MOTION IIT-JEE|AIEEE CBSE|SAT|NTSE OLYMPIADS
Nurturing potential through education

CHEMISTRY
TARGET IIT JEE

ORGANIC CHEMISTRY, IIT-JEE 2013

ACIDITY & BASICITY

THEORY AND EXERCISE BOOKLET

CONTENTS

394 - Rajeev Gandhi Nagar Kota, Ph. No. 0744-2209671, 93141-87482, 93527-21564
IVRS No. 0744-2439051, 0744-2439052, 0744-2439053 www.motioniitjee.com, email-hr.motioniitjee@gmail.com

IIT-JEE Syllabus :

Acidity & Basicity

Inductive and resonance effects on acidity and basicity of organic acids and bases; basicity of substituted anilines and aliphatic amines,

Acidity & Basicity

$HA \rightleftharpoons H^{\oplus} + \ddot{A}^{\ominus}$

Acid Conjugate base

Note : More stable the conjugate base (i.e., $\ddot{A}^{\ominus}$), more will be the forward reaction which results more acidic nature of HA.

Ex.1 Compare the acidic strength of the following acids.

(a) C – C – C – COOH (b) C = C – C – COOH (c) C ≡ C – C – COOH

Sol. The acid whose conjugate base is most stable will be more acidic.

After forming conjugate base from the above acids.

(a) $C-C-\boxed{C-COO^{-}}$ (sp^3) (b) $C=C-\boxed{C-COO^{-}}$ (sp^2) (c) $C\equiv C-\boxed{C-COO^{-}}$ (sp)

It is clear that sp hybridised carbon being most electronegative will decrease e^- density from O most effectively making the conjugate base most stable.

c > b > a (acidic strength)

Ex.2 Which is more acidic between the two

(a) CHF_3 (b) $CHCl_3$

Sol. $CHF_3 > CHCl_3$

If we consider the –I effect of F and Cl But this effect will not be considered here

After the removal of proton

(a) $\ominus C(F)(F)F$ (b) $\ominus C(Cl)(Cl)Cl$

(vacant d-orbital available where C will coordinate its electron) (pπ – dπ bonding)

⇒ a < b (acidic strength)

Ex.3 Compare the acidic strength of the following

(a) CHF_3 (b) $CHCl_3$

(c) $CHBr_3$ (pπ – dπ bonding in Br is not as much as effective as in Cl due to large size of Br)

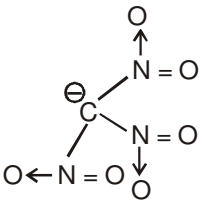
Sol. $CHCl_3 > CHBr_3 > CHF_3$

Ex.4 Compare the acidic strength of the following

(a) $CH(CN)_3$ (b) $CH(NO_2)_3$ (c) $CHCl_3$

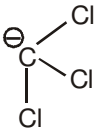
Sol. After removing H^+

$^{-}C(C\equiv N)(C\equiv N)(C\equiv N)$ (Resonance) In its resonating structure, –ve charge will be on N)



(Resonance) (– In its resonating structure –ve charge will reside on O

⇒ more effective Resonance



(pπ – dπ)

b > a > c

* –ve charge on O is more stable than –ve charge on N as O is more electronegative than N.

* Pπ – dπ Resonance < Actual Resonance

Ex.5 Compare the acidic strength of the following

(a) $CH \equiv CH$ (b) $CH_2 = CH_2$ (c) $CH_3 - CH_3$

Sol. $\underset{\downarrow}{CH \equiv \bar{C}} > \underset{\downarrow}{CH_2 = \bar{C}H} > \underset{\downarrow}{CH_3 - \overset{\ominus}{C}H_2}$

sp sp2 sp3

(Stability of the conjugate base)

⇒ a > b > c (acidic strength)

Ex.6 Compare the acidic strength of the following :

(a) $CH_3 - CH_2 - CH_2 - COOH$

(b) $CH_3 - CH_2 - \underset{\displaystyle Cl}{\underset{|}{CH}} - COOH$

(c) $CH_3 - CH_2 - \underset{\displaystyle F}{\underset{|}{CH}} - COOH$

(d) $CH_3 - CH_2 - \underset{\displaystyle NO_2}{\underset{|}{CH}} - COOH$

Sol. **d > c > b > a**

Ex.7 Compare the acidic strength of the following :

(a) H_2O (b) H_2S (c) H_2Se (d) H_2Te

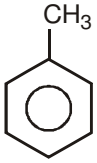
Sol. Conjugate base is in an stability order

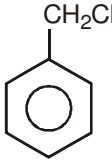
$\bar{O}H < H\bar{S} < H\bar{S}e < H_2Te$

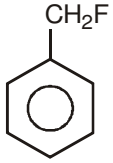
⇒ $H_2O < H_2S < H_2Se < H_2Te$ (acidic strength)

Ex.8 Compare the acidic strength of the following compound

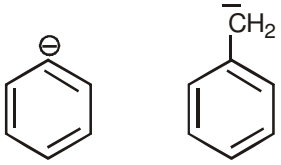
(a) 

(b) 

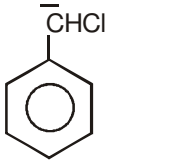
(c) 

(d) 

Sol. After forming conjugate base of the above

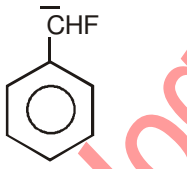


–ve charge is not in resonance



pπ – dπ bonding due vacant d-orbital of Cl

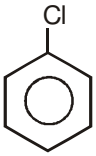
(most stable)

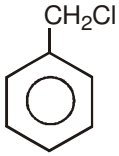


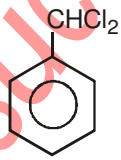
C – I effect of F decrease e⁻ density from C making the carbanion stable

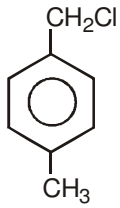
c > d > b > a

Ex.9 Compare the reactivity of the following compounds with 1 mole of $AgNO_3$

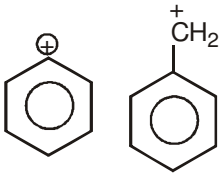
(a) 

(b) 

(c) 

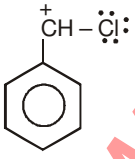
(d) 

Sol. After removing Cl^-

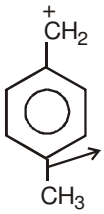


(+ve charge is not on resonance

∴ least stable)



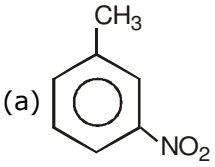
(most stable as L.P. of Cl will be coordinated to +ve charge completing the octet of each atom and making the corbocation most stable)

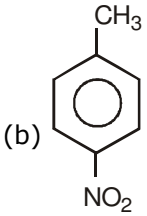


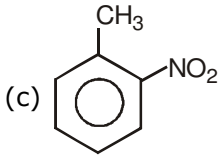
(By hyper conjugation)

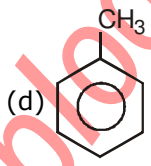
extent of +ve charge decreases stability increases

Ex.10 Compare the acidic strength

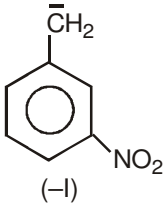


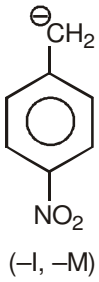


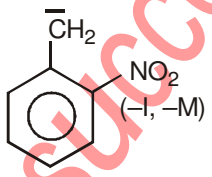


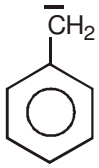


Sol. After making conjugate base









c > b > a > d

BASIC STRENGTH

$A^+ - H$

Basic strength directly depends on the availibility of lone pair for H^+

Ex.11 Compare the basic strength of following

Sol.

(a) NH_3
(b) PH_3
(c) AsH_3
(d) SbH_3
(e) BiH_3

Basic strength

Ex.12 Compare the basic strength of the following

(a) $\bar{C}H_3$ (b) $\bar{N}H_2$ (c) $\bar{O}H$ (d) $\bar{F}$

Sol. $\bar{C}H_3$, $\bar{N}H_2$, $\bar{O}H$, $\bar{F}$

$CH_4 < NH_3 < H_2O < HF$

(acidic strength)

$\overset{\ominus}{C}H_3 > \overset{\ominus}{N}H_2 > \bar{O}H > \bar{F}$

(Basic strength)

* Strong Acids have weak conjugate base.

$\overset{\ominus}{C}H_3 > \overset{\ominus}{N}H_2 > \bar{O}H > F$

(Nucleophilicity)

* For the same period
less electronegativity, more nucleophilicity as more electronegative element has less tendencey to give its electron pair.

Ex.13 Which is more basic $\bar{O}H$ or $H\bar{S}$?

Sol. $\bar{O}H > H\bar{S}$

Which is more basic NH_3 or $\overset{\ominus}{N}H_2$

forming conjugate acid

$\overset{+}{N}H_4 > NH_3$ (acidity)

$\therefore$ $NH_3 < \overset{\ominus}{N}H_2$ (Basicity)

COMPARISON OF BASICITY OF AMMONIA AND ALKYL AMINES :

Ex.14 Compare the basic strength of the following NH_3, CH_3NH_2, $(CH_3)_2NH$, $(CH_3)_3N$

Factors which affect the basicity of Amines

(1) steric effects

(2) Inductive effect

(3) solvation effect.

- The base whose conjugate acid is more stable will be more acidic forming conjugate acid of the given base

$\overset{+}{N}H_4$, $CH_3\overset{+}{N}H_3$, $(CH_3)_2\overset{+}{N}H_2$, $(CH_3)_3\overset{+}{N}H$

Stability order of conjugate acid

$(CH_3)_3\overset{+}{N}H > (CH_3)_2\overset{+}{N}H_2 > CH_3\overset{+}{N}H_3 > \overset{+}{N}H_4$

(due to +I effect)

Therefore basic strength

$(CH_3)_3N > (CH_3)_2NH > CH_3NH_2 > NH_3$

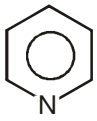
(vapor phase or gaseous is phase or in Non polar solvent)

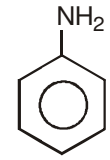
In Aqueous solution or in polar solvent

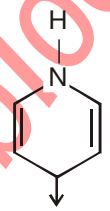
$(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$

- In aqueous solution, the conjugate acids form H-bonds (intermolecular) with water molecules and stabilise them selves conjugat acid of 1° amine which has largest no. of H-atoms form maximum H-bond with water and is most stable. Consequently 1° amine is most basic.
- Due to steric effect 1° amine is considered more basic as compared to 3° amine as lone pair is hindered by three alkyl group and less available for H^+.
  Considering the combined effect of the three (Inductive, solvation and steric effect) we can conclude that
  $2° > 1° > 3° > NH_3$
- Aromatic amines are least basic as their lone pair is in conjugation and less avaibable for protonation.

Ex.15 Compare the basic strength of the following

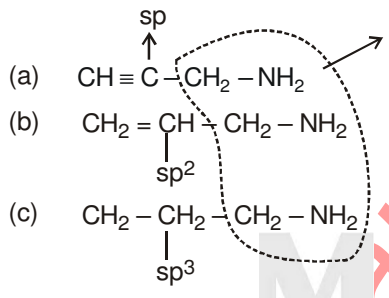
(a) 
(no Resonance as ring will break if we draw the resonating structure)
⇓
(most basic)

(b) 
(Resonance)

(c) 

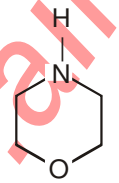
(if L.P. will be participate in Resonance, then molecule becomes aromatic)
∴ Hence L.P. will have a greater tendency to take part in Resonance and will be less available for H^+
∴ This compound will be least basic.

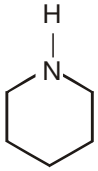
Ex.16 Compare the basic strength of the following



Sol. sp hybridised carbon being most electronegative will attract e^- density from nitrogen and will make it less available for H^+. Hence basicity decreases.
c > b > a

Ex.17 Compare the basic strength

(a) 
(–I of O at attracts e^- density from N making it less basic)

(b) 

a < b

Ex.18 Compare the basicity of the following compounds

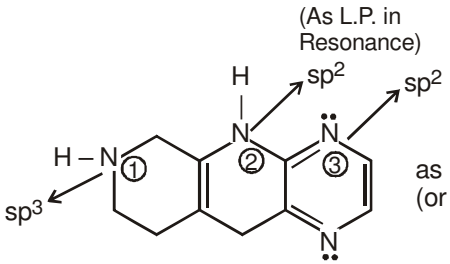
(a) $CH_3 - CH_2 - CH = CH - \ddot{N}H_2$ (b) $CH_3 - CH_2 - \underset{\downarrow}{CH_2}(sp^3) - CH_2 - NH_2$

(c) $CH_2 = CH - \underset{\downarrow}{CH_2}(sp^2) - CH_2 - NH_2$ (d) $CH \equiv \underset{\downarrow}{C}(sp) - CH_2 - CH_2 - NH_2$

Sol. In part (a) the lone pair of nitrogen in Resonance therefore will be less available for H^+ making it least basic among all followed by sp, sp^2, sp^3 hybridised carbon atoms.

b > c > d > a

Ex.19 Compare the basicity of the numbered nitrogen atoms.



as L.P. is not in Resonance (or in conjugation)

Sol. The planerity of ring will be destroyed if L.P. will take part in Resonance.

Basicity order of Nitrogen follows the order

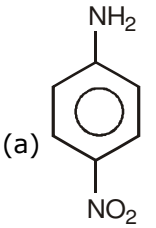
$N(sp^3) > N(sp^2) > N(sp)$

1 > 3 > 2

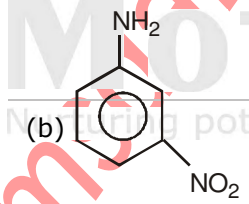
sp^2 sp^2

(In this sp^2, l.p. is in Resonance with ring hence will be less available for H^+ therefore it will be least basic)

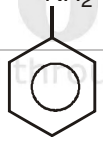
Ex.20 Compare the basic strength of the following



(a)



(b)



(c)

Sol. In part (a) NO_2 is at p-position Hence will attract e^- density by both –M and –I

In part (b) NO_2 is at m-position hence will attract e^- density by –I only

There is no such effect in part (c)

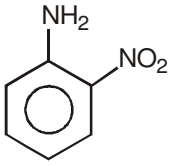
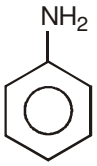
⇒ Availibity of L.P. on nitrogen in part (a) is minimum followed by b and then c.

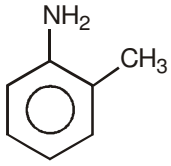
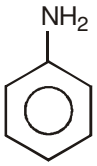
c > b > a

Ortho effect :

The ortho substituted aniline are less basic than aniline and ortho substituted benzoic acids are more acidic than benzoic acid.

- Ortho effect is valid only for benzoic acid and aniline.

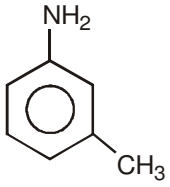
e.g.  < 

Also  < 

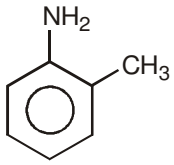
Ex.21 Compare the basic strength of the following :

(a) 

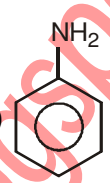
(+I, Hyperconjugation)

(b) 

(+I)

(c) 

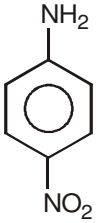
(+I)

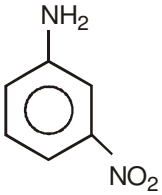
(d) 

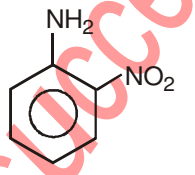
Sol. **a > b > d > c**

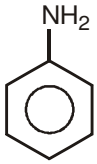
* Due to ortho effect d > c
if c is less basic than d then it will be certainly less basic than b as b is more basic than d.

Ex.22 Compare the basic strength of the following :

(a) 

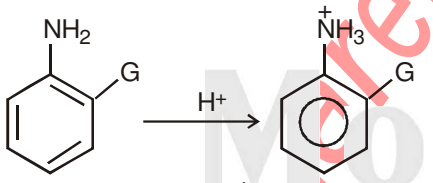
(b) 

(c) 

(d) 

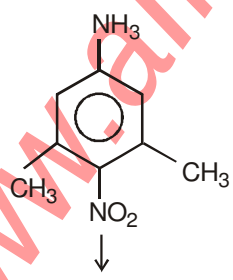
Sol. Do your selves

S.I.P → Steric inhibition of Protonation (ortho effect)

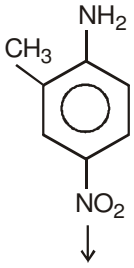


after protonation, repulsion increases therefore ortho substituted aniline is less basic than aniline

S.I.R → Steric inhibition of resonance

(a) 

(Shows only –I effect)

(b) 

(Shows –I as well as – M this means delocalisation of e^- is more)

Exercise - I

ACIDITY OR ACIDIC STRENGTH

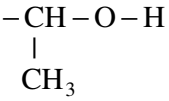
Q.1 Write the correct order of acidic strength of following compounds:

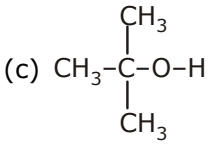
(i) (a) H–F (b) H–Cl (c) H–Br
(d) H–I

Sol.

(ii) (a) CH_4 (b) NH_3 (c) H_2O
(d) H–F

Sol.

(iii) (a) $CH_3–CH_2–O–H$ (b) 

(c) 

Sol.

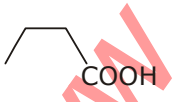
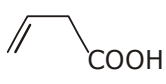
(iv) (a) $F–CH_2–CH_2–O–H$
(b) $NO_2–CH_2–CH_2–O–H$
(c) $Br–CH_2–CH_2–O–H$
(d) $\overset{\oplus}{N}H_3 – CH_2 – CH_2 – O – H$

Sol.

Q.2 Write the correct order of acidic strength of following compounds:

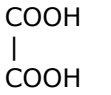
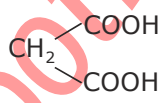
(i) (a) CH_3COOH (b) CH_3CH_2OH
(c) C_6H_5OH (d) $C_6H_5SO_3H$

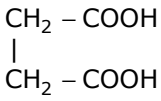
Sol.

(ii) (a)  (b) 

(c) 

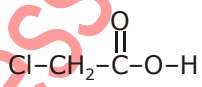
Sol.

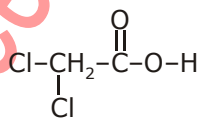
(iii) (a)  (b) 

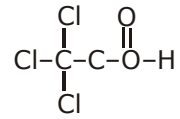
(c) 

Sol.

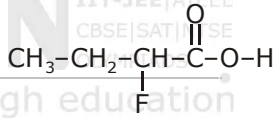
Q.3 Write correct order of acidic strength of following compounds:

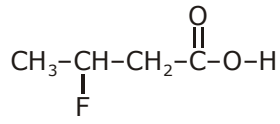
(i) (a) 

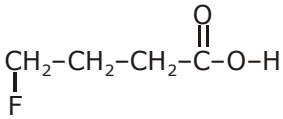
(b) 

(c) 

Sol.

(ii) (a) 

(b) 

(c) 

Sol.

(iii) (a) $NO_2-CH_2-\overset{\overset{O}{\|}}{C}-O-H$

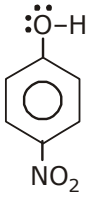
(b) $F-CH_2-\overset{\overset{O}{\|}}{C}-O-H$

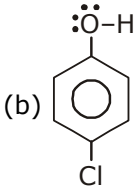
(c) $Ph-CH_2-\overset{\overset{O}{\|}}{C}-O-H$

(d) $CH_3-CH_2-\overset{\overset{O}{\|}}{C}-O-H$

Sol.

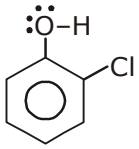
Q.4 Write correct order of acidic strength of following compounds:

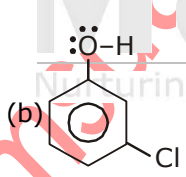
(i) (a) 

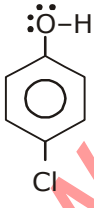
(b) 

(c) 

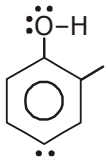
Sol.

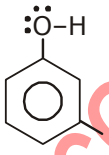
(ii) (a) 

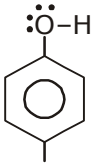
(b) 

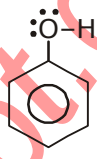
(c) 

Sol.

(iii) (a) 

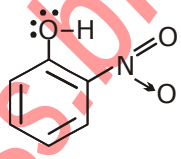
(b) 

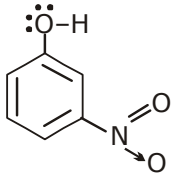
(c) 

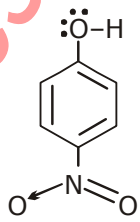
(d) 

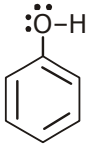
Sol.

Q.5 Write correct order of acidic strength of following compounds:

(i) (a) 

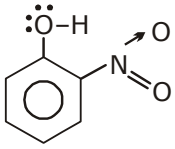
(b) 

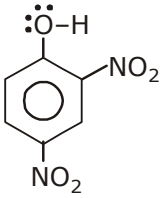
(c) 

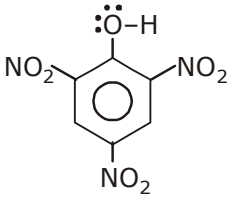
(d) 

Sol.

(ii) (a) 

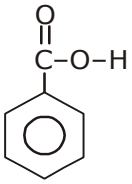
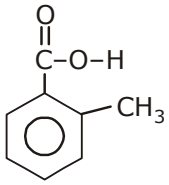
(b) 

(c) 

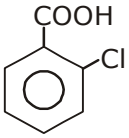
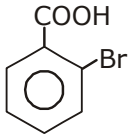
(d) 

Sol.

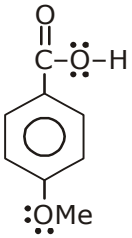
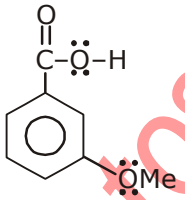
Q.6 Write correct order of acidic strength of following compounds:

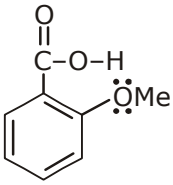
(i) (a)  (b) 

Sol.

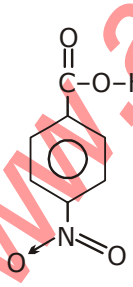
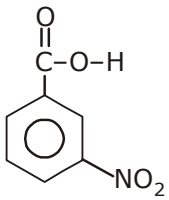
(ii) (a)  (b) 

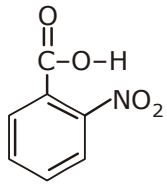
Sol.

(iii) (a)  (b) 

(c) 

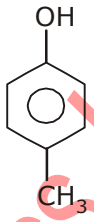
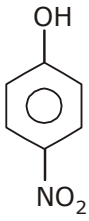
Sol.

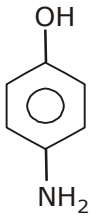
(iv) (a)  (b) 

(c) 

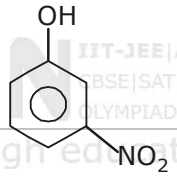
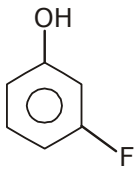
Sol.

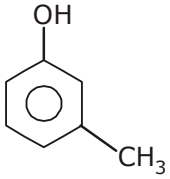
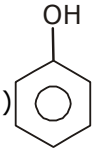
Q.7 Select the strongest acid in each of the following sets :

(i) (a)  (b) 

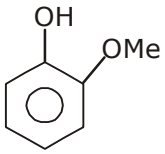
(c)  (d) 

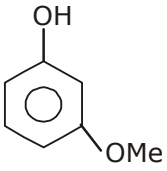
Sol.

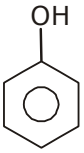
(ii) (a)  (b) 

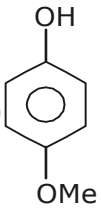
(c)  (d) 

Sol.

(iii) (a) 

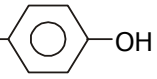
(b) 

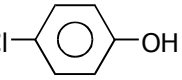
(c) 

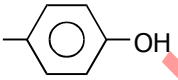
(d) 

Sol.

Q.8 Arrange the given phenols in their decreasing order of acidity:

(I) C_6H_5–OH (II) 

(III) 

(IV) 

Select the correct answer from the given code:

(A) IV > III > I > II (B) IV > II > III > I

(C) IV > III > II > I (D) IV > I > III > II

Sol.

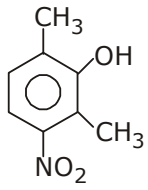
Q.9 Which one of the following is the most acidic?

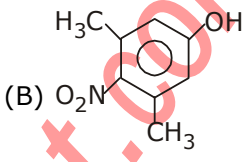
(A)  (B) 

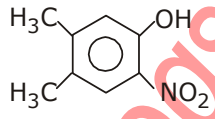
(C)  (D) $CH_2=CH-CH_3$

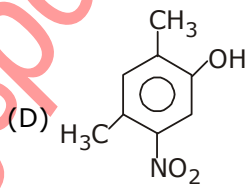
Sol.

Q.10 Which one of the following phenols will show highest acidity?

(A) 

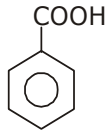
(B) 

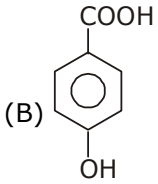
(C) 

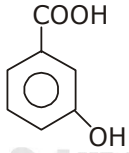
(D) 

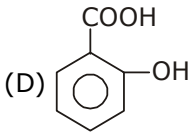
Sol.

Q.11 Which of the following is weakest acid?

(A) 

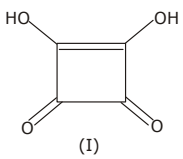
(B) 

(C) 

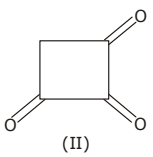
(D) 

Sol.

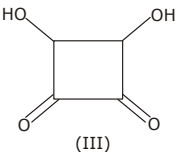
Q.12 The correct pKa order of the follwoing acids is :



(I)



(II)



(III)

(A) I > II > III (B) III > II > I

(C) III > I > II (D) I > III > II

Sol.

Q.13 Arrange pH of the given compounds in decreasing order:

(1) Phenol (2) Ethyl alcohol

(3) Formic acid (4) Benzoic acid

(A) 1 > 2 > 3 > 4 (B) 2 > 1 > 4 > 3

(C)3 > 2 > 4 > 1 (D) 4 > 3 > 1 > 2

Sol.

Q.14 Arrange acidity of given compounds in decreasing order:

(I) $CH_3–NH–CH_2–CH_2–OH$

(II) $CH_3–NH–CH_2–CH_2–CH_2–OH$

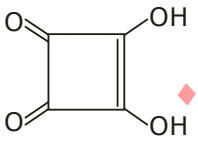
(III) $(CH_3)_3\overset{\oplus}{N}–CH_2–CH_2–OH$

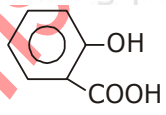
(A) III > I > II (B) III > II > I

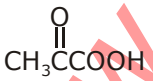
(C) I > II > III (D) II > I > III

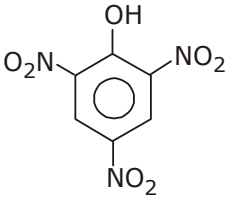
Sol.

Q.15 Consider the following compound

(A) 

(B) 

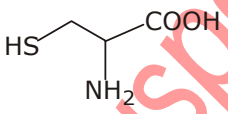
(C) 

(D) 

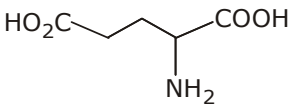
Which of the above compounds reacts with $NaHCO_3$ giving CO_2

Sol.

Q.16 Say which pk_a belong to which functional group in case of following amino acids :

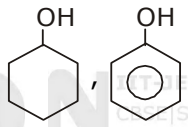
(i) cysteine :  1.8, 8.3 & 10.8

Sol.

(ii) glutamic acid :  : 2.19, 4.25, 9.67

Sol.

Q.17 Record the following sets of compounds according to increasing pK_a (= – log Ka)

(a)  , cyclohexane carboxylic acid.

Sol.

(b) 1-butyne, 1-butene, butane

Sol.

(c) Propanoic acid, 3-bromopropanoic acid, 2-nitropropanoic acid

Sol.

(d) Phenol,o-nitrophenol, o-cresol

Sol.

(e) Hexylamine, aniline, methylamine

Sol.

Q.18 Explain which is a stronger acid.

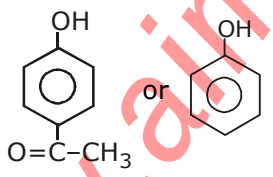
(a) CH_3CH_3 $BrCH_2NO_2$

(b) $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$ & $CH_3-\overset{\overset{O}{\|}}{C}-CH_2CN$

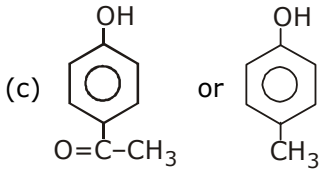
(c) $CH_3 - CHO$ $CH_3 - NO_2$

Sol.

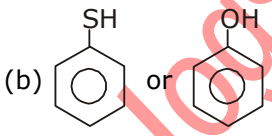
Q.19 Explain which is a weaker acid.

(a)  or

Sol.

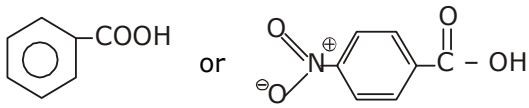
(c) 

Sol.

(b) 

Sol.

Q.20 Which of the following would you predict to be the stronger acid ?

(a) 

Sol.

(b) $CH_3 - CH_2 - CH_2 - OH$ or $CH_3 - CH = CH - OH$

Sol.

(c) $CH_3 - CH = CH - CH_2 - OH$ or $CH_3 - CH = CH - OH$

Sol.

Exercise - II

BASICITY OR BASIC STRENGTH

Q.1 Write increasing order of basic strength of following:

(i) (a) $F^{\ominus}$ (b) $Cl^{\ominus}$

(c) $Br^{\ominus}$ (d) $I^{\ominus}$

Sol.

(ii) (a) $CH_3^{\ominus}$ (b) $NH_2^{\ominus}$

(c) $OH^{\ominus}$ (d) $F^{\ominus}$

Sol.

(iii) (a) $R-NH_2$ (b) $Ph-NH_2$

(c) $R-\overset{\overset{O}{\|}}{C}-NH_2$

Sol.

(iv) (a) NH_3 (b) $MeNH_2$

(c) Me_2NH (d) Me_3N (Gas phase)

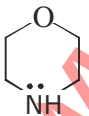
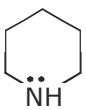
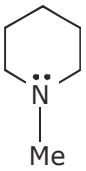
Sol.

(v) (a) NH_3 (b) $MeNH_2$

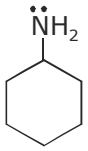
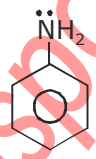
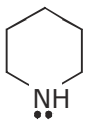
(c) Me_2NH (d) Me_3N (in H_2O)

Sol.

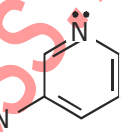
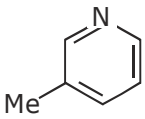
Q.2 Write increasing order of basic strength of following:

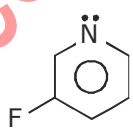
(i) (a)  (b)  (c) 

Sol.

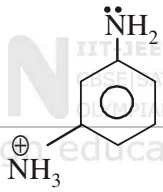
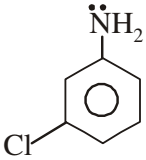
(ii) (a)  (b)  (c) 

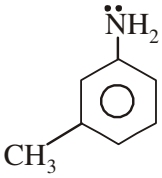
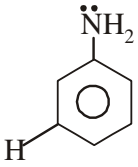
Sol.

(iii) (a)  (b) 

(c) 

Sol.

(iv) (a)  (b) 

(c)  (d) 

Sol.

Q.3 Write increasing order of basic strength of following:

(i) (a) $CH_3-CH_2-\ddot{N}H_2$ (b) $CH_3-CH=\ddot{N}H$

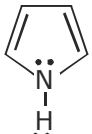
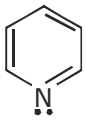
(c) $CH_3-C\equiv\ddot{N}$

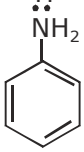
Sol.

(ii) (a) $CH_3-\overset{\overset{O}{\|}}{C}-\ddot{N}H_2$ (b) $CH_3-CH_2-\ddot{N}H_2$

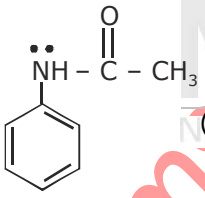
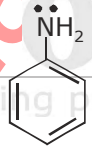
(c) $CH_3-\overset{\overset{NH}{\|}}{C}-\ddot{N}H_2$ (d) $NH_2-\overset{\overset{NH}{\|}}{C}-\ddot{N}H_2$

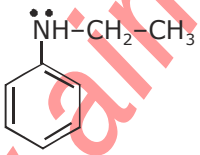
Sol.

(iii) (a)  (b) 

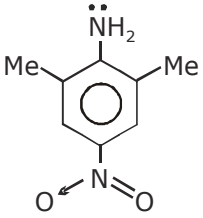
(c) 

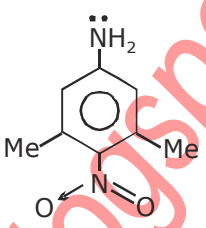
Sol.

(iv) (a)  (b) 

(c) 

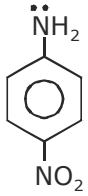
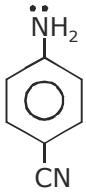
Sol.

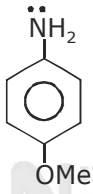
(v) (a) 

(b) 

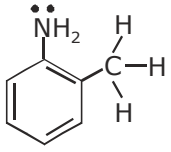
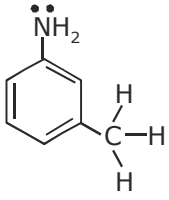
Sol.

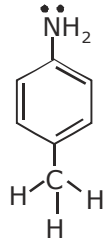
Q.4 Write increasing order of basic strength of following:

(i) (a)  (b) 

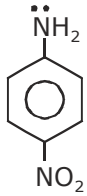
(c)  (d) 

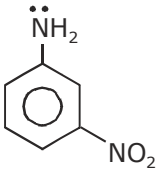
Sol.

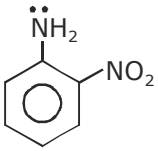
(ii) (a  (b) 

(c) 

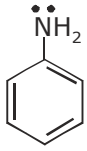
Sol.

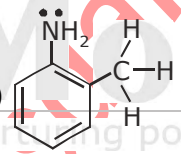
(iii) (a) 

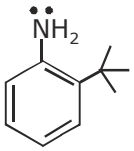
(b) 

(c) 

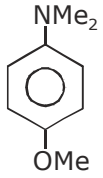
Sol.

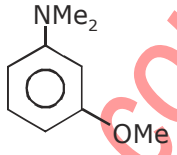
(iv) (a) 

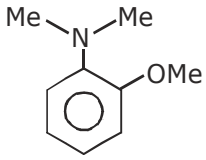
(b) 

(c) 

Sol.

(v) (a) 

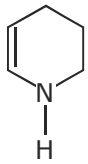
(b) 

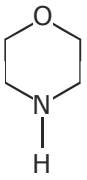
(c) 

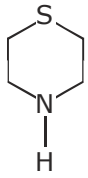
Sol.

Q.5 Select the strongest base in following compound :

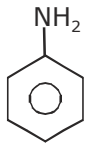
(i) (a) 

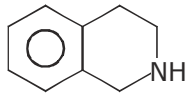
(b) 

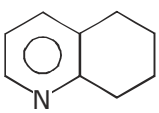
(c) 

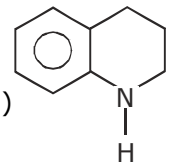
(d) 

Sol.

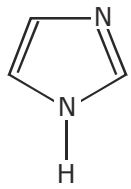
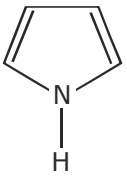
(ii) (a) 

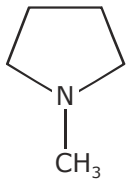
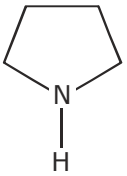
(b) 

(c) 

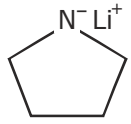
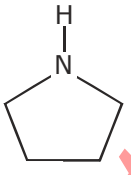
(d) 

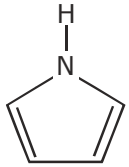
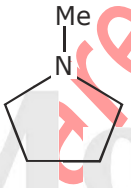
Sol.

(iii) (a)  (b) 

(c)  (d) 

Sol.

(iv) (a)  (b) 

(c)  (d) 

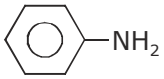
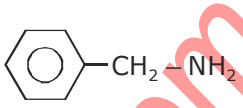
Sol.

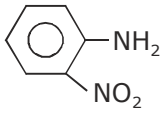
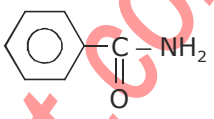
Q.6 Arrange the following compound in decreasing order of their basicity.

(i) (a) $H_2C = CHNa$ (b) CH_3CH_2Na

(c) CH_3CH_2ONa (d) $HC \equiv CNa$

Sol.

(ii) (a)  (b) 

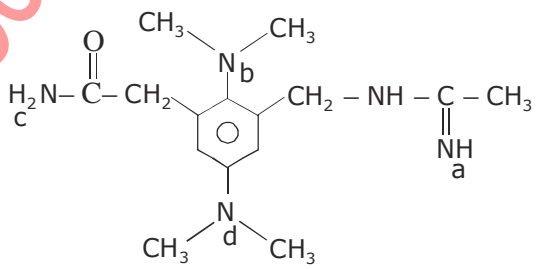
(c)  (d) 

Sol.

(iii) (a) HO^- (b) NH_3 (c) H_2O

Sol.

Q.7 Basicity order in following compound is :



(A) b > d > a > c (B) a > b > d > c

(C) a > b > c > d (D) a > c > b > d

Sol.

Q.8 Consider the following bases:

(I) o-nitroaniline (II) m-nitroaniline

(III) p-nitroaniline

The decreasing order of basicity is:

(A) II > III > I (B) II > I > III

(C) I > II >III (D) I > III > II

Sol.

Q.9 Consider the basicity of the following aromatic amines:

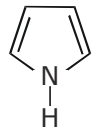
(I) aniline (II) p-nitroaniline
(III) p-methoxyaniline (IV) p-methylaniline

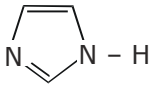
The correct order of decreasing basicity is:

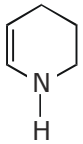
(A) III > IV > I > II (B) III > IV > II > I
(C) I > II > III > IV (D) IV > III > II > I

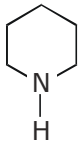
Sol.

Q.10 Which one of the following is least basic in character?

(A) 

(B) 

(C) 

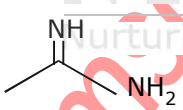
(D) 

Sol.

Q.11 In each of the following pair of compounds, which is more basic in aqueous solution? Give an explanation for your choice:

(a) CH_3NH_2 or CF_3NH_2

Sol.

(b) CH_3CONH_2 or 

Sol.

(c) n-$PrNH_2$ or CH_3CN

Sol.

(d) $C_6H_5N(CH_3)_2$ or 2,6-dimethyl-N-N-dimethylaniline

Sol.

(e) m-nitroaniline or p-nitroaniline

Sol.

Q.12 From the following pair, select the stronger base:

(a) p-methoxy aniline or p-cyanoaniline

Sol.

(b) pyridine or pyrrole

Sol.

(c) CH_3CN or $CH_3CH_2NH_2$

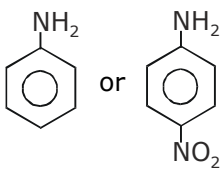
Sol.

Q.13 Choose the member of each of the following pairs of compunds that is likely to be the weaker base.

(a) H_2O or $H_3O^{\oplus}$ (b) H_2S, HS^-, S^{2-}
(c) Cl^-, SH^- (d) F^-, OH^-, NH_2^-, CH_3^-
(e) HF, H_2O, NH_3 (f) OH^-, SH^-, SeH^-

Sol.

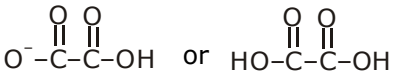
Q.14 Explain which compound is the weaker base.

(a) 

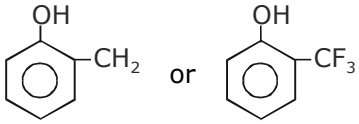
Sol.

(b) $CH_2 = CH - CH = CH - CH_2^-$ or $CH_2 = CH - CH_2^-$

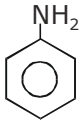
Sol.

(c) 

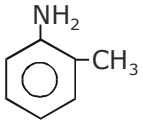
Sol.

(d) 

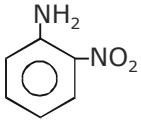
Q.15 Rank the following amines in increasing basic nature.

(a) 

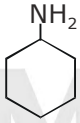
(i)



(ii)

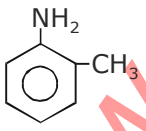


(iii)

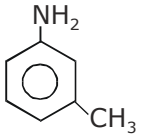


(iv)

Sol.

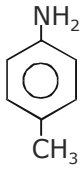
(b) 

(i)

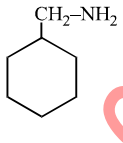


(ii)

Sol.



(iii)



(iv)

Sol.

Q.16 Arrange the basic strength of the following compounds.

(a) OH^- CH_3COO^- Cl^-

(i) (ii) (iii)

Sol.

(b) $CH \equiv C^-$ $CH_2 = CH^-$ $CH_3CH_2^-$

(i) (ii) (iii)

Sol.

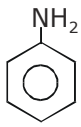
(c) (i) $CH_2 = CHCH_2NH_2$

(ii) $CH_3CH_2CH_2NH_2$

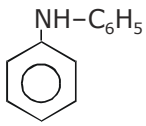
(iii) $CH \equiv C - CH_2NH_2$

Sol.

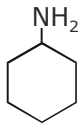
Q.17 Arrange the basic strength of the following compounds.

(a) 

(i)

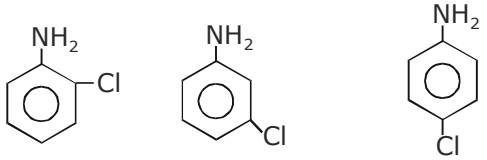


(ii)



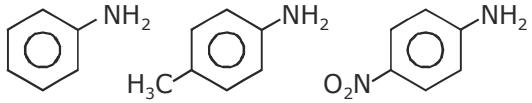
(iii)

Sol.

(b) 

(i) (ii) (iii)

Sol.

(c) 

(i) (ii) (iii)

Sol.

Q.18 Arrange the following compounds in order of increasing basicity.

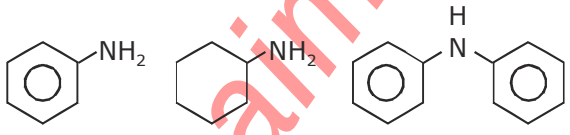
(a) CH_3NH_2, $CH_3\overset{\oplus}{N}H_3$, CH_3NH^-

(b) CH_3O^-, CH_3NH^-, $CH_3CH_2^-$

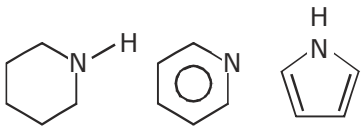
(c) $(CH_3)_3CH=CH^-$, $CH_3CH_2CH_2^-$, $CH_3C\equiv C^-$

Sol.

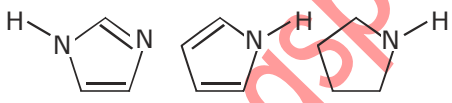
Q.19 Rank the amines in each set in order of increasing basicity.

(a) 

Sol.

(b) 

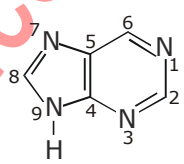
Sol.

(c) 

Sol.

Q.20 

Pyrimidine Imidazole



Purine

Among the following which statement(s) is/are ture:

(A) Both N of pyrimidine are of same basic strength

(B) In imidazole protonation takes places on N–3.

(C) Purine has 3 basic N.

(D) Pyrimidine imidazole and purine all are aromatic

Sol.

Answers

Exercise-I

Q.1 (i) d > c > b > a (ii) d > c > b > a (iii) a > b > c (iv) d > b > a > c

Q.2 (i) d > a > c> b (ii) c > b > a (iii) a > b > c

Q.3 (i) c > b > a (ii) a > b > c (iii) a > b > c > d

Q.4 (i) a > b > c (ii) a > b > c (iii) d > b > c > a

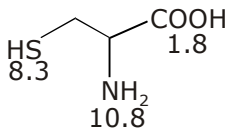
Q.5 (i) c > a > b > d (ii) d > c > a > b

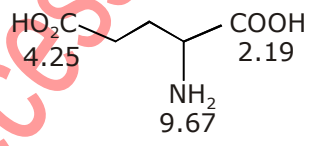
Q.6 (i) b > a (ii) b > a (iii) c > b > a (iv) c > a > b

Q.7 (i) b (ii) a (iii) b Q.8 C Q.9 B Q.10 C

Q.11 B Q.12 B Q.13 B Q.14 A

Q.15 A, B, C, D

Q.16 (i) cysteine : 

(ii) glutamic acid : 

Q.17 (a) 3 < 2 < 1; (b) 1 < 2 < 3; (c) 3 < 2 < 1; (d) 2 < 1 < 3; (e) 2 < 3 < 1

Q.18 (a) 2; (b) 2; (c) 2 Q.19 (a) 2; (b) 2; (c) 2 Q.20 (a) 2; (b) 2; (c) 2

Exercise-II

Q.1 (i) a > b > c > d (ii) a > b > c> d (iii) a > b > c (iv) a < b < c < d
(v) c > b> d> a

Q.2 (i) a < b < c (ii) c > a > b (iii) b > c > a (iv) c > d > b > a

Q.3 (i) a > b > c (ii) d > c > b > a (iii) b > c > a (iv) c > b > a (v) b > a

Q.4 (i) d > c > b > a (ii) c > b > a (iii) b > a > c (iv) a > b > c (v) c > a > b

Q.5 (i) d (ii) b (iii) a (iv) a Q.6 (i) b > a > d > c (ii) b > a > c > d (iii) a > b > c

Q.7 B Q.8 A Q.9 A Q.10 A

Q.11 (a) i, (b) ii, (c) i, (d) ii, (e) i Q.12 (a) i, (b) i, (c) ii

Q.13 (a) 2; (b) 1; (c) 1; (d) 1; (e) 1; (f) 3 Q.14 (a) 2; (b) 1; (c) 2; (d) 2

Q.15 (a) 3 < 2 < 1 < 4; (b) 1 < 2 < 3 < 4 Q.16 (a) 1 > 2 > 3; (b) 1 < 2 < 3; (c) 3 < 1 < 2

Q.17 (a) 2 < 1 < 3; (b) 1 < 2 < 3; (c) 2 > 1 > 3 Q.18 (a) 2 < 1 < 3; (b) 1 < 2 < 3; (c) 3 < 1 < 2

Q.19 (a) 2 > 1> 3, (b) 1 > 2 > 3, (c) 1 > 3 > 2, Q.20 A, B, C, D

ACIDITY & BASICITY

EXERCISE - 1 HINT & SOLUTON

Q.1

(i) (a) $H - F \rightarrow F^-$ (b) $H - Cl \rightarrow Cl^-$ (c) $H - Br \rightarrow Br^-$ (d) $H - I \rightarrow I^-$

In group we see the size factor more the size, more stable the anion, more the acidity.

d > c > b > a (acidic strength)

(ii) (a) $CH_4 \xrightarrow{-H^+} {}^-CH_3$ (b) $NH_3 \xrightarrow{-H^+} NH_2^-$ (c) $H_2O \xrightarrow{-H^+} OH^-$ (d) $H - F \xrightarrow{-H^+} F^-$

In period we see the E.N. factor more the electron negativity, more stable the anion, more the acidity.

E.N. order $\Rightarrow {}^-F > {}^-OH > {}^-NH_2 > {}^-CH_3$

Acidity order = d > c > b > a

(iii) (a) $CH_3 - CH_2 - O - H \rightarrow +I(CH_3) - CH_2 - {}^-O$

More stable

(b) $CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{|}}{CH} - O - H \rightarrow CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{|}}{CH} - O^-$

2(+I) effect

(c) $CH_3 - \underset{\displaystyle CH_3}{\overset{\displaystyle CH_3}{|}}{C} - O - H \rightarrow (CH_3)_3 - C - O^-$

Three + I group less stable

(acidic strength)a > b > c

(iv) (a) $F - CH_2 - CH_2 - O - H \Rightarrow F - CH_2 - CH_2 - O^-$

(b) $NO_2 - CH_2 - CH_2 - O - H \Rightarrow NO_2 - CH_2 - CH_2 - O^-$

(c) $Br - CH_2 - CH_2 - O - H \Rightarrow Br - CH_2 - CH_2 - O^-$

(d) $\overset{\oplus}{N}H_3 - CH_2 - CH_2 - O - H \Rightarrow \overset{\oplus}{N}H_3 - CH_2 - CH_2 - O^-$

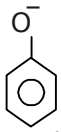
–I order = $-\overset{\oplus}{N}H_3 > -NO_2 > -F > -Br$

acidic strength = d > b > a > c

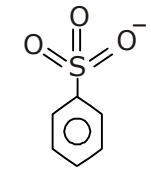
Q.2(i) (a) $CH_3 - COOH \xrightarrow{-H^+} CH_3 - \underset{\displaystyle O}{\overset{\displaystyle ||}{C}} - O^-$

(b) $CH_3 - CH_2 - OH \xrightarrow{-H^+} +I(CH_3) - CH_2 - {}^-O$

(c) $C_6H_5OH \xrightarrow{-H^+} C_6H_5 - O^-$

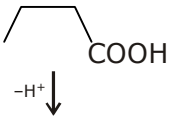
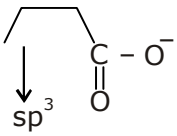


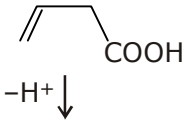
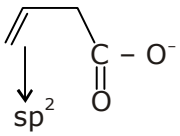
(Phenoxide ion)

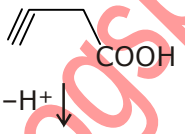
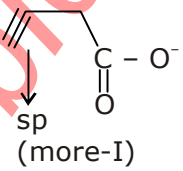
(d) $C_6H_5SO_3^-$  [–I order – C(=O) – R > Ph]

(More the resonating structures, more the stability)

d > a > c > b

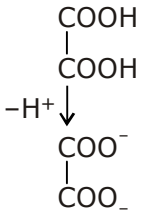
(ii) (a)  

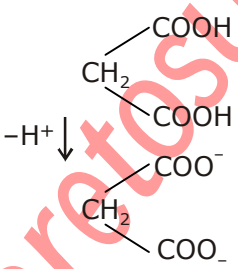
(b)  

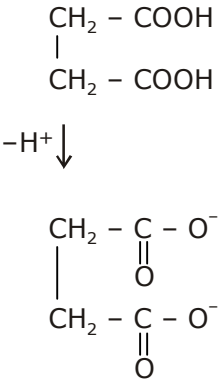
(c)  

Stability = C > b > a

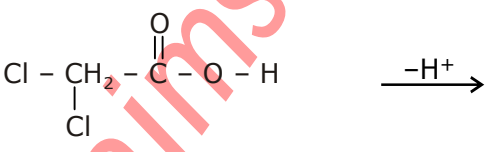
acidity = c > b > a

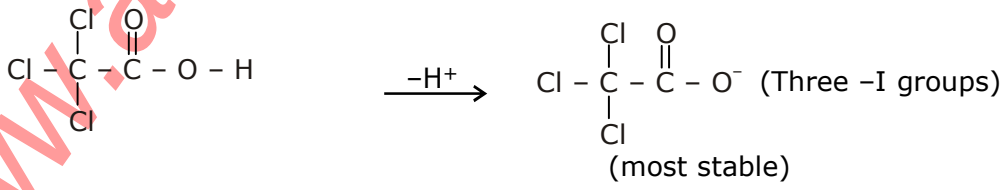
(iii) (a) 

(b) 

(c) 

Q.3 (a) $Cl-CH_2-\overset{O}{\overset{\|}{C}}-O-H \xrightarrow{-H^+}$ $Cl-CH_2-\overset{O}{\overset{\|}{C}}-O^-$ (one -I group)

(b)  (two -I grop)

(c)  (most stable)

Ans. c > b > a

(ii) (a) $CH_3 - CH_2 - \underset{F}{\underset{|}{CH}} - \overset{O}{\overset{\|}{C}} - O - H \xrightarrow{-H^+} CH_3 - CH_2 - \underset{F}{\underset{|}{CH}} - \overset{O}{\overset{\|}{C}} - O^-$

(b) $CH_3 - \underset{F}{\underset{|}{CH}} - CH_2 - \overset{O}{\overset{\|}{C}} - O - H \xrightarrow{-H^+} CH_3 - \underset{F}{\underset{|}{CH}} - CH_2 - \overset{O}{\overset{\|}{C}} - O^-$

(c) $\underset{F}{\underset{|}{CH_2}} - CH_2 - CH_2 - \overset{O}{\overset{\|}{C}} - O - H \xrightarrow{-H^+} \underset{F}{\underset{|}{CH_2}} - CH_2 - CH_2 - \overset{O}{\overset{\|}{C}} - O^-$

In this type of case are see "DNP" rule.

"DNP" → Distance, Number, Power

Acidic strength = a > b > c

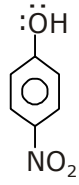
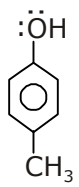
(iii) (a) $NO_2 - CH_2 - \overset{O}{\overset{\|}{C}} - O - H \xrightarrow{-H^+} NO_2 - CH_2 - \overset{O}{\overset{\|}{C}} - O^-$

(b) $F - CH_2 - \overset{O}{\overset{\|}{C}} - O - H \xrightarrow{-H^+} F - CH_2 - \overset{O}{\overset{\|}{C}} - O^-$

(c) $Ph - CH_2 - \overset{O}{\overset{\|}{C}} - O - H \xrightarrow{-H^+} Ph - CH_2 - \overset{O}{\overset{\|}{C}} - O^-$

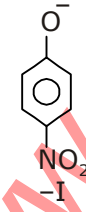
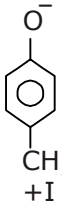
(d) $CH_3 - CH_2 - \overset{O}{\overset{\|}{C}} - OH \xrightarrow{-H^+} CH_3 - CH_2 - \overset{O}{\overset{\|}{C}} - O^-$

Acidic Strength : a > b > c > d

Q.4(i) (a)  (b)  (c) 

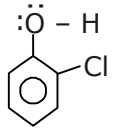
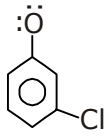
(strongel acid)

↓ ↓ ↓

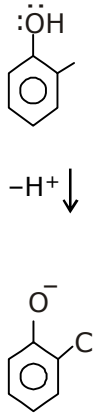
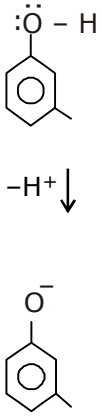
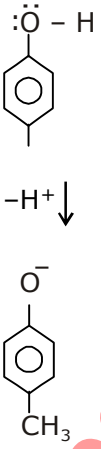
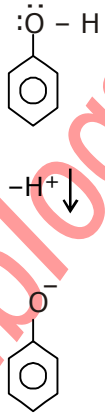
  

(most stable conjugate base)

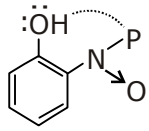
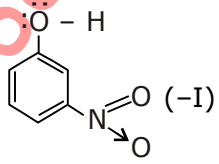
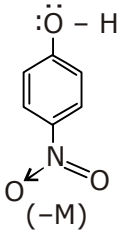
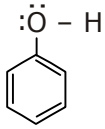
Acidic strength = a > b > c

(ii) (a)  (b)  (c) 

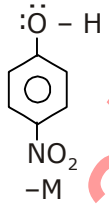
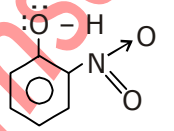
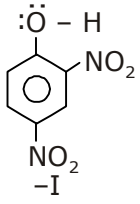
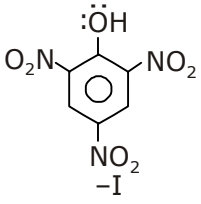
Inductive effect by distance decreases.
Acidity order a > b > c

(iii) (a)  (b)  (c)  (d) 

stability of Conjugate base : d > b > c > a
acidity order : d > b > c > a

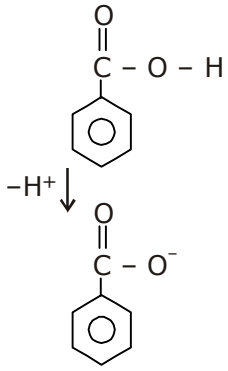
Q.5(i) (a) 
(–M) Hydrogen Bonding
(b)  (–I) (c) 
(–M)
(d) 

Acidity order = c > a > b > d

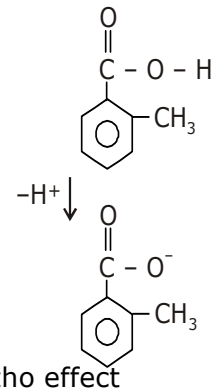
(ii) (a) 
–M
(b) 
H–Bonding
(–M)
(c) 
–I
(d) 
–I

Acidity order = d > c > a > b

Q.6(i) (a)



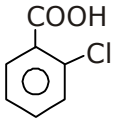
(b)



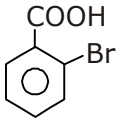
Due to ortho effect
COOH goes out of plane
So max. acidity

b > a

(ii) (a)

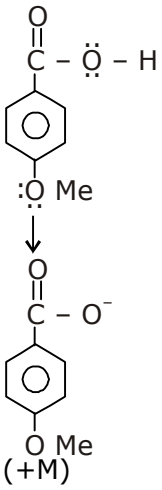


(b)

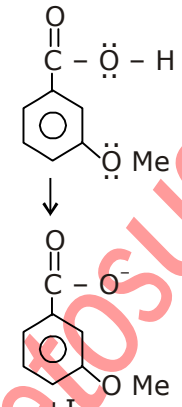


Br is more bulky then Cl ortho effect

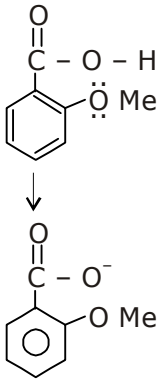
(iii) (a)



(b)



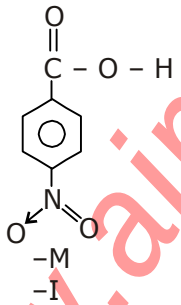
(c)



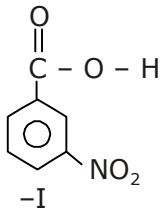
Ortho effect max. acidity

Acidity order c > b > a

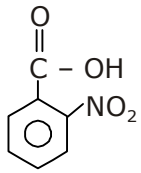
(iv) (a)



(b)

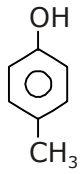
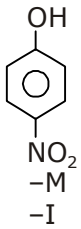
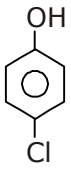
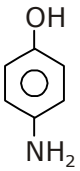


(c)

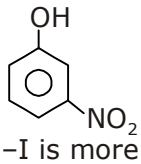
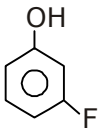
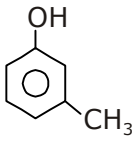
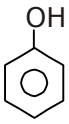


Ortho effect

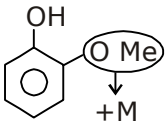
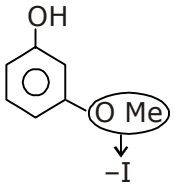
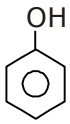
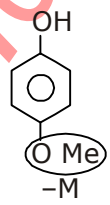
Acidity order = c > a > b

Q.7(i) (a)  (b)  (c)  (d) 

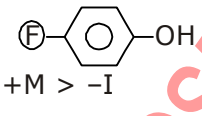
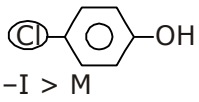
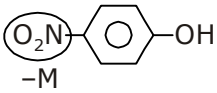
Strongest acid ⇒ (b)

(ii)  –I is more (b)  (c)  (d) 

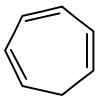
So maximum acidity.

(iii)(a)  (b)  (c)  (d) 

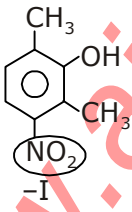
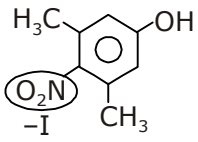
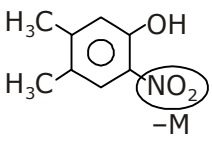
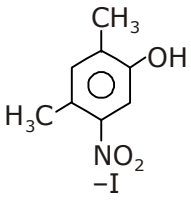
acidity ∝ with drawing tendency of group.
so (b) max. acidity.

Q.8 (I) C_6H_5 – OH (II)  (III)  (iv) 

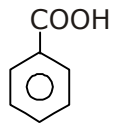
IV > III > II > I

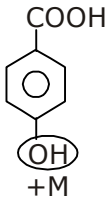
Q.9 (A)  (b)  (c)  (d) CH_2 – CH – CH_3

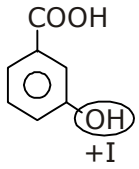
The conjugate base of compound (b) is most stable due to aromaticity (i.e. )

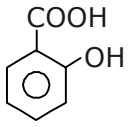
Q.10 (A)  (B)  (C)  (D) 

Maximum acidity (C). Ans. (C)

Q.11 (A) 

(B) 

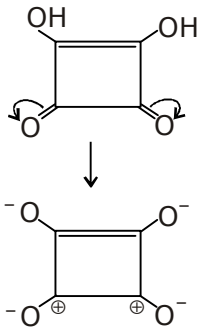
(C) 

(D) 

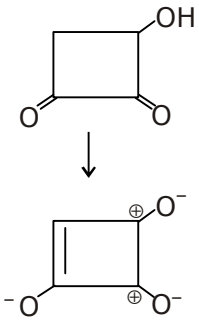
(ortho effect)

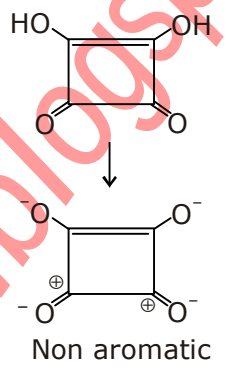
(most acidic)

Compound (B) is less acidic due to (+M) effect of –OH group because it is present on pera position.

Q.12 (I) 

4 eq. Aromatic R.S.

(II) 

(III) 

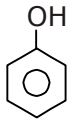
Non aromatic

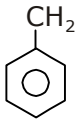
$$\text{acidity} \propto \frac{1}{Pk_a}$$

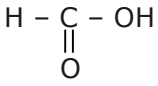
acidity (ka) order = I > II > III

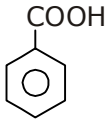
Pk_a order = III > II > I

Q.13 (1) Phenol (2) Ethyl alcohol (3) Formic acid (4) Benzoic acid

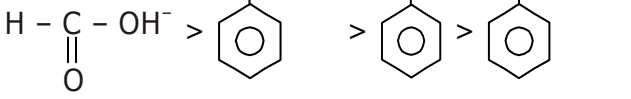








$$pH \propto \frac{1}{\text{acidity}} \propto \frac{1}{\text{stability of conjugate Base}}$$

Stability of conjugate base = 

Q.14 (I) $CH_3 - NH - CH_2 - CH_2 - OH \longrightarrow CH_3 - NH - CH_2 - CH_2 - O^-$

(II) $CH_3 - NH - CH_2 - CH_2 - CH_2 - OH \longrightarrow CH_3 - NH - CH_2 - CH_2 - CH_2 - O^-$

(III) $(CH_3)_3\overset{\oplus}{N} - CH_2 - CH_2 - OH \longrightarrow N(\overset{\oplus}{C}H_3)_3 - CH_2 - CH_2 - O^-$

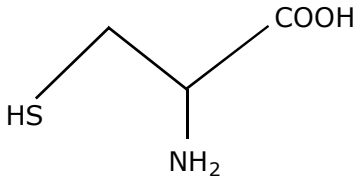
Strong –I effect

Acidity order = III > I > II

Q.15 Compound which are stronger acid than H_2CO_3 gives CO_2 with $NaHCO_3$.

→ Compound (A), (B), (C), (D) all are stronger acid than H_2CO_3.

16. (i) Cysteine :



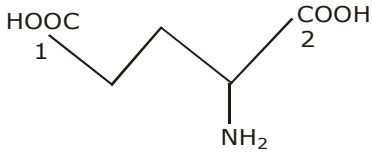
Acidity $\propto \frac{1}{Pk_a}$

Acidity order = $-COO^{\ominus} > -S^{\ominus} > -NH^{\ominus}$

pka order = $-NH_2 > -S > -COOH$

10.8 8.3 1.8

(ii) glutomic acid :



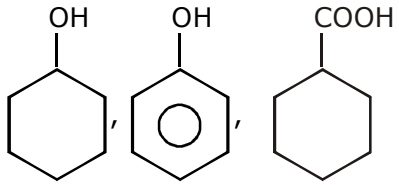
acidity : $-COOH > -NH_2$

acidity of $-COOH$ (2) > $-COOH$ (1) due to $-I$ effect to $-\ddot{N}H_2$

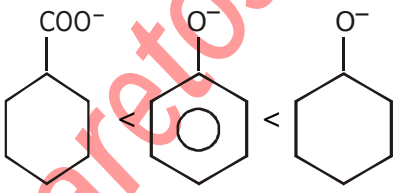
order of acidity : $-COOH$ (2) > $-COOH$ (1) > $-NH_2$

order of Pka : $-NH_2$ > $-COOH$ (1) > $-COOH$ (2)

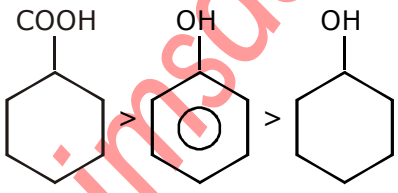
17. (a)



acidity stablity of CB =



acidity =



P_{ka} order = 3 < 2 < 1

(b) 1 - butyne, 1-butene, butane

$CH_3 - CH_2 - \underset{\downarrow}{C}(sp) \equiv CH$ (4, 3, 2, 1)

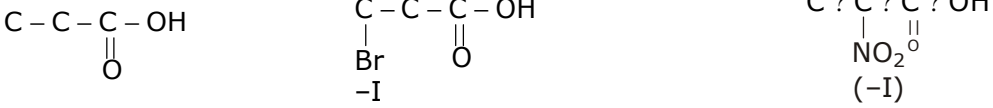
$CH_3 - CH_2 - \underset{\downarrow}{CH}(sp^2) = CH_2$

$CH_3 - CH_2 - \underset{\downarrow}{CH_2}(sp^2) - CH_3$

acidity order = 1 > 2 > 3

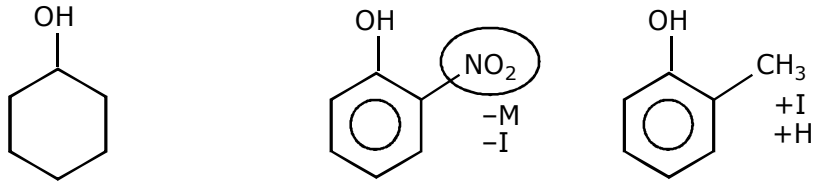
Pk_a order = 1 < 2 < 3

(c) Prophanoic acid, 3-Bromo propanoic acid 2-nitro propanoic acid



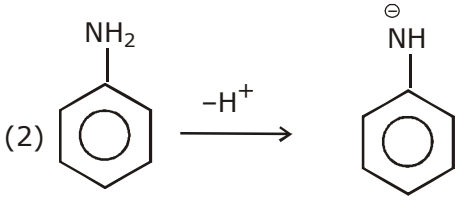
acidity 3 > 2 > 1
pk_a order 3 < 2 < 1

(d) Phenol, O-nitrophenol, O-cresol



acidity order = 2 > 1 > 3
P_{Ka} order = 2 < 1 < 3

(e) (1) $CH_3-CH_2-CH_2-CH_2-CH_2-NH_2 \rightarrow CH_3-CH_2-CH_2-CH_2-CH_2-CH_2-\overset{\ominus}{N}H$

(2) 

(3) $CH_3-NH_2 \xrightarrow{-H^+} CH_2-NH^{\ominus}$

acidity $\propto$ stability of conjugate Base
stability order = 2 > 3 > 1
acidity order = 2 > 3 > 1
P_{ka} = 2 < 3 < 1

18. (a) CH_3-CH_2-Br & CH_3-NO_2 (b) $CH_3-\overset{O}{\overset{\|}{C}}-CH_3$ (C) CH_3-CHO

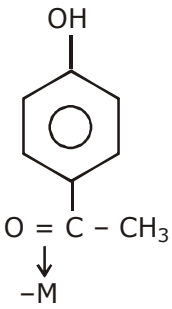
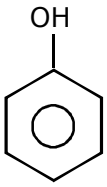
(1) $\overset{+I}{CH_3}-\overset{\ominus}{C}H-Br$ & $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CN$ CH_3-NO_2

(2) $\overset{\ominus}{C}H_2-NO_2$ (1) $\overset{\ominus}{C}H_2-\overset{O}{\overset{\|}{C}}-CH_3$ (1) $\overset{\ominus}{C}H_2-\overset{O}{\overset{\|}{C}}-H$

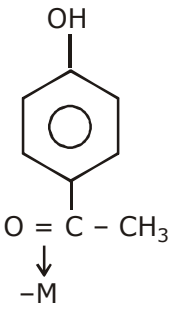
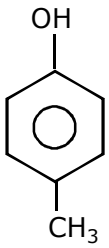
$\overset{-I}{}$

(2) is stronger acid (2) $CH_3-\overset{O}{\overset{\|}{C}}-\overset{\ominus}{C}H-CN$ (2) $\overset{\ominus}{C}H_2-NO_2$

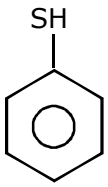
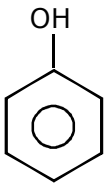
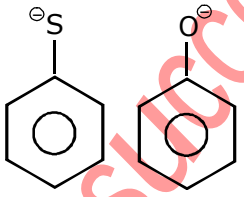
(2) > (1) (2) > (1) (2) > (1)

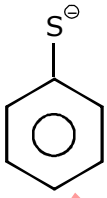
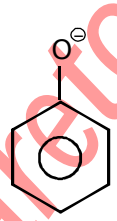
19.  as (2)  acidity $\propto$ – M effect

So (2) is weaker acid

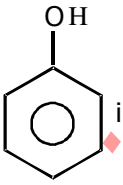
(b)  as (2) 

So (2) is weaker acid

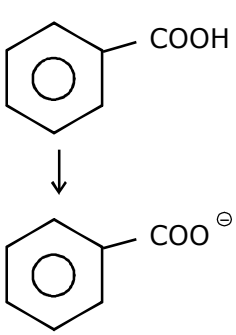
(c)  or  

Stability of C.B. =  . > 

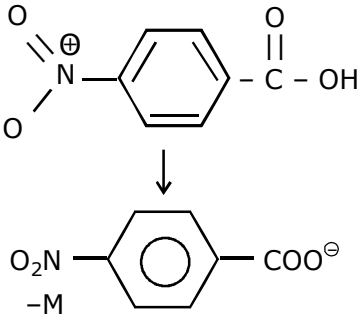
Acidity $\propto$ stability of C.B.

So  is weaker acid

20.



or



acidity $\propto$ – M effect
so (2) is more acidic

(b) $CH_3 - CH_2 - CH_2 - OH$ or $CH_3 - CH = CH - OH$

$\downarrow$ $\downarrow$

$CH_3 - CH_2 - CH_2 - O^{\ominus}$ $CH_3 - CH = CH - O^{\ominus}$

Showing Resonance so more acidic

So (2) is stronger acid

(c) $CH_3 - CH = CH - CH_2 - OH$ or $CH_3 - CH = CH - OH$

$\downarrow$

(d) $CH_3 - CH = CH - CH_2 - O^{\ominus}$ (2) $CH_3 - CH = CH - O^{\ominus}$

Show Resonance so more acidic

so (2) is stronger acid

EXERCISE - 2 HINT & SOLUTON

Q.1 (i) Basicity $\propto \frac{1}{\text{Stability of anion}}$

Stability order $F^- < Cl^- < Br^- < I^-$ (size)
Basicity order $F^- > Cl^- > Br^- > I^-$

(ii) Stability order $CH_3^- < NH_2^- < OH^- < F^-$ (E.N.)

Basicity order $CH_3^- > NH_2^- > OH^- > F^-$

(iii) $R - \ddot{N}H_2$
ℓ.p. localised
(more basic)

Pn $\ddot{N}H_2$
ℓ.p. delocalised
(weak base)

R – C(=O) $\ddot{N}H_2$
ℓ.p. more delocalised
(least base)

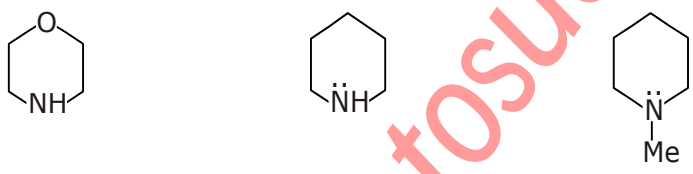
basicity order a > b > c

(iv) In gas phase basicity $\propto$ (+I) effect.
Basicity order

$NH_3 < \underset{+I}{Me} \rightarrow NH_3 < \underset{+I}{Me} \rightarrow NH \leftarrow \underset{+I}{Me} < \underset{+I}{Me} \rightarrow N \leftarrow \underset{+I}{Me}$
(Me, +I on N)

(v) In H_2O, 3°-amine is less basic than 1°-amine due to less solvation.
Basicity order : 2°–amine > 1°–amine > 3°–amine > NH_3

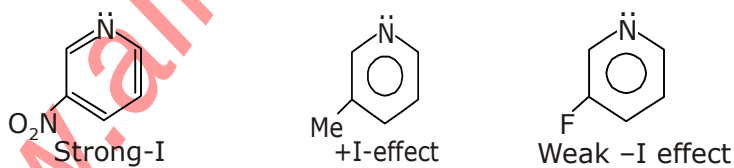
Q.2 (i)



(ii)

Basicity c > a > b

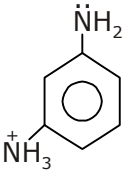
(iii)

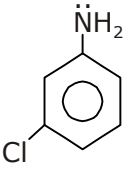


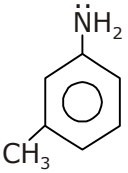
Basicity $\propto \frac{1}{(-I) \text{ effect}}$

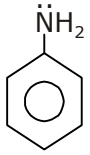
$\propto$ (+I) effect

Basicity b > c > a

(iv) (a) 
Strong-I-effect of $-\overset{+}{N}H_3$, least basic

(b) 
Weak –I effect of –Cl, less basic

(c) 
+I effect of $-CH_3$, most basic

(d) 
No effect of any group. Weaker than C, but stronger than a & b compound.

Q.3(i) (a) $CH_3\ CH_2\ \ddot{N}H_2$ (sp^3)
Least electronegative. most basic
order a > b > c

(b) $CH_3 - CH = \ddot{N}H$ (sp^2)

(c) $CH_3 - C \equiv \ddot{N}$ (sp)
most electronegative least basic.

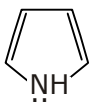
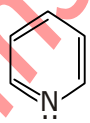
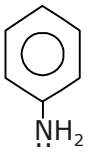
(ii) (a) $CH_3 - \underset{\underset{O}{\|}}{C} - \ddot{N}H_2$
least basic, l.p. of nitrogen is delocalised.

(b) $CH_3CH_2\ddot{N}H_2$
Lone pair localised

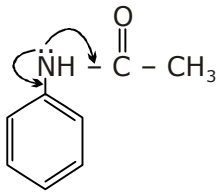
(c) $CH_3 - \underset{\underset{\ddot{N}H}{\|}}{C} - \ddot{N}H_2$
More basic due to delocalisation of only one l.p.

(d) $\ddot{N}H_2 - \underset{\underset{\ddot{N}H}{\|}}{C} - \ddot{N}H_2$
Most basic, due to more delocalisation of l.p.

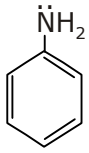
Basicity order d > c > b > a

(iii) (a)  (b)  (c) 

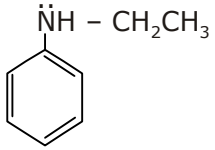
* Compound 'a' is least basic, because l.p. of Nitrogen will more take participate in resonance due to aromaticity.
* Compound 'b' is most basic, because its l.p. is localised.
* Compound 'c' is more basic than 'b' because its l.p. is delocalised.

(iv) 

l.p. of nitrogen is in conjugation with benzene as well as $-\overset{\overset{O}{\|}}{C}-CH_3$, least basic.

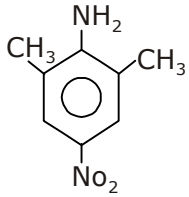


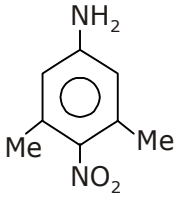
l.p. of nitrogen is in conjugation only with benzene. it is more basic than compound 'a'.



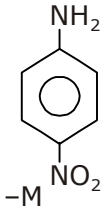
due to extra +I effect of $-CH_2CH_3$ group, compound 'c' is most basic than a & b.

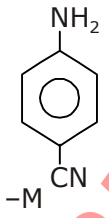
order c > b > a

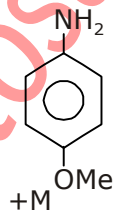
(v) 

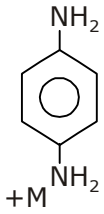


Compound a is least basic than b, due to ortho effect of two $-CH_3$ group.

Q.4(i) 





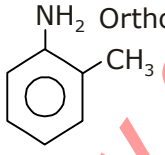


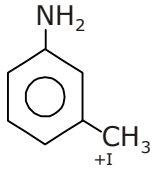
Order of −M $-NO_2 > -CN$

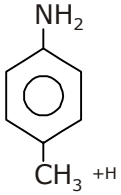
Order of +M $-NH_2 > -OMe$

Basicity $\propto +M \propto \frac{1}{-M}$

∴ Basicity order d > c > b > a

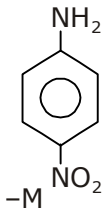
(ii) 

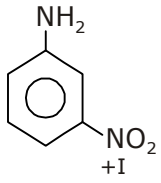


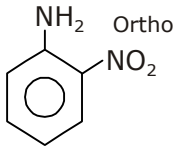


Compound C is most basic due to +H effect of $-CH_3$ group. But compound a is least basic due to ortho effect of $-CH_3$ group.

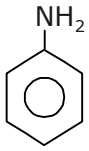
Basicity order c > b > a

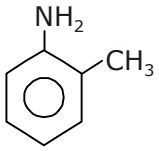
(iii) (a) 

(b) 

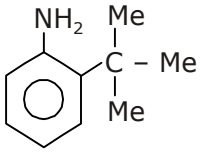
(c) 

Order b > a > c

(iv) 

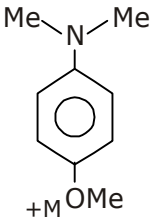


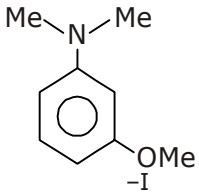
Ortho effect, less basic

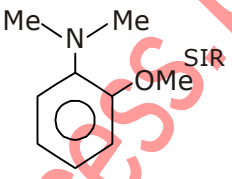


Greater ortho effect, least basic.

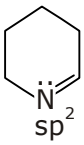
Order a > b > c

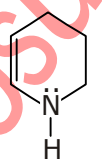
(v) 



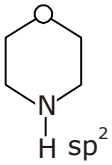


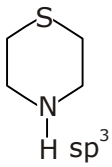
Order c > a > b

Q.5(i) (a) 

(b) 

sp^2 & delocalisation of l.p.

(c) 

(d) 

In compound 'd', hybridisation of N is sp^3. i.e. less electronegative and –I effect of S is less.

(ii)[b] In compound b, N atom is sp^3 hybridised, and l.p. of nitrogen is localised.

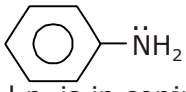
(iii) Compound a is most basic because charge density on double bonded nitrogen is very high due to resonance.

(iv) In compound a, the e^- charge density is very high due to –ve charge.

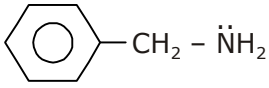
Q.6(i) $\text{Basicity} \propto \frac{1}{\text{E.N. of anion}}$

Order of E.N.

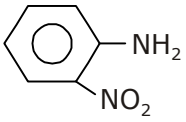
$CH_3CH_2^- < CH_2 = CH^- < HC \equiv C^- < CH_3CH_2O^-$

(ii) (a) 

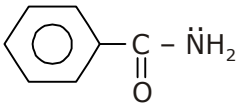
l.p. is in conjugation only with benzene ring.

(b) 

l.p. localised, most basic

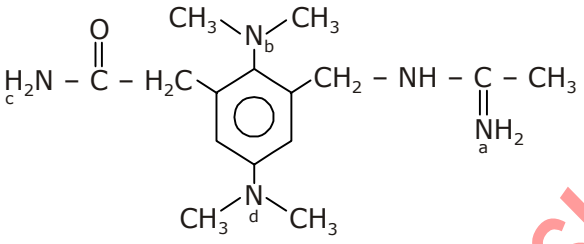
(c) 

Ortho effect

(d) 

l.p. is in conjugation with $-\overset{\overset{O}{\|}}{C}-$ group. Which is most with drawing.

Order : b > a > c > d

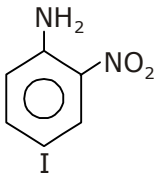
Q.7 

a is most basic due to high charge density.

b is more basic than d and c due to ortho effect.

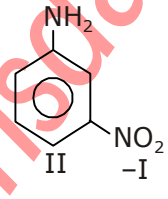
c is least basic because l.p. of nitrogen is conjugated with $-\overset{\overset{O}{\|}}{C}-$ group.

Order : a > b > d > c

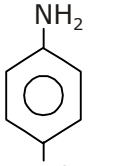
Q.8 

I

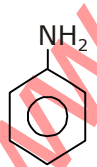
least basic due to ortho effect

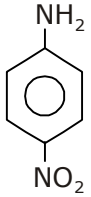


II $-I$

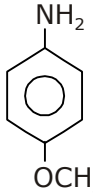


III $-M$

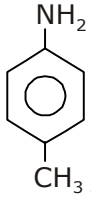
Q.9 (I) 

(II) 

NO_2 $-M$

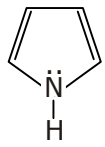
(III) 

OCH_3 $+M$

(IV) 

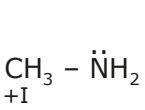
CH_3 $+H$

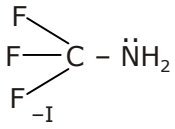
Order : III > IV > I > II

Q.10 

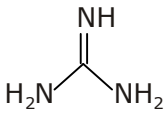
This lone pair very much delocalised because of getting Aromaticity so do not donate lone pair so it is least basic.

Q.11 (a) CH_3NH_2 or CF_3NH_2





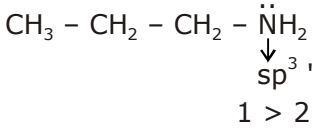
have more tendensity to donate the pair of e^-.

(b) CH_3CONH_2 or 

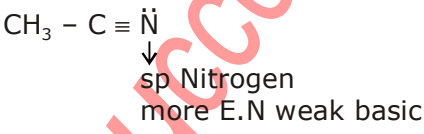
In aquous solution 2° are more basic because of solvation energy.

2 > 1

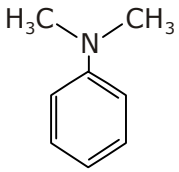
(c) n-Pr NH_2 or CH_3CN

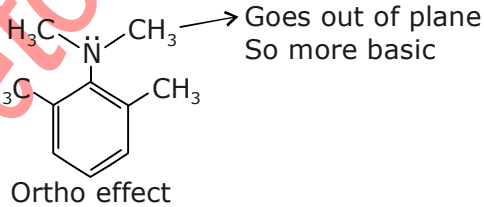


1 > 2



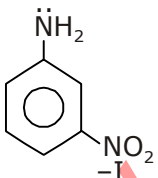
(d) $C_6H_5N(CH_3)_2$ or 2,6-di methyl-N, N-dimethyl aniline.

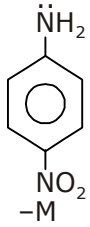




Ortho effect
So 2 > 1

(e) m-Nitro aniline or p-nitro aniline

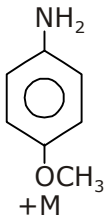




So more basic 1 > 2

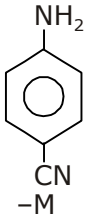
Q.12

(a) p-methoxy aniline or p-cyano aniline



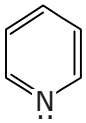
+M

So more basic 1 > 2

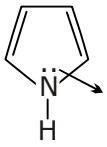


−M

(b) Puridine or Pyrrole



Localised lone pair



Delocalised lone pair so least basic.

(c) $CH_3C \equiv N$ or $CH_3CH_2\ddot{N}H_2$

↓ ↓

sp nitrogen so less basic sp^3 Nitrogen 2 > 1

Q.13 (a) $H_2\ddot{O}$ or H_3O^+

(2) +ve charged spcie is weak base.

(b) H_2S, $-SH$, S^{2-}

(1) Neutral so weak base More −ve charge more donating tendency.

(c) Cl^-, ^-SH

(1) $S \longrightarrow Cl$ E.N. ↑ size small

More sable

less basic

(d) F^- OH^- NH_2^- CH_3^-

CH_3^- NH_2^- OH^- F^-

Size ↓

(1) F^- So more stable less basic

(e) $H\ddot{\underset{\cdot\cdot}{F}}:$, $H_2\ddot{O}$, $\ddot{N}H_3$

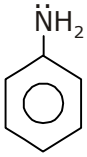
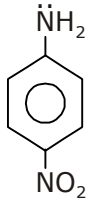
'F' more electronegative so do not donate the pair of e^- so less basic.

(f) $\bar{O}H$ $\bar{S}H$ $Se\bar{H}$

Big size

−ve charge stable, So weak base.

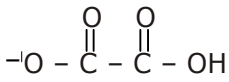
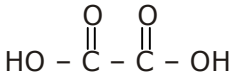
$$\text{Basicity} \propto \frac{1}{\text{Stability}}$$

Q.14 (a)  or 

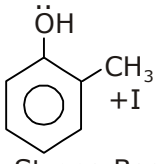
–M so more tendency to donate the pair of e^- of NH_2 in the ring. So weak base

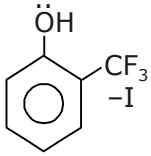
(b) $CH_2 = CH - CH = CH - \bar{C}H_2$ or $CH_2 = CH - CH_2^-$

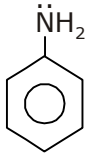
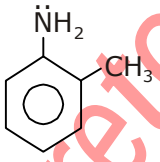
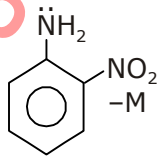
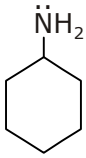
long resonance
So –ve charge delocalised
So weak base

(c)  or 

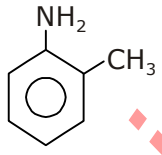
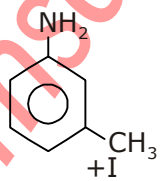
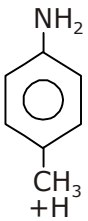
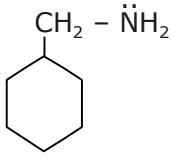
Anions are more Basic than Neutral.
So (2) is a weak base.


Strong Base

or 
Weak Base

Q.15(a) (i)  (ii) 
Ortho effect
(iii)  (iv) 
Localised l.p. of N

3 < 2 < 1 < 4

(b) (i) 
Ortho effect
(ii) 
(iii) 
(iv) 

1 < 2 < 3 < 4

Q.16(a) (i) $\bar{O}H$ (ii) $CH_3\bar{C}OO$ (iii) $\bar{Cl}$

Stability – $\bar{Cl} > CH_3\bar{C}OO > \bar{O}H$

Basicity order : $\underset{1}{\bar{O}H} > \underset{2}{CH_3\bar{C}OO} > \underset{3}{\bar{Cl}}$

(b) (i) $CH \equiv C^-$ (ii) $CH_2 = CH^-$ (iii) $CH_3CH_2^-$

Stability = (i) > (ii) > (iii)

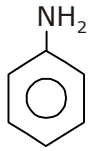
Basicity = (i) < (ii) < (iii)

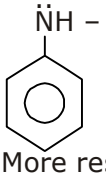
(c) (i) $\overset{sp^2}{CH_2} = CH - CH_2 - \ddot{N}H_2$

(ii) $\overset{sp^3}{CH_3} - CH_2 - CH_2 - \ddot{N}H_2$

(iii) $\underset{sp}{CH \equiv C} - CH_2 - \ddot{N}H_2$

Basic strength : 3 < 1 < 2

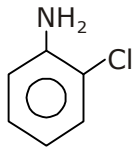
Q.17(a) (i) 

(ii) 

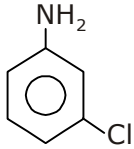
More resonance
More delocalised
so least basic

(iii) 

(ii) < (i) < (iii)

(b) (i) 

Ortho effect

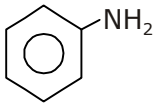
(ii) 

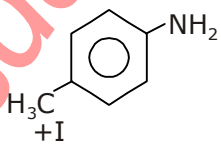
More –I

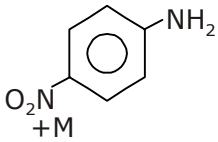
(iii) 

Less –I

1 < 2 < 3

(c) 

(ii) 

(iii) 

2 > 1 > 3

Q.18 (a) CH_3NH_2 (Neutral), $CH_3{}^+NH_3$ (+ve charged), CH_3NH^- (–ve charged)

2 < 1 < 3

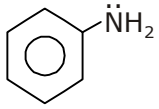
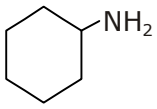
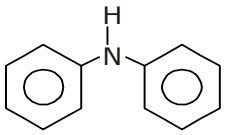
(b) CH_3O^-, CH_3NH^-, $CH_3CH_2^-$

More E.N. more stable 1 < 2 < 3

(c) $\underset{\downarrow}{CH_3CH} = \underset{sp^2}{\bar{C}H}$, $CH_3\underset{\downarrow}{CH_2}\underset{sp^3}{\bar{C}H_2}$, $CH_3 - \underset{\downarrow}{C} \equiv \underset{sp}{\bar{C}}$

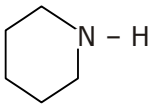
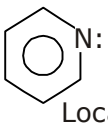
Stability = 3 > 1 > 2

Basicity order = 3 < 1 < 2

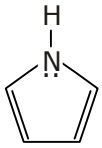
Q.19 (a)   

More resonance
least basic

2 > 1 > 3

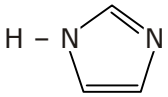
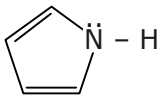
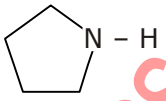
(b)  

Localised l.p.

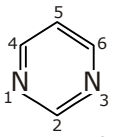


l.p. Delocalised

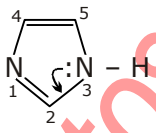
1 > 2 > 3

(c)   

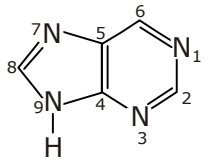
Participate in
resonance so
least basic

Q.20 

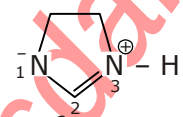
Pyrimidine
Localised lone pair
of N, $6\pi e^-$,aromatic



Imidazole
Protonation takes
place on N–1



Purine
Three basic 'N'
N1, N3, N7



$6\pi e^-$
aromatic

So (A), (C) & (D) are aromatic.