}} \overset{\mathsf{C}}{\underset{\mathsf{II}}} \overset{\mathsf{C}}{\mathsf{C}} \overset{\mathsf{C}}{\underset{\mathsf{II}}} \overset{\mathsf{C}}{\mathsf{C}} \overset{\mathsf{C}}{\underset{\mathsf{II}}} \overset{\mathsf{C}}{\mathsf{C}} \overset{\mathsf{C}}{\underset{\mathsf{N}}} \overset{\mathsf{C}}{\mathsf{C}} \overset{\mathsf{C}}{\underset{\mathsf{N}}} \overset{\mathsf{C}}{\mathsf{C}} \overset{\mathsf{C}}{\underset{\mathsf{N}}} \overset{\mathsf{C}}{\mathsf{C}} \overset{\mathsf{C}}{\mathsf{C$$

Stability order of conjugate acids is P > R > Q > S. Hence basicity order is I > III > II > IV.

8.\*





- Due to + M effect of OH group and hyperconjugation of CH<sub>3</sub> group
- **9.\*** Bond length is internuclear distance between two covalently bonded atom in a molecule. Bond length order is

(1) C - H < C = C < C - O < C - CBond length /pm 107 134 143 154

- 10.  $CF_{a}-COOH > CCI_{a}-COOH > HCOOH > CH_{a}COOH$  (K order) (K  $\pi \Psi$  (M = 1)
- Acetyl acetone is liquid and exist mainly as III due to intramolecular H-bonding and the correct answer is
   III > II > I.

However in aquous medium, the correct answer is II > III > I.

- **12.**<sup>\*</sup>  $-NO_2$  group is most deactivating group due to strong -I and -M effect.
- **13.** All compounds show tautomerism.



14. 18  $\sigma$  and  $2\pi$  bonds in both keto and enol form of ethyl acetoacetate.

**15.** Hyperconjugation possible in 
$$CH_3$$
 due to presence of  $\alpha$ -H

16. 
$$CH_3$$
— $CH=CH\_CH_2$ — $CH_2$ — $CH_3$ — $CH=CH\_CH_2$ — $CH_3$ 

- **17.**  $CH_3 \xrightarrow{I}_{C\oplus} C\oplus_{CH_3}$  is less stable than  $CH_2 \xrightarrow{\oplus}_{CH_2} CH_2$
- **18.**  $NH_2$   $\rightarrow$  Delocalised lone pair of nitrogen atom with Benzene ring in any amine

aryl amine

 $\longrightarrow$  lone pair of electrons of nitrogen atom are not delocalized in alkyl amine. (Alkyl amine)

CH<sub>3</sub>−C≡C sp hybridisation

Steric Number (1 $\sigma$  + 1 –ve charge)  $\longrightarrow$  sp

- **20.** It is known that basic need for the existance of Keto-enol tautomers is the presence of at least one hydrogen atom at adjacent sp<sup>3</sup> carbon of carbonyl carbon.
- 21. Only III

19.

 $\alpha$ -H at bridge head carbon never show tautomerism.



## 22. (II > III > I)

Acidic strength  $\alpha$  –I, –M effect

-I effect depand upon distance so II have stronger -I effect than III.

24. Electron withdrawing groups (-I & -M effect) decreases basic strength of aniline while electron donating groups (+I and +M effect) increases basic strength of aniline at para positions.



So, the correct order of basic strength of following compounds is -II < II.

**25.** Definition of electrophile

Example of positively charged electrophile is  $NO_2^{\oplus}$  (nitronium ion) Example of neutral electrophile is SO<sub>3</sub>.

- 26. Alkynes more acidic than alkenes which are further more acidic than alkanes due to the different electro negativity of sp, sp<sup>2</sup> and sp<sup>3</sup> hybride carbon (order of electro negativity =  $C_{sp} > C_{sp}^2 > C_{sp}^3$ ) +I effect decreases the acidic strength of alkynes so the overall order of acidic strength will be CH=CH > CH<sub>3</sub>-C=CH > CH<sub>2</sub>=CH<sub>2</sub> > CH<sub>3</sub>-CH<sub>3</sub>
- **27.** Due to the presence of three strong electron withdrawing groups (–M effect) at ortho and para positions, picric acid (2,4,6-trinitro phenol) is more acidic compound.
- **28.** Both are correct order of **–I effect** –NH<sub>2</sub> < –OR < –F –NR<sub>2</sub> <–OR <–F
- **29.** Ph- $\dot{O}$ -H  $\longrightarrow$  lone pair of oxygen in conjugation so less basic and difficult to protonated (Phenol)
- **30.**  $K_b$  of methyl substituted amines in auous solution depand upon combined effect of +I of methyl and solubility in H<sub>2</sub>O by H-bonding and order is  $K_b = (CH_3)_2NH > CH_3-NH_2 > (CH_3)_3N$

**31.** 
$$CH_3 - C - CH - CH_3$$
  
 $H_3 - C - CH - CH_3$   
 $H_3 - C - CH - CH_3$   
 $H_3 - CH_3 - CH_3$ 

PART - II

6. Among the given compounds, only  $CH_3 NH_3 CI^-$  is the ionic compound, hence dissociation constant is maximum for it.

... dissociation constant

$$\mathsf{K} = \frac{[\mathsf{CH}_3\mathsf{NH}_3^+][\mathsf{CI}^-]}{[\mathsf{CH}_3\mathsf{NH}_3^+\mathsf{CI}^-]}$$

7. In pyrrole and aniline lone pair of electrons on N-atom involved in delocalization and pyridine has sp<sup>2</sup> nitrogen but piperidine has no such delocalization and it is a secondary amine. Hence, it is highly basic.



- 9. +I and hyperconjugation +I तथा अतिसयुग्मन
- **12.**  $(4n + 2)\pi$  electrons and cyclic, planar structure are the essential conditions for aromaticity.
- **13.** In structure (3), N atoms forms five bonds, ie has 10 electrons which is not possible due to absence of d-orbitals. Structure (3) is highly unstable or we can say this structure in not possible.
- **14.** In benzinidazole, lone pair of Nx is not involved in delocalisation, hence it is more basic. The lone pair of Ny takes part in delocalisation, hence not available for donation. Thus Ny is non basic.



benzinidazole

ш

- **15.** In gaseous phase basic strength depends upon electronic effect : ( $K_{b} \propto + I$  effect).
- **16.** Substituent with strong +R effect, + I effect and weaker –I effect increases the basicity. Hence pK<sub>b</sub> decreases. Also, alkylamines are stronger bases than arylamines. So, the order is (4).
- **17.** Weaker acids have higher  $pK_a OCH_3$  at meta-position exerts only -I effect, hence increases the acidity.

-I effect order :  $-NO_2 > -OCH_3 > -CI.$ 

- **19.** -NO<sub>2</sub> group, being strong electron-withdrawing, disperses the -ve charge, hence stabilizes the concerned carbanion.
- **20.**  $CH_3C \equiv CCH_3$ , being symmetrical, has the lowest dipole moment.

22. 
$$\begin{array}{c} \overset{\Pi}{\longleftarrow} \overset{-H^+}{\longrightarrow} \overset{\Theta}{\bigoplus} \text{ (more stable due to aromaticity)} \\ \overset{H}{\longleftarrow} \overset{-H^+}{\longrightarrow} \overset{\Theta}{\bigoplus} \text{ Anti aromatic (least stable)} \\ \overset{H}{\longleftarrow} \overset{-H^+}{\longrightarrow} \overset{\Theta}{\bigoplus} \text{ Stable by resonance} \\ \text{Acidia patture a stability of acciumate acian (base)} \end{array}$$

Acidic nature  $\alpha$  stability of conjugate anion (base) i > iii > ii



**25.** 
$$K_b = CH_3 - CH_2 - N$$

N, N, Diethylethylomine

+I effect of  $C_2H_5$  – group more than  $CH_3$ – group.

**26.** Ortho nitrophenol is more acidic than meta nitro phenol because at ortho position NO<sub>2</sub> group show –m effect but at meta, —NO<sub>2</sub> gp show only –I ether.



**29.** Ph–CH<sub>2</sub>–NH<sub>2</sub> (Benzylamine) have –I effect of Phenyl group while CH<sub>3</sub>–CH<sub>2</sub>–NH<sub>2</sub> have +I effect.

## PART - III

- 1.  $CH_3$  group has + I effect, as number of  $-CH_3$  group increases the inductive effect increases.
- **2.** HCOO<sup>-</sup> exists as

$$O \rightarrow H - C = O$$
 [Identical resonating structures]

So, the carbon-oxygen bonds are found to be of equal length.

**3.** Except the amines containing tertiary butyl group, all lower aliphatic amines are stronger bases than ammonia because of + I (inductive). The alkyl groups, which are electron releasing groups, increase the electron density around the nitrogen there by increasing the availability of the lone pair of electrons to proton or lewis acids and making the amine more basic.

Thus the relative strength is in order  $(CH_3)_2$  NH >  $CH_3$ NH<sub>2</sub> > NH<sub>3</sub>.

4. Lone pairs of  $\hat{N}$  are not taking part in conjugation whereas in other options lone pairs are taking part in conjugation.



E.W.G. increases the acidity of benzoic acid, o-isomer will have higher acidity than corresponding m and p isomer due to ortho effect.

7. Due to resonance of electron pair in aniline, basic strength decreases. In benzylamine electron pair is not involved in resonance.



Decreasing order of basic strength is 4 > 3 > 2 > 1.

 The order of stability of free radical is as follows: tertiary > secondary > primary.

> Benzyl free radicals are stabilised by resonance and hence are more stable than alkyl free radicals. Further as the number of phenyl group attached to the carbon atom holding the odd electron increases, the stability of a free radical increases accordingly i.e.

$$(\mathsf{CH}_3)_2 \dot{\mathsf{C}}\mathsf{H} < (\mathsf{CH}_3)_3 \dot{\mathsf{C}} < (\mathsf{C}_6\mathsf{H}_5)_2 \dot{\mathsf{C}}\mathsf{H} < (\mathsf{C}_6\mathsf{H}_5)_3 \dot{\mathsf{C}}$$

**9.** Effect of substituent on the acid strength of aliphatic acids.

(i) Acidity decreases as the + I - effect of the alkyl group increases.

(ii) Acidity decreases as the - I-effect decreases.

(iii)On the basis of given information the relative order of increasing acid strength of the given compounds:  $(CH_3)_2 COOH < CH_3 COOH < CH_3 OCH_2 COOH < CF_3 COOH$ 

**10.** The increasing order of basicity of the given compounds is

$$(CH_3)_2 NH > CH_3 NH_2 > (CH_3)_3 N > C_6 H_5 NH_2$$

Due to the +I effect of alkyl groups the electron density on nitrogen increases and thus the availability of the lone pair of electrons to proton increases and hence the basicity of amines also increases. So aliphatic amines are more basic than aniline.

In case of tertiary amine  $(CH_3)_3 N$ , the covering of alkyl groups over nitrogen atom from all sides makes the approach and bonding by a proton relatively difficult, hence the basicity decreases. Electron withdrawing  $(C_6H_5-)$  groups decreases electron density on nitrogen atom and thereby decreasing basicity.



**14.** 
$$CH_3 = \overset{\square}{C} = CH_2 = CH_2 = CH_3 \Longrightarrow CH_3 = \overset{\square}{C} = CH = CH_2 = CH_3$$



Therefore acidity order is :

$$\mathsf{D} > \mathsf{C} > \mathsf{A} > \mathsf{B}.$$

6. 
$$\begin{array}{c} OH \\ O \\ NO_2 \end{array} > \begin{array}{c} OH \\ O \\ CI \end{array} > \begin{array}{c} OH \\ O \\ CH \end{array} > \begin{array}{c} OH \\ O \\ CH_3 \end{array} > \begin{array}{c} OH \\ O \\ OCH_3 \end{array} \\ OCH_3 \end{array}$$

1

electron releasing group decreases and electron withdrawing group increases acidic strength.

17. The order of stability of carbocation will be

18. Order of basic strength of aliphatic amine in aqueous solution is as follows.

order of 
$$K_b$$
:  $(CH_3)_2 \dot{N}H > CH_3 \dot{N}H_2 > (CH_3)_3 \dot{N} > C_6 H_5 \dot{N}H_2$   
As we know  $pK_b = -\log K_b$ 

so  $(CH_3)_2 \dot{N}$  will have smallest pK<sub>b</sub> value.

19. All are aromatic compounds except

It is non aromatic so least resonance stabilised.

- **20.** Imidine is more basic than 2° amine followed by 1° amine.
- **21.** The conjugate base of  $CH(CN)_3$  is  $C(CN)_3$  and in  $C(CN)_3$  the negative charge is extensively delocalized.
- 22. Greater the –I effect, greater will be the acidity.

**25.** 
$$CH_3 - CH_2 - NH > CH_3 - CH_2 - NH_2 > CH_3 - N - CH_3 > Ph - N - H$$

- **26.** Electron withdrawing group increases acidic strength and Electron releasing group decreases acidic strength.
- **27.** Neither of B, or C, nor D, follow the Huckel's rule of  $4n + 2\pi e^{-1}$  for aromaticity.
- **28.** Lone pair of electons in 'a' and 'e' are used in delocalisation.
- **29.** Acidic strength  $\infty$  Stability of conjugate base E.N.  $\rightarrow$  sp carbon > sp<sup>2</sup> carbon > sp<sup>3</sup> carbon