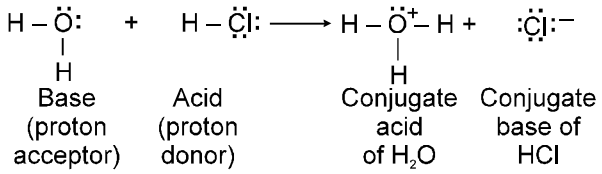
ACIDIC STRENGTH & BASIC STRENGTH

Acidic strength : It can be explained by Bronsted -Lowry of Lewis concept.

(1) The Bronsted - Lowry concept of Acids and Bases

According to it - an acid is a substance that can donate a proton, and a base is a substance that can accept a proton.

Consider, that gaseous hydrogen chloride dissolves in water :

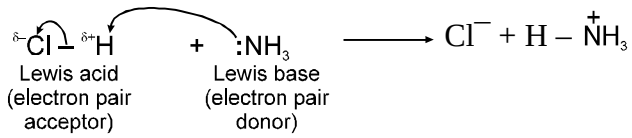


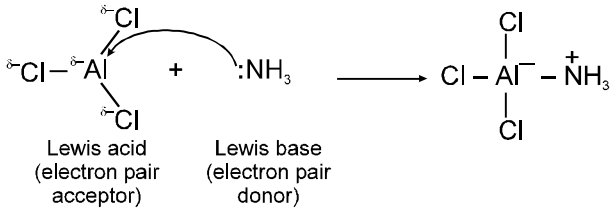
Hydrogen chloride, a very strong acid, transfers its proton to water. Water acts as a base and accepts the proton. The products that result from this reaction are hydronium ion (H_3O^+) and chloride ion (Cl^-).

The molecule or ion that forms when an acid donates its proton is called the **conjugate base** of that acid. (The chloride ion is the conjugate base of HCl). The molecule or ion that is formed when a base accepts a proton is called the **conjugate acid** of that base.

(2) The Lewis concept of Acids and Bases

Lewis proposed that acids are electron pair acceptors and bases are electron pair donors. For example aluminium chloride, reacts with ammonia in the same way that a proton donor does. Using curved arrows to show the donation of the electron pair of ammonia (the Lewis base), it can be given as :





(I) Relative acidic strength of hydrocarbons

Being most electronegative the sp hybridised carbon atom of ethyne or terminal alkyne polarizes its C – H bond to the greatest extent causing its H to be most positive therefore ethyne is most acidic. Hence acidic strength order is

$HC \equiv CH > H_2C = CH_2 > H_3C - CH_3$

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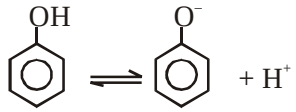
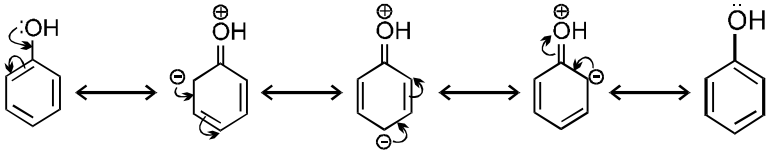
(II) Acidic Strength of Phenols :

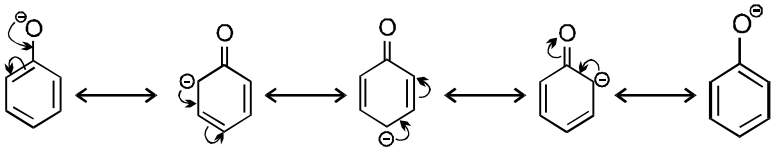
When phenol ionises, the phenoxide ion is more stabilised by resonance than the unionised phenol.



Resonating structrures of phenol are :

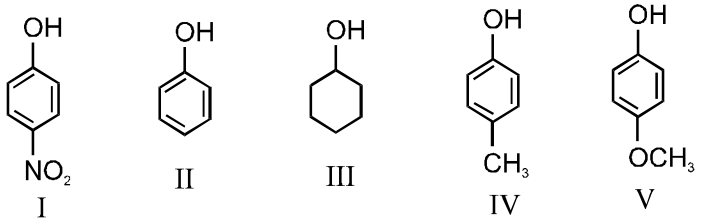


Resonating structures of phenoxide ion are :



Groups which are – I, – M increases acidic character of phenol by effectively dispersing negative charge of phenoxide ion. However +I, and + M groups decreases acidic strength.

Example :

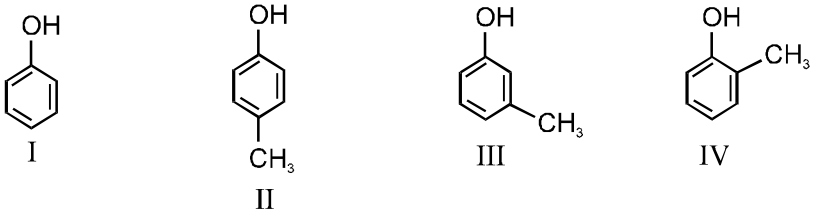


I II III IV (Cresol) V

Acid strength order : I > II > IV > V > III ($-NO_2$ show –M & –I while $-OCH_3$ show –I and +M)

So nitrophenol will be most acidic followed by phenol. Amongst cresol and methoxyphenol, methoxyphenol has + M effect of – OCH_3 which increases electron density hence decrease acidic strength

Example



I II III IV

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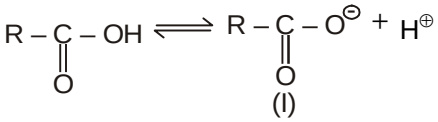
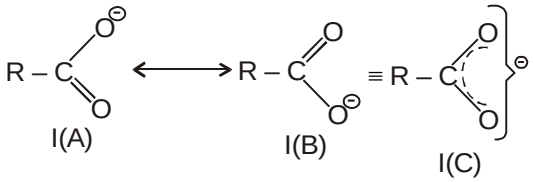
Acid strength order : I > III > II > IV

CH_3 have + I effect so all methylphenols (cresols) are less acidic than phenol (I). Amongst cresols p- and o- CH_3 are increasing the electron density due to their hyper conjugation but ortho isomer has viable + I effect also, which will help in destabilising phenoxide ion therefore o- is least acidic. Since at meta position only + I works it has least electron density amongst the cresols

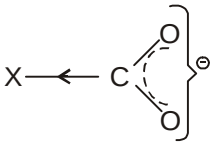
(III) Acidic strength of Carboxylic Acids :



$RCOO^-$ (I) exists as two equivalent cannonical structures I(A) and I(B). This ion is resonance stablised and resonance hybrid structure is I(C), while RCOOH has two non equivalent resonating structures making it less stable.



Electron withdrawing group (–I effect) stablises the anion and hence, increases acidic nature.



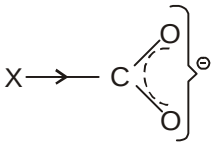
Ex. 1 $F - CH_2 - COOH > Cl - CH_2COOH > Br - CH_2COOH > I - CH_2COOH$

Increasing acid strength

Ex. 2 $Cl - \underset{\underset{Cl}{|}}{\overset{\overset{Cl}{|}}{C}} - COOH > Cl - \underset{|}{\overset{Cl}{C}}H - COOH > Cl - CH_2COOH > CH_3COOH$

Increasing acid strength

Electron releasing group (+ I effect) destabilises the anion and hence decreases acidic nature.



Ex. 3 $HCOOH > CH_3COOH > CH_3 - CH_2 - COOH$

Ex. 4 $\begin{matrix}COOH\\|\\COOH\end{matrix} > CH_2\begin{matrix}\diagup COOH\\\diagdown COOH\end{matrix} > \begin{matrix}CH_2 - COOH\\|\\CH_2 - COOH\end{matrix}$

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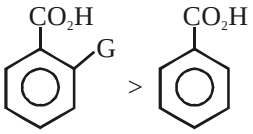
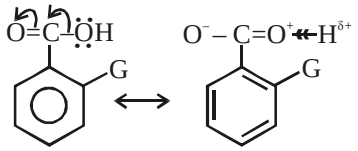
Ortho effect :

Ortho derivative of benzoic acid is generally more acidic than benzoic acid itself. It is called ortho effect

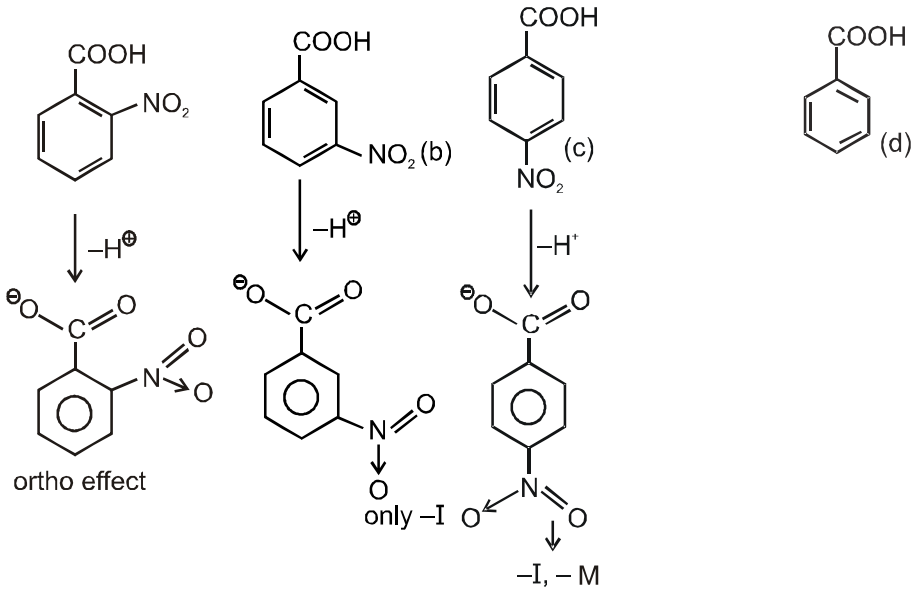


Explanation :

At ortho position when group G is attached, there will be steric repulsion between group G and $-CO_2H$ group, due to which $-CO_2H$ group is partially out of plane. So resonance of phenyl group w.r.t. $-\overset{\overset{O}{\|}}{C}-$ decreases and resonance of –OH group w.r.t. $-\overset{\overset{O}{\|}}{C}-$ increases, +ve charge on oxygen atom increases, –I effect increases, acidity increases.

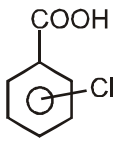


Example : If substitutent is –I and –M ($-NO_2$)



K_a order = ortho > para > meta > benzoic acid

Example : If substitutent is (–I > +M) – Cl, Br, F, I



K_a order = ortho > meta > para > benzoic acid

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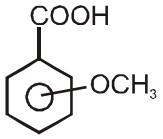
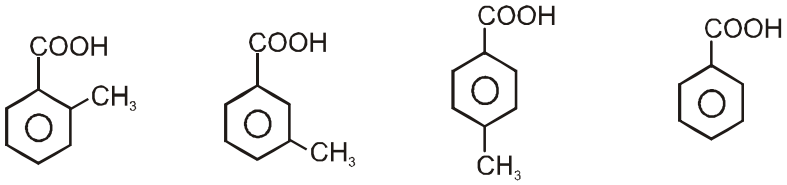
Example : If substitutent is (+M > –I) $-OCH_3$



K_a order = meta ≈ ortho > benzoic acid > para

Example : If substitutent is (+I, +H) – R (Alkyl group)



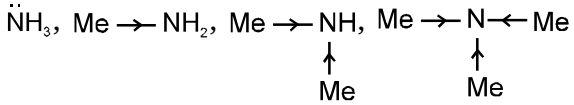
K_a order = ortho > benzoic acid > meta > para

BASIC STRENGTH

(I) Aliphatic Amines

Ease of protonation is the basic nature. Increasing strength of nitrogenous bases is related to readiness with which they are prepared to take up protons.

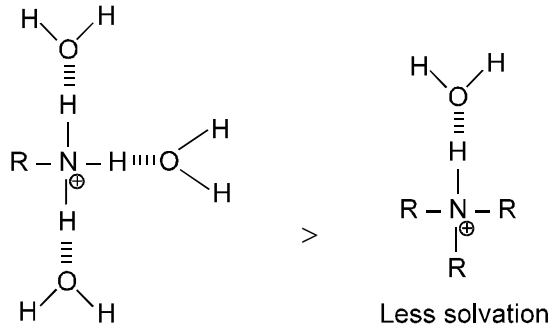
Consider the following molecules



By considering + I effect of methyl in above example we may expect basic nature as

$NH_3 < MeNH_2 < Me_2NH < Me_3N$ **(Which is not true always)**

This is due to the fact that basic strength of an amine in water is determined not only by ease of electron donation (protonation) of N atom but also by the extent to which cation so formed can undergo **SOLVATION** and become stabilised by H atom attached to N atom. Greater is possibility of solvation via H bonding by water. Alkyl groups are hydrophobic and inhibits H bonding hence solvation.



More solvation

Less solvation

Thus, due to two opposite effects i.e. solvation of cation and + I effect, the jumbled order comes to be

$Me_2NH > Me – NH_2 > Me_3N > NH_3$

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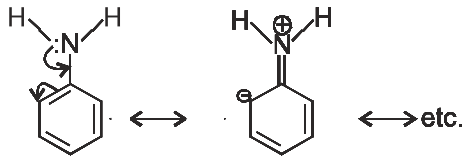
It is also interesting to note that in gas phase basicity order of amines follows the usual order of $Me_3N > Me_2NH > MeNH_2 > NH_3$ (Since only + I effect works and no solvation effect persists). Similarly on the same reasons ethyl amines and other amine follows the following order for basic strength:

$Et_3N > Et_2NH > EtNH_2 > NH_3$ (gas phase)

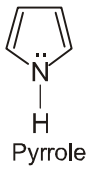
$Et_2NH > Et_3N > EtNH_2 > NH_3$ (water as solvent)

(II) Aromatic amines (Ph – $\ddot{N}H_2$) or Anilines :



When the lone pair lies in conjugation with a multiple bond, system can get resonance stabilisation. Aniline is a weaker base than NH_3 because it has delocalised lone pair.

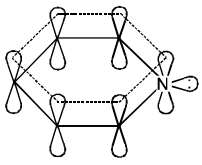
Example :



Pyrrole

Pyridine

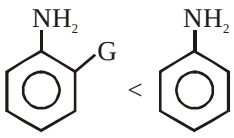
In pyrrole lone pairs are involved in resonance therefore it is less basic. But in pyridine lone pairs are in perpendicular plane of π orbitals therefore not involved in resonance



Pyridine

Ortho effect

Ortho derivative of aniline is generally less basic than aniline itself. It is called ortho effect



druring protonation N change its hybridisation from sp^2 to sp^3. Steric crowding around N increases. If G is occupied at ortho position then steric crowding further increases, stability of protonated product decreases, basicity decreases.

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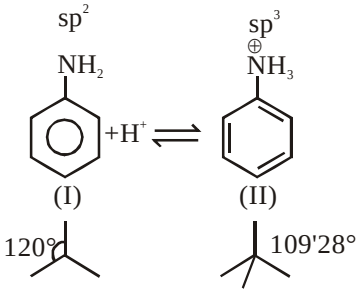
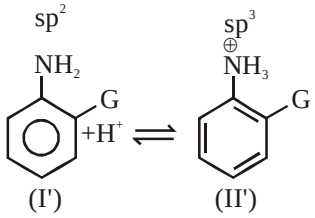


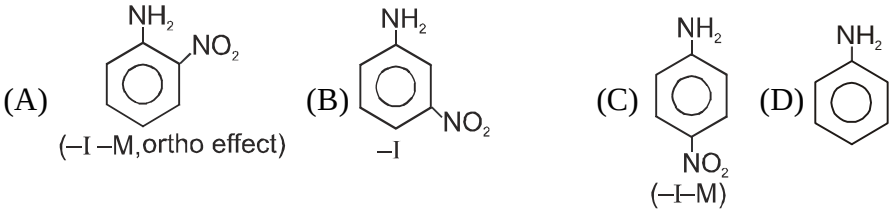
change of hybridisation causes steric repulsion.



steric crowding further increases, stability of II' further decreases basicity order to I' < I

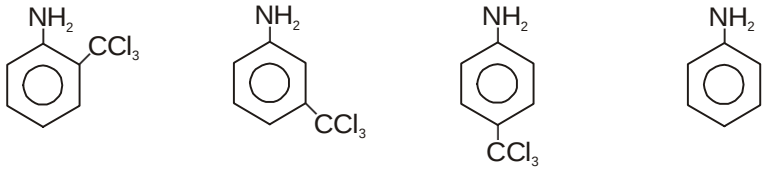
Example : Arrange the following in their basic strength

(i) G = (–M, –I); NO_2



Solution : (Aniline > m > p > o).

(ii) G = (–I); CCl_3



Solution : (Aniline > m > p > o).

Basic Strength

* Acid amides are weaker bases

* Ability to donate e^-

* Check stability of conjugate acid

1.

$$\begin{array}{cccc} I^- & Cl^- & Br^- & F^- \\ \downarrow & \downarrow & \downarrow & \downarrow \\ HI & HCl & HBr & HF \end{array}$$

IV > III > II > I as the acidic character decreases from 1→IV, the basic character ↑

2.

$$\begin{array}{cccc} {}^-CH_3 & {}^-NH_2 & {}^-OH & {}^-F \\ \downarrow & \downarrow & \downarrow & \downarrow \\ CH_4 & NH_3 & H_2O & HF \end{array}$$

I > II > III > IV → as E.N. ↑ , –ve charge becomes more stable and basic ↓

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3. $RO^- > RS^-$

$\downarrow \quad \downarrow$

ROH RSH

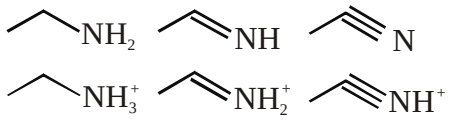
I > II as smaller the size, more will be the charge density.

4. $R_3N \quad R_3P$

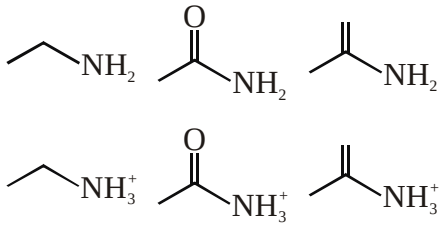
$\downarrow \quad \downarrow$

$^+NR_3H \quad ^+PR_3H$

I > II , smaller the size, better the overlapping

5. 

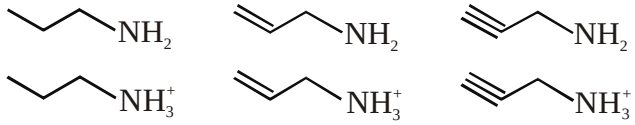
I > II > III as s character ↑, acidity ↑

6. 

I > III > II, I - Localized

II - Dispersed on O $\Rightarrow$ highly delocalize

III - Dispersed on C $\Rightarrow$ moderately localize

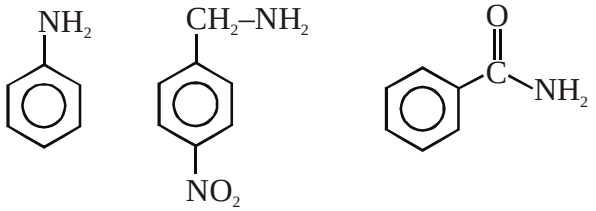
7. 

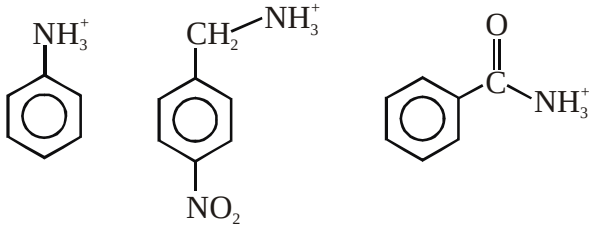
I > II > III as I effect decreases from sp^3 C $\rightarrow$ sp C.

8. $HC \equiv C^- \quad CH_2 = CH^- CH_3 - CH_2^-$

$HC \equiv CH \quad CH_2 = CH_2 CH_3 - CH_3$

III > II > I as decreases from 1 $\rightarrow$ III.

9. 



II > I > III

II - Localized L.P.

I - e^- dispersed on C

III - e^- dispersed on O

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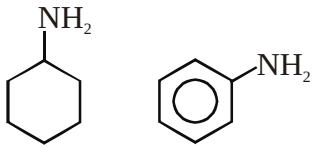
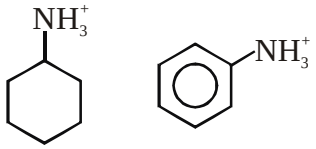
10. 

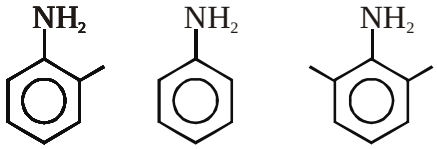


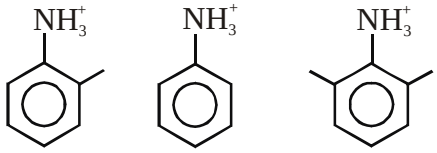
I > II due to localized L.P.

11. Ph_3N Ph_2NH $Ph–NH_2$

Ph_3NH^+ $Ph_2NH_2^+$ $Ph–NH_3^+$ III > II > I delocalized of e^- decreases from

$I \rightarrow III$

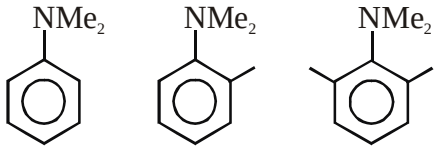
12. 

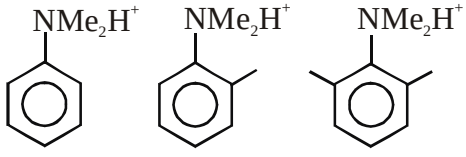


low SE

III < I < II

high SE

13. 



2 ortho substituted

III < I < II

delocalized one ortho substituted

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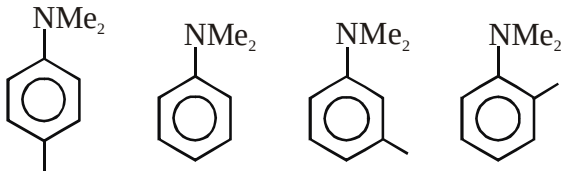
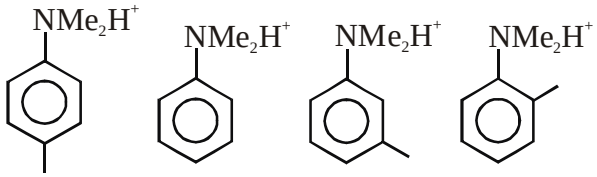
14.





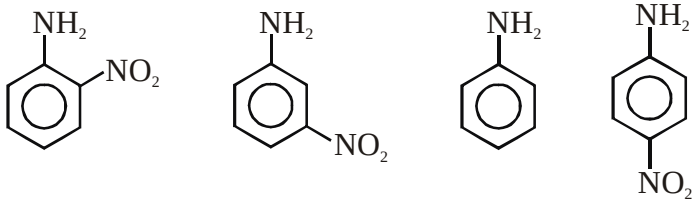
IV > I > III > II

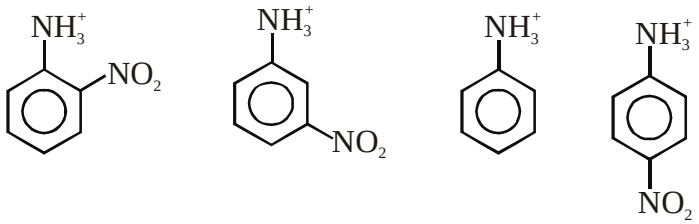
↓ ↘ ↘

localized +H +I

L.P.

15.



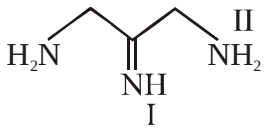


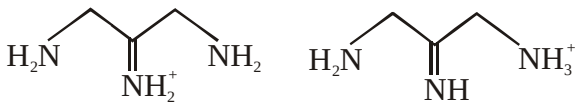
III > II > IV > I

↓ ↓ ↓

–I –R SE

16.





II > I , sp^2N is acidic than sp^3 N

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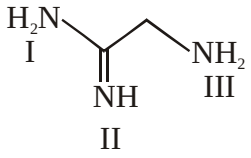
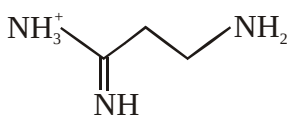
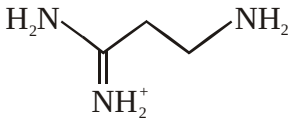
17. 

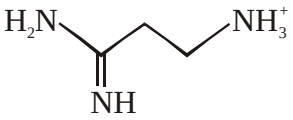
II



III

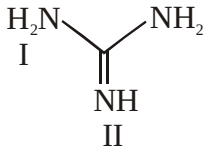


I



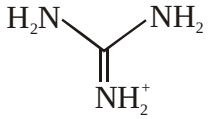
II

(delocalized) (identical R.S.) (localized) II > III > I

18. 

II

(Guanidine) → most basic



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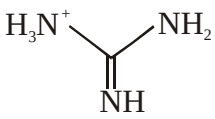
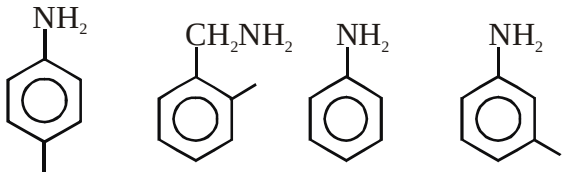
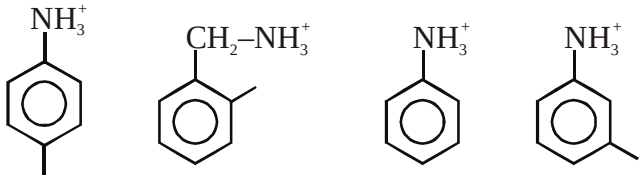


II > I due to 3 identical R.S.

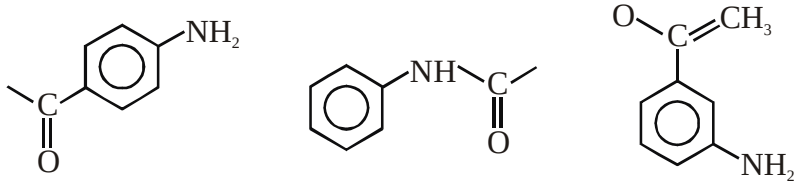
19. 

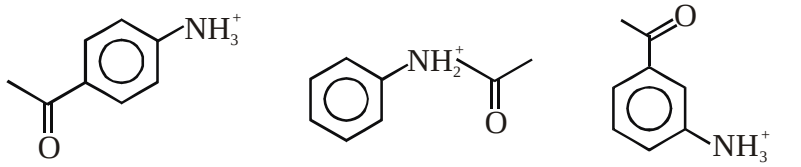


II I IV III

(Stabilizing + H) (Localized L.P) (Stabilized by +I)

So, II > I > IV > III

20. 



III > I > II

–I –R e^- displace on O

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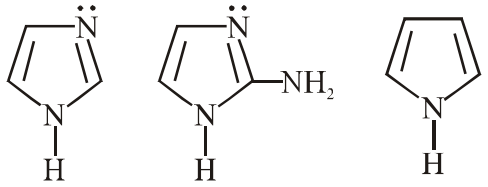
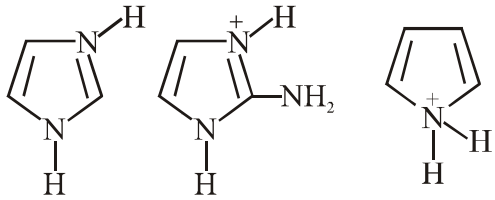
21.

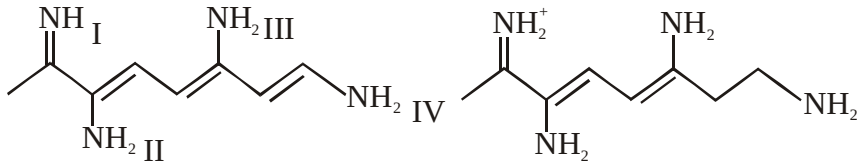


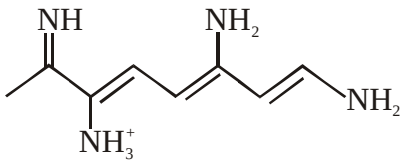


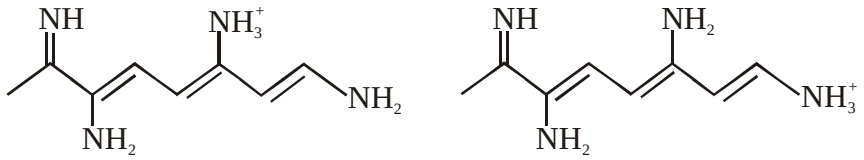
II > I > III

(Moderate R.S.) (Max R.S.) (Delocalization by Resonance)

22.







Localized L.P. ⟵ I > II > III > IV ⟶ sp^2 N

stability as e^- approxy on N

Longest dispersal of L.P.

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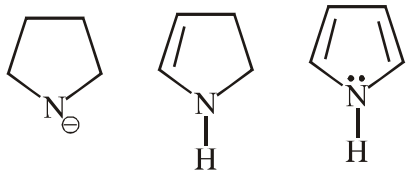
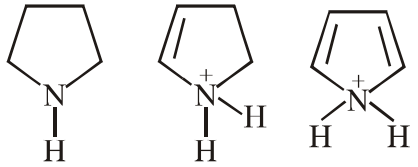
23. 

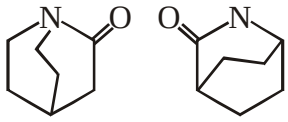


long
resonance
↑
Localized ⟵ I > II > III ⟶ Longestresonance of l.p.

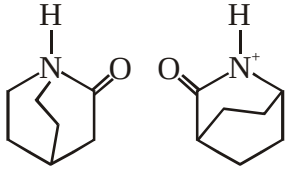
24. NaOH $NaHCO_3$

I > II

as NaOH > $NaHCO_3$
↓
–ve charge is dispersed on O

25. 

I > II as l.p. is localized by bredt's rule


I > II as l.p. is localized by bredt's rule.

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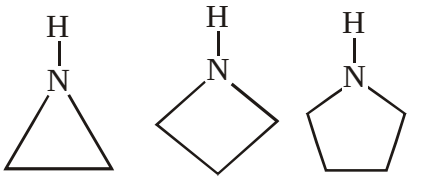
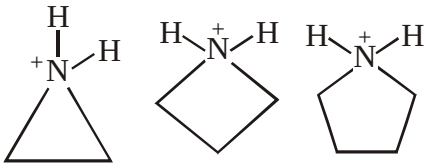
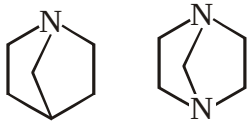
26.

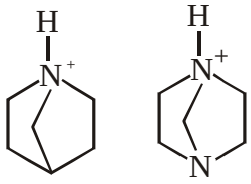




III > II > I by more +1 or less strain.

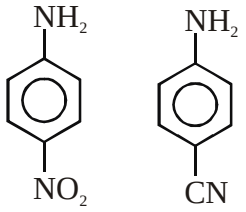
27.

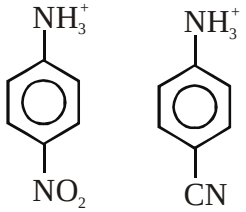




I > II ans N is II attracts the L.P.

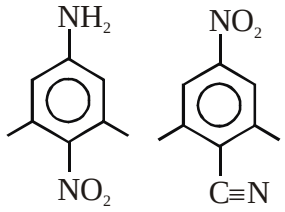
28.



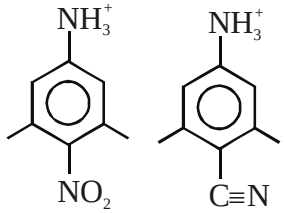


II > I, tendency of resonance in I > II (–R)

29.



I > II, due to SIR, I $\rightarrow$ –I II $\rightarrow$ –R



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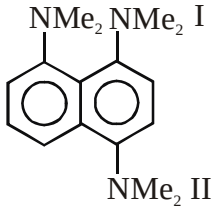
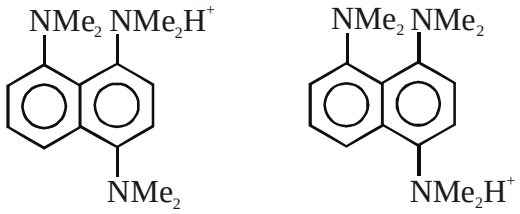
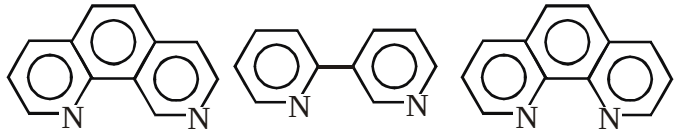
30.





I > II as after accepting H^+ it forms a strong chelate

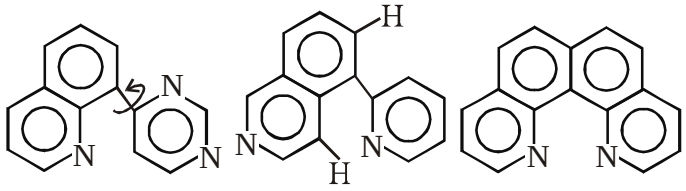
31.



III > II > I

I (more e^- density attracts H^+ more to from chelate)

32.



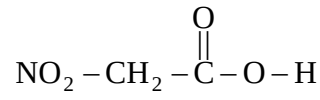
III > I > II

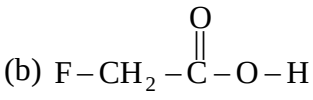
V. strong chelate

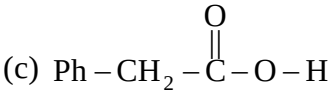
in one position it can form strong chelate with N

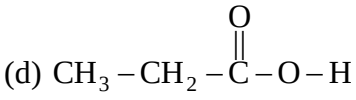
EXERCISE # O-I

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

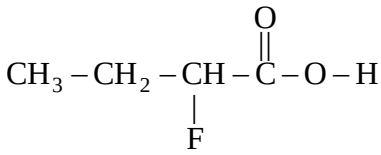
(i) (a) 

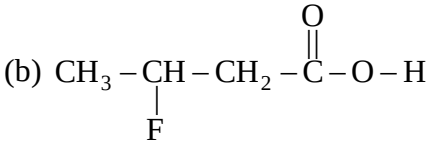
(b) 

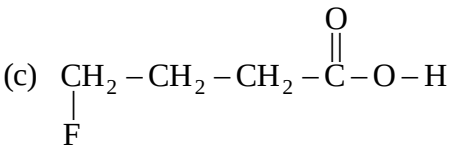
(c) 

(d) 

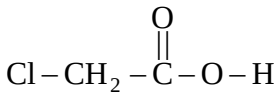
AB0001

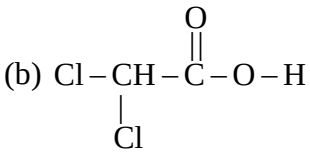
(ii) (a) 

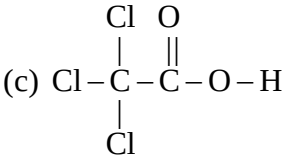
(b) 

(c) 

AB0002

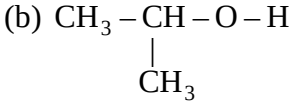
(iii) (a) 

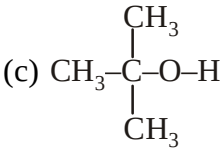
(b) 

(c) 

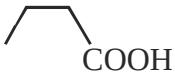
AB0003

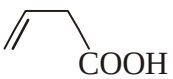
(iv)(a) $CH_3–CH_2–O–H$

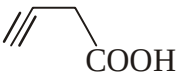
(b) 

(c) 

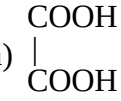
AB0004

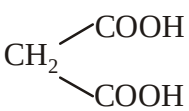
(v) (a) 

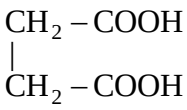
(b) 

(c) 

AB0005

(vi) (a) 

(b) 

(c) 

AB0006

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

AB0007

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

AB0008

(ix)(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) $\overset{\oplus}{N}H_3–CH_2–CH_2–O–H$

AB0009

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

AB0010

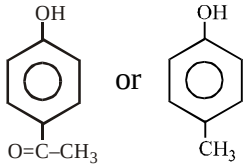
2. Explain which is a stronger acid.

(a) CH_3CH_3 or $BrCH_2NO_2$

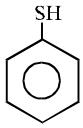
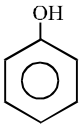
AB0011

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

AB0012

(c)  or

AB0013

(d)  or 

AB0014

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

(a) Benzoic acid or para-nitrobenzoic acid

AB0015

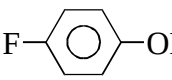
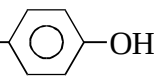
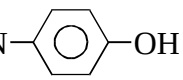
(b) $CH_3–CH_2–CH_2–OH$ or $CH_3–CH = CH – OH$

AB0016

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

AB0017

4. Arrange the given phenol & its derivative 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

AB0018

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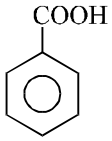
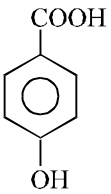
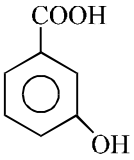
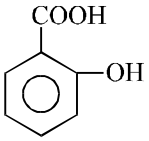
5. Which one of the following is the most acidic?

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

AB0019

6. Which of the following is weakest acid?

(A)  (B)  (C)  (D) 

AB0020

7. 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

AB0021

8. Arrange acidity of given compounds in decreasing order:

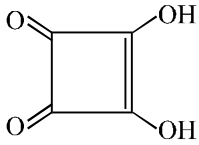
(I) $CH_3-NH-CH_2-CH_2-OH$ (II) $CH_3-NH-CH_2-CH_2-CH_2-OH$

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

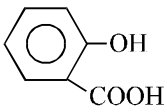
(A) III > I > II (B) III > II > I (C) I > II > III (D) II > I > III

AB0022

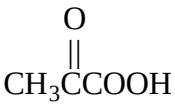
9. Consider the following compound



I



II



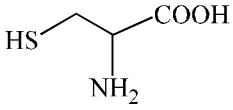
III

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

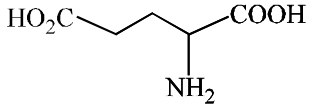
(A) I, II and III (B) I and III (C) II and III (D) I and II

AB0023

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

(i) cysteine :  1.8, 8.3 & 10.8

AB0024

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

AB0025

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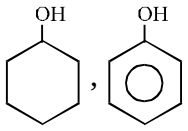
11. Record the following sets of compounds according to increasing pK_a (= – log Ka)

(a)  , cyclohexane carboxylic acid.

AB0026

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

AB0027

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

AB0028

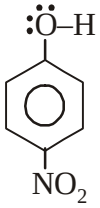
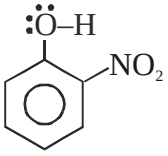
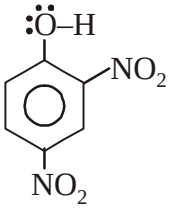
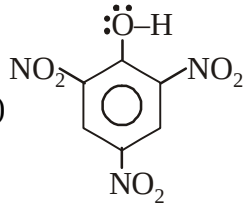
(d) Phenol,o-nitrophenol, o-cresol

AB0029

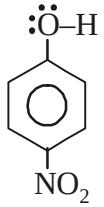
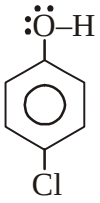
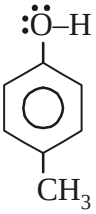
(e) Hexylamine, aniline, methylamine

AB0030

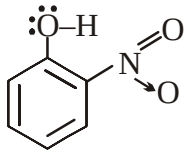
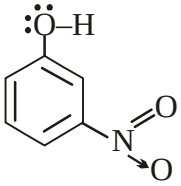
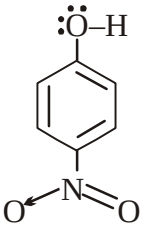
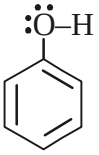
12. Write correct order of acidic strength of following compounds:

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

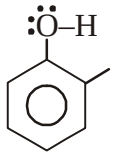
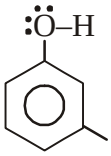
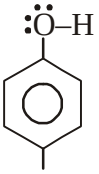
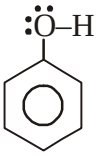
AB0031

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

AB0032

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

AB0033

(iv)(a)  (b)  (c)  (d) 

AB0034

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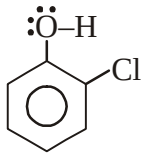
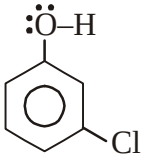
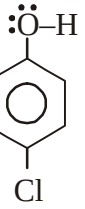
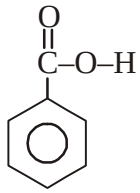
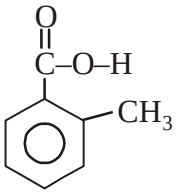
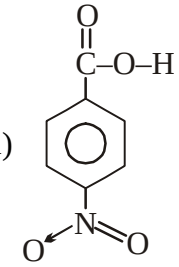
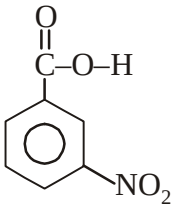
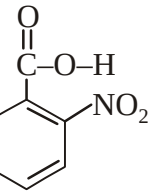
(v) (a)  (b)  (c) 

AB0035

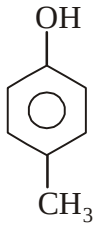
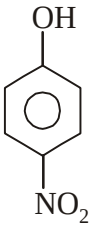
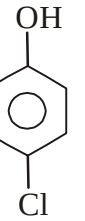
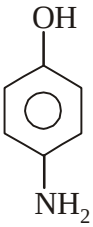
(vi)(a)  (b) 

AB0036

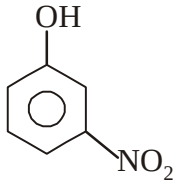
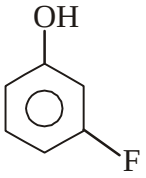
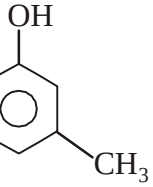
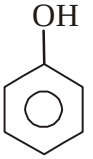
(vii) (a)  (b)  (c) 

AB0037

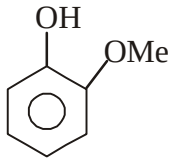
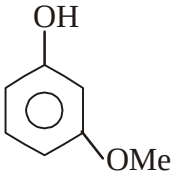
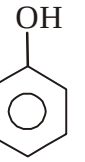
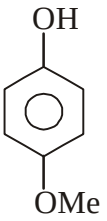
13. Select the strongest acid in each of the following sets :

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

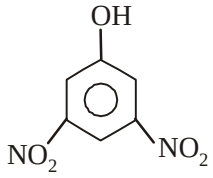
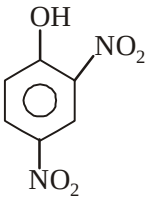
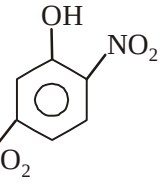
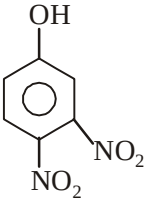
AB0038

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

AB0039

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

AB0040

(iv)(a)  (b)  (c)  (d) 

AB0041

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14. The strongest acid is :

(A)HF (B) CH_3CO_2H (C) HF + SbF_5 (D) H_2S

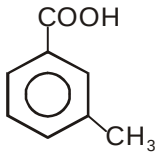
AB0042

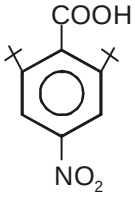
15. The weakest acid (does not show acidic character) is :

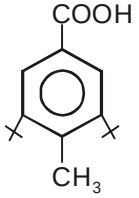
(A)HC ≡ CH (B) $CH_2 = CH_2$ (C) Me_3CH (D) Ph_3CH

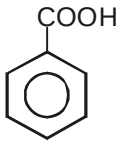
AB0043

16. Which of the following is most acidic :

(A) 

(B) 

(C) 

(D) 

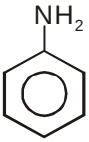
AB0044

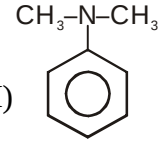
Paragraph for Question 17 to 18

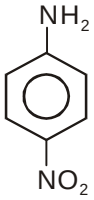
The most important condition for resonance to occur is that the involved atoms in resonating structure must be coplanar or nearly coplanar for maximum delocalisation. If this condition does not fulfil, involved orbitals cannot be parallel to each other and as a consequence delocalisation cannot occcur. Bulky groups present on adjacent atoms inhibit the planarity of atoms involved in resonance. This phenomenon is known as steric inhibition of resonance. Steric inhibition of resonance has profound effect on

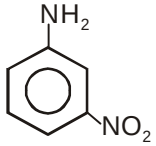
(1) Physical properties (2) Acidity and basicity (3) Reactivity of organic compounds

17. Arrange the following in the decreasing order of basicity :

(I) 

(II) 

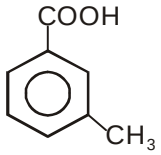
(III) 

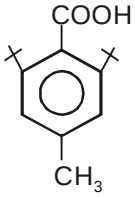
(IV) 

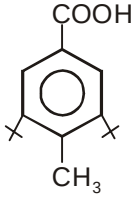
(A) I > II > III > IV (B) IV > III > II > I (C) II > I > IV > III (D) I > IV > III > II

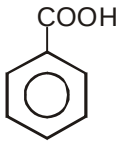
AB0045

18. Which of the following is most acidic :

(A) 

(B) 

(C) 

(D) 

AB0046

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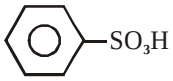
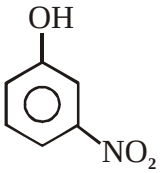
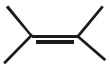
19. How many following compounds are more acidic than water ?

(a)  (b) HCl (c) $CH_3 - C \equiv CH$ (d)

(e)  (f) (g) (h) 

(i) NaOH

AB0047

20. Select correct order regarding acidic strength of given compounds :

(1) o-methylbenzoic acid (2) m-methylbenzoic acid

(3) p-methylbenzoic acid (4) benzoic acid

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

AB0048

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EXERCISE # O-II

1. Write decreasing order of basic strength of following :

(i) (a) CH_3^- (b) NH_2^- (c) OH^- (d) F^-

AB0049

(ii) (a) F^- (b) Cl^- (c) Br^- (d) I^-

AB0050

(iii) (a) NH_3 (b) $MeNH_2$ (c) Me_2NH (d) Me_3N (in H_2O)

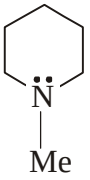
AB0051

(iv) (a) NH_3 (b) $MeNH_2$ (c) Me_2NH (d) Me_3N (Gas phase)

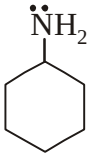
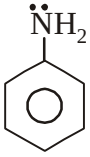
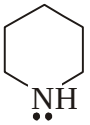
AB0052

(v) (a) $R–NH_2$ (b) $Ph–NH_2$ (c) $R-\overset{\overset{O}{\|}}{C}-NH_2$

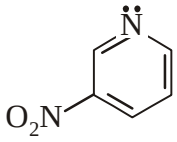
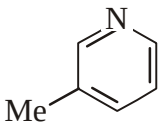
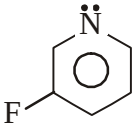
AB0053

(vi) (a) (b) (c) 

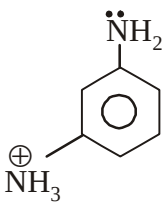
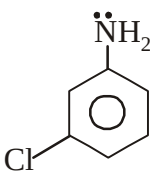
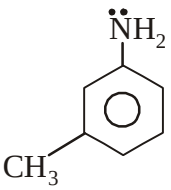
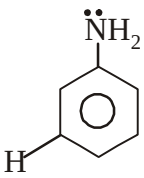
AB0054

(vii)(a)  (b)  (c) 

AB0055

(viii) (a)  (b)  (c) 

AB0056

(ix) (a)  (b)  (c)  (d) 

AB0057

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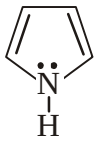
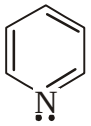
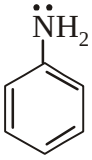
2. Write decreasing order of basic strength of following :

(i) (a) $CH_3–CH_2–\ddot{N}H_2$ (b) $CH_3–CH=\ddot{N}H$ (c) $CH_3–C\equiv\ddot{N}$

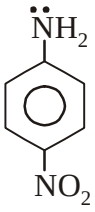
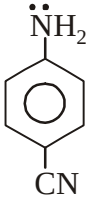
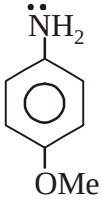
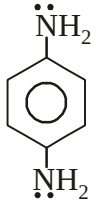
AB0058

(ii) (a) $CH_3-\underset{\underset{O}{\|}}{C}-\ddot{N}H_2$ (b) $CH_3–CH_2–\ddot{N}H_2$ (c) $CH_3-\underset{\underset{\ddot{N}H}{\|}}{C}-\ddot{N}H_2$ (d) $\ddot{N}H_2-\underset{\underset{\ddot{N}H}{\|}}{C}-\ddot{N}H_2$

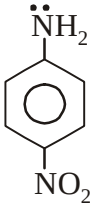
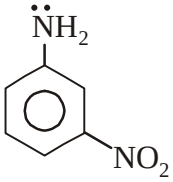
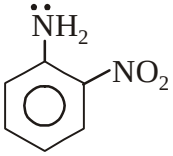
AB0059

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

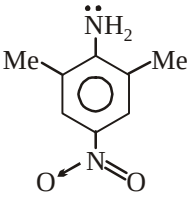
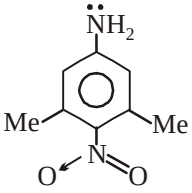
AB0060

(iv) (a)  (b)  (c)  (d) 

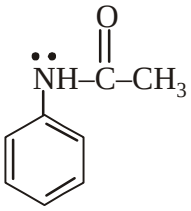
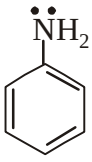
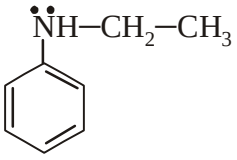
AB0061

(v) (a)  (b)  (c) 

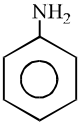
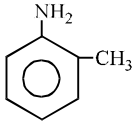
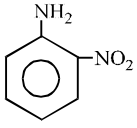
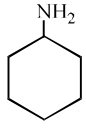
AB0062

(vi) (a)  (b) 

AB0063

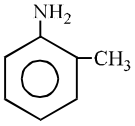
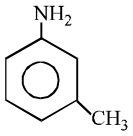
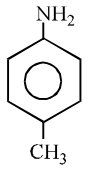
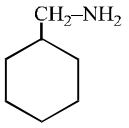
(vii)(a)  (b)  (c) 

AB0064

(viii) (a)  (b)  (c)  (d) 

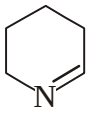
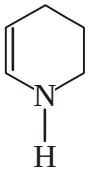
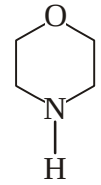
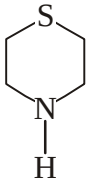
AB0065

node06\B0BO-BA\Kota \JEE(Advanced)\Leader \Che\Sheet \Acidic Strength and Basic Strength \Eng.p65

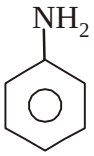
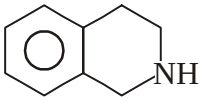
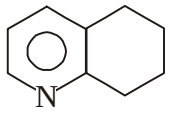
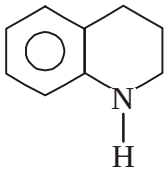
(ix) (a)  (b)  (c)  (d) 

AB0066

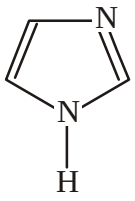
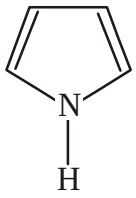
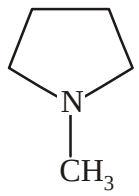
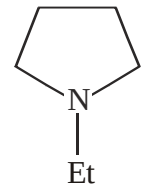
3. Select the strongest base in following compound :

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

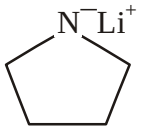
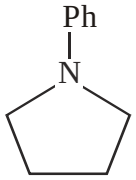
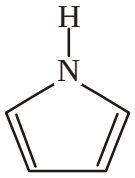
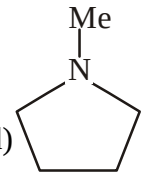
AB0067

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

AB0068

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

AB0069

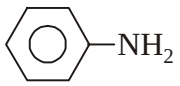
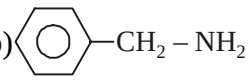
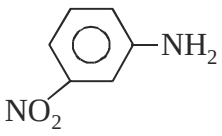
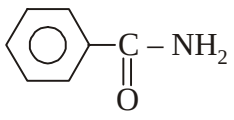
(iv) (a)  (b)  (c)  (d) 

AB0070

4. Arrange the following compound in decreasing order of their basicity.

(i) (a) $H_2C = CHNa$ (b) CH_3CH_2Na (c) CH_3CH_2ONa (d) $HC \equiv CNa$

AB0071

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

AB0072

(iii) (a) HO^- (b) NH_3 (c) H_2O (d) HSO_4^-

AB0073

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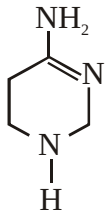
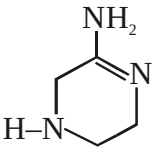
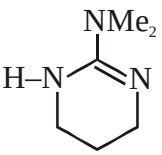
5. Correct decreasing order of basic strength -


(I)


(II)


(III)

Of following compound -

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

AB0074

6. 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

AB0075

7. Consider the basicity of the following aromatic amines:

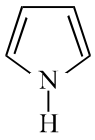
(I) aniline (II) p-nitroaniline (III) p-methoxyaniline (IV) p-methylaniline

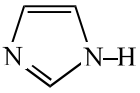
The correct order of decreasing basicity is:

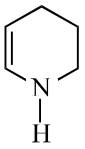
(A) III > IV > I > II (B) III > IV > II > I (C) I > II > III > IV (D) IV > III > II > I

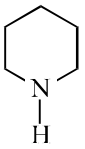
AB0076

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

(A) 

(B) 

(C) 

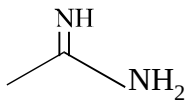
(D) 

AB0077

9. 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

AB0078

(b) CH_3CONH_2 or 

AB0078

(c) $CH_3CH_2CH_2NH_2$ or CH_3CN

AB0078

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

AB0078

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10. 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^+

AB0079

(b) Cl^-, SH^-

AB0079

(c) F^-, OH^-, NH_2^-, CH_3^-

AB0079

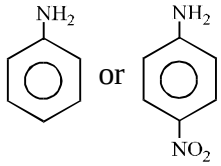
(d) HF, H_2O, NH_3

AB0079

(e) OH^-, SH^-, SeH^-

AB0079

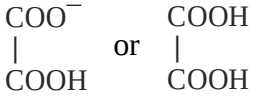
11. Explain which compound is the weaker base.

(a)  or

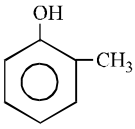
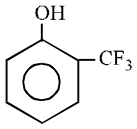
AB0080

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

AB0080

(c)  or

AB0080

(d)  or 

AB0080

12. Arrange the basic strength of the following compounds.

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

(i) (ii) (iii)

AB0081

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

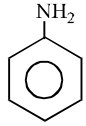
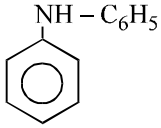
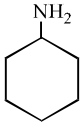
(i) (ii) (iii)

AB0082

(c) $CH_2 = CHCH_2NH_2$ $CH_3CH_2CH_2NH_2$ $CH \equiv C - CH_2NH_2$

(i) (ii) (iii)

AB0083

(d)   

(i) (ii) (iii)

AB0084

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13. Arrange the following compounds in order of increasing basicity.

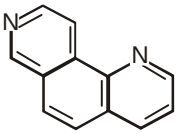
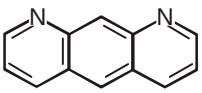
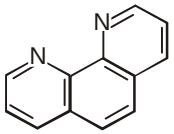
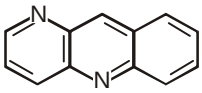
(a) CH_3NH_2, $CH_3NH_3^{\oplus}$, CH_3NH^{-}

AB0085

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

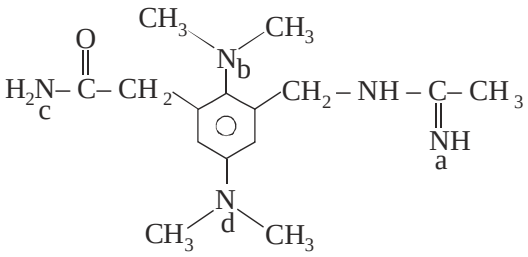
AB0085

14. Which of the following is most basic :

(A)  (B)  (C)  (D) 

AB0086

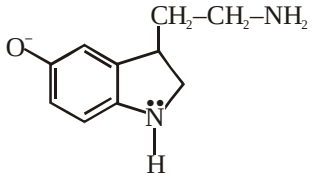
15. Basicity order of N in following compound is :



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

AB0087

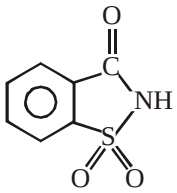
16. The conjugate base of serotonin (used as tranquilisers) is given as follows :



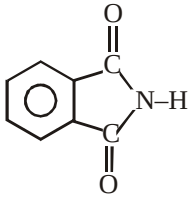
How many basic groups present in following compound ?

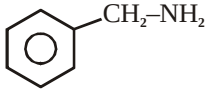
AB0088

17. The structure of saccharin is given as follows :

 [Provided N is the donor atom in all cases]

How many following compounds are more basic than saccharin ?

(i) $CH_3-\underset{\underset{NH}{\|}}{C}-NH_2$ (ii) $H_2N-\underset{\underset{NH}{\|}}{C}-NH_2$ (iii) $CH_3-\underset{\underset{O}{\|}}{C}-NH_2$ (iv) 

(v)  (vi)

AB0089

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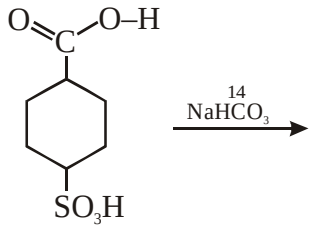
EXERCISE # S-I

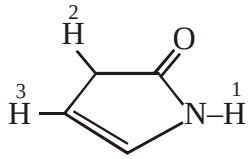
1. In given reaction Gas liberated is/are



(A) CO_2 & SO_3 (B) SO_3 & $^{14}CO_2$ (C) $^{14}CO_2$ only (D) SO_2 only

AB0090

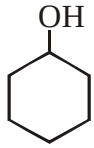
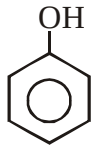
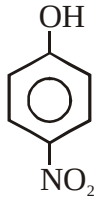
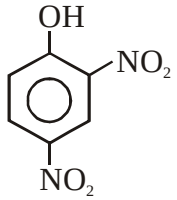
2. Arrange marked atom in decreasing order of acidic strength



(A) 1 > 2 > 3 (B) 3 > 2 > 1 (C) 2 > 1 > 3 (D) 2 > 3 > 1

AB0091

3.

Column - I	**Column-I**
(A) 	(P) React with NaOH
(B) 	(Q) React with $NaHCO_3$
(C) 	(R) React with NaH
(D) 	(S) React with Na
	(T) React with $NaNH_2$

AB0092

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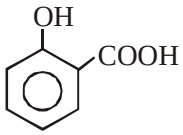
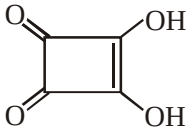
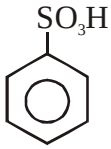
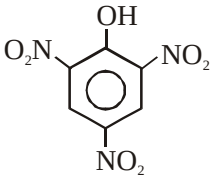
4. Compound which can give effevescences with $NaHCO_3$

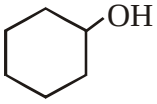
(i)  (Salicylic acid)

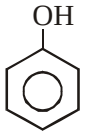
(ii)  (Squaric acid)

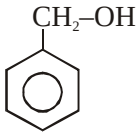
(iii)  (Benzene sulphonic acid)

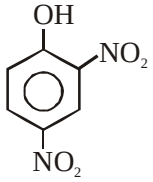
(iv)  (Picric acid)

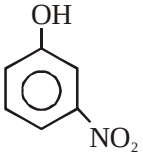
(v) Ph–CH=CH–COOH (cinnamic acid)

(vi) 

(vii) 

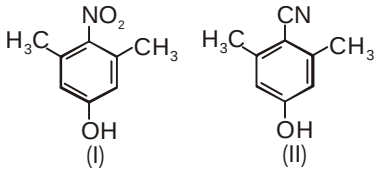
(viii) 

(ix) 

(x) 

AB0093

5. **Statement-1 :** For the given two compounds-I is more acidic than compounds-II.



(I) (II)

and

Statement-2 : Due to presence of $-CH_3$ group at ortho positions to $-NO_2$; the plane of $-NO_2$ deviates, w.r.t plane of ring.

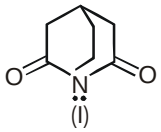
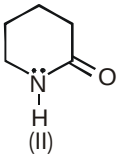
(A) Statement-1 is True, Statement-2 is True ; Statement-2 is a correct explanation for Statement-1.

(B) Statement-1 is True, Statement-2 is True ; Statement-2 is NOT a correct explanation for Statement-1.

(C) Statement-1 is True, Statement-2 is False.

(D) Statement-1 is False, Statement-2 is True.

AB0094

6. **Statement 1** :  (I) is more basic than  (II)

and

Statement 2 : Lone pair electrons on nitrogen in compound (I) does not participate in resonance.

(A) Statement-1 is True, Statement-2 is True ; Statement-2 is a correct explanation for Statement-1.

(B) Statement-1 is True, Statement-2 is True ; Statement-2 is NOT a correct explanation for Statement-1.

(C) Statement-1 is True, Statement-2 is False.

(D) Statement-1 is False, Statement-2 is True.

AB0095

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7. Match Column-I with Column-II.

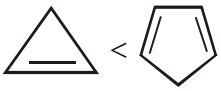
Column - I (Facts)

(A) Guanidine $H_2N-\underset{\underset{NH}{\|}}{C}-NH_2$ is example of strong base

(B) Carbanion stability $\bar{C}Cl_3 > \bar{C}F_3$

(C) Alkyne is more acidic than alkene

(D) Acidity :



Column - II (Reasons)

(P) Resonance stabilisation of conjugate acid of strong base.

(Q) Due to s-character of central atoms

(R) Due to d-orbital resonance

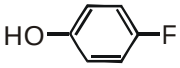
(S) Due to formation of aromatic anion

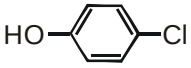
(T) Stability of conjugate base due to more number of identical resonating structure

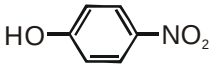
AB0096

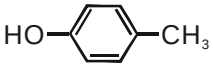
8. Match Column-I with Column-II.

Column - I (Compounds)

(A) 

(B) 

(C) 

(D) 

Column - II (pKa)

(P) 7.15

(Q) 10.14

(R) 9.98

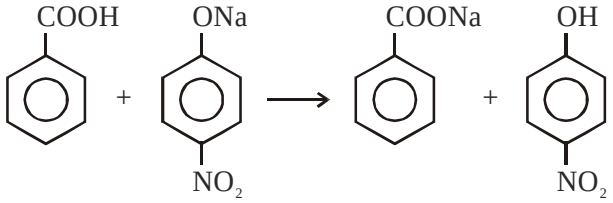
(S) 9.38

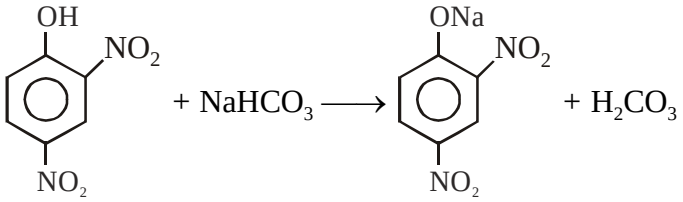
(T) pKa is more than phenol

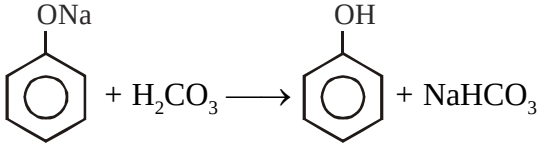
AB0097

(Comprehension) (Q.9 to Q.11)

Observe the following feasible reactions :

(i) 

(ii) 

(iii) 

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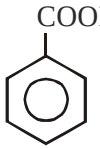
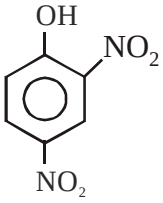
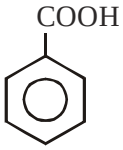
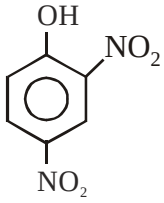
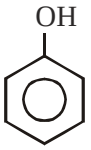
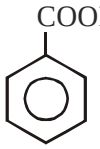
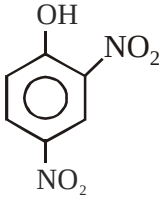
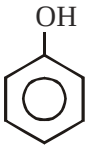
Answer the following question :

9. Which of the following is the correct order of acidic strength.

(A)  >  > H_2CO_3 >

(B)  >  >  > H_2CO_3

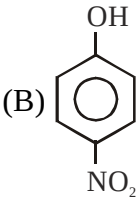
(C)  > H_2CO_3 >  > 

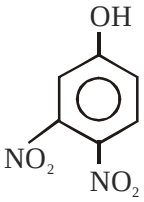
(D) None

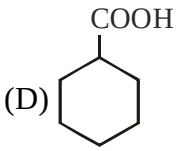
AB0098

10. Which of the following compound does not react with $NaHCO_3$

(A)

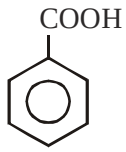
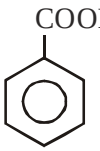
(B) 

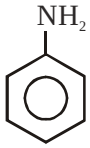
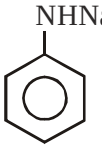
(C) 

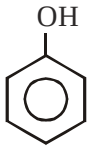
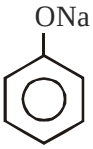
(D) 

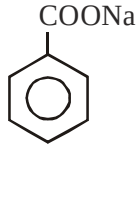
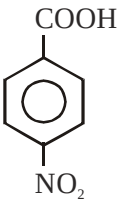
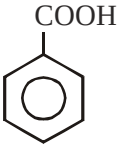
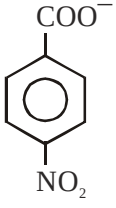
AB0099

11. Identify the feasible reactions

(A)  + $NaHCO_3 \longrightarrow$  + $H_2O + CO_2$

(B)  + $NaHCO_3 \longrightarrow$  + $H_2O + CO_2$

(C)  + $NaHCO_3 \longrightarrow$  + $H_2O + CO_2$

(D)  +  $\longrightarrow$  + 

AB0100

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12. Identify the non-feasible reaction

(A) $CH_3–C \equiv CH + NH_2^- \rightleftharpoons CH_3—C \equiv \overset{\bullet\bullet}{\underset{\bullet\bullet}{C}}^- + NH_3$

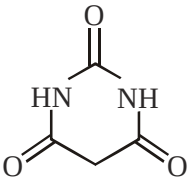
(B) $CH_3CH_2—OH + NaH \rightleftharpoons CH_3CH_2ONa + H_2$

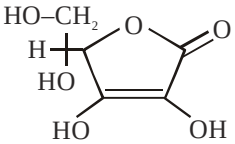
(C) $CH_3—OH + NaOH \rightleftharpoons CH_3ONa + H_2O$

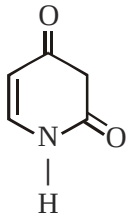
(D) $HC{\equiv}CH + NaOH \rightleftharpoons HC{\equiv}CNa + H_2O$

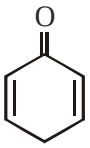
AB0101

13. Select the number of compounds in which deprotonation gives aromatic anion :

(A) 
Barbituric acid

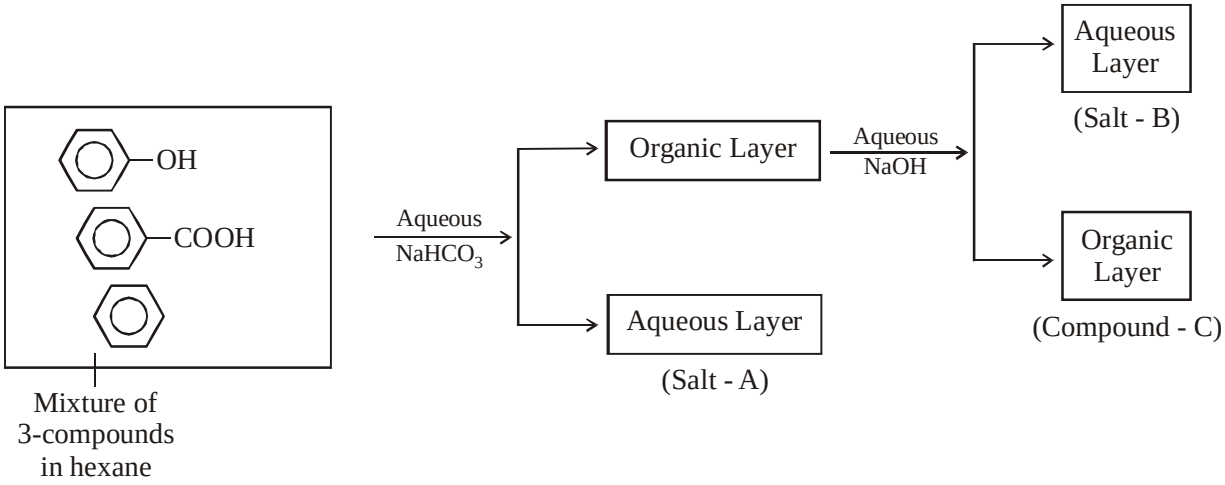
(B) 
Ascorbic acid
(Vitamin-C)

(C) 

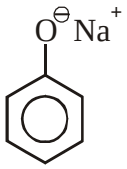
(D) 

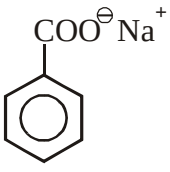
AB0102

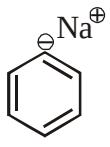
Paragraph for Questions 14 and 15



14. Identify salt 'A' ?

(A) 

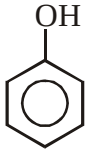
(B) 

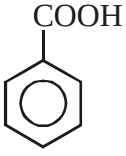
(C) 

(D) All of these

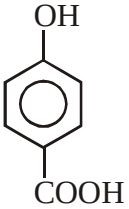
AB0103

15. Identify compound 'C' ?

(A) 

(B) 

(C)

(D) 

AB0103

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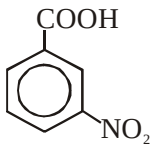
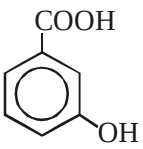
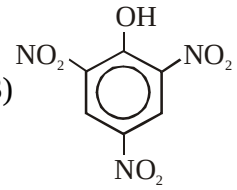
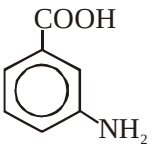
EXERCISE # (JEE-MAIN)

1. Picric acid is - **[AIEEE-2002]**

(1)  (2)  (3)  (4) 

AB0104

2. Which of the following speices acts both as bronsted acid & base – **[AIEEE-2002]**

(1) NH_3 (2) OH^- (3) $HSO_4^{\ominus}$ (4) 1 and 3 both

AB0105

3. The correct order of increasing basic nature for the bases NH_3, CH_2NH_2 and $(CH_3)_2NH$ is- **[AIEEE-2003]**

(1) $CH_3NH_2 < NH_3 < (CH_3)_2NH$ (2) $(CH_3)_2NH < NH_3 < CH_3NH_2$

(3) $NH_3 < CH_3NH_2 < (CH_3)_2NH$ (4) $CH_3NH_2 < (CH_3)_2NH < NH$

AB0106

4. Consider the acidity of the carboxylic acids- **[AIEEE-2004]**

(i) PhCOOH (ii) o–$NO_2C_6H_4COOH$

(iii) p-$NO_2C_6H_4COOH$ (iv) m-$NO_2C_6H_4COOH$

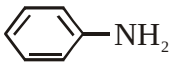
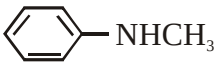
which of the following is the correct order of acidity-

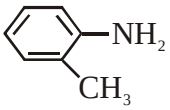
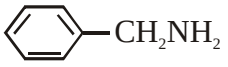
(1) i > ii > iii > iv (2) ii > iv > iii > i

(3) ii > iv > i > iii (4) ii > iii > iv > i

AB0107

5. Which of the following is the strongest base - **[AIEEE-2004]**

(1)  (2) 

(3)  (4) 

AB0108

6. Among the following acids which has the lowest pk_a value- **[AIEEE-2005]**

(1) CH_3CH_2COOH (2) $(CH_3)_2CHCOOH$

(3) HCOOH (4) CH_3COOH

AB0109

7. Amongest the following the most basic compound is- **[AIEEE-2005]**

(1) p-nitro aniline (2) Acetanilide

(3) Aniline (4) Benzylamine

AB0110

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8. What is the conjugate base of OH^-? **[AIEEE-2005]**

(1) H_2O (2) O_2 (3) O^{2-} (4) O^-

AB0111

9. Among the following acids which has the lowest pK_a value? **[AIEEE-2005]**

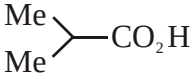
(1) HCOOH (2) CH_3COOH

(3) CH_3CH_2COOH (4) $(CH_3)_2CH–COOH$

AB0112

10. The correct order of increasing acid strength of the compounds is **[AIEEE-2006]**

(a) CH_3CO_2H (b) $MeOCH_2CO_2H$

(c) CF_3CO_2H (d) 

(1) d < a < c < b (2) d < a < b < c

(3) a < d < c < b (4) b < d < a < c

AB0113

11. Which one of the following is the strongest base in aqueous solution ? **[AIEEE-2007]**

(1) Trimethylamine (2) Aniline

(3) Dimethylamine (4) Methylamine

AB0114

12. The correct order of increasing basicity of the given conjugate base (R=CH_3) is :- **[AIEEE-2010]**

(1) $RCO\bar{O} < HC \equiv \bar{C} < \bar{N}H_2 < \bar{R}$ (2) $RCO\bar{O} < HC \equiv \bar{C} < \bar{R} < \bar{N}H_2$

(3) $\bar{R} < HC \equiv \bar{C} < RCO\bar{O} < \bar{N}H_2$ (4) $RCO\bar{O} < \bar{N}H_2 < HC \equiv \bar{C} < \bar{R}$

AB0115

13. The strongest acid amongst the following compounds is ? **[AIEEE-2011]**

(1) $CH_3CH_2CH(Cl)CO_2H$ (2) $ClCH_2CH_2CH_2COOH$

(3) CH_3COOH (4) HCOOH

AB0116

14. The correct order of acid strength of the following compounds :-

A. Phenol B. p-Cresol

C. m-Nitrophenol D. p- Nitrophenol

is :- **[AIEEE-2011]**

(1) C > B > A > D (2) D > C > A > B

(3) B > D > A > C (4) A > B > D > C

AB0117

15. In the following compounds : **[JEE(Main)-2012]**

(I) (II) (III) (IV)

the order of basicity is as follows :

(1) IV > III > II > I (2) II > III > I > IV

(3) I > III > II > IV (4) III > I > II > IV

AB0118

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16. The most basic compound among the following is :- **[JEE(Main)-2012]**

(1) Acetanilide (2) Benzylamine

(3) p-Nitro aniline (4) Aniline

AB0119

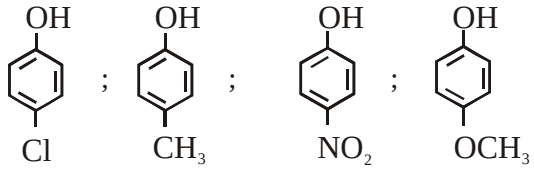
17. The order of basicity of amines in gaseous state is :- **[JEE(Main)-2013]**

(1) $3° > 2° > NH_3 > 1°$ (2) $1° > 2° > 3° > NH_3$

(3) $NH_3 > 1° > 2° > 3°$ (4) $3° > 2° > 1° > NH_3$

AB0120

18. Arrange the following compounds in order of decreasing acidity : **[JEE(Main)-2013]**



(I) (II) (III) (IV)

(1) II > IV > I > III (2) I > II > III > IV

(3) III > I > II > IV (4) IV > III > I > II

AB0121

19. The conjugate base of hydrazoic acid is :- **[JEE(Main)-2014]**

(1) HN_3^- (2) N_3^- (3) N_2^- (4) N^{-3}

AB0122

20. Which one of the following compounds will not be soluble in sodium bicarbonate ? **[JEE(Main)-2014]**

(1) Benzene sulphonic acid (2) Benzoic acid

(3) o-Nitrophenol (4) 2, 4, 6 - Trinitrophenol

AB0123

21. Considering the basic strength of amines in aqueous solution, which one has the smallest pK_b value ? **[JEE(Main)-2014]**

(1) $(CH_3)_3N$ (2) $C_6H_5NH_2$ (3) $(CH_3)_2NH$ (4) CH_3NH_2

AB0124

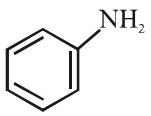
22. Among the following oxoacids, the correct decreasing order of acid strength is : **[JEE(Main)-2014]**

(1) $HClO_4 > HClO_3 > HClO_2 > HOCl$ (2) $HClO_2 > HClO_4 > HClO_3 > HOCl$

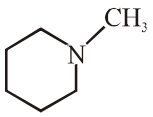
(3) $HOCl > HClO_2 > HClO_3 > HClO_4$ (4) $HClO_4 > HOCl > HClO_2 > HClO_3$

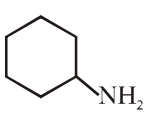
AB0125

23. Among the following compounds, the increasing order of their basic strength is:-

(I) 

(II)

(III) 

(IV) 

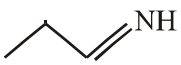
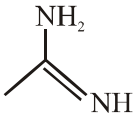
(1) (II) < (I) < (III) < (IV) (2) (I) < (II) < (IV) < (III) **[JEE(Main)-On-Line 2017]**

(3) (II) < (I) < (IV) < (III) (4) (I) < (II) < (III) < (IV)

AB0126

node06\B0BO-BA\Kota \JEE(Advanced)\Leader \Che\Sheet \Acidic Strength and Basic Strength\Eng.p65

24. The increasing order of basicity of the following compounds is : **[JEE(Main)-2018]**

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

(1) (b) < (a) < (c) < (d) (2) (b) < (a) < (d) < (c)

(3) (d) < (b) < (a) < (c) (4) (a) < (b) < (c) < (d)

AB0127

25. The correct decreasing order for acid strength is :- **[JEE(Main)-Jan-2019]**

(1) $NO_2CH_2COOH > NCCH_2COOH > FCH_2COOH > ClCH_2COOH$

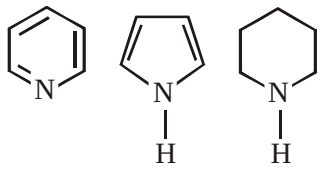
(2) $FCH_2COOH > NCCH_2COOH > NO_2CHCOOH > ClCH_2COOH$

(3) $NO_2CH_2COOH > FCH_2COOH > CNCH_2COOH > ClCH_2COOH$

(4) $CNCH_2COOH > O_2NCH_2COOH > FCH_2COOH > ClCH_2COOH$

AB0128

26. Arrange the following amines in the decreasing order of basicity: **[JEE(Main)-Jan-2019]**

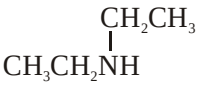
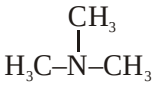
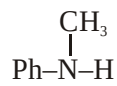


(I) (II) (III)

(1) I > II > III (2) III > II > I (3) I > III > II (4) III > I > II

AB0129

27. The increasing basicity order of the following compounds is : **[JEE(Main)-Jan-2019]**

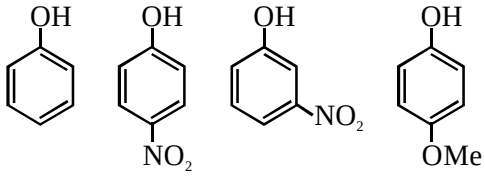
(A) $CH_3CH_2NH_2$ (B)  (C)  (D) 

(1) (D)<(C)<(A)<(B) (2) (A)<(B)<(D)<(C)

(3) (A)<(B)<(C)< (D) (4) (D)<(C)<(B)<(A)

AB0130

28. The increasing order of the pKa values of the following compounds is : **[JEE(Main)-Jan-2019]**



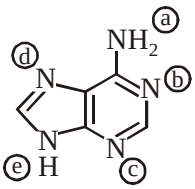
A B C D

(1) D < A < C < B (2) B < C < D < A

(3) C < B < A < D (4) B < C < A < D

AB0131

29. In the following compound, **[JEE(Main)-Jan-2019]**



the favourable site/s for protonation is/are :-

(1) (b), (c) and (d) (2) (a) (3) (a) and (e) (4) (a) and (d)

AB0132

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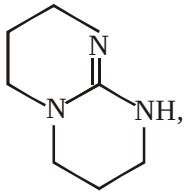
30. The correct order for acid strength of compounds **[JEE(Main)-Jan-2019]**
$CH{\equiv}CH$, $CH_3{-}C{\equiv}CH$ and $CH_2{=}CH_2$
is as follows :
(1) $CH \equiv CH > CH_2 = CH_2 > CH_3{-}C \equiv CH$ (2) $HC \equiv CH > CH_3 - C \equiv CH > CH_2 = CH_2$
(3) $CH_3{-}C \equiv CH > CH_2 = CH_2 > HC \equiv CH$ (4) $CH_3{-}C \equiv CH > CH \equiv CH > CH_2 = CH_2$

AB0133

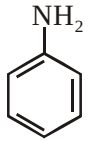
31. The increasing order of pK_b for the following compounds will be : **[JEE(Main)-Jan-2020]**
$NH_2 - CH = NH$,
(A)



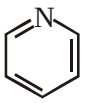
(B)
CH_3NHCH_3
(C)
(1) (A) < (B) < (C) (2) (C) < (A) < (B) (3) (B) < (A) < (C) (4) (B) < (C) < (A)

AB0134

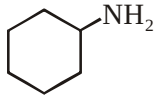
32. The decreasing order of basicity of the following amines is : **[JEE(Main)-Jan-2020]**



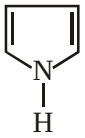
(I)



(II)



(III)



(IV)

(1) (I) > (III) > (IV) > (II) (2) (III) > (I) > (II) > (IV)
(3) (III) > (II) > (I) > (IV) (4) (II) > (III) > (IV) > (I)

AB0135

33. The increasing order of basicity for the following intermediates is (from weak to strong)
(i) $H_3C - \overset{\ominus}{C}(CH_3)_2$ **[JEE(Main)-Jan-2020]**
(ii) $H_2C = CH - \overset{\ominus}{C}H_2$
(iii) $HC{\equiv}\overset{\ominus}{C}$ (iv) $\overset{\ominus}{C}H_3$ (v) $\overset{\ominus}{C}N$
(1) (v) < (i) < (iv) < (ii) < (iii) (2) (iii) < (i) < (ii) < (iv) < (v)
(3) (v) < (iii) < (ii) < (iv) < (i) (4) (iii) < (iv) < (ii) < (i) < (v)

AB0136

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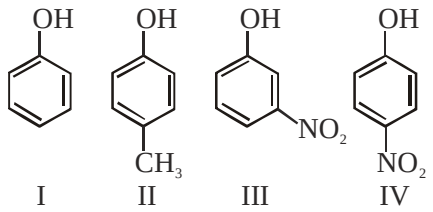
EXERCISE # (J-ADVANCED)

1. In the following compounds **[IIT-JEE-1996]**



I II III IV

The order of acidity is -

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

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

AB0137

2. Although phenoxide ion has more number of resonating structures than benzoate ion, benzoic acid is a stronger acid than phenol. Why ? **[IIT-JEE-1997]**

AB0138

3. Amongst the following, the most basic compound is - **[IIT-JEE-2000]**

(A) $C_6H_5NH_2$

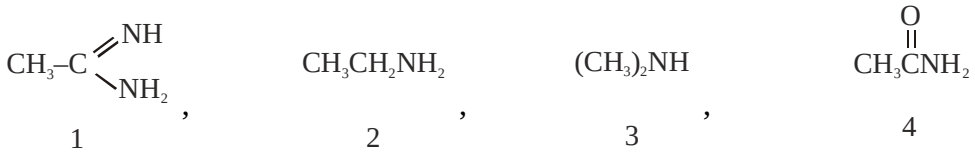
(B) $p–NO_2–C_6H_4NH_2$

(C) $m–NO_2–C_6H_4NH_2$

(D) $C_6H_5CH_2NH_2$

AB0139

4. The correct order of basicities of the following compounds is : **[IIT-JEE-2001]**



1 , 2 , 3 , 4

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

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

AB0140

5. **Statement-I :** p-Hydroxybenzoic acid has a lower boiling point that o-hydroxybenzoic acid.

Because

Statement-II : o-Hydroxybenzoic acid has intramolecular hydrogen bonding. **[IIT-JEE-2003]**

(A) Statement-I is True, Statement-II is True ; Statement-II is a correct explanation for Statement-I

(B) Statement-I is True, Statement-II is True; Statement-II is NOT a correct explanation for Statement-I

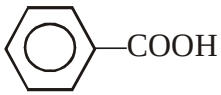
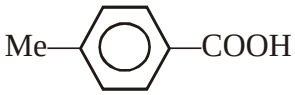
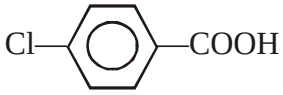
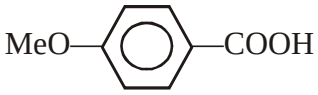
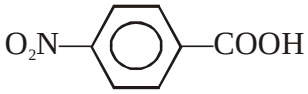
(C) Statement-I is True, Statement-II is False.

(D) Statement-I is False, Statement-II is True.

AB0141

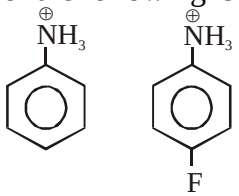
node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Chm\Sheet\Acidic Strength and Basic Strength\Eng.p65

6. Match K_a values with suitable acid : **[IIT-JEE-2003]**

K_a	Acid
(A) 3.3×10^{-5}	(p) 
(B) 4.2×10^{-5}	(q) 
(C) 6.3×10^{-5}	(r) 
(D) 6.4×10^{-5}	(s) 
(E) 30.6×10^{-5}	(t) 

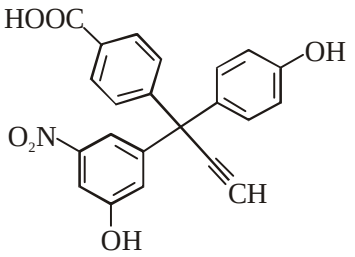
AB0142

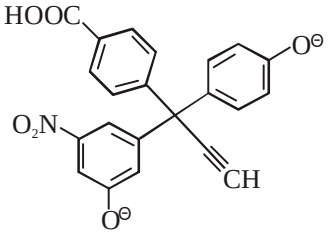
7. (a) Which of the following is more acidic and why ? **[IIT-JEE-2004]**

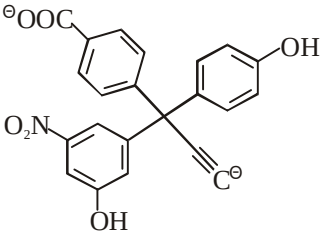


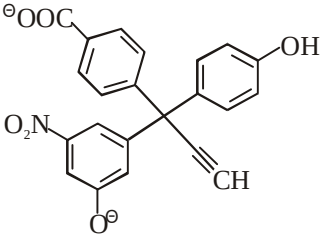
(I) (II)

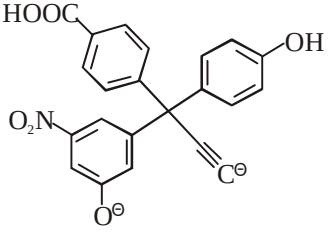
AB0143

8.  A. The product (A) will be : **[IIT-JEE-2007]**

(A) 

(B) 

(C) 

(D) 

AB0144

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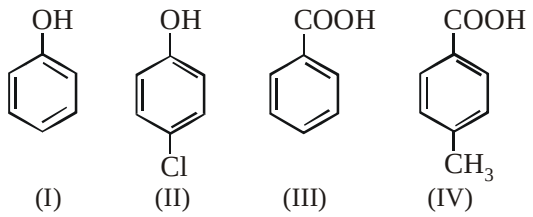
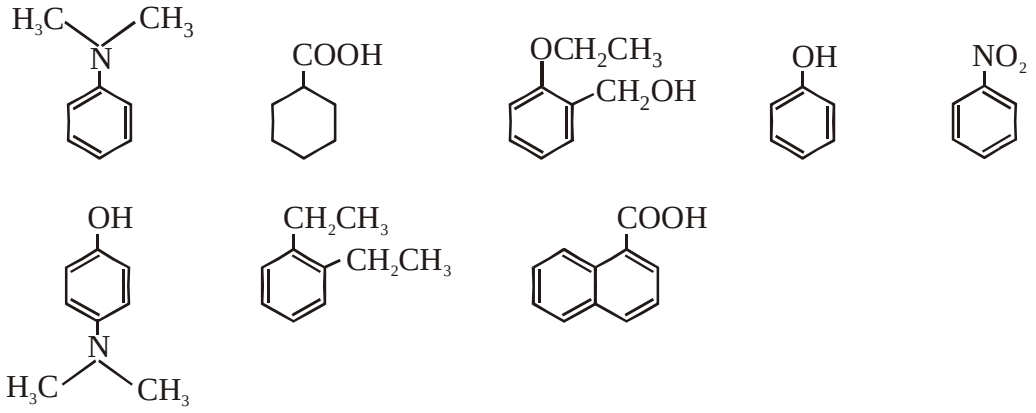
9. The correct acidity order of the following is : **[IIT-JEE-2009]**



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

AB0145

10. Amongst the following, the total number of compounds soluble in aquesous NaOH is: **[IIT-JEE-2010]**



AB0146

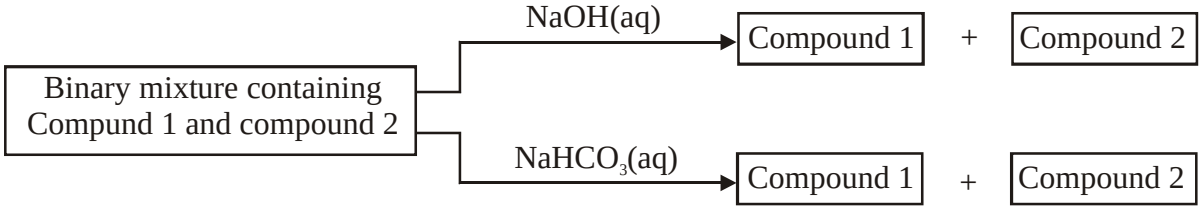
11. Among the following compounds, the most acidic is **[IIT-JEE-2011]**
(A) p-nitrophenol (B) p-hydroxybenzoic acid
(C) o-hydroxybenzoic acid (D) p-toluic acid

AB0147

12. The carboxyl functional group (–COOH) is present in - **[IIT-JEE-2012]**
(A) picric acid (B) barbituric acid (C) ascorbic acid (D) aspirin

AB0148

13. Identify the binary mixtures (s) that can be separated into the individual compounds, by differential extraction, as shown in the given scheme - **[IIT-JEE-2012]**



(A) C_6H_5OH and C_6H_5COOH (B) C_6H_5COOH and $C_6H_5CH_2OH$
(C) $C_6H_5CH_2OH$ and C_6H_5OH (D) $C_6H_5CH_2OH$ and $C_6H_5CH_2COOH$

AB0149

node06\B0BO-BA\Kota\JEE(Advanced)\Leader\Che\Sheet\Acidic Strength and Basic Strength\Eng.p65

14. The compound that does NOT liberate CO_2, on treatment with aqueous sodium bicarbonate solution, is - **[JEE-ADVANCED-2013]**

(A) Benzoic acid (B) Benzenesulphonic acid (C) Salicylic acid (D) Carbolic acid (phenol)

AB0150

15. Hydrogen bonding plays a central role in the following phenomena **[JEE-ADVANCED-2014]**

(A) Ice floats in water

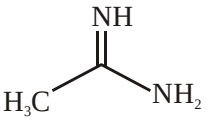
(B) Higher Lewis basicity of primary amines than tertiary amines in aqueous solutions

(C) Formic acid is more acidic than acetic acid

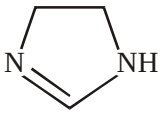
(D) Dimerisation of acetic acid in benzene

AB0151

16. The order of basicity among the following compounds is **[JEE-ADVANCED-2017]**



I



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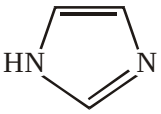

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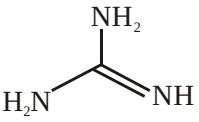

IV

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

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

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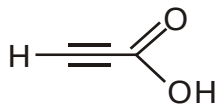
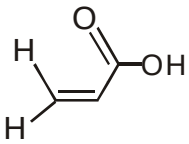
17. The correct order of acid strength of the following carboxylic acids is -

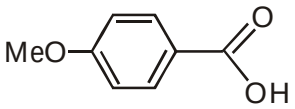
[JEE-ADVANCED-2019]



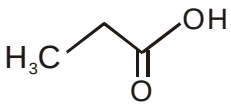
I



II



III



IV

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

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

AB0153

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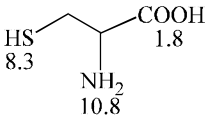
ANSWER-KEY

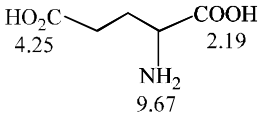
EXERCISE # O-I

1. **(i) a > b > c > d,** **(ii) a > b > c ,** **(iii) c > b > a,** **(iv) a > b > c,**
(v) c > b > a, **(vi) a > b > c** **(vii) d > c > b > a ,** **(viii)d > c > b > a,**
(ix) d > b > a > c, **(x) d > a > c> b**

2. **(a) 2 ; (b) 2 ; (c) 1 ; (d) 1** **3.** **(a) 2 ; (b) 2 ; (c) 2** **4.** **(C)**

5. **(B)** **6.** **(B)** **7.** **(B)** **8.** **(A)** **9.** **(A)**

10. **(i) cysteine :** 

(ii) glutamic acid : 

11. **(a) 3 < 2 < 1 ; (b) 1 < 2 < 3 ; (c) 3 < 2 < 1 ; (d) 2 < 1 < 3 ; (e) 2 < 3 < 1**

12. **(i) d > c > a > b,** **(ii) a > b > c,** **(iii) c > a > b > d,** **(iv) d > b > c > a,**
(v) a > b > c, **(vi) b > a** **(vii) c > a > b**

13. **(i) b , (ii) a, (iii) b , (iv) b** **14.** **(C)** **15.** **(C)** **16.** **(B)**

17. **(C)** **18.** **(B)** **19.** **(4)** **20** **(C)**

EXERCISE - O-II

1. **(i) a > b> c> d,** **(ii) a > b > c > d,** **(iii) c > b> d> a ,** **(iv) d > c > b > a**
(v) a > b > c, **(vi) c > b > a** **(vii) c > a > b,** **(viii) b > c > a,** **(ix) c > d > b > a**

2. **(i) a > b > c,** **(ii) d > c > b > a,** **(iii) b > c > a,** **(iv) d > c > b > a,**
(v) b > a > c, **(vi) b > a,** **(vii) c > b > a,** **(viii) d > a > b > c**
(ix) d > c > b > a

3. **(i) d, (ii) b, (iii) a, (iv) a**

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

5. **(A)** **6. (A)** **7. (A)** **8. (A)**

9. **(a) i , (b) ii , (c) i , (d) ii** **10. (a) 2 ; (b) 1 ; (c) 1 ; (d) 1 ; (e) 3**

11. **(a) 2; (b) 1;(c) 2; (d) 2** **12. (a) 1 > 2 > 3 ; (b) 1 < 2 < 3 ; (c) 3 < 1 < 2 ; (d) 2 < 1 < 3**

13. **(a) 2 < 1 < 3 ; (b) 1 < 2 < 3** **14. (C)** **15. (B)**

16. **3, 3 basic groups are** $\overset{..}{N}H_2$; –NH–; O^- **17.** **(6)**

EXERCISE # S-I

1. **(C)** **2.** **(C)**

3. **(A) – R, S, T ; (B) – P, R, S, T ; (C) – P, Q, R, S, T ; (D) – P, Q, R, S, T**

4. **(i) , (ii) (iii) (iv), (v) (ix)** **5. (D)** **6.** **(A)**

7. **(A) – P,T ; (B) – R; (C) – Q ; (D) – S, T** **8.** **(A) – R ; (B) – S; (C) – P ; (D) – Q, T**

9. **(A)** **10.** **(A)** **11.** **(A, D)** **12.** **(D)**

13. **(A, B, C, D)** **14.** **(B)** **15.** **(C)**

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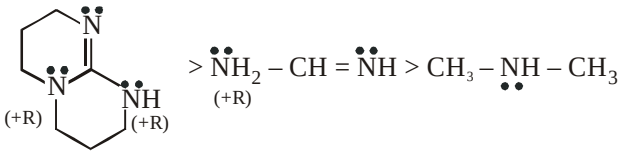
EXERCISE # JEE-MAIN

1.	**(3)**	**2.**	**(4)**	**3.**	**(3)**	**4.**	**(4)**	**5.**	**(4)**
6.	**(3)**	**7.**	**(4)**	**8.**	**(3)**	**9.**	**(1)**	**10.**	**(2)**
11.	**(3)**	**12.**	**(1)**	**13.**	**(1)**	**14.**	**(2)**	**15.**	**(3)**
16.	**(2)**	**17.**	**(4)**	**18.**	**(3)**	**19.**	**(2)**	**20.**	**(3)**
21.	**(3)**	**22.**	**(1)**	**23.**	**(3)**	**24.**	**(2)**		
25.	**Ans. (1)**	**26.**	**Ans. (4)**	**27.**	**Ans. (1)**	**28.**	**Ans. (4)**		
29.	**Ans. (1)**	**30.**	**Ans. (2)**						

31. Ans. (3)

Sol. Base strength order



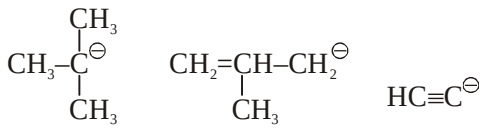
(B) (A) (C)

pk_b order (C > A > B)

32. Ans. (3)

33. Ans. (3)

Sol.



(i) (ii) (iii)

(iv) (v)

Basic strength order : (i) > (iv) > (ii) > (iii) > (v)

EXERCISE # J-ADVANCED

1.	**(D)**	**2.**	**Benzoate has equivalent resonating structures**					**3.**	**(D)**
4.	**(B)**	**5.**	**(D)**	**6.**	**A-(s) ; B-(q) ; C-(p) ; D-(r) ; E-(t)**				
7.	**(II is most acidic)**	**8.**	**(C)**	**9.**	**(A)**	**10.**	**(4)**	**11.**	**(C)**
12.	**(D)**	**13.**	**(B, D)**	**14.**	**(D)**	**15.**	**(A, B, D)**		
16.	**(D)**	**17.**	**Ans. (D)**						

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