General Organic Chemistry-II

Section (A) : Basic strength

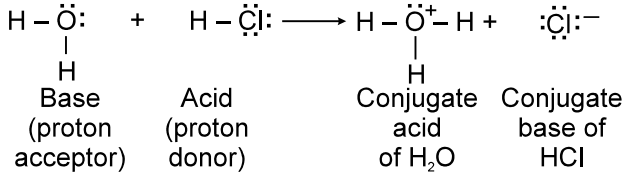
Th1. Bases

D1: **(a) Arhenius base:** Base is a substance that can donate (or loose) OH^- ions in H_2O.

D2: **(b) The Bronsted Lowry definition of acids and bases:**

An acid is a substance that can donate (or loose) a proton, and a base is a substance that can accept a proton.

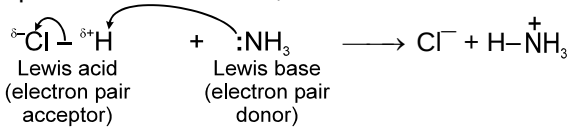
Let us consider, an example of this concept, the reaction that occurs when gaseous hydrogen chloride dissolves in water :

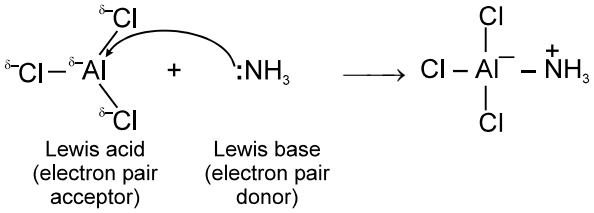


D3: **(c) The Lewis definition of acids and bases:**

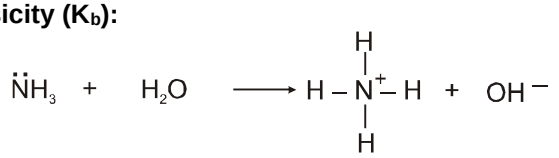
Lewis proposed that acids are electron pair acceptors and bases are electron pair donors.

For example aluminiumchloride, reacts with ammonia in the same way that a proton donor does.





(d) Basicity (K_b):



$$K_b = \frac{[NH_4^+]\ [OH^-]}{[NH_3]} \quad \Rightarrow \quad pK_b = -\log K_b$$

Basicity order in periodic table:

(1) Basic strength decreases down the group,

(2) Basic strength decreases along the period because electron neagativity increases, so electron donor tendency decreases.

1.1 Aliphatic bases:

(1) On the basis of +I effect basic strength of amines should be $3^o > 2^o > 1^o > NH_3$

But this order is applicable only when the amines are in gaseous state or in case of non-polar aprotic solvent.

(2) Basic strength of nitrogeneous compound depends upon the hybridised state of nitrogen

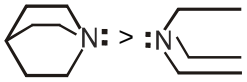
$$R{-}CH_2{-}CH_2{-}NH_2 > R{-}CH_2{-}CH{=}NH > R{-}CH{=}CH{-}NH_2 > R{-}C{\equiv}N$$

sp^3 (localised) sp^2 (localised) sp^2 (delocalised) sp

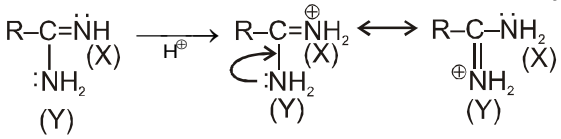
(3) More electronegative atom (–I group) will decrease the basic strength

$CH_3{-}CH_2{-}CH_2{-}NH_2 > CH_2{=}CH{-}CH_2{-}NH_2 > H{-}C{\equiv}C{-}CH_2{-}NH_2$

(4) Cyclic amines are more basic than acyclic amines of same nature



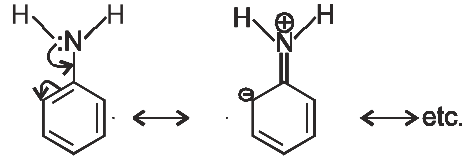
(5) Amidines are more basic in nature because their conjugate acid are more stable due to resonance.



Nitrogen (X) is more basic than nitrogen (Y).

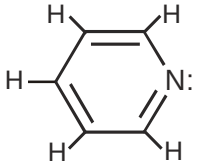
Th2. Basic strength of aromatic amines and substituted anilines:

(a) Aniline: Lone pair of aniline lies in conjugation with a multiple bond, it resides in '2p' atomic orbital, so that it can get resonance stabilisation and hence, basic strength decreases. So, Aniline is a weaker base than NH_3.

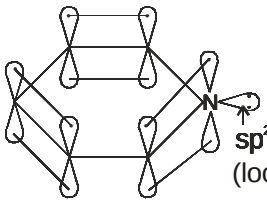


(b) Pyridine (C_5H_5N) : 6-π electrons, aromatic

S.F. :



A.O. Diagram:

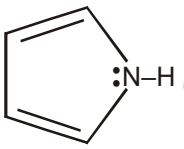


sp² hybrid orbital (localised lone pair)

Lone pair of N in pyridine is localised so it is more basic than aniline.

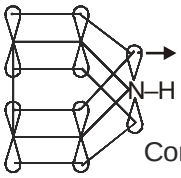
(c) Pyrrole (C_4H_5N:) : 6-π electrons, aromatic

S.F. :



(sp²)

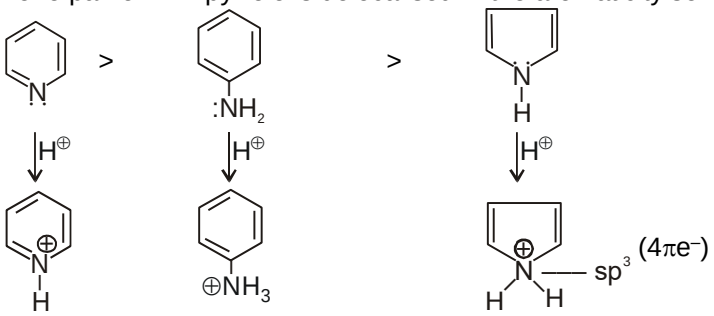
A.O. Diagram:



(lone pair in 2p A.O.)

Complete delocalisation of e^-

Lone pair of N in pyrrole is delocalised in the aromaticity so it is very less basic than aniline.

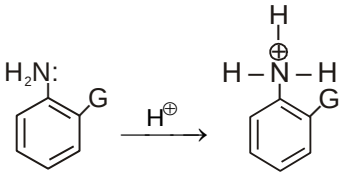


Aromatic Aromatic Non-aromatic

(d) Ortho substituted anilines :

Electron releasing groups (ERG) +M, HC, +I increases the K_b and
Electron withdrawing groups (EWG) –m, –I decreases the K_b

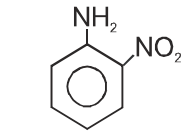
Steric effect of ortho-substituent in aniline (ortho effect) :

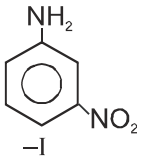


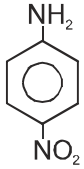
(conjugate acid)

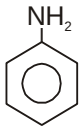
(i) Ortho-substituted anilines are mostly weaker bases than aniline itself.
(ii) Ortho-substituent causes steric hinderance to solvation in the product (conjugate acid i.e. cation).
(iii) The small groups like $-NH_2$ or –OH do not experience (SIR) due to small size.

Ex. (a) G = (–M, –I); NO_2


(–I –M, ortho effect)

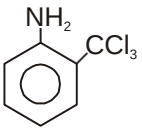

–I

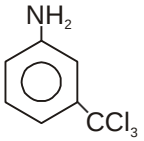

(–I–M)

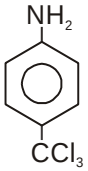


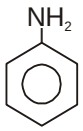
(Aniline > m > p > o).

(b) G = (–I); CCl_3





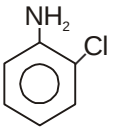


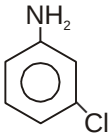


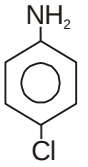
(Aniline > p > m > o).

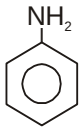
Only (–I) decides the order.

(c) G = (–I > + m); Cl





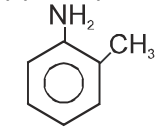


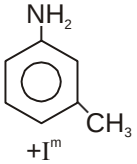


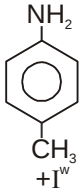
(Aniline > p > m > o)

Only (–I) decides the order.

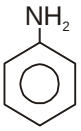
(d) G = (+I, HC); If R = $-CH_3$ (Toluidines)


Ortho effect,
+I
HC


$+I^m$

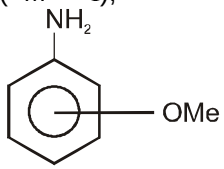

$+I^w$

HC → more dominating



p > m > aniline > o

(e) G = (+M > –I);



K_b order : p > Aniline > o > m

General basicity order :

$$R_3\overset{\ominus}{C} > R_2\overset{\ominus}{C}H > R-\overset{\ominus}{C}H_2 > \overset{\ominus}{C}H_3 > \overset{\ominus}{P}h > Ph\overset{\ominus}{C}H_2 > \overset{\ominus}{N}H_2 > Ph_2\overset{\ominus}{C}H > Ph_3\overset{\ominus}{C} > \overset{\ominus}{H} > R-C\equiv\overset{\ominus}{C} > R\overset{\ominus}{C}\underset{\underset{O}{\|}}{C}H_2$$


$\approx R-\overset{\ominus}{O} \gtrsim \overset{\ominus}{O}H \gtrsim CH_3\overset{\ominus}{O} > CO_3^{2-} > Ph\overset{\ominus}{O} > R\overset{\ominus}{S} > RCO\overset{\ominus}{O} > O\overset{\ominus}{C}N > H_2O > \overset{\ominus}{Cl}$

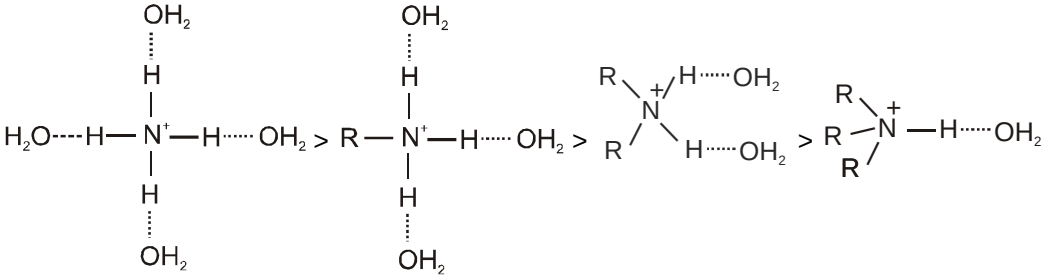
Th3. Solvent effect in bases :

The trend is not regular in the aqueous state as evident by their pKb values given in Table.

Name of amine	pK_b	Name of amine	pK_b
Methanamine	3.38	N,N-Diethylethanamine	3.25
N-Metheylmethanamine	3.27	Phenylmethanamine	4.70
N, N-Dimethylmethanamine	4.22	Aniline	9.38
Ethanamine	3..29	N-Methylaniline	9.30
N-Ethylethanamine	3.00	N,N-Dimethylaniline	8.92

Table : pK_b Values of Amines in Aqueous Phase (Ref. NCERT)

In the aqueous phase, the substituted ammonium cations get stabilised not only by electron releasing effect of the alkyl group (+I) but also by solvation with water molecules. The greater the size of the ion (Alkyl groups are hydrophobic and inhibits H bonding and solvation.), lesser will be the solvation and the less stabilised is the ion. The order of solvation of ions are as follows:



Ammonium ion 1^0 2^0 3^0

Greater is the stability of the substituted ammonium cation, stronger should be the corresponding amine as a base.

On the basis of above two sequences, we can say that the basic strength of amines is the combined effect of inductive effect, steric hindrance and solvation.

$R_2NH > RNH_2 > R_3N > NH_3$ (if R = CH_3) ..... (1)

$R_2NH > R_3NH > RNH_2 > NH_3$ (if R = C_2H_5) .....(2)

Th4. Reactions of bases :

(i) **Nature of aqueous solution:** Amines combine with water to form alkyl ammonium hydroxides. This gives hydroxide ions in solution, thus the aqueous solution of amines is basic in nature.

$RNH_2 + HOH \rightleftharpoons \overset{+}{R}NH_3OH^- \rightleftharpoons [RNH_3]^+ + OH^-$

1º Amine

$R_2NH + HOH \rightleftharpoons R_2\overset{+}{N}H_2OH^- \rightleftharpoons [R_2NH_2]^+ + OH^-$

2º Amine

The aqueous solution of amines behave like NH_4OH and gives the precipitate of ferric hydroxide with ferric chloride.

$3RNH_3OH + FeCl_3 \longrightarrow Fe(OH)_3 + 3RNH_3Cl$

Brown ppt.

(ii) **Aliphatic and aromatic amines form salt because of their basic nature:**

$RNH_2 + H_2O \longrightarrow \overset{+}{R}NH_3\overset{-}{O}H$

Alkylammoniumhydroxide

$RNH_2 + HCl \longrightarrow \overset{+}{R}NH_3\overset{-}{C}l$

Alkylammoniumchloride

$RNH_2 + H_2SO_4 \longrightarrow (\overset{+}{R}NH_3)_2\, SO_4^{-2}$

Similarly we get

$C_6H_5NH_2 + H_2O \longrightarrow C_6H_5\overset{+}{N}H_3\overset{-}{O}H$

Aniliniumhydroxide

$C_6H_5NH_2 + HCl \longrightarrow C_6H_5\overset{+}{N}H_3\overset{-}{C}l$ or $C_6H_5NH_2 : HCl$

Aniliniumchloride Anilinehydrochloride

Salts of amines are ionic compounds and hence water soluble.

Section (E) : Acidic strength

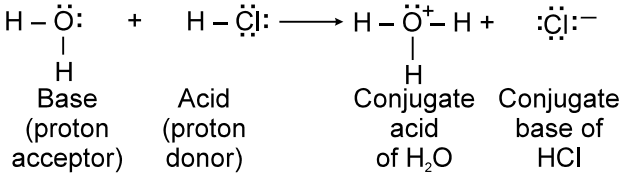
Th5. Acids

D4: **(a) Arhenius acid:** An acid is a substance that can donate (or loose) a proton in H_2O.

D5: **(b) The Bronsted Lowry definition of acids and bases:**

An acid is a substance that can donate (or loose) a proton, and a base is a substance that can accept a proton.

Let us consider, an example of this concept, the reaction that occurs when gaseous hydrogen chloride dissolves in water :

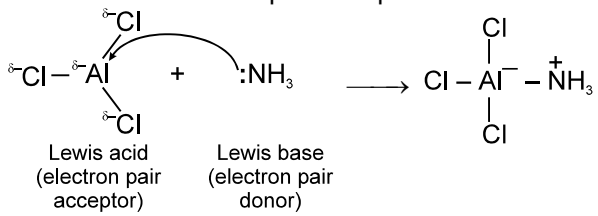


Hydrogen chloride, a very strong acid, transfers its proton to water. Water acts as a base and accepts the proton. The products that result from this reaction are a hydronium ion (H_3O^+) and a chloride ion (Cl^-).

The molecule or ion that forms when an acid loses 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.

D6: **(c) The Lewis definition of acids and bases**

Lewis proposed that acids are electron pair acceptors and bases are electron pair donors.



(d) Acid dissociation constant (K_a) :

$$RCOOH + H_2O \rightleftharpoons RCOO^- + H_3O^+$$

$$K_{eq} = \frac{[RCOO^-]\ [H_3O^+]}{[RCOOH]\ [H_2O]}$$

$$K_a = \frac{[RCOO^-]\ [H_3O^+]}{[RCOOH]}$$

$$pK_a = -\log K_a$$

5.1 Relative acidity of hydrocarbons :

Being most electronegative the sp hybridised carbon atom of ethyne polarizes its C–H bond to the greatest extent causing its H to be most positive therefore ethyne is most acidic hydrocarbon.

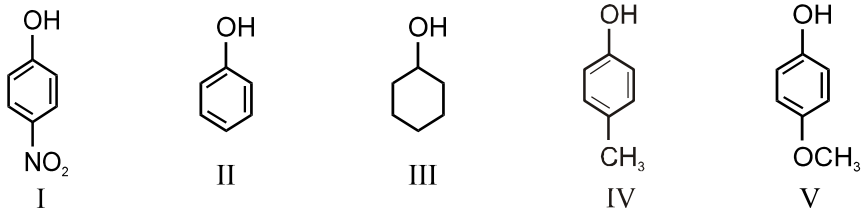
$HC \equiv CH > H_2C = CH_2 > H_3C - CH_3$

5.2 Acidity of phenols :

The phenoxide ion is more stabilised by resonance than the unionised phenol.

Groups which are –I, –m increases acidic character of phenol because effectively dispersing the negative charge of phenoxide ion. Alternatively + I and + m groups decreases acid strength.

Ex. (a)

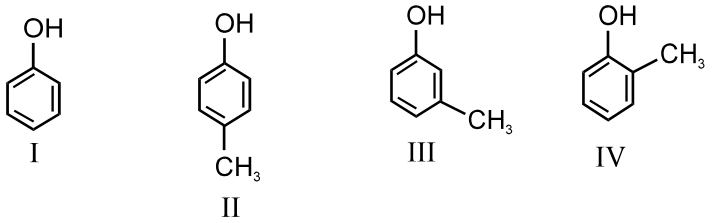


Ans. Acid strength order : I > II > IV > V > III

Sol. Step-1. III will be least acidic as it has no dispersion of negative charge (No delocalisation of negative charge).

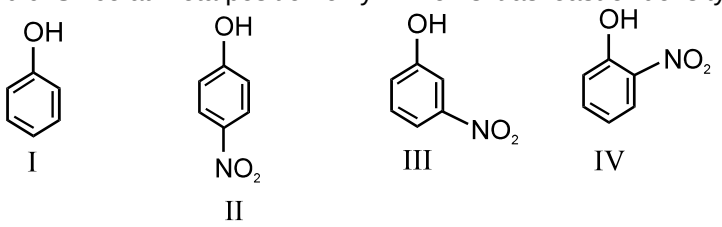
Step-2. Since –I, –m group will increase acid strength, Nitrophenol will be most acidic followed by phenol,

Step-3. Amongst cresol and methoxyphenol, methoxyphenol has +M effect of $-OCH_3$ which increases e^- density hence decrease acidic strength

Ex. (b) 

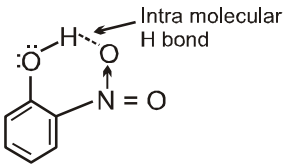
Ans. Acid strengh order: I > III > II > IV

Sol. Step-1: Notice that CH_3 have +I effect so all methylphenols (cresols) are less acidic than phenol (I).
Step-2: Now amongst cresols p- and o-CH_3 are increasing the e^- 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 as least e^- density amongst the cresol.

Ex. (c) 

Ans. Acid strength order: II > IV > III > I

Sol. Step-1 : In nitrophenols –I effect of NO_2 will help to increase acidic strength hence phenol is least acidic amongst all nitrophenols
Step-2 : Only –I effect is applicable in meta nitrophenol it will be number three. Now –o, –p have both –I and –m effect of NO_2 group over OH and in this particular case para isomer is more acidic than ortho since



H is trapped by NO_2 group.

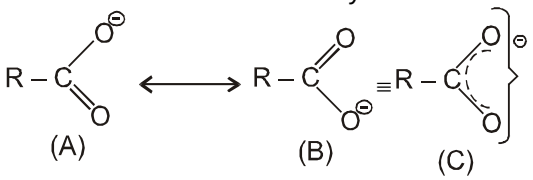
Table : pK_a values of some phenols and Ethanol. **(Ref. NCERT)**

Compound	Formula	pKa	Compound	Formula	pKa
o-Nitrophenol	o–O_2N–C_6H_4–OH	7.2	o-Cresol	o-CH_3–C_6H_4–OH	10.2
m-Nitrophenol	m–O_2N–C_6H_4–OH	8.3	m-Cresol	m-$CH_3C_6H_4$–OH	10.1
p-Nitrophenol	p-O_2N–C_6H_4–OH	7.1	p-Cresol	p-CH_3–C_6H_4–OH	10.2
Phenol	C_6H_5–OH	10	Ethanol	C_2H_5OH	15.9

From the above data, you will note that phenol is million times more acidic than ethanol.

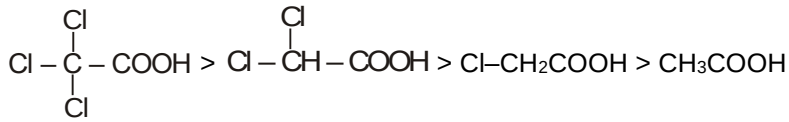
5.3 Acidity of carboxylic acids :

Conjugate base of carboxylic acid exists as two equivalent cannonical structures (A) and (B). This ion is resonance stablised and resonance hybrid structure is (C).

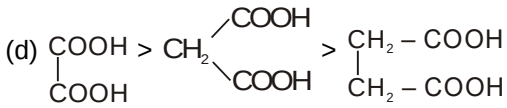


Electron withdrawing group (–M, –I effect) increases acidic nature.
Electron releasing group (+M, +I effect) decreases acidic nature.

Ex. (a) F–CH_2–COOH > Cl–CH_2COOH > Br–CH_2COOH > I–CH_2COOH

(b) 

(c) HCOOH > CH_3COOH > CH_3–CH_2–COOH

(d) 

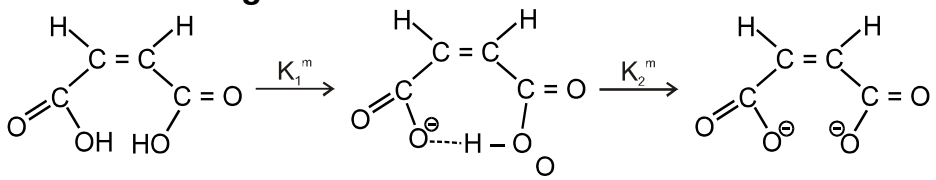
The effect of the following groups in increasing acidicty order is **[Ref. NCERT]**

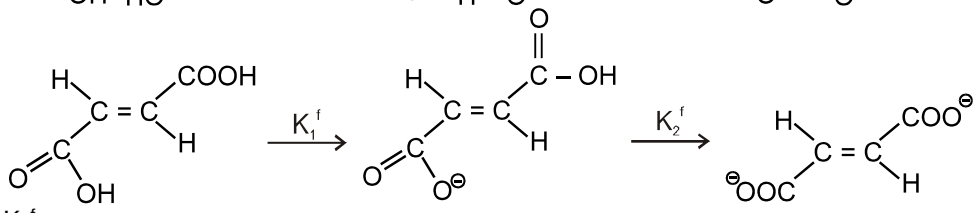
Ph < I < Br < Cl < F < CN < NO_2 < CF_3

Thus, the following acids are arranged in order of decreasing acidity (based on pK_a values) :

CF_3COOH > CCl_3COOH > $CHCl_2COOH$ > NO_2CH_2COOH > $NC–CH_2COOH$ > FCH_2COOH > $ClCH_2COOH$ > $BrCH_2COOH$ > $HCOOH$ > $ClCH_2CH_2COOH$ > C_6H_5COOH > $C_6H_5CH_2COOH$ > CH_3COOH > CH_3CH_2COOH

5.4 Comparison between two geometrical isomers :

Maleic acid : 

Fumaric acid : 

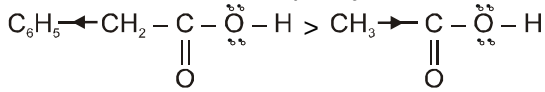
Now K_1^m > K_1^f

Since the conjugate base is stabilised by intramolecular H bonding.

But K_2^f > K_2^m Since in maleate ion, after donation of $H^{\oplus}$ two $–COO^{\ominus}$ groups faces each other and makes system unstable. In fumarate ion this repulsion is minimised.

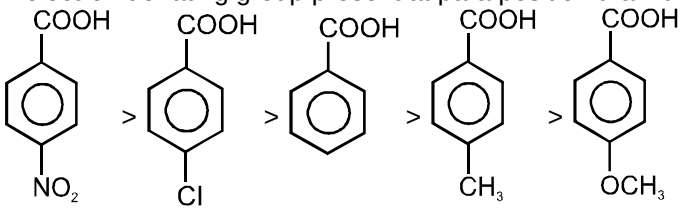
5.5 Acidic strength of substituted benzoic acids :

Formic acid is more acidic than benzoic acid while phenyl acetic acid is more acidic than acetic acid.

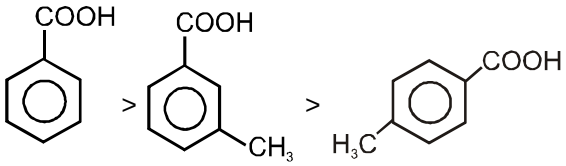
HCOOH > PhCOOH > 

Electron withdrawing group attached to benzene ring will increase the acidic strength while electron releasing group decreases acidic strength.

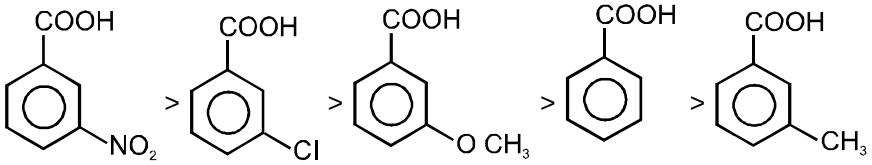
If electron donating group present at para position than it is always less acidic than benzoic acid.



Also it is less acidic then meta substituted benzoic acid.



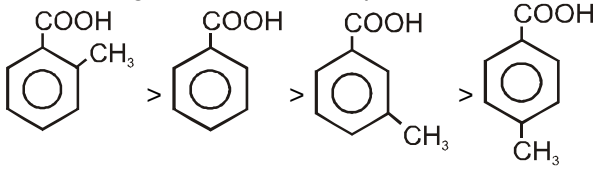
On the other hand if e^- withdrawing group is present at meta position then it is more acidic than benzoic acid.



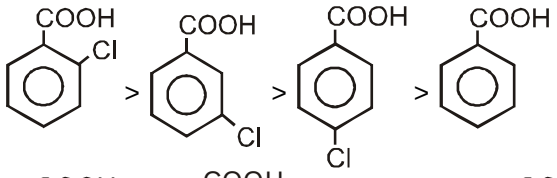
Th6. Ortho effect :

D6. It is common observation that generally ortho substituted benzoic acids are more acidic as compared to their isomers and benzoic acids itself. This is called ortho effect (which is combined effect of steric hindrance, crowding & electronic effect) in benzoic acid. However exceptions are seen.

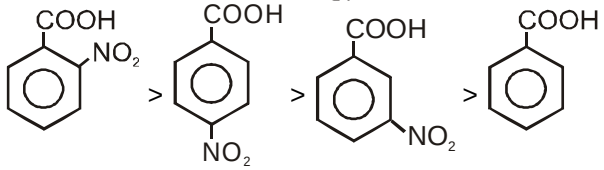
Ex. (a)



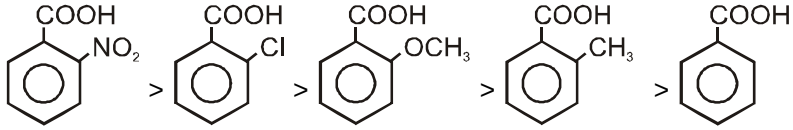
(b)



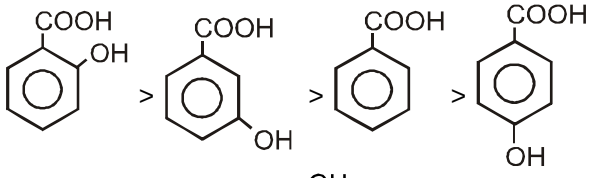
(c)



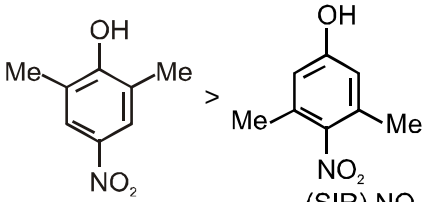
(d)



(e)



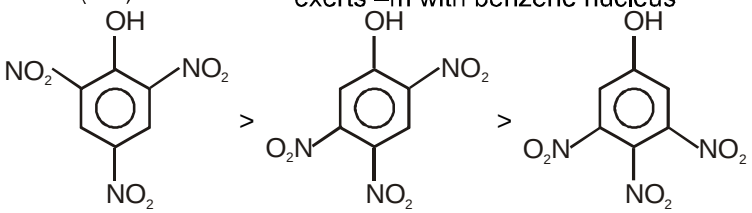
(f)



(–m)

(SIR) NO_2 not in plane, so NO_2group does not exerts –m with benzene nucleus

(g)



(picric acid)

Section (F) : Feasible reactions of acids and bases

Th7. Reaction of acid with salt:

(1) NaX + HY $\longrightarrow$ NaY + HX

Salt of Weak acid Strong Acid

Remark: A stronger acid displaces the weaker acid from weak acid metal salt. The weaker acid is released out as a gas or liquid or precipitates out as a solid. The weaker acid cannot displace the stronger acid from the salt.

1. $2\ NaCl + H_2SO_4 \longrightarrow Na_2SO_4 + 2HCl$
2. $Na_2SO_4 + 2HCl \longrightarrow$ No reaction
3. $CH_3COONa + CH_3SO_3H \longrightarrow CH_3COOH + CH_3SO_3Na$ (feasible)
4. $CH_3COONa + PhOH \longrightarrow PhONa + CH_3COOH$ (not feasible)

Section (G) : Tautomerism

Th8. Tautomerism

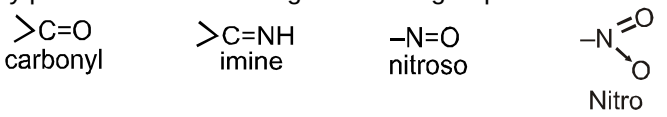
D7: Definition :

Tautomerism is a phenomenon by which a single compound exists in two or more readily interconvertible structures that differ in the relative positions of at least one atomic nucleus, generally hydrogen.

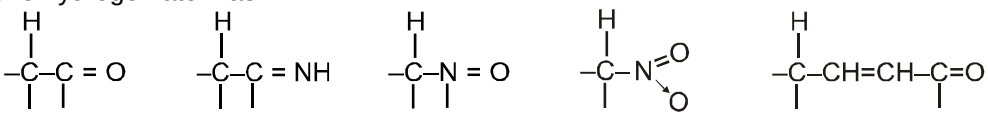
These two isomers remain in dynamic equilibrium and can be isolated also give different lab test.

Conditions :

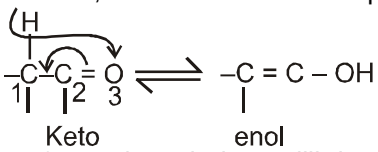
1. Usually present in the following functional groups



2. Basic need for its existence is attachment of these groups with the sp^3 hybridised C-atom having atleast one hydrogen atom as –



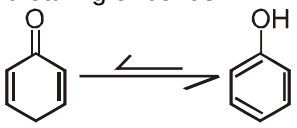
To get tautomer of above structures α-hydrogen atom is shifting to more electronegative atom attached to double bond (i.e. hydrogen atom from 1st atom to 3rd atom) and double bond is developed between 1,2-atom from 2,3-atom. This can be represented as:



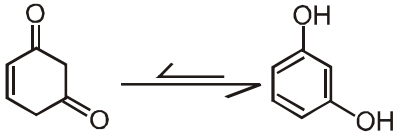
These two forms (remain in equilibrium) are called tautomers of each other. The interconvertibility of tautomers is a chemical reaction which involves making and breaking of bonds.

Ex. (a) $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$ (I) $\rightleftharpoons$ $CH_2=\overset{\overset{OH}{|}}{C}-CH_3$ (II)

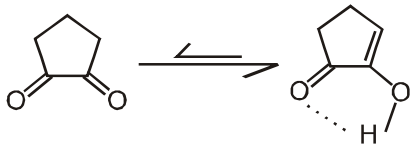
(b)



(c)

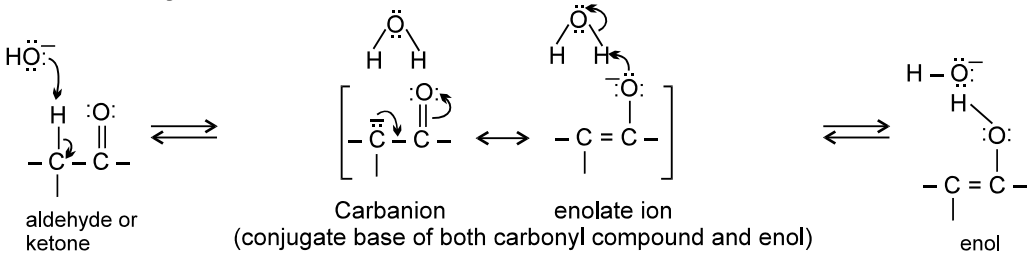


(d)



Th9. Keto-enol tautomerisation :

9.1 (A) Base-catalyzed enolization :

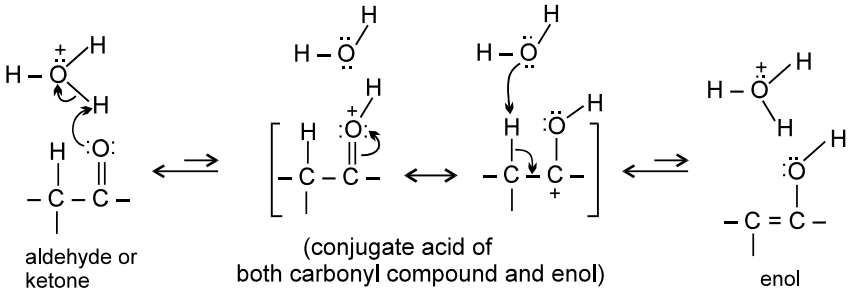


(conjugate base of both carbonyl compound and enol)

Protonation of the carbanion by water on the α-carbon gives back the carbonyl compound. Protonation on oxygen gives the enol. Notice that the enolate ion is the conjugate base of both the carbonyl compound and the enol.

(B) Acid-catalyzed enolization :

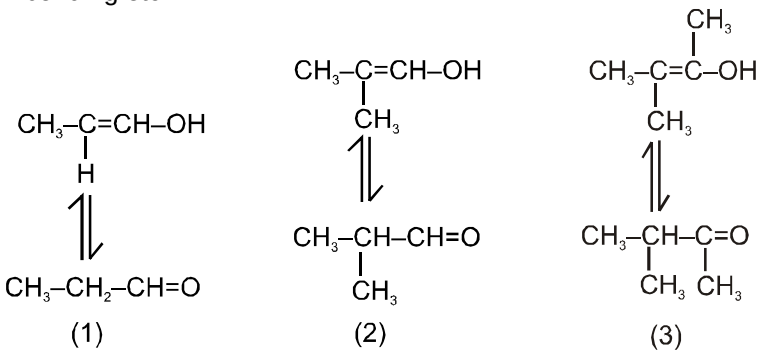
Involves the conjugate acid of the carbonyl compound. Recall that this ion has carbocation characteristics. Loss of the proton from oxygen gives back the starting carbonyl compound; loss of the proton from the α-carbon gives the enol. Notice that an enol and its carbonyl isomer have the same conjugate acid.



9.2 % Enol content in the carbonyl compounds :

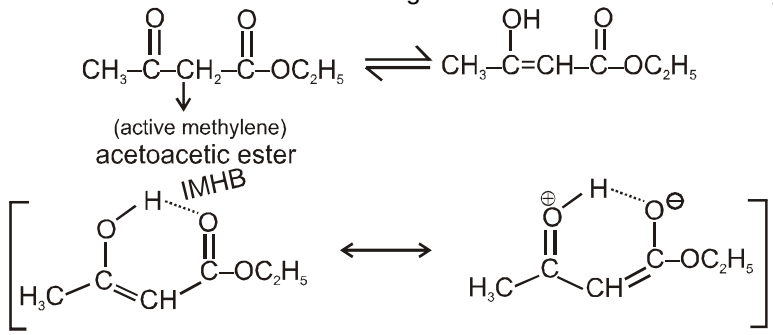
(a) For monocarbonyl % Enol is very less

(b) Enol content increases with increase in the stability of enol by resonance, hyperconjugation, hydrogen bonding etc.



Decreasing order of enol content for above carbonyl compounds is : 3 > 2 > 1.

(c) For a carbonyl compound having active methylene group percentage of enol content will be more because enolic form has intramolecular H-bonding and also it will be stabilised by resonance.



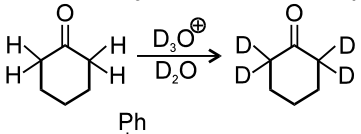
(d) If active methylene group is more acidic then enol content will be more.

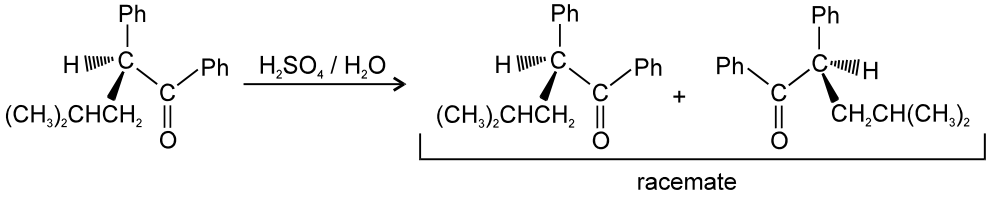
For example in acetyl acetone ($CH_3–\overset{O}{\overset{\|}{C}}–CH_2–\overset{O}{\overset{\|}{C}}–CH_3$) enolic content is 75–76% while it is 7–8% in acetoacetic ester because ester group shows less electron withdrawing nature than keto group.

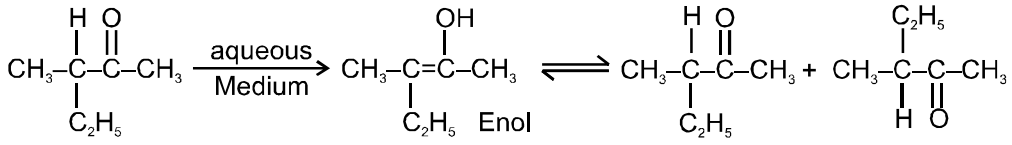
(e) Percentage of enol content is more in non-polar media while % of keto form is more in polar media.

Th10. Racemisation and D-exchange :

Exchange of α-hydrogen from deuterium as well as racemization at the α-carbon are catalyzed not only by bases but also by acids due to the phenomenon of tautomerisation.

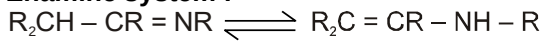
1.  (D-exchange)

2. 

3. 

Th10. Other examples of tautomers *(not to be done in class only for the reference of students)*

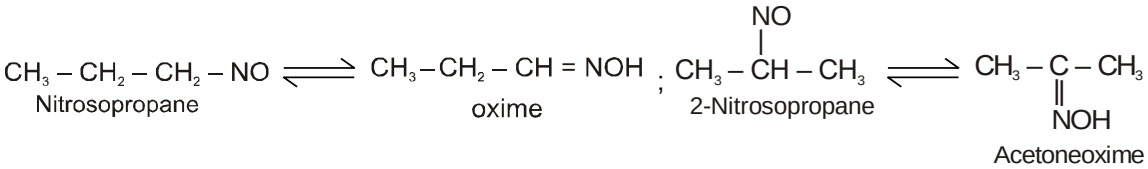
(a) Imine-Enamine system :



Among these two tautomers, enamines are stable only when there is no hydrogen on the nitrogen, otherwise the imine form predominates.

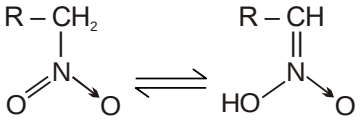
(b) Nitroso-oxime system:

Like primary and secondary nitro compounds, primary and secondary nitroso compounds also exhibit tautomerism with their more stable isonitroso or oxime form.

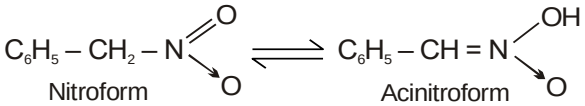


(c) Nitro-Acinitro system:

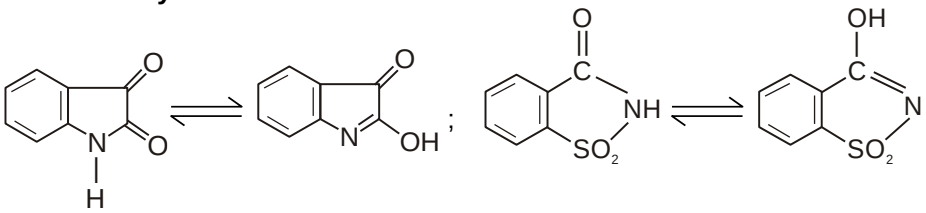
The acidic nature of the nitro compounds gives rise to the belief that the nitro compounds exist in two forms, a more stable or normal nitro form and the less stable acinitro form.



The stability of the nitro form is more as compared to the acinitro form because it is stabilised by resonance.



(d) Lactam-Lactim system :



CHECK LIST

Definitions (D)		
D1 :	Arhenius base	☐
D2 :	Bronsted base	☐
D3 :	Lewis definition of acids and bases	☐
D4 :	Arhenius acid	☐
D5 :	Bronsted acid	☐
D6 :	Lewis definition of acids and bases	☐
D7 :	Ortho effect	☐
D8 :	Tautomerism	☐

Theories (Th)		
Th1 :	Bases	☐
Th2 :	Basic strength of aromatic amines and substituted anilines	☐
Th3 :	Solvent effect in bases	☐
Th4 :	Reactions of bases	☐
Th5 :	Acids	☐
Th6 :	Ortho effect	☐
Th7 :	Reactions of acids with salts	☐
Th8 :	Tautomerism	☐
Th9 :	Keto-enol tautomerisation	☐
Th10:	Racemisation and D-exchange	☐
Th11:	Other examples of tautomers	☐

Exercise-1

Marked questions are recommended for Revision.
चिन्हित प्रश्न दोहराने योग्य प्रश्न है।

PART - I : SUBJECTIVE QUESTIONS

भाग - I : विषयात्मक प्रश्न (SUBJECTIVE QUESTIONS)

Section (A) : Basic strength

खण्ड **(A) :** क्षारीय सामर्थ्यता

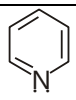
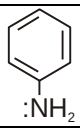
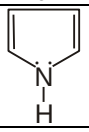
A-1. Compare the basic strength of the following compounds:
(निम्न यौगिको की क्षारीय सार्म्थयता की तुलना कीजिए :)

$C_2H_5O^-$ **(I)** $C_2H_5^-$ **(II)** $C_2H_5NH^-$ **(III)** NH_2^- **(IV)** F^- **(V)**

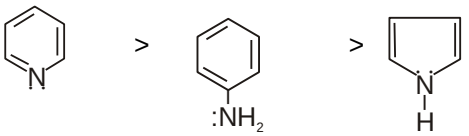
Ans. II > III > IV > I > V

Sol. In a period left to right electron negativity increases so electron donation tendency decreases.
आर्वत मे बांये से दांये जाने पर विद्युतऋणता बढ़ती है। अतः इलेक्ट्रॉन दान करने की क्षमता घटती है।

A-2. Compare the basic strength of the following compounds :
निम्नलिखित यौगिकों की क्षारीय सामर्थ्य की तुलना कीजिए :

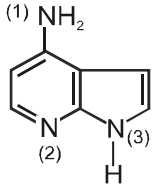
(a)	$PhNH_2$	Ph_2NH	Ph_3N
(b)			
(c)	$CH_3–\underset{\displaystyle Ph}{\underset{\vert}{CH}}–NH_2$	$CH_3–CH_2–\underset{\displaystyle Ph}{\underset{\vert}{\ddot{N}H}}$	$Ph–CH_2–CH_2–NH_2$

Ans. (a) $PhNH_2$ > Ph_2NH > Ph_3N

(b) 

(c) $Ph–CH_2–CH_2–NH_2$ > $CH_3–\underset{\displaystyle Ph}{\underset{\vert}{CH}}–NH_2$ > $CH_3–CH_2–\underset{\displaystyle Ph}{\underset{\vert}{\ddot{N}H}}$

A-3. Which of the following group is most basic in the given compounds :
दिये गये यौगिक में निम्न में से कौनसा समूह सबसे अधिक क्षारीय है :



Ans. 2

A-4. Which of the following is a stronger base ? Give reason to justify your answer.
निम्न में से कौनसा प्रबल क्षार है? अपना उत्तर सही कारण सहित दे।

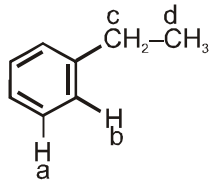
$CH_2 = CH – \ddot{N}H_2$ (I) $\qquad$ $CH_2 = \ddot{N} – CH_3$ (II)

Ans. I is less basic than II because, in compound (I) the lone pair of electrons is involved in resonance but not in II.
I, II से कम क्षारीय है क्योंकि (I) यौगिक में एकाकी इलैक्ट्रॉन युग्म अनुनाद में भाग लेते है जबकि II यौगिक में नहीं।

Section (B) : Acidic Strength

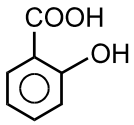
खण्ड **(B) :** अम्लीय सामर्थ्यता

B-1. Which 'H' atom is most acidic in the following compounds.
निम्न यौगिकों में कौनसा 'H' परमाणु अधिक अम्लीय है।

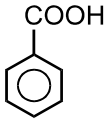
(I) $\overset{a}{CH_3}-\overset{b}{CH}=\overset{c}{CH_2}$ (II) $\overset{a}{CH_3}-\overset{O}{\overset{\|}{C}}-\overset{b}{CH_2}-\overset{O}{\overset{\|}{C}}-\overset{c}{H}$ (III) 

Ans. I - a, II - b, III - c, (acidic strength $\propto$ stability of conjugate base)
I - a, II - b, III - c, (अम्लीय सामर्थ्यता $\propto$ सयुग्मित क्षार का स्थायित्व)

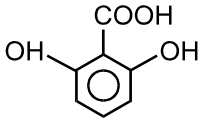
B-2. Arrange the following in decreasing order of acidity (निम्न को अम्लीयता के घटते हुए क्रम में व्यवस्थित करें।)



I

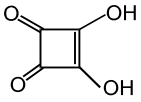


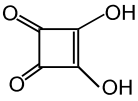
II

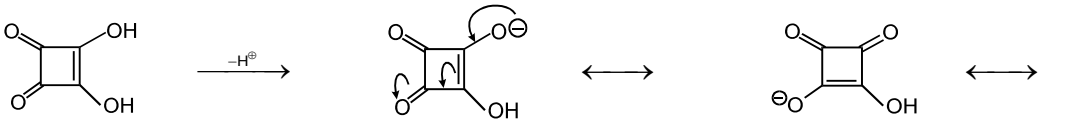


III

Ans. III > I > II (acidic strength $\propto$ stability of conjugate base) In III conjugate base is highly stabilised by intra molecular H-bonding.
III > I > II (अम्लीय सार्म्थयता $\propto$ सयुग्मित क्षार का स्थायित्व) III में संयुग्मित क्षार अन्तः आण्विक हाइड्रोजन बंध द्वारा अधिक स्थायित्व प्राप्त करता है।

B-3. The given compound X =  is a strong acid. Justify this statement.

यौगिक X =  एक प्रबल अम्ल है। इस कथन का सही स्पष्टीकरण कीजिए।

Ans. 

etc. इत्यादि

Its conjugate base (anion) is resonance stabilised like $RCOO^{\ominus}$ anion of carboxylic acid.
इसका संयुग्मित क्षार (ऋणायन) अनुनादी स्थायित्व रखता है। जैसे काबॉसिलिक अम्ल का $RCOO^{\ominus}$ ऋणायन।

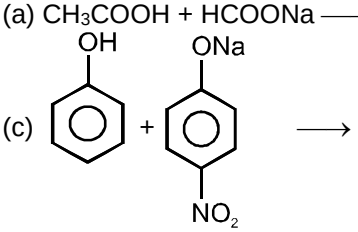
Section (C) : Feasible Reactions of Acids and Bases

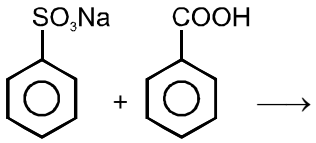
खण्ड **(C) :** अम्ल तथा क्षार की सुसंगत अभिक्रियाएँ

C-1. Which of the follwing reactions is/are feasible ?
निम्न में से कौनसी अभिक्रियाऐं सुसंगत हैं ?

(a) $CH_3COOH + HCOONa \longrightarrow$

(b) $HC \equiv C - Na + H_2O \longrightarrow$

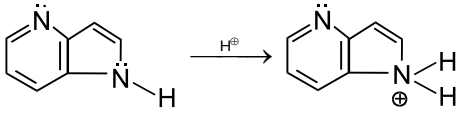
(c) 

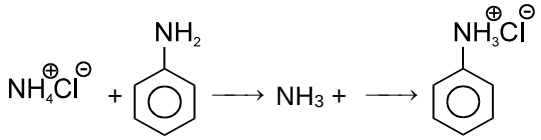
(d) 

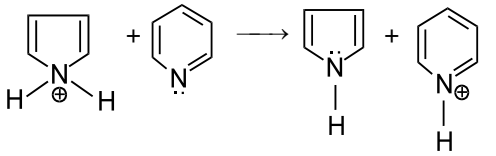
Ans. (a) Not feasible (सुसंगत नहीं) (b) Feasible (सुसंगत)
(c) Not feasible (सुसंगत नहीं) (d) Not feasible (सुसंगत नहीं)

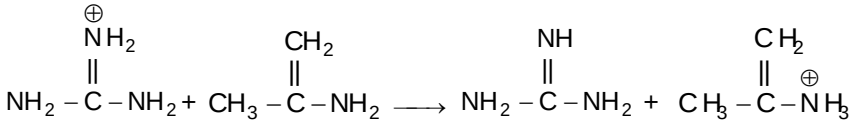
Sol. Stronger acid displace the weaker acid from the salt of weaker acid.
प्रबल अम्ल, दुर्बल अम्ल के लवण से दुर्बल अम्ल को विस्थापित कर देता है।

C-2. Which of the following reaction is feasible?
निम्न में से कौनसी अभिक्रिया सुसंगत हैं ?

(a) 

(b) 

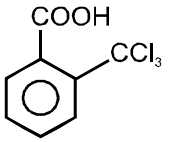
(c) 

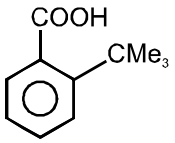
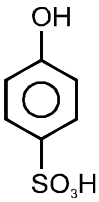
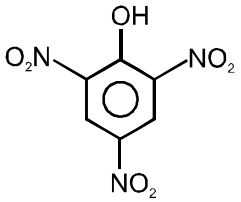
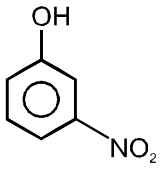
(d) 

Ans. (c) Strong base accept H^+ ions so this reaction is feasible.
(c) प्रबल क्षार H^+ आयन को ग्रहण करता है। अतः यह अभिक्रिया सुसंगत है।

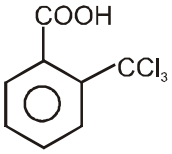
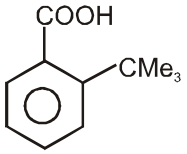
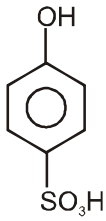
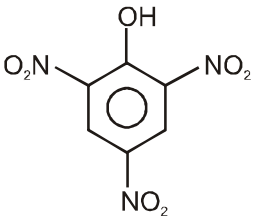
Sol. On the basis of availability of electron pair. (इलैक्ट्रॉन युग्म की उपलब्धता के आधार पर)

C-3. Which of the following acids (given below) react with $NaHCO_3$ and liberate $CO_2(g)$?
कितने अम्ल (नीचे दिये गये) $NaHCO_3$ के साथ क्रिया कर $CO_2(g)$ निष्कासित करते हैं?

$CCl_3–COOH$ $CH_3–CH_2–OH$  HCl

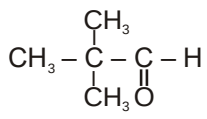
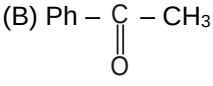
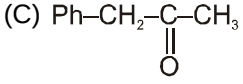
Ans. (i, iii, iv, v, vi, vii)

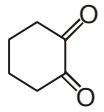
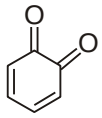
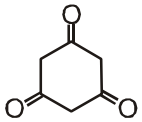
Sol. $CCl_3–COOH$, HCl,  ,  ,  , 

Section (D) : Tautomerism

खण्ड **(D) :** चलावयवता

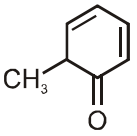
D-1. Which of the following compounds can exhibit tautomerism ?
निम्न में से कौनसा यौगिक चलावयवता प्रदर्शित करता ?

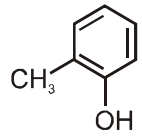
(A)  (B)  (C)  (D) 

(E)  (F)  (G)  (H) 

Sol. B, C, E, G, H can show tautomerism.
Sol. B, C, E, G, H चलावयवता दर्शाते है।

D-2. Write the tautomers of the following compounds :
दिये गये यौगिको के चलावयवी लिखिए :

(P) $CH_3-\overset{\overset{O}{\|}}{C}-CH_3$ (Q) $CH_3–CH=NH$ (R) $CH_3-\underset{\underset{CH_3}{|}}{CH}-NO_2$ (S) 

Sol. (P) $CH_3-\overset{\overset{OH}{|}}{C}=CH_2$ (Q) $CH_2=CH–NH_2$ (R) $CH_3-\underset{\underset{CH_3}{|}}{C}=N\begin{matrix}\nearrow O\\ \searrow OH\end{matrix}$ (S) 

D-3. Monocarbonyl compounds have very small percentage enol form at equilibrium. Explain.
मोनोकार्बोनिल यौगिको में साम्यवस्था पर ईनॉल रूप बहुत कम होता है, समझाइये।

Sol. In Monocarbonyl Keto form is more stable due to greater strength of the carbon-oxygen double bond as compared to the carbon carbon double bond.
मोनोकार्बोनिल यौगिको में कीटो रूप अधिक स्थायी होता है क्योकि कार्बन–ऑक्सीजन द्विबन्ध, कार्बन–कार्बन द्विबन्ध की तुलना में अधिक स्थायी होता है।

PART - II : ONLY ONE OPTION CORRECT TYPE

भाग - II : केवल एक सही विकल्प प्रकार (ONLY ONE OPTION CORRECT TYPE)

Section (A) : Basic strength

खण्ड **(A) :** क्षारीय सामर्थ्यता

A-1. The correct basic strength order of following anions is :
निम्न ऋणायनों में क्षारीय सामर्थ्य का सही क्रम है :

(A) $CH_3–\overset{\ominus}{C}H_2 > \overset{\ominus}{N}H_2 > CH_2=\overset{\ominus}{C}H > CH\equiv\overset{\ominus}{C} > H\overset{\ominus}{O} > \overset{\ominus}{F}$

(B) $\overset{\ominus}{N}H_2 > CH_3–\overset{\ominus}{C}H_2 > CH_2=\overset{\ominus}{C}H > CH\equiv\overset{\ominus}{C} > \overset{\ominus}{F} > H\overset{\ominus}{O}$

(C*) $CH_3–\overset{\ominus}{C}H_2 > CH_2=\overset{\ominus}{C}H > \overset{\ominus}{N}H_2 > CH\equiv\overset{\ominus}{C} > H\overset{\ominus}{O} > \overset{\ominus}{F}$

(D) $\overset{\ominus}{F} > H\overset{\ominus}{O} > CH\equiv\overset{\ominus}{C} > CH_2=\overset{\ominus}{C}H > \overset{\ominus}{N}H_2 > CH_3–\overset{\ominus}{C}H_2$

Sol. Basicity is inversely related to stability of anions. क्षारीयता ऋणायनों के स्थायित्व के व्युत्क्रमानुपाती होती है।

A-2. Which of the following shows the correct order of decreasing basicity in gas phase ?
निम्न में से कौनसा क्रम गैसीय अवस्था में क्षारीयता के सही घटते हुए क्रम को प्रदर्शित करता है?

(A*) $(CH_3)_3N > (CH_3)_2NH > CH_3NH_2 > NH_3$ (B) $(CH_3)_2NH > (CH_3)_3N > CH_3NH_2 > NH_3$
(C) $(CH_3)_2NH > CH_3NH_2 > (CH_3)_3N > NH_3$ (D) $(CH_3)_2NH > CH_3NH_2 > NH_3 > (CH_3)_3N$

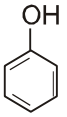
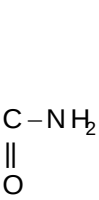
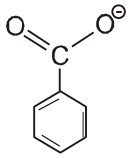
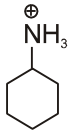
Sol. $(CH_3)_3N > (CH_3)_2NH > CH_3NH_2 > NH_3$

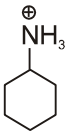
A-3. Find the order of basic strength. (If R = Me)? क्षारीय सामर्थ्य का क्रम बताइये। (यदि R = Me) ?

(I) $R_4N^+OH^-$ (II) R_3N (III) R_2NH (IV) RNH_2
(A*) I > III > IV > II (B) IV > III > I > II (C) II > IV > III > I (D) II > IV > I > III

Sol. (A) Anionic bases are stronger than neutral bases and (2º Amine > 1º Amine > 3º Amine > NH_3)
(A) ऋणायनिक क्षार उदासीन क्षार से अधिक क्षारीय होते है एवं (2º एमीन > 1º एमीन > 3º एमीन > NH_3)

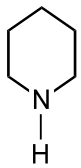
A-4. Which of the following cannot be a base? निम्न में से कौन क्षार नही हो सकता?

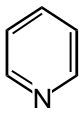
(A)  (B)  (C)  (D*) 

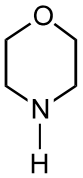
Sol. 

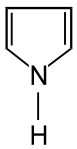
It does not have any lone pair of electrons to donate to $H^{\oplus}$ ion.
इसके पास $H^{\oplus}$ को देने के लिये कोई एकाकी इलैक्ट्रॉन युग्म नहीं है।

A-5. Select the basic strength order of following molecules ?
निम्नलिखित यौगिकों के लिये क्षारीय सामर्थ्य का सही क्रम होगा ?


(I) Piperidine
(I) पिपरीडीन


(II) Pyridine
(II) पिरीडीन

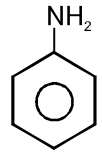

(III) Morpholine
(III) मोर्फोलीन

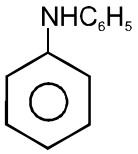

(IV) Pyrrole
(IV) पायरोल

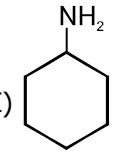
(A) (IV) > (I) > (III) > (IV)
(B) (III) > (I) > (IV) > (II)
(C) (II) > (I) > (III) > (IV)
(D*) (I) > (III) > (II) > (IV)

Sol. (I) sp^3 'N', (III) sp^3 'N' and – I effect, (II) sp^2 'N' , (IV) Aromaticity (lp delocalised)
Sol. (I) sp^3 'N', (III) sp^3 'N' एवं – I प्रभाव, (II) sp^2 'N', (IV) एरोमेटिकता (lp विस्थानिकृत)

A-6. Arrange the following in increasing order of pKa value ?
निम्न को pKa मान के बढते हुये क्रम में व्यवस्थित कीजिए ?

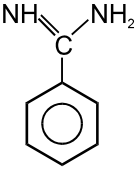
(I) 
(A*) II < I < III

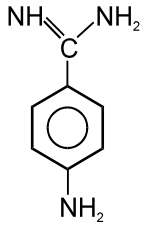
(II) 
(B) III < I < II

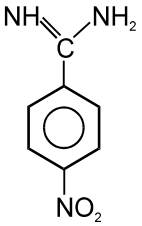
(III) 
(C) III < II < I

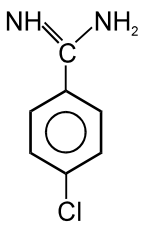
(D) II < III < I

A-7. Select the decreasing order of relative basic strengths of following species :
नीचे दिये गये यौगिकों के लिये क्षारीय सामर्थ्य का घटता हुआ क्रम बताइए :

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

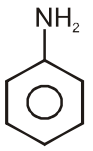
(II) 
(B) III > I > IV > II

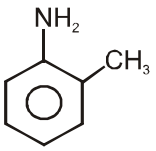
(III) 
(C) III > IV > I > II

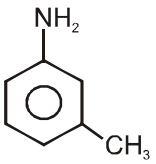
(IV) 
(D*) II > I > IV > III

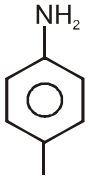
Sol. II $\rightarrow$ + M effect III $\rightarrow$ – NO_2 (–M effect) IV $\rightarrow$ – I effect
II $\rightarrow$ + M प्रभाव III $\rightarrow$ – NO_2 (–M प्रभाव) IV $\rightarrow$ – I प्रभाव

A-8. Select the basic strength order of following molecule :
निम्न अणुओं की क्षारीय सामर्थ्य के क्रम का चयन करिये :


(I)


(II)


(III)


(IV)

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

Section (B) : Acidic strength

खण्ड **(B) :** अम्लीय सामर्थ्यता

B-1. Among the following compounds, the strongest acid is :
निम्नलिखित यौगिकों में से सर्वाधिक प्रबल अम्लीय यौगिक कौनसा है :

(A) HC ≡ CH (B) C_6H_6 (C) C_2H_6 (D*) CH_3OH

Sol. Conjugate base of (D) has negative charge on oxygen.
(D) के संयुग्मी क्षार में ऋणात्मक आवेश ऑक्सीजन के पास है।

B-2. Which of the following is not correct decreasing K_a order.
निम्नलिखित में से कौनसा K_a के घटते हुये क्रम में नहीं है।

(A*) $CH_4 > NH_3 > H_2O > HF$ (B) $CH_3–OH > CH_3–NH_2 > CH_3–F > CH_3–CH_3$
(C) HI > HBr > HCl > HF (D) $PhOH > H_2O > C_2H_5OH > CH_3–C\equiv CH$

Sol. Acidic strength is directly related to stability of conjugate base.
(अम्लीय सामर्थ्य संयुग्मी क्षार के स्थायित्व के समानुपाती है।)

B-3. Which of the following acid has the smallest dissociation constant ?
निम्न में से किस अम्ल का वियोजन स्थिरांक निम्नतम है ?

(A) $CH_3–\underset{\displaystyle NO_2}{\underset{|}{CH}}–COOH$ (B) $O_2N–CH_2–CH_2–COOH$

(C*) $Cl–CH_2–CH_2–COOH$ (D) $NC–CH_2–CH_2–COOH$

B-4. Find the strongest acid among the following compounds is :
नीचे दिये गये यौगिकों में प्रबलतम अम्ल का चयन कीजिए :

(A) $HOOC–(CH_2)_2–COOH$ (B*) $H_3N^{\oplus}–(CH_2)_2–COOH$
(C) $F–(CH_2)_2–COOH$ (D) $CH_3–(CH_2)_2–COOH$

Sol. $H_3N^{\oplus}–(CH_2)_2$ – COOH has strongest acid due to strong –I effect of $-\overset{\oplus}{N}H_3$.

Sol. $H_3N^{\oplus}–(CH_2)_2$ – COOH, $-\overset{\oplus}{N}H_3$ के प्रबल –I प्रभाव के कारण प्रबलतम अम्ल है।

B-5. Which of the following option shows the correct order of decreasing acidity :
निम्न में से कौनसा विकल्प अम्लीयता के सही घटते हुए क्रम को प्रदर्शित करता है :

(A) $PhCO_2H > PhSO_3H > PhCH_2OH > PhOH$ (B) $PhSO_3H > PhOH > PhCH_2OH > PhCO_2H$
(C) $PhCO_2H > PhOH > PhCH_2OH > PhSO_3H$ (D*) $PhSO_3H > PhCO_2H > PhOH > PhCH_2OH$

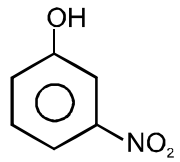
Sol. $PhSO_3H > PhCO_2H > PhOH > PhCH_2OH$.

B-6. Arrange increasing order of acidic strength of following dibasic acids :
(I) oxalic acid, (II) succinic acid, (III) malonic acid, (IV) adipic acid

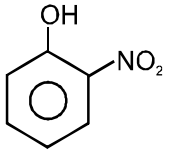
(A) III < II < I < IV (B) II < III > I > IV (C*) I > III > II > IV (D) II > I > III < IV

निम्न द्विक्षारकीय अम्लों को अम्लीय सामर्थ्य के बढ़ते हुए क्रम में व्यवस्थित कीजिए :
(I) ऑक्सेलिक अम्ल, (II) सक्सीनिक अम्ल, (III) मैलोनिक अम्ल, (IV) एडीपिक अम्ल

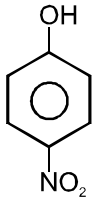
(A) III < II < I < IV (B) II < III > I > IV (C*) I > III > II > IV (D) II > I > III < IV

B-7. 

I



II



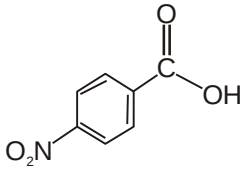
III

Arrange above phenol in increasing order of pK_a value :
उपरोक्त फीनॉल को pK_a मान के बढते हुये क्रम में व्यवस्थित कीजिए :

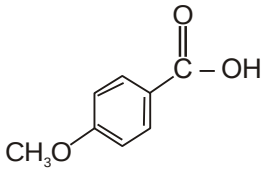
(A) I < II < III (B) III < I < II (C*) III < II < I (D) I < III < II

Sol. pK_a order (pK_a का क्रम) : I < II < III

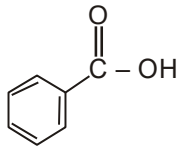
B-8. Order of K_a of following acids is : निम्नलिखित अम्लों को K_a के क्रम में व्यवस्थित करो :



I



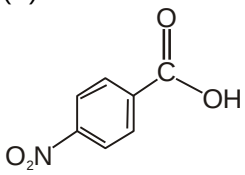
II



III

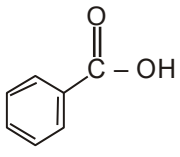
(A) I > II > III (B) II > I > III (C*) I > III > II (D) III > I > II

Sol.



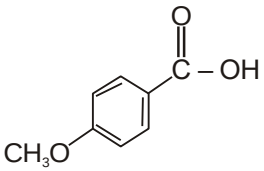
I

>



III

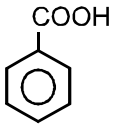
>



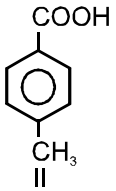
II

(Strong –I, –M effect of $–NO_2$ group) (+M effect of $–OCH_3$ group)
($–NO_2$ समूह का प्रबल –I, –M प्रभाव) ($–OCH_3$ समूह का प्रबल +M प्रभाव)

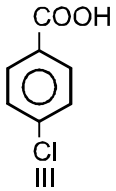
B-9. Arrange the following compounds in increasing order of their acidic strength.
निम्न यौगिकों को अम्लीय सामर्थ्य के बढ़ते हुये क्रम में व्यवस्थित करे।



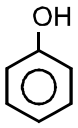
I



II



III

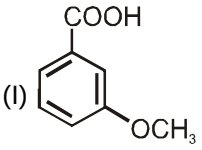


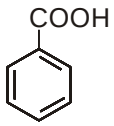
IV

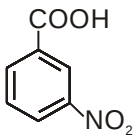
(A*) IV < II < I < III (B) I < II < III < IV (C) IV < II < III < I (D) I < III < II < IV

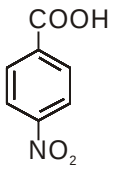
Sol. $–Cl \rightarrow –I > +M$; $–CH_3 \rightarrow$ H.C. and तथा +I

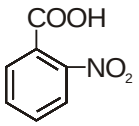
B-10. Find the order of K_a of following compounds : निम्न यौगिकों के K_a मान का क्रम ज्ञात करे :

(I) 

(II) 

(III) 

(IV) 

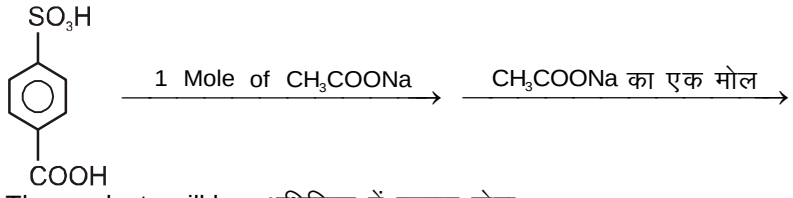
(V) 

(A) I < II < III < IV < V (B) IV < I < III < II < V (C) III < II < I < IV < V (D*) II < I < III < IV < V

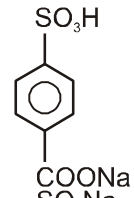
Sol. On the basis of stability of conjugate base due to electronic effects.
(इलैक्ट्रॉनिक प्रभाव के कारण संयुग्मी क्षार के स्थायित्व क्रम के आधार पर)

Section (C) : Feasible Reactions of Acids and Bases

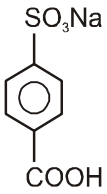
खण्ड **(C) :** अम्ल तथा क्षार की सुसंगत अभिक्रियाएँ

C-1. 

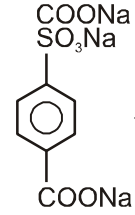
The products will be : अभिक्रिया में उत्पाद होगा :

(A) 

+ CH_3COOH

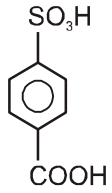
(B*) 

+ CH_3COOH

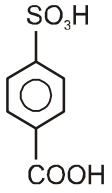
(C) 

+ CH_3COOH

(D) Reaction is not feasible (अभिक्रिया सुसंगत नहीं हैं)

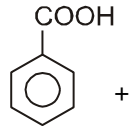
Sol. 

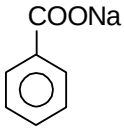
is more acidic than CH_3COOH.

हल. CH_3COOH की तुलना में यौगिक 

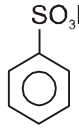
अधिक अम्लीय है।

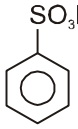
C-2. Which of the following reactions is not feasible? निम्न में से कौनसी अभिक्रियाएँ सुसंगत नहीं है?

(A) 

+ $NaHCO_3$ ⟶ 

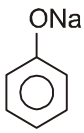
+ $H_2O + CO_2$

(B) 

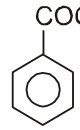
+ $NaHCO_3$ ⟶ 

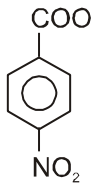
+ $H_2O + CO_2$

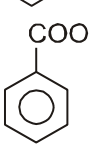
(C*) 

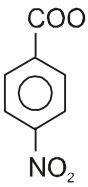
+ $NaHCO_3$ ⟶ 

+ $H_2O + CO_2$

(D) 

+ 

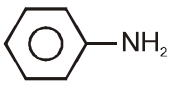
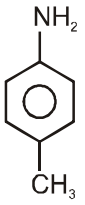
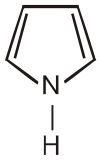
⟶ 

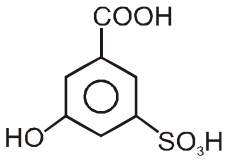
+ 

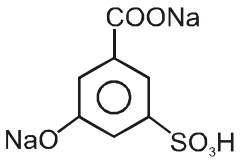
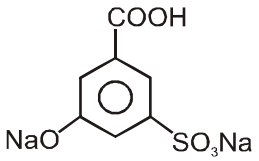
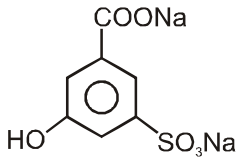
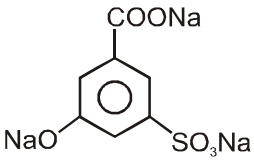
Sol. The stronger acid displaces the weaker acid from the salt of weaker acid.

हल. प्रबल अम्ल, दुर्बल अम्ल के लवण में से दुर्बल अम्ल को विस्थापित करता है।

C-3. Which of the following will accept H^+ from NH_4^+ ion. निम्न में से कौनसा NH_4^+ आयन से H^+ ग्रहण करेगाः

(A)  (B)  (C)  (D*) $CH_3–CH_2–NH_2$

C-4.  $\xrightarrow[NaHCO_3]{2\ Mole}$ Product (उत्पाद)

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

Section (D) : Tautomerism

खण्ड **(D) :** चलावयवता

D-1. Keto-enol tautomerism does not observe in : कीटो–ईनॉल चलावयवता निम्न में से किसमें नहीं होगीः

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

Sol. Due to absent of α-hydrogen with respect to C=O.

हल. C=O के सापेक्ष α-हाइड्रोजन की अनुपस्थिति के कारण।

D-2. The enolic form of acetone contains :

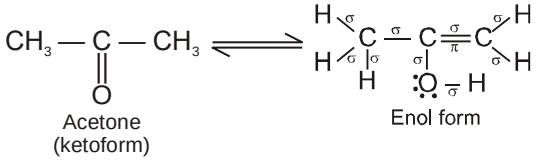
(A*) 9 σ bonds, 1 π bond and 2 lone pairs (B) 8 σ bond, 2 π bond and 2 lone pairs

(C) 10 σ bond, 1 π bond and 1 lone pair (D) 9 σ bond, 2 π bond and 1 lone pair

एसीटोन के ईनॉलिक रूप में उपस्थित है :

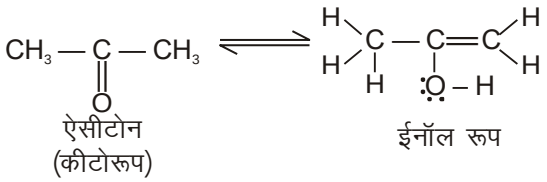
(A*) 9 σ बंध, 1 π बंध तथा 2 एकाकी इलैक्ट्रॉन युग्म (B) 8 σ बंध, 2 π बंध तथा 2 एकाकी इलैक्ट्रॉन युग्म

(C) 10 σ बंध, 1 π बंध तथा 1 एकाकी इलैक्ट्रॉन युग्म (D) 9 σ बंध, 2 π बंध तथा 1 एकाकी इलैक्ट्रॉन युग्म

Sol. 

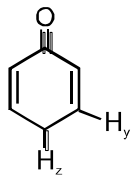
Acetone (ketoform) Enol form

9 σ bonds; 1 π bonds and 2 lonepairs.

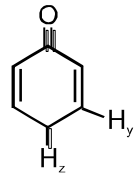


ऐसीटोन (कीटोरूप) ईनॉल रूप

9 σ बंध; 1 π बंध और 2 एकाकी इलैक्ट्रॉन युग्म

D-3. Molecule  can be enolised by which hydrogen ?

(A) y–H (B*) z–H (C) both (D) None of these

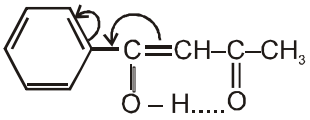
यौगिक  कौनसी हाइड्रोजन द्वारा ईनॉलीकृत होगा ?

(A) y–H (B*) z–H (C) दोनों (D) इनमें से कोई नहीं

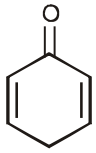
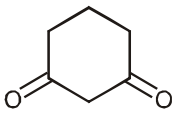
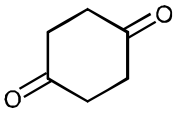
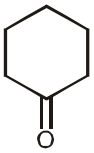
D-4. Which among the following compound will give maximum enol content in solution :
दिये गये यौगिकों में से कौनसे यौगिक का विलयन में ईनॉल घटक अधिकतम होगा।

(A*) $C_6H_5-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$ (B) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$

(C) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-CH_2-CH_3$ (D) $CH_3-\overset{O}{\overset{\|}{C}}-CH_2-COOC_2H_5$

Sol. 

D-5. Arrange the following in decreasing order of percentage enol content.
निम्न को ईनॉल घटक प्रतिशत के घटते हुए क्रम में व्यवस्थित कीजिए।

(i)  (ii)  (iii)  (iv) 

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

PART - III : MATCH THE COLUMN

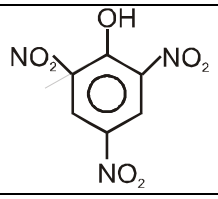
भाग - III : कॉलम को सुमेलित कीजिए (MATCH THE COLUMN)

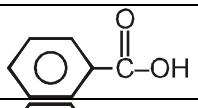
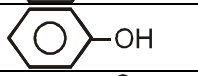
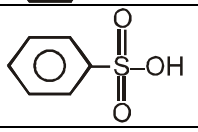
1. Match the column मिलान कीजिए :

	Column-I (Keto) कॉलम-**I (**कीटो**)**		**Column-II (% enol)** कॉलम-**II (%** ईनॉल**)**
(A)	$CH_3 - CH = O$	(x)	95 %
(B)	$Ph-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-Ph$	(y)	76 %
(C)	$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-OEt$	(z)	0.0001 %
(D)	$CH_3-\overset{O}{\overset{\|}{C}}-CH_2-\overset{O}{\overset{\|}{C}}-CH_3$	(w)	7.2 %

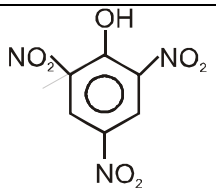
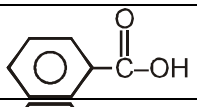
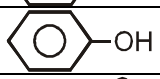
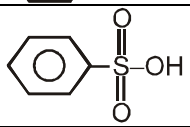
Ans (A - z) ; (B - x) ; (C - w) ; (D - y)

2. Match the column :

	Column-I		**Column-II**
(A)	$NaHCO_3$ will react with	(p)	

(B)	Na will react with	(q)	
(C)	NaOH will react with	(r)	
(D)	$NaNH_2$ will react with	(s)	

मिलान कीजिए :

	कॉलम-I		कॉलम-II
(A)	$NaHCO_3$ किसके साथ क्रिया करेगा	(p)	
(B)	Na किसके साथ क्रिया करेगा	(q)	
(C)	NaOH किसके साथ क्रिया करेगा	(r)	
(D)	$NaNH_2$ किसके साथ क्रिया करेगा	(s)	

Ans. (A - p,q,s) ; (B - p,q,r,s) ; (C - p,q,r,s) ; (D - p,q,r,s)

Exercise-2

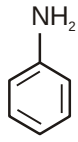
Marked questions are recommended for Revision.

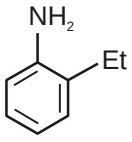
चिन्हित प्रश्न दोहराने योग्य प्रश्न है।

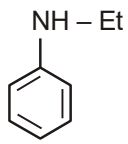
PART - I : ONLY ONE OPTION CORRECT TYPE

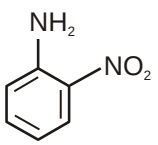
भाग-I : केवल एक सही विकल्प प्रकार (ONLY ONE OPTION CORRECT TYPE)

1. Correct basic strength order is : क्षारीय सामर्थ्य का सही क्रम है :

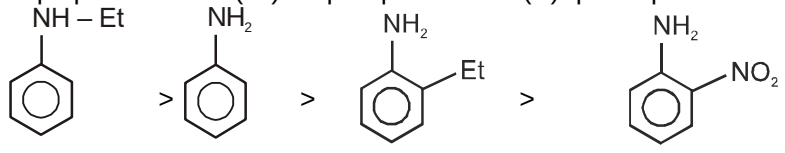

p


q


r


s

(A) r > q > p > s (B*) r > p > q > s (C) q > r > p > s (D) r > q > s > p

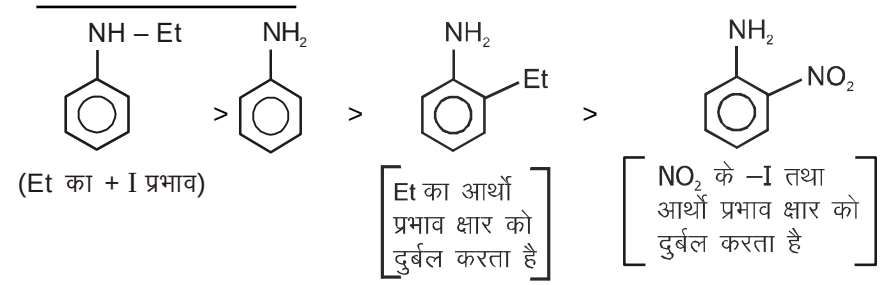
Sol.(B) 

(+ I effect of Et)

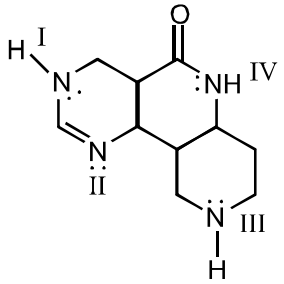
ortho effect of Et is base weakening effect

– I & ortho effect of NO_2 are base weakening effects

Sol.(B)

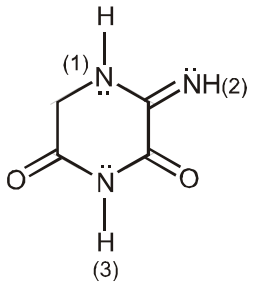


2. The order of basic strength of the given basic nitrogen atoms is :
निम्नलिखित यौगिक में दिये गये क्षारीय नाइट्रोजन परमाणुओं की क्षारीय सामर्थ्य का सही क्रम है :



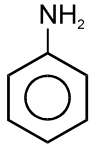
(A) III > II > I > IV (B) III > I > II > IV (C) I > III > II > IV (D*) II > III > I > IV

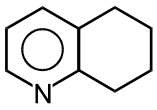
3. In the labelled N-atoms which is correct basic strength order :
अंकित नाइट्रोजन परमाणु में सही क्षारीय सामर्थ्य का क्रम है :

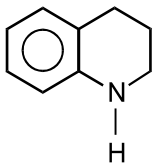


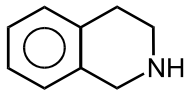
(A*) 2 > 1 > 3 (B) 3 > 1 > 2 (C) 2 > 3 > 1 (D) All are equally basic
(A*) 2 > 1 > 3 (B) 3 > 1 > 2 (C) 2 > 3 > 1 (D) सभी समान रूप से क्षारीय है।

4. Choose the strongest base among the following : निम्न में प्रबलतम क्षार का चयन कीजिये :

(A) 

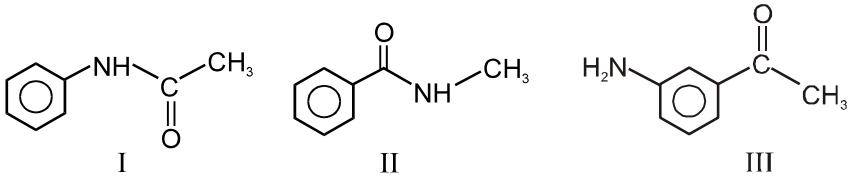
(B) 

(C) 

(D*) 

Sol. Only in (D) the ℓ.p of N atom is not involved in resonance with benzene ring.
केवल (D) में N परमाणु का एकाकी युग्म बेंजीन वलय के साथ अनुनाद में सम्मित नहीं है।

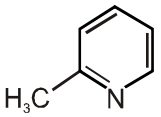
5. Select the basic strength order of following molecules?
निम्नलिखित यौगिकों के लिये क्षारीय सामर्थ्य का सही क्रम होगा ?

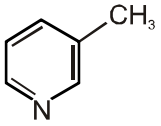


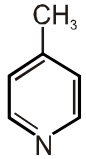
(A*) III > II > I (B) II > III > I (C) I > III > II (D) III > I > II

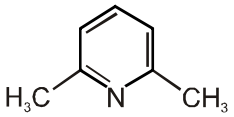
Sol. III > II > I
The basicity order is inversaly related to delocalisation of lone pair.
क्षारीय सामर्थ्य एकाकी इलैक्ट्रॉन युग्म के विस्थानीकरण के व्युत्क्रमानुपाती होता है।

6. Which is the weakest base among the followings? निम्न में से कौनसा दुर्बलतम क्षार है :

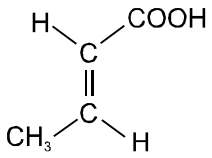
(A) 

(B) 

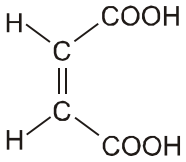
(C) 

(D*) 

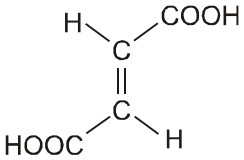
7. Write the order of K_{a_1} values of following acids : दिये गये अम्लो के K_{a_1} को घटते हुए क्रम में लिखिए :



(I)



(II)

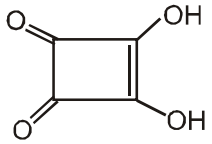


(III)

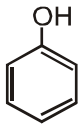
(A*) II > III > I (B) I > III > II (C) III > II > I (D) II > I > III

Sol. On the basis of electronic effect and hydrogen bonding. (इलेक्ट्रॉनिक प्रभाव एवं हाइड्रोजन बन्ध के आधार पर)

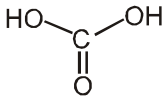
8. The acid strength order is : अम्लीय सामर्थ्य का क्रम हैं :



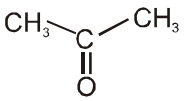
I



II



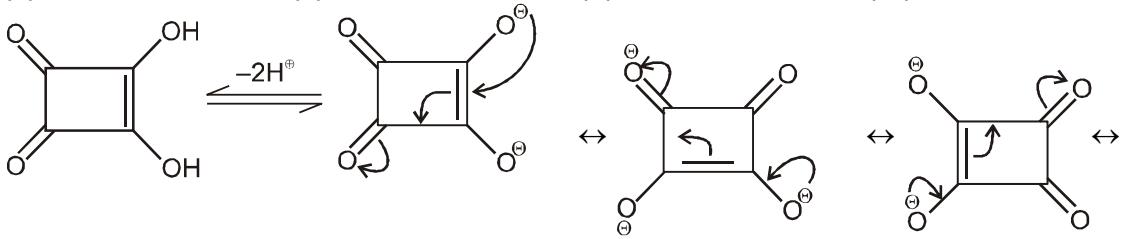
III



IV

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

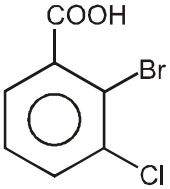
Sol.

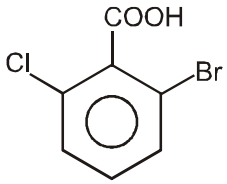


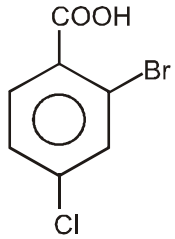
System is aromatic in nature. So, to gain aromaticity $H^{\oplus}$ are easily released.
यौगिक एरोमैटिक प्रकृति का है इसलिये एरोमैटिकता बढ़ाने के लिये $H^{\oplus}$ आसानी से दे देता है।

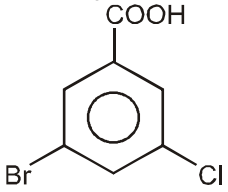
9. (X) ($C_6H_3ClBrCOOH$) are a dihalosubstituted benzoic acids. The strongest acid among all isomers is -
(X) ($C_6H_3ClBrCOOH$) एक डाईहैलो प्रतिस्थापित बेन्जोइक अम्ल है, इसके सभी समावयवीयों में से प्रबलतम अम्ल होगा

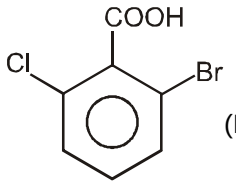
[Acid Base, Test Bank]

(A) 

(B*) 

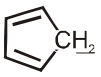
(C) 

(D) 

Sol. 

(Due to ortho effect) (ओर्थो प्रभाव के कारण)

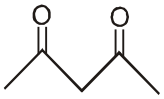
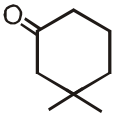
10. The order of acidity of the H-atoms underlined in the following compounds is in the order :
निम्न यौगिकों में रेखांकित H परमाणु की अम्लीयता का क्रम है :

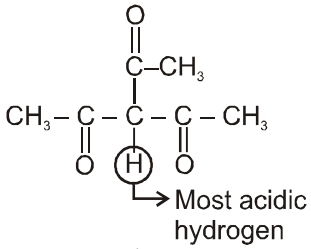
(I) Ph-$C\underline{H_2}$-CH_3 (II) Ph–CH=CH–$C\underline{H_3}$ (III) Ph-CH=$C\underline{H_2}$ (IV) 

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

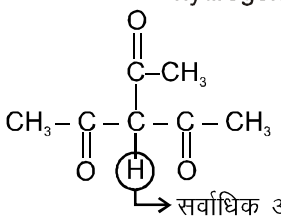
Sol. IV > II > I > III
Structure IV is most acidic as the conjugate base is aromatic.
संरचना IV सर्वाधिक अम्लीय है क्योंकि इसका संयुग्मी क्षार एरोमैटिक है।

11. Most acidic hydrogen is present in : निम्न में सर्वाधिक अम्लीय हाइड्रोजन उपस्थित हैं :

(A)  (B)  (C*) $(CH_3CO)_3CH$ (D) $(CH_3)_3COH$

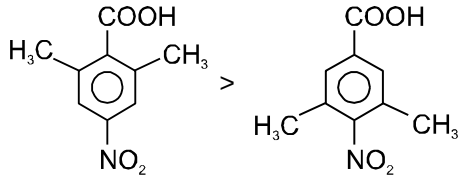
Sol. (C) 

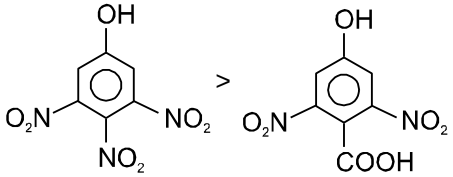
(Active methylene group).

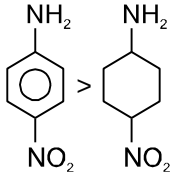
हल : (C) 

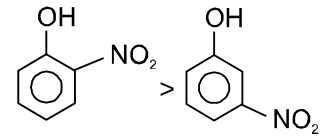
(सक्रिय मेथिलीन समूह)

12. The correct orders are : दिये गये यौगिकों में सही क्रम है :

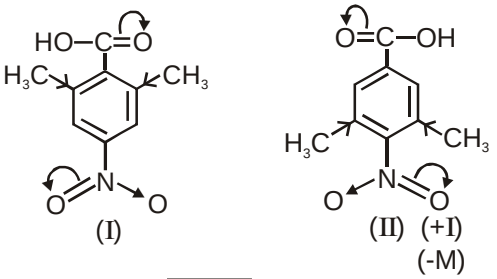
(A*)  Acid strength (अम्लीय सामर्थ्य)

(B)  Acid strength (अम्लीय सामर्थ्य)

(C)  Basic strength (क्षारीय सामर्थ्य)

(D)  Boiling point (क्वथनांक बिन्दु)

Sol.

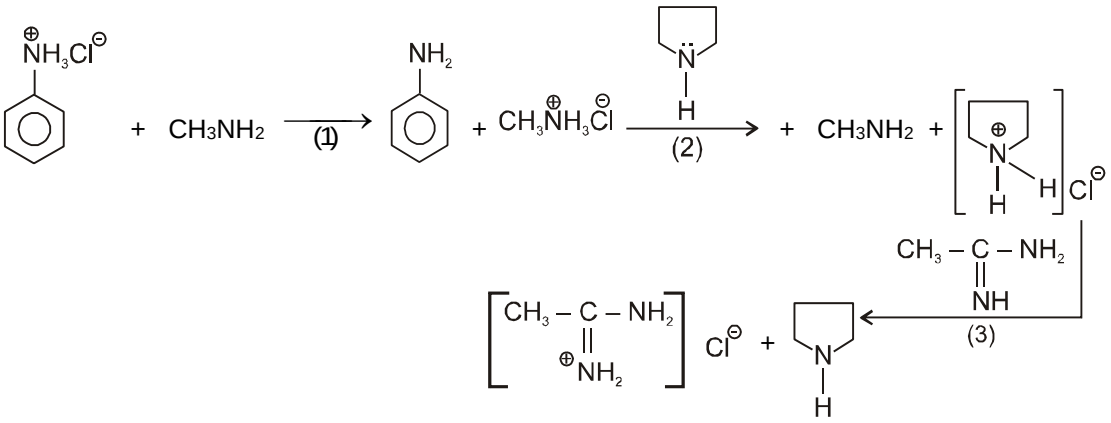


(I) (II) (+I) (-M)

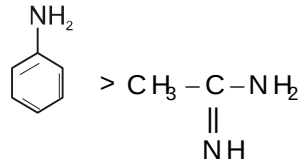
acidic order is $\boxed{I > II}$. due to the presence of ortho effect on – COOH group

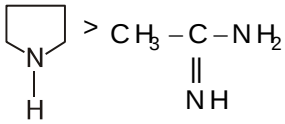
अम्लीयता का क्रम $\boxed{I > II}$ है। – COOH समूह पर ऑर्थो प्रभाव की उपस्थिति के कारण

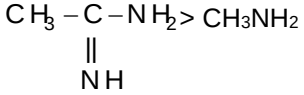
13. Observe the following sequence of reactions :
निम्न अभिक्रिया क्रम को ध्यान पूर्वक देखिये :

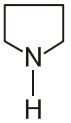


Select the correct option regarding the relative basic strength (K_b) :
क्षारीय सामर्थ्य (K_b) के सन्दर्भ में सही विकल्प का चयन कीजिए :

(A) 

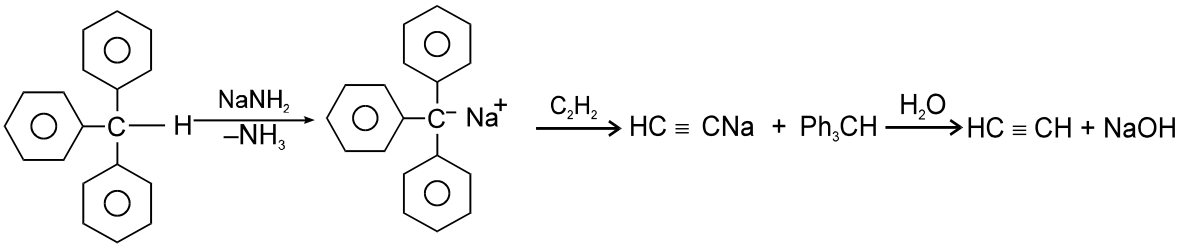
(B) 

(C*) 

(D) CH_3NH_2 > 

Sol. On the basis of availability of electron pair. (इलैक्ट्रॉन युग्म की उपलब्धता के आधार पर)

14. Order of K_a which can be predicted by following reaction is :
निम्नलिखित अभिक्रिया के आधार पर K_a का क्रम क्या होगा :



(A) $NH_3 > Ph_3CH > C_2H_2 > H_2O$ (B*) $H_2O > HC \equiv CH > Ph_3CH > NH_3$

(C) $HC \equiv CH > H_2O > Ph_3CH > NH_3$ (D) $Ph_3CH > HC \equiv CH > H_2O > NH_3$

Sol. On the basis of stability of conjugate base due to electronegativity.
(विद्युतऋणता के कारण संयुग्मी क्षार के स्थायित्व क्रम के आधार पर)

15. The gases produced in the following reactions are respectively
निम्न अभिक्रियाओं से उत्पन्न गैंस क्रमशः होगी –

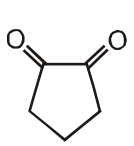
I : $CH_3NH_2 + NH_4Br \longrightarrow$

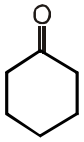
II : $CH_3SO_3H + NaHCO_3 \longrightarrow$

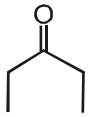
III : $CH_3-\underset{\underset{O}{\|}}{C}-NH_2 + NaH \longrightarrow$

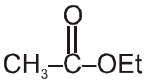
(A) NH_3, NH_3, CO_2 (B) NH_3, SO_2, H_2 (C) NH_3, SO_2, NH_3 (D*) NH_3, CO_2, H_2

16. Decreasing order of enol content of the following compounds in liquid phase
निम्न यौगिकों की द्रव अवस्था में ईनॉल घटक प्रतिशत का घटता हुआ क्रम है :


(1)


(2)


(3)



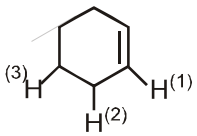
(4)

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

PART - II : SINGLE AND DOUBLE VALUE INTEGER TYPE

भाग - II : एकल एवं द्वि–पूर्णांक मान प्रकार (SINGLE AND DOUBLE VALUE INTEGER TYPE)

1. Consider following compound, which H-atom deprotonated first ?
निम्न यौगिक में कौनसे हाइड्रोजन परमाणु का विप्रोटिनीकरण पहले होगा ?

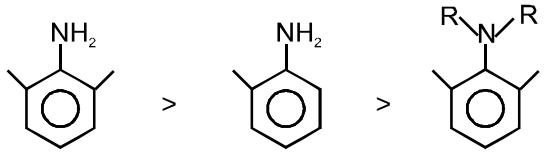


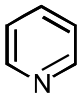
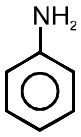
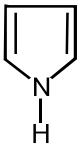
Ans. 2

2. How many of the following are correct orders for Basic Strength :
निम्न में से कितनों का क्षारीय सामर्थ्य का क्रम सही है :

S_1 : $CH_3-\underset{\underset{CH_3}{|}}{NH} > CH_3-NH_2 > CH_3-\underset{\underset{CH_3}{|}}{N}-CH_3$

S_2 : $C_2H_5-\underset{\underset{C_2H_5}{|}}{NH} > C_2H_5-\underset{\underset{C_2H_5}{|}}{NH}-C_2H_5 > C_2H_5-NH_2$

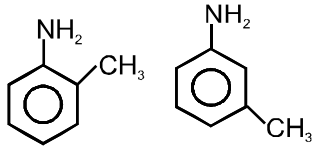
S_3 :  > >

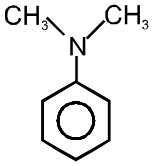
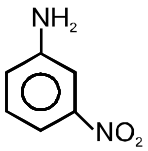
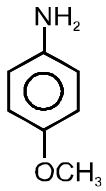
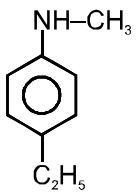
S_4 :  >  > 

S_5 :  >  > $C_2H_5–NH_2$

Ans. 4 (S_1, S_2, S_4, S_5)

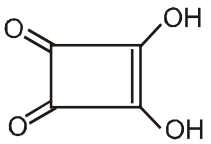
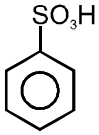
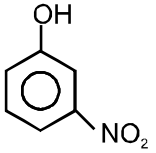
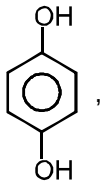
3. How many following compounds are more basic than aniline.
निम्न में से कितने यौगिक एनीलिन से अधिक क्षारीय है।

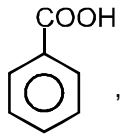
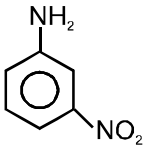
 $CH_3–CH_2= NH$

Ans. 5 (ii, iii, iv, vi, vii)

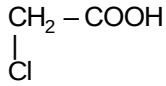
4. How many of the following compounds give CO_2 on reaction with $NaHCO_3$.
निम्न में से कितने यौगिक $NaHCO_3$ के साथ अभिक्रिया पर CO_2 देते है।

 , HCl,  ,  ,  ,

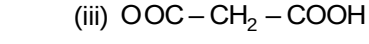
 , HCOOH, $C_2H_5–OH$, CH_3COOH, 

Ans. 6 (i, ii, iii, vi, vii, ix)

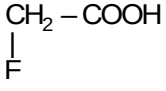
5. How many of the following are more acidic than HCOOH.
निम्न में से कितने HCOOH की तुलना में अधिक अम्लीय है।

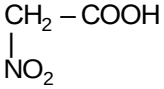
(i) 

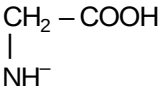
(ii) $CH_3–COOH$

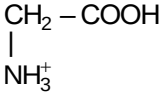
(iii) 

(iv) $NC–CH_2–COOH$

(v) 

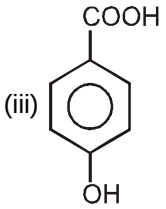
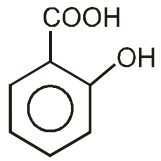
(vi) 

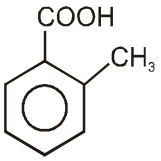
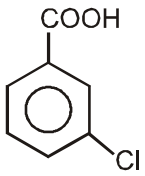
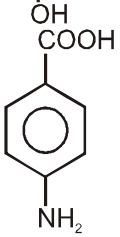
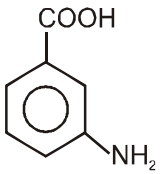
(vii) 

(viii) 

Ans. 5 (i, iv, v, vi, viii)

6. How many of the following compound have less pKa than benzoic acid :
निम्न में से कितने यौगिकों का pKa मान बैन्जोइक अम्ल से कम है।

(i) HCOOH (ii) CH_3COOH (iii)  (iv) 

(v)  (vi)  (vii)  (viii) 

Ans. 5 (i, iv, v, vi, viii)

7. 90 g of acetic acid react with excess of $NaHCO_3$ then what volume of CO_2 will produce at S.T.P. Write your answer in terms of nearest integer.
S.T.P. पर 90 ग्राम एसीटिक अम्ल $NaHCO_3$ के आधिक्य के साथ क्रिया करता है तब CO_2 का कितना आयतन निर्मित होगा। अपना उत्तर समीपस्थ पूर्णांक में दीजिए।

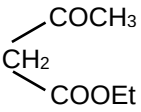
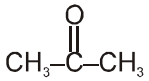
Ans. 34

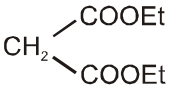
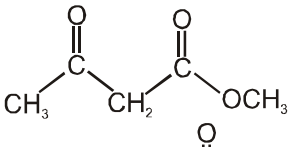
Sol. $CH_3COOH + NaHCO_3 \longrightarrow CH_3COONa + H_2O + CO_2$

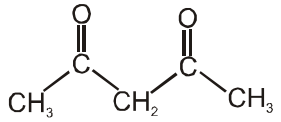
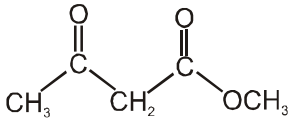
$n = \frac{90}{60} = 1.5$

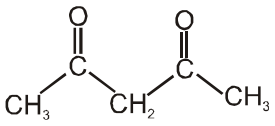
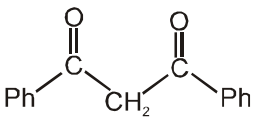
$v = 22.4 \times 1.5 = 33.6 \approx 34$

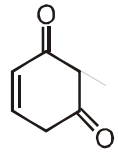
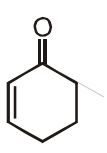
8. In how many of the following pairs first will have higher enol content than second.
निम्न में से कितने यौगिकों के युग्म प्रथम यौगिक द्वितीय की तुलना में अधिक ईनॉल घटक रखता है।

(i)  & 

(ii)  & 

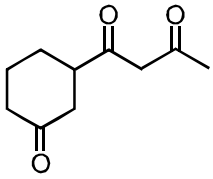
(iii)  & 

(iv)  & 

(v)  & 

Ans. 3

9. Consider the following compound and write number of enolizable H-atom
निम्न यौगिक में उपस्थित ईनोलीकरण योग्य H-परमाणु की संख्या लिखिए।



Ans 10

PART - III : ONE OR MORE THAN ONE OPTIONS CORRECT TYPE

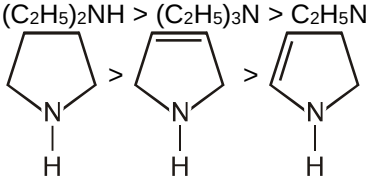
भाग - III : एक या एक से अधिक सही विकल्प प्रकार

1. Which of the following is/are correct for basic strength : **[Made by SNC_2015]**
क्षारीय सामर्थ्य के लिए निम्न में से कौनसे विकल्प सही है/हैं :

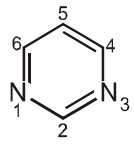
(A) $(CH_3)_2NH > (CH_3)_3N > CH_3NH_2 > NH_3$

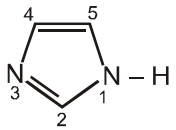
(B*) $(C_2H_5)_2NH > (C_2H_5)_3N > C_2H_5NH_2 > NH_3$

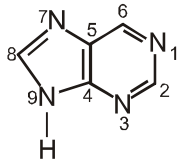
(C*) $PhNH_2 > Ph_2NH > Ph_3N$

(D*) 

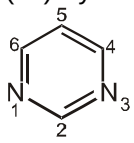
2.

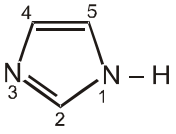

Pyrimidine

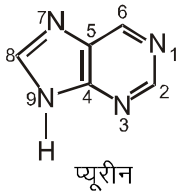

Imidazole


Purine

Among the following which statement(s) is/are correct :
(A*) Both N of pyrimidine are same basic strength
(B*) In imidazole protonation take places on N-3.
(C*) In purine only one lone pair of N is delocalised.
(D*) Pyrimidine, imidazole and purine all are aromatic.

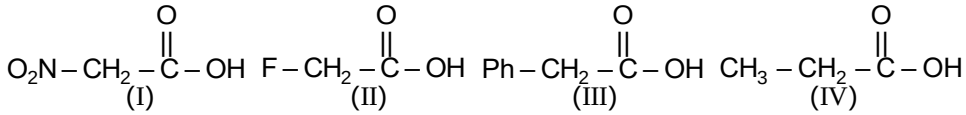

पिरीमिडीन


इमेडेजोल


प्यूरीन

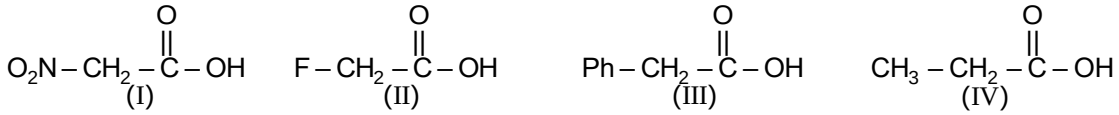
निम्न में से कौनसे कथन सही है/हैं :
(A*) पिरीमिडीन के दोनों N परमाणु समान क्षारीय सामर्थ्य रखते है।
(B*) इमेडेजोल में प्रोटीनीकरण N–3 पर होता है।
(C*) प्यूरीन में केवल एक एकाकी इलेक्ट्रॉन युग्म विस्थानीकृत है।
(D*) पिरीमिडीन, इमेडेजोल तथा प्यूरीन सभी एरोमैटिक है।

3. Consider the following compounds


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

Which statement is/are correct :
(A*) I > II > III > IV (Acidic strength order) (B) I is most acidic because of – M effect of $-NO_2$ group
(C*) I is most acidic because of – I effect of $-NO_2$ group
(D*) IV is least acidic because of + I Effect.

निम्न यौगिकों के लिए कौनसा (से) कथन सही है/हैं



(A*) I > II > III > IV (अम्लीय सामर्थ्य का क्रम)

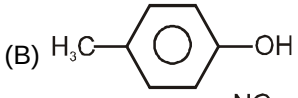
(B) $-NO_2$ समूह के –M प्रभाव के कारण I अधिक अम्लीय है

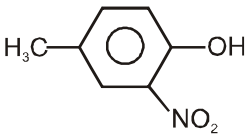
(C*) $-NO_2$ समूह के –I प्रभाव के कारण I अधिक अम्लीय है

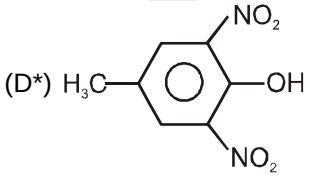
(D*) +I प्रभाव के कारण IV की अम्लीयता सबसे कम है।

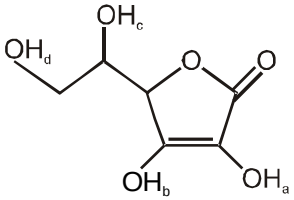
4. Carbolic acid is less acidic than : कार्बोलिक अम्ल किससे कम अम्लीय है :

(A*) CH_3COOH

(B) 

(C*) 

(D*) 

5. 

Observe the compound and choose correct statement :

(A) It has carboxylic acid group

(B*) It is Ascorbic acid

(C*) H_b is most acidic Hydrogen atom

(D) H_a is least acidic Hydrogen atom

उपरोक्त यौगिक के लिए सही कथन का चयन कीजिए :

(A) इसमें कार्बोक्सिलिक अम्ल समूह है

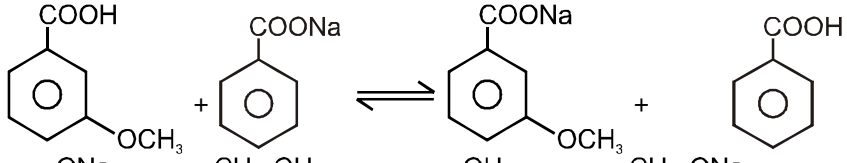
(B*) यह एस्कोर्बिक अम्ल है

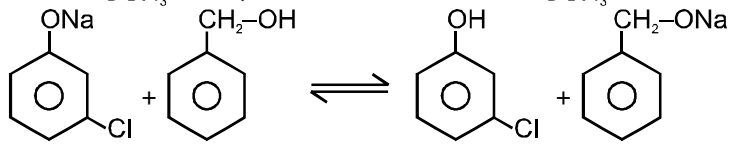
(C*) H_b अधिक अम्लीय हाइड्रोजन परमाणु है

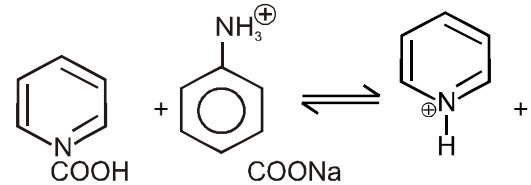
(D) H_a कम अम्लीय हाइड्रोजन परमाणु है

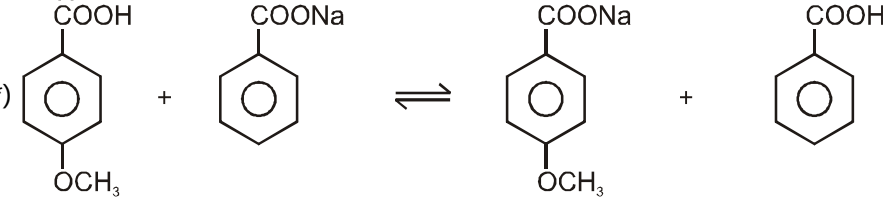
6. Which of the following reactions favour backward direction?

निम्न में से कौनसी अभिक्रिया पश्च दिशा के लिए अनुकूल है?

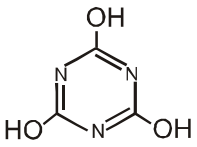
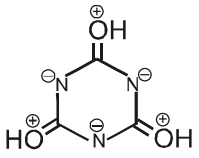
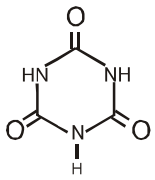
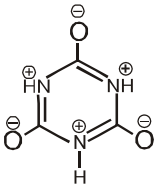
(A) 

(B*) 

(C) 

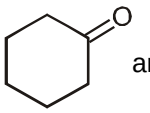
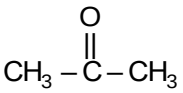
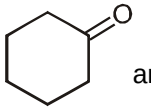
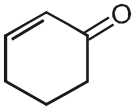
(D*) 

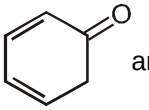
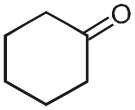
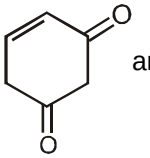
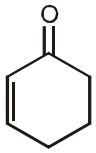
7. The **correct** statement(s) concerning the structures P, Q, R & S is/are
संरचनाओं P, Q, R तथा S के संबंध में सही कथन होगें।

(P)  **(Q)**  **(R)**  **(S)** 

(A*) Q & S are not resonating structures (B*) R & S are resonating structures
(C*) P & R are tautomers (D*) P & Q are resonating structures
(A*) Q और S अनुनादी संरचना नहीं है। (B*) R और S अनुनादी संरचना है।
(C*) P और R चलावयवी है। (D*) P और Q अनुनादी संरचना है।

8. Among the given pairs, in which pair second compound has less enol content :
कौनसे यौगिकों के युग्म में द्वितीय यौगिक कम ईनॉल घटक रखता है।

(A*)  and तथा  (B)  and तथा 

(C*)  and तथा  (D*)  and तथा 

PART - IV : COMPREHENSION

भाग - IV : अनुच्छेद (COMPREHENSION)

Read the following passage carefully and answer the questions.
निम्न अनुच्छेद को ध्यानपूर्वक पढ़िये तथा प्रश्नों के उत्तर दीजिए।

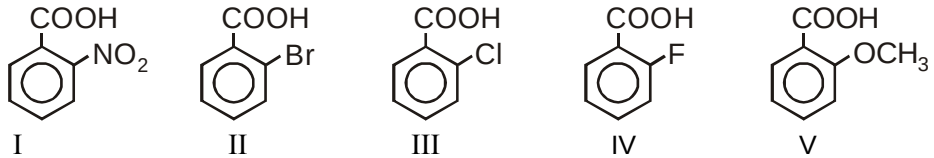
Comprehension # 1

Ortho effect is a special type of effect that is shown by o-substituents. This ortho-effect operates at the benzoic acids irrespective of the polar type. Nearly all o-substituted benzoic acid are stronger than benzoic acid. Benzoic acid is a resonance stabilised and so the carboxyl group is coplanar with the ring. An o-substituent tends to prevent this coplanarity.

अनुच्छेद **# 1**

ऑर्थो प्रभाव एक विशिष्ट प्रकार का प्रभाव होता है जो कि o-प्रतिस्थायी द्वारा दर्शाया जाता है। आर्थो प्रभाव बेन्जोइक अम्ल में प्रेक्षित होता है, चाहे प्रतिस्थापी का कोई भी ध्रुवीय प्रभाव हो। लगभग सभी o-प्रतिस्थापी बेन्जोइक अम्ल स्वयं बेन्जोइक अम्ल की अपेक्षा अधिक प्रबल होते हैं। बेन्जोइक अम्ल एक अनुनाद द्वारा स्थायित्व पाता है एंव इसलिये कार्बोक्सिल समूह वलय के साथ समतलीय होता है लेकिन o-प्रतिस्थापी इस समतलीयता को रोकने का प्रयास करता है।

1. What is the order of K_a of following compounds ? निम्न यौगिकों में K_a का क्रम क्या है ?

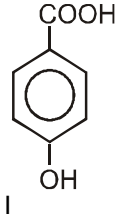


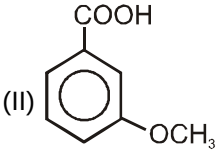
I II III IV V

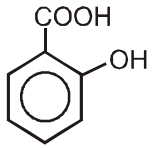
(A*) I > II > III > IV > V (B) II > I > III > IV > V (C) V > IV > III > I > II (D) III > II > I > V > IV

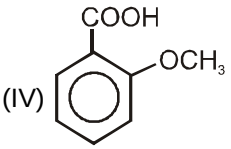
Sol. On the basis of electronic effect because ortho effect is common in all the above. (इलेक्ट्रॉनिक प्रभाव के आधार पर क्योकि ऑर्थो प्रभाव उक्त सभी में समान होता है।)

2. Which among the following will be the strongest acid ?
निम्न में से कौनसा प्रबलतम अम्ल होगा ?

(I) 

(II) 

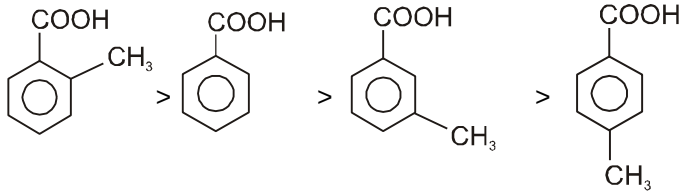
(III) 

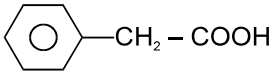
(IV) 

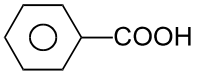
(A) I (B) II (C*) III (D) IV

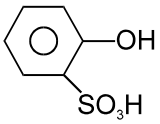
Sol. On the basis of hydrogen bonding because ortho effect is not observed by OH group.
(हाइड्रोजन बन्ध के आधार पर क्योंकि ऑर्थो प्रभाव OH समूह द्वारा प्रेक्षित नहीं होता)

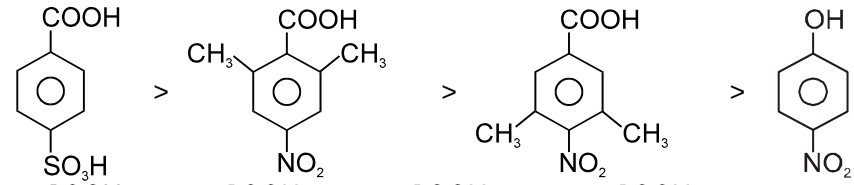
3. Which of the following is/are correct pK_a order ?
निम्नलिखित में से कौनसे विकल्पों में pK_a के क्रम का सही निर्धारण किया गया है ?

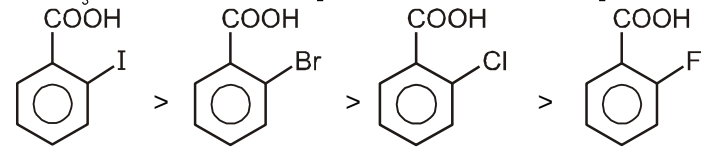
(A) 

(B*) $CH_3 - COOH >$ 

$>$ 

$>$ 

(C) 

(D) 

Sol. On the basis of electronic effect and ortho effect. (इलैक्ट्रॉनिक प्रभाव तथा ऑर्थो प्रभाव के आधार पर)

Comprehension # 2

The lone pair of amines makes them basic. They react with acids to form acid-base salts. Amines are more basic than alcohols, ethers and water. When an amine is dissolved in water, an equilibrium is established, where water acts as an acid and transfer a proton to the amine. The basic strength of an amine can be measured by basicity constant K_b.
Arylamines are less basic than alkylamines because the lone pair of nitrogen is delocalised with the aromatic ring and are less available for donation.
Substituted arylamines can be either more basic or less basic than aniline, depending on the substitutent. ERG substituents, such as $–CH_3$, $–NH_2$ and $–OCH_3$ increases the basicity and EWG substituents, such as –Cl, $–NO_2$ and –CN decreases basicity. While sp^2-hybridized nitrogen atom in pyridine is less basic than the sp^3-hybridized nitrogen in an alkylamine.

अनुच्छेद **# 2**

एमीनों के एकाकी इलैक्ट्रॉन युग्म (lone pair) उन्हें क्षारीय बनाते है। वे अम्लों से क्रिया कर अम्ल–क्षार लवण बनाते हैं। एमीन, एल्कोहॉल, ईथर एवं पानी की अपेक्षा अधिक क्षारीय हैं। जब किसी एमीन को जल में विलेय किया जाता है, तो एक साम्य स्थापित होता है, जिसमें पानी एक अम्ल की तरह कार्य करता है और एमीन को प्रोटॉन स्थानांतरित करता है। एमीन की क्षार सामर्थ्य क्षारीयता स्थिरांक K_b द्वारा ज्ञात की जा सकती है।
एरिलएमीन, एल्किलएमीन की अपेक्षा कम क्षारीय होती है, क्योंकि नाइट्रोजन पर उपस्थित एकाकी इलैक्ट्रॉन युग्म एरोमैटिक वलय के π इलैक्ट्रॉन के साथ विस्थानीकृत हो जाता है तथा दान के लिये कम उपलब्ध होते हैं।

प्रतिस्थापी एरिलएमीन एनिलीन की अपेक्षा या तो अधिक क्षारीय या कम क्षारीय हो सकते है, जो कि प्रतिस्थापी पर निर्भर करता है। ERG प्रतिस्थापी जैसे कि $–CH_3$, $–NH_2$ और $–OCH_3$ क्षारीयता को बढ़ाते हैं और EWG प्रतिस्थापी जैसे –Cl, $–NO_2$ और –CN क्षारीयता को कम करते हैं। जबकि पिरिडीन में sp^2-संकरित नाइट्रोजन परमाणु, एल्किलएमीन में sp^3-संकरित नाइट्रोजन की अपेक्षा कम क्षारीय होता है।

4. Select the correct order of K_b.

(A) CH_3NH_2 > NaOH (B) Pyridine > $CH_3–\ddot{N}H–CH_3$

(C*) p-Methyl aniline > p-Chloroaniline > p-Amino acetophenone

(D) p-Bromoaniline > p-Nitroaniline > p-Amino benzaldehyde

क्षारीय सामर्थ्य के सन्दर्भ में सही विकल्प चुनिये।

(A) CH_3NH_2 > NaOH (B) पिरीडीन > $CH_3–\ddot{N}H–CH_3$

(C*) p-मेथिल एनिलीन > p-क्लोरोएनिलीन > p-एमीनों एसीटोफिनॉन

(D) p-ब्रोमोएनिलीन > p-नाइट्रोएनिलीन > p-एमीनोबैन्जैल्डिहाइड

Sol. On the basis of electronic effect. (इलेक्ट्रॉनिक प्रभाव के आधार पर)

5. pK_b order of the following compound is :

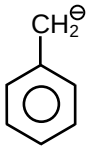
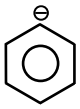
निम्न यौगिको का pK_b क्रम है :

(I) NH_2OH (II) NH_2NH_2 (III) NH_3 (IV) H_2O

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

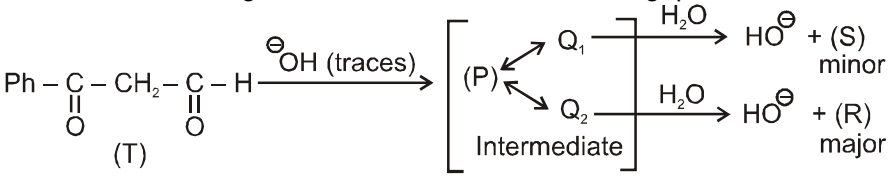
6. The most basic carbanion is : **(GOCE-CAC(O)_E_203)**

सर्वाधिक क्षारीय कार्बऋणायन है–

(A)  (B) $CH\equiv\overset{\ominus}{C}$ (C)  (D*) 

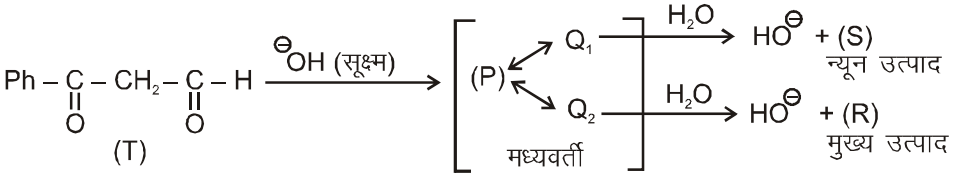
Comprehension # 3

Observe the following reaction and answer the following questions :



अनुच्छेद **# 3**

दिये गये अभिक्रिया का प्रेक्षण कीजिये एवं निम्न प्रश्नो के उत्तर दीजिये :

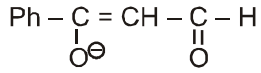


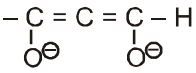
7. The product 'R' is **:** उत्पाद 'R' है :

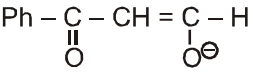
(A) $Ph–\underset{OH}{\overset{|}{C}}=C=\underset{OH}{\overset{|}{C}}–H$ (B) $Ph–\underset{O}{\overset{\|}{C}}–CH=\underset{OH}{\overset{|}{C}}–OH$

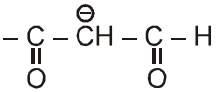
(C) $Ph–\underset{O}{\overset{\|}{C}}–CH=\underset{OH}{\overset{|}{C}}–H$ (D*) $Ph–\underset{OH}{\overset{|}{C}}=CH–\underset{O}{\overset{\|}{C}}–H$

8. The structure of Q_1 is : Q_1 की संरचना है :

(A) 

(B) 

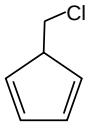
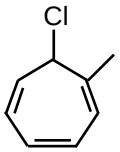
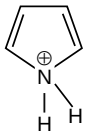
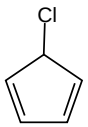
(C*) 

(D) 

Comprehension # 4

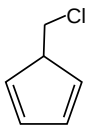
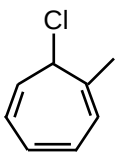
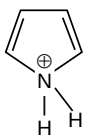
Answer Q.9, Q.10 and Q.11 by appropriately matching the information given in the three columns of the following table.

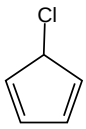
Column-1, 2 & 3 containing starting material, reaction condition & electronic effect / intermediate respectively.

Column-1		**Column-2**		**Column-3**	
(I)		(i)	$SbCl_5$ / $AlCl_{3(Anhy.)}$	(P)	Rearrangement
(II)		(ii)	Na	(Q)	Resonance
(III)		(iii)	H^+	(R)	Hyperconjugation
(IV)		(iv)	NaOH	(S)	Carbocation intermediate

अनुच्छेद **# 5**

कॉलम-1, 2 व 3 में क्रमशः प्रारम्भिक अभिकारक, अभिक्रिया परिस्थितियाँ एवं इलेक्ट्रॉनिक प्रभाव/मध्यवर्ती दिये गये है।

कॉलम**-1**		कॉलम**-2**		कॉलम**-3**	
(I)		(i)	$SbCl_5$ / $AlCl_{3(Anhy.)}$	(P)	पुर्नविन्यास
(II)		(ii)	Na	(Q)	अनुनाद
(III)		(iii)	H^+	(R)	अतिसंयुग्मनप्रभाव

(IV)		(iv)	NaOH	(S)	कार्बधनायन मध्यवर्ती

9._ Which combination will give hydrogen gas ?a
कौनसे युग्म में उत्पाद H_2 गैस प्राप्त होगी ?
(A) (III) (iii) (P) (B) (II) (ii) (R) (C*) (IV) (ii) (Q) (D) (I) (iii) (P)

10._ In which product formation is not possible ?
कौनसे युग्म में उत्पाद प्राप्त नहीं होता है ?
(A) (I) (ii) (Q) (B) (II) (i) (R) (C) (III) (ii) (Q) (D*) (IV) (i) (S)

11._ In which amongs the following aromatic product will not form ?
कौनसे युग्म में ऐरोमेटिक उत्पाद प्राप्त नहीं होता है ?
(A*) (I) (i) (P) (B) (II) (i) (Q) (C) (III) (iv) (Q) (D) (IV) (ii) (Q)

Exercise-3

PART - I : JEE (ADVANCED) / IIT-JEE PROBLEMS (PREVIOUS YEARS)

भाग - I : JEE (ADVANCED) / IIT-JEE (पिछले वर्षो) के प्रश्न

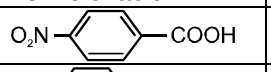
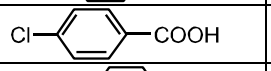
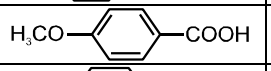
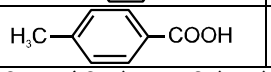
*** Marked Questions may have more than one correct option.**
***** चिन्हित प्रश्न एक से अधिक सही विकल्प वाले प्रश्न है -

1. Which of the following acid has the lowest value of acid dissociation constant : **[JEE-02(S), 3/90]**
निम्नलिखित में से कौन–से अम्ल के लिये अम्लीय वियोजन स्थिरांक (acid dissociation constant) का मान न्यूनतम है?
(A) $CH_3CHFCOOH$ (B) FCH_2CH_2COOH (C*) $BrCH_2CH_2COOH$ (D) $CH_3CHBrCOOH$

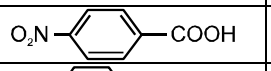
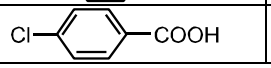
Sol. Acidic strength $\propto$ Dissociation constant of acid. In given acids order of acidic strength
CH_3 CHFCOOH > $CH_3CHBrCOOH$ > FCH_2CH_2COOH > $BrCH_2CH_2COOH$
Hence in these smallest dissociation constant for $BrCH_2$ —CH_2COOH

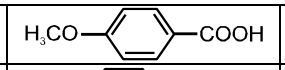
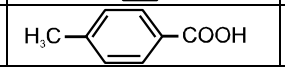
Sol. अम्लीय सामर्थ्य $\propto$ अम्ल का वियोजन स्थिरांक। अतः दिये गये अम्लों का अम्लीय सामर्थ्य निम्न होगा
CH_3 CHFCOOH > $CH_3CHBrCOOH$ > FCH_2CH_2COOH > $BrCH_2CH_2COOH$
इन सभी में $BrCH_2$ —CH_2COOH का वियोजन स्थिरांक सबसे कम है।

2. Match the K_a values : **[JEE-03(M), 2/60]**

	Compounds		**K_a**
(a)	Benzoic acid	(i)	3.3×10^{-5}
(b)		(ii)	6.3×10^{-5}
(d)		(iii)	30.6×10^{-5}
(e)		(iv)	6.4×10^{-5}
(f)		(v)	4.2×10^{-5}

निम्नलिखित यौगिकों, का दिये गये K_a के मान से उचित मिलान कीजिए।

	यौगिक		**K_a**
(a)	बैन्जोइक अम्ल	(i)	3.3×10^{-5}
(b)		(ii)	6.3×10^{-5}
(d)		(iii)	30.6×10^{-5}

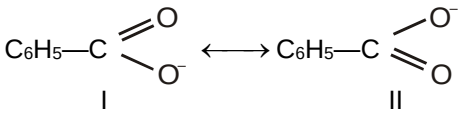
(e)		(iv)	6.4×10^{-5}
(f)		(v)	4.2×10^{-5}

Ans. (a) – (ii) (b) – (iii) (c) – (iv) (d) – (i) (e) – (v)

Sol. As we know that acid strength of acid $\propto K_a$. So higher the value of K_a, higher the acidic strength of acid.

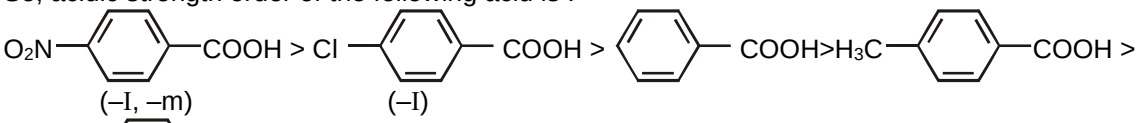
Strength of acid $\propto$ Rate of formation of proton or stability of conjugate base.

In carboxylic acid, acidic character is due to resonance stabilization of their carboxylate ion, like in benzoic acid.

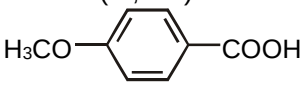


I II

So, acidic strength order of the following acid is :



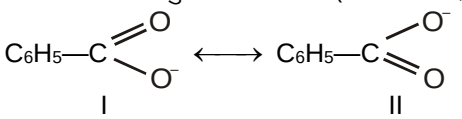
(–I, –m) (–I)



(+m)

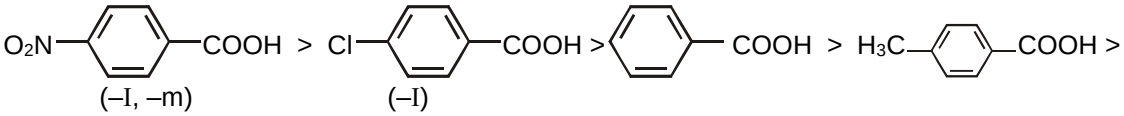
Sol. जैसा कि हम जानते हैं कि अम्ल की अम्लीय सामर्थ्य $\propto K_a$; इसलिये K_a का मान अधिक होगा तो अम्ल की सामर्थ्य भी अधिक होगी।

अम्ल की सामर्थ्य $\propto$ प्रोटोन के संभवन की दर या संयुग्मी क्षार का स्थायित्व कार्बोक्सिलिक अम्ल में, अम्लीय गुण कार्बोक्सिलेट आयन के अनुनादी स्थायित्व (जैसा बेन्जोइक अम्ल में होता है) के कारण आते है।

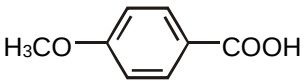


I II

i.e. निम्न अम्लो का अम्लीय सामर्थ्य का क्रम :



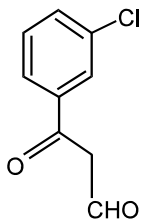
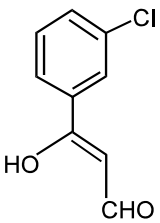
(–I, –m) (–I)

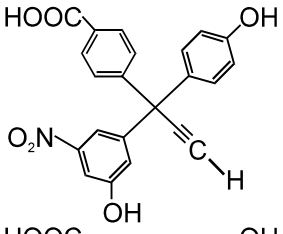


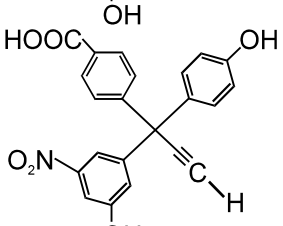
(+m)

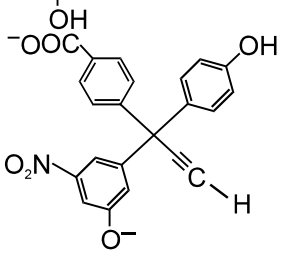
3. Compound A of molecular formula $C_9H_7O_2Cl$ exists in keto form and predominantly in enolic form 'B'. On oxidation with $KMnO_4$'A' gives m-Chlorobenzoic acid. Identify 'A' and 'B'. **[JEE(M)-03]**

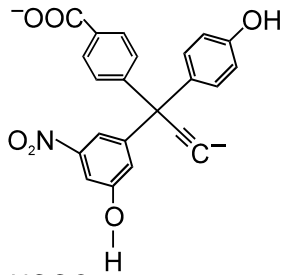
यौगिक 'A' जिसका अणुसूत्र $C_9H_7O_2Cl$ है, कीटो अवस्था में पाया जाता है तथा यह ईनॉल अवस्था 'B' में भी मुख्य रूप से पाया जाता है। $KMnO_4$ के साथ ऑक्सीकरण पर 'A' m-क्लोरोबेन्जोईक अम्ल देता है। अतः 'A' तथा 'B' की पहचान कीजिए। **[JEE(M)-03]**

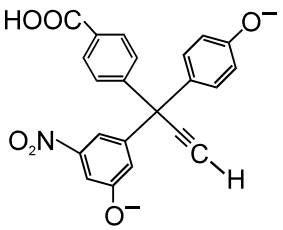
Sol. A.  B. 

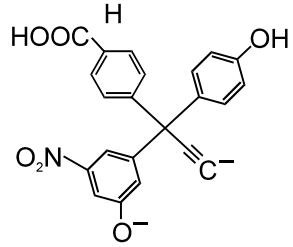
4.  $\xrightarrow{2 \text{ moles } NaNH_2}$ A , The product A will be - **[JEE-03(S), 3/84]**

 $\xrightarrow{2 \text{ मोल } NaNH_2}$ A , अभिक्रिया में उत्पाद 'A' होगा ? **[JEE-03(S), 3/84]**

(A*) 

(B) 

(C) 

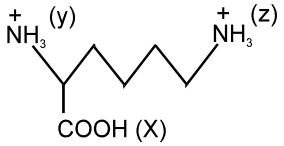
(D) 

Sol. Acidity of hydrogens –COOH > PhOH > > –C≡C–H (also NO_2 group increases acidic strength) hence if only two moles of base is taken then $H^{\oplus}$ will come out from –COOH and PhOH.

Sol. हाइड्रोजन की अम्लीयता –COOH > PhOH > > –C≡C–H (NO_2 समूह अम्लीय सामर्थ्य को बढाता है) यदि क्षार के दो मोल लिये जाये तो, –COOH तथा PhOH का $H^{\oplus}$ पहले निष्कासित होगा।

5. What is the acidity order of x, y & z ? **[JEE-04(S), 3/84]**

दिये गये यौगिक में x, y और z की अम्लीय सामर्थ्य का निम्न में से सही क्रम होगा? **[JEE-04(S), 3/84]**



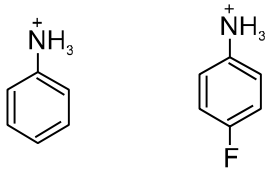
(A*) x > y > z (B) x > z > y (C) y > z > x (D) z > y > x

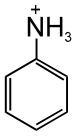
Sol. –COOH is stronger acid than $-\overset{\oplus}{N}H_3$ and –I group increases acidic strength.

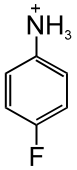
Sol. –COOH समूह $-\overset{\oplus}{N}H_3$ की अपेक्षा प्रबल अम्ल है, और –I समूह अम्ल सामर्थ्य को बढाता है।

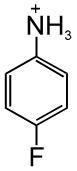
6. Which one of the following two compounds is the stronger acid? Explain why? **[JEE 2004, 4/60]**

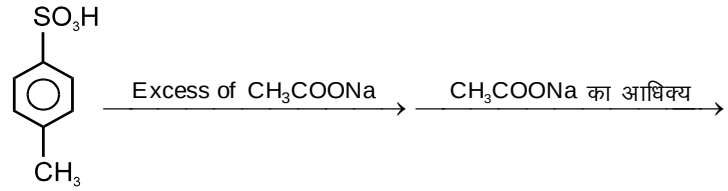
निम्न दोनों यौगिकों में कौन सा एक यौगिक प्रबलतम अम्ल है? व्याख्या कीजिए क्यों ? **[JEE 2004, 4/60]**



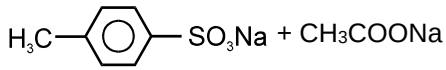
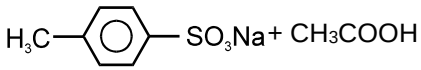
Ans. 

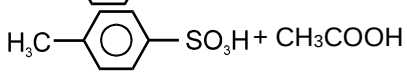
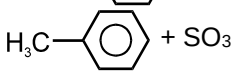
Sol.  is less acidic due to inter molecular H-bonding and +m effect of fluorine atom.

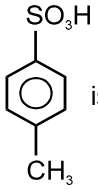
Sol.  कम अम्लीय है क्योंकि इसमें अन्तरआण्विक H-बंधन होता है तथा फ्लुओरीन परमाणु का +m प्रभाव लगता है।

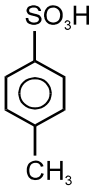
7.  **[JEE-05(S), 3/84]**

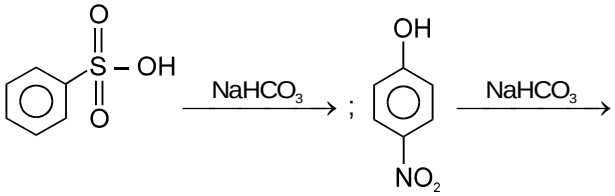
The products will be : उपरोक्त अभिक्रिया में उत्पाद होगें ?

(A)  (B*) 

(C)  (D) 

Sol.  is more acidic than CH_3COOH

हल. CH_3COOH की तुलना में यौगिक  अधिक अम्लीय है।

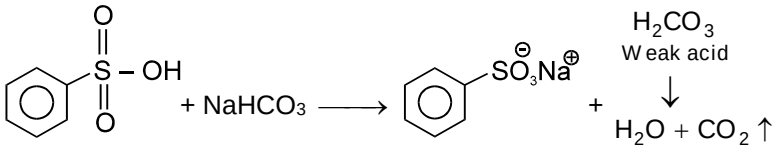
8. 

Benzenesulphonic acid and para nitrophenol react with $NaHCO_3$ separately. The gases produced are respectively. **[JEE-06, 3/184]**

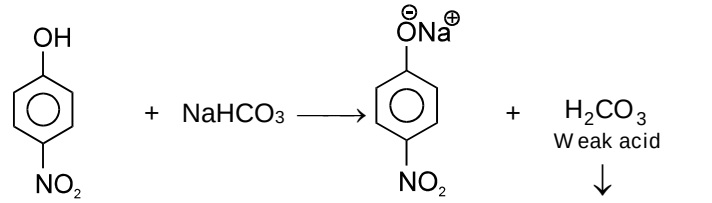
बैन्जीन सल्फोनिक अम्ल और पैरानाइट्रोफीनॉल $NaHCO_3$ के साथ पृथक–पृथक अभिक्रिया करते है, तो अभिक्रिया में प्राप्त गैसीय उत्पाद क्रमशः होगे? **[JEE-06, 3/184]**

(A) SO_2, CO_2 (B) SO_2, CO (C) SO_2, NO_2 (D*) CO_2, CO_2

Sol.

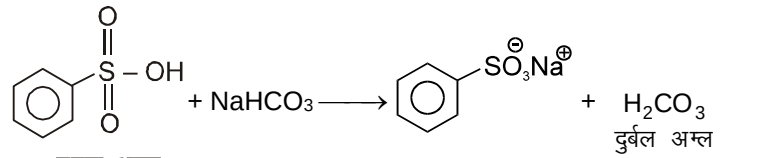


strong acid

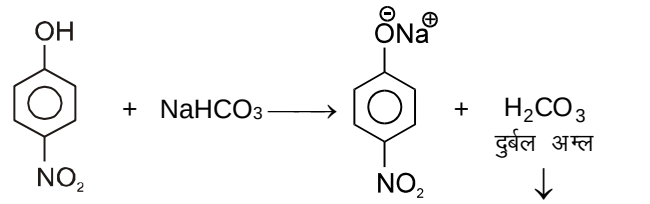


strong acid

हल.



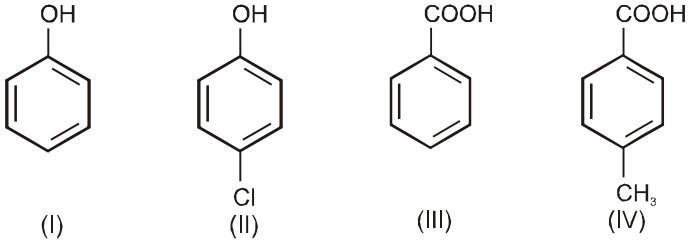
प्रबल अम्ल



प्रबल अम्ल

9. The correct acidity order of the following is : **[JEE-09, 3/160]**

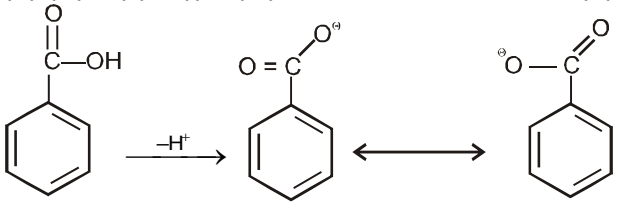
नीचे दिये हुए यौगिकों की अम्लीयता का सही क्रम है : **[JEE-09, 3/160]**



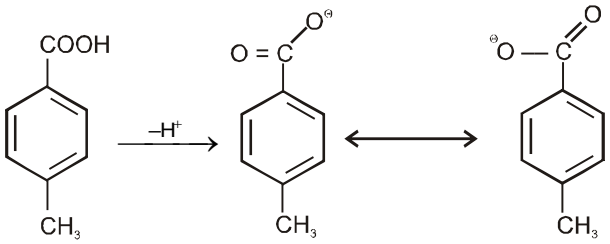
(I) (II) (III) (IV)

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

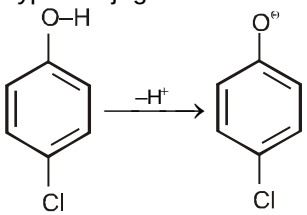
Sol.



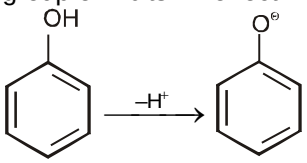
More stable conjugate base (carboxylate anion, –ve charge always on oxygen atom).



More stable conjugate base (carboxylate anion, –ve charge always on oxygen atom).+ I and hyperconjugative effect of – CH_3 group decreases stability of benzoate anion.

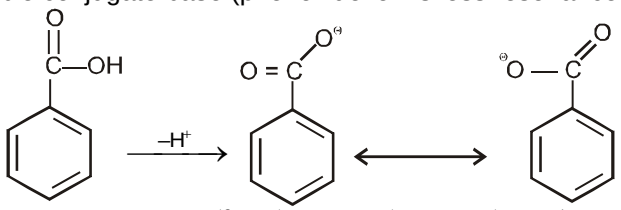


Less stable conjugate base (phenoxide ion is less resonance stabilized than benzoate anion). –Cl group exhibits – I effect.

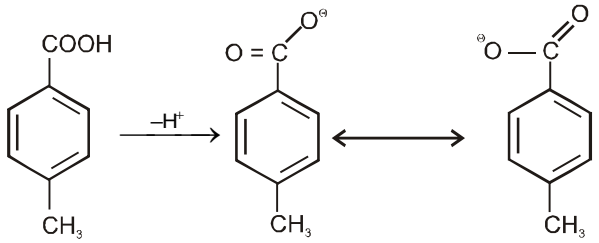


Less stable conjugate base (phenoxide ion is less resonance stabilized than benzoate anion).

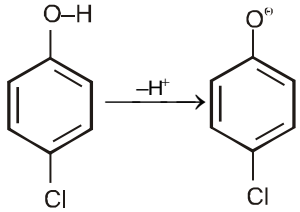
हल.



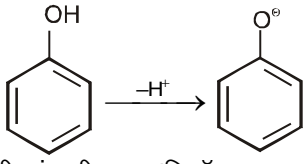
अधिक स्थायी संयुग्मी क्षार (कार्बोक्सिलेट आयन में –ve आवेश सदैव ऑक्सीजन पर होता है)।



अधिक स्थायी संयुग्मी क्षार (कार्बोक्सिलेट आयन में –ve आवेश सदैव ऑक्सीजन पर होता है।) $–CH_3$ के +I तथा अतिसयुग्मन प्रभाव के कारण संयुग्मी क्षार का स्थायित्व घटता है।

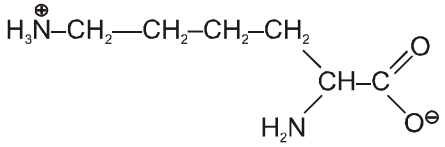


कम स्थायी संयुग्मी क्षार (फिनॉक्साइड आयन, बेन्जोऐट आयन से कम अनुनाद स्थाई है।)–Cl का –I प्रभाव प्रदर्शित होता है।



कम स्थायी संयुग्मी क्षार (फिनॉक्साइड आयन, बेन्जोऐट आयन से कम अनुनादी स्थायी है)।

10. The total number of basic groups in the following form of lysine is : **[JEE-10, 3/163]**
लाइसीन के निम्न रूप में क्षारीय समूहों की कुल संख्या है : **[JEE-10, 3/163]**



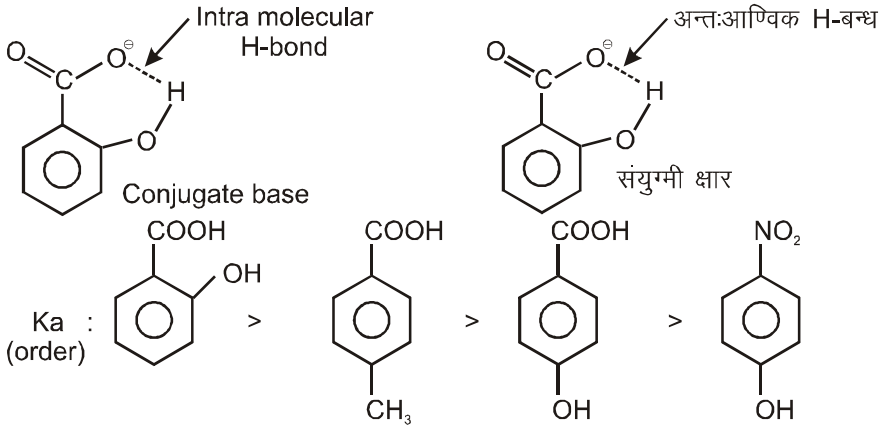
Ans. 2

Sol. $-NH_2$ and $-COO^{\ominus}$ are two basic groups.

Sol. $-NH_2$ तथा $-COO^{\ominus}$ दो क्षारीय समूह हैं।

11. Among the following compounds, the most acidic is : **[JEE-11, 3/180]**
(A) p-nitrophenol (B) p-hydroxybenzoic acid
(C*) o-hydroxybenzoic acid (D) p-toluic acid
निम्न यौगिकों में से सबसे अधिक अम्लीय है : **[JEE-11, 3/180]**
(A) p-नाइट्रोफीनॉल (B) p-हाइड्रॉक्सीबेंजोइक अम्ल
(C*) o-हाइड्रॉक्सीबेंजोइक अम्ल (D) p- टॉलूइक अम्ल

Sol.



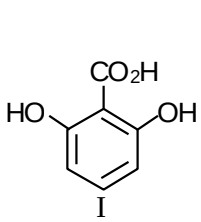
Due to intramolecular hydrogen bonding in conjugate base of ***o***-Hydroxybenzoic acid, it is strongest acid.
o-हाइड्रोक्सी बेन्जोइक अम्ल के संयुग्मी क्षार में अन्तःआण्विक हाइड्रोजन बन्ध के कारण यह प्रबल अम्ल होगा।

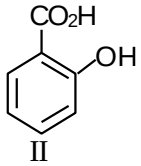
12. The compound that does **NOT** liberate CO_2, on treatment with aqueous sodium bicarbonate solution, is:
[JEE(Advanced) 2013, 2/120]
(A) Benzoic acid (B) Benzenesulphonic acid
(C) Salicylic acid (D*) Carbolic acid (Phenol)
यौगिक जो जलीय सोडियम बाइकार्बोनेट विलयन द्वारा अभिक्रिया कर CO_2 नहीं देता है, वह है
[JEE(Advanced) 2013, 2/120]
(A) बेन्जोइक अम्ल (B) बेन्जीनसल्फोनिक अम्ल (C) सेलिसिलिक अम्ल (D) कार्बोलिक अम्ल (फीनॉल)

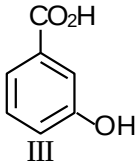
Sol. Phenol is less acidic than H_2CO_3 and does not liberate CO_2.

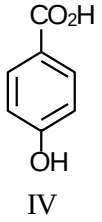
Sol. फिनॉल, H_2CO_3 से कम अम्लीय है। अतः ये CO_2 गैस का निष्कासन नहीं करेगा।

13. The correct order of acidity for the following compounds is **[JEE(Advanced) 2016, 3/124]**
निम्नलिखित यौगिकों की अम्लता का सही क्रम है **[JEE(Advanced) 2016, 3/124]**


I


II


III


IV

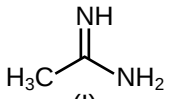
(A*) I > II > III > IV (B) III > I > II > IV (C) III > IV > II > I (D) I > III > IV > II

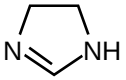
Sol. Due to ortho effect, ortho substituted benzoic acid is more acidic than meta & para isomers.
ऑर्थो प्रभाव के कारण, ऑर्थो प्रतिस्थापि बेन्जोइक अम्ल की अम्लीयता उसके मेटा एवं पेरा समावयवी से अधिक होती है।

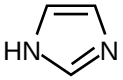
or या

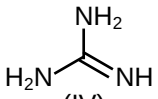
Due to strong hydrogen bond in conjugate base of ortho hydroxybenzoic acid, it is more acidic than its meta & para isomers. ऑर्थो हाइड्रॉक्सी बेन्जोइक अम्ल के सयुग्मी क्षार में प्रबल हाइड्रोजन बन्ध के कारण अम्लीयता उसके मेटा एवं पैरा समावयवी से अधिक होती है।

14. The order of basicity among the following compounds is **[JEE(Advanced) 2017, 3/122]**
निम्नलिखित यौगिकों में क्षारकता का क्रम है। **[JEE(Advanced) 2017, 3/122]**


(I)

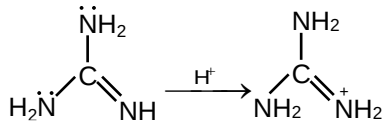
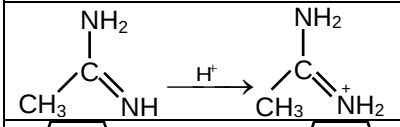
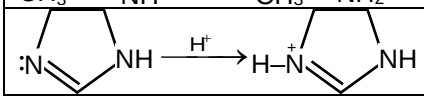

(II)


(III)


(IV)

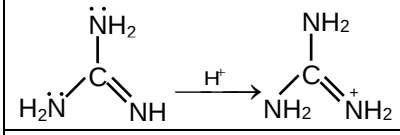
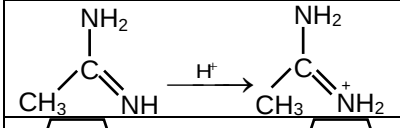
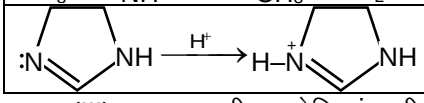
(A) II > I > IV > III (B) I > IV > III > II (C) IV > II > III > I (D*) IV > I > II > III

Sol.

	→	The conjugate acid is stabilized by resonance with two different $-NH_2$ group.
	→	The conjugate acid is stabilized by resonance with one $-NH_2$ group and by hyperconjugation of $-CH_3$ group.
	→	The conjugate acid is stabilized by resonance with only one NH_2 group.

(III) Least basic, as the LP is used in aromaticity.

हल **:**

	→	संयुग्मी अम्ल दो $-NH_2$ समूहों के अनुनाद के द्वारा स्थायीकृत होता है।
	→	संयुग्मी अम्ल एक $-NH_2$ समूह के अनुनाद तथा $-CH_3$ समूह के अतिसंयुग्मन के द्वारा स्थायीकृत होता है।
	→	संयुग्मी अम्ल केवल एक NH_2 समूह के अनुनाद के द्वारा स्थायीकृत होता है।

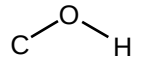
(III) न्यूनतम क्षारीय क्योकि एंकाकी इलेक्ट्रॉन युग्म ऐरोमेटिकता में भाग लेता है।

PART - II : JEE (MAIN) / AIEEE PROBLEMS (PREVIOUS YEARS)

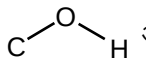
भाग - II : JEE (MAIN) / AIEEE (पिछले वर्षो) के प्रश्न

JEE(MAIN) ONLINE PROBLEMS

1. Which one of the following statements is **not** correct ? **[JEE(Main) 2014 Online (11-04-14), 4/120]**

(1) Alcohols are weaker acids than water.
(2) Acid strength of alcohols decreases in the following order $RCH_2OH > R_2CHOH > R_3COH$.
(3*) Carbon-oxygen bond length in methanol, CH_3OH is shorter than that of C–O bond length in phenol.
(4) The bond angle  in methanol is 108.9º.

निम्न कथनों में से कौनसा सही नहीं है ? **[JEE(Main) 2014 Online (11-04-14), 4/120]**

(1) ऐल्कोहालें पानी की तुलना में दुर्बल अम्ल हैं।
(2) ऐल्कोहालों की अम्ल शक्ति इस क्रम में घटती जाती है– $RCH_2OH > R_2CHOH > R_3COH$
(3*) मैथेनाल, CH_3OH में कार्बन–ऑक्सीजन आबन्ध की लम्बाई फिनाल में C–O आबन्ध की लम्बाई से छोटी होती है।
(4) मेथेनाल में  आबन्ध कोण 108.9º होता है।

2. Which one of the following compounds will not be soluble in sodium bicarbonate ?
[JEE(Main) 2014 Online (19-04-14), 4/120]

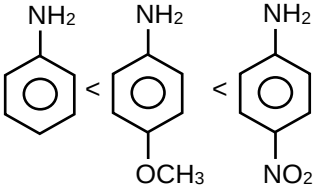
(1) 2,4,6-Trinitrophenol (2) Benzoic acid
(3*) o-Nitrophenol (4) Benzene sulphonic acid

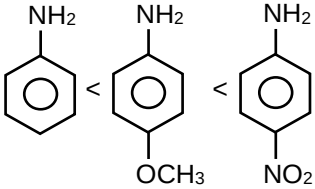
इनमें से कौन–सा यौगिक सोडियम बाइकार्बोनेट मे नही घुलेगा ? **[JEE(Main) 2014 Online (19-04-14), 4/120]**

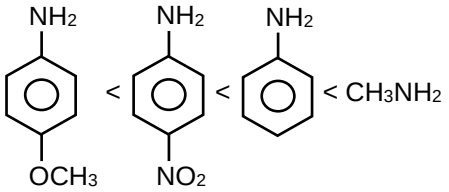
(1) 2,4,6-ट्राईनाइट्रोफिनॉल (2) बैन्ज्रोइक ऐसिड
(3*) o-नाइट्रोफिनॉल (4) बैन्ज्रीन सल्फानिक ऐसिड

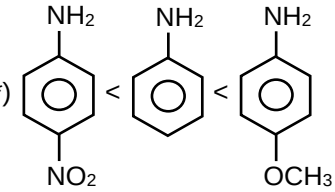
3. Arrange the following amines in the order of increasing basicity :
[JEE(Main) 2015 Online (10-04-15), 4/120]

निम्न ऐमीनो को बढती हुई क्षारकता के क्रम में व्यवस्थित कीजिए। **[JEE(Main) 2015 Online (10-04-15), 4/120]**

(1) CH_3NH_2 < 

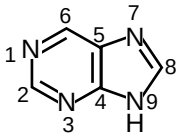
(2)  < CH_3NH_2

(3) 

(4*)  < CH_3NH_2

Sol. $CH_3–NH_2$ pKa = 10.64
pKa = 4.62
pKa = 0.98
pKa = 5.29

4. The "N" which does not contribute to the basicity for the compound is :
वह "N" जो निम्न यौगिक की क्षारीय प्रवृत्ति में योगदान नहीं देता है, वह है :
[JEE(Main) 2016 Online (10-04-16), 4/120]

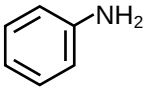
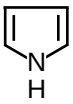
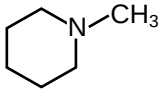
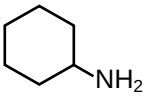


(1) N 7 (2) N 1 (3*) N 9 (4) N 3

Sol. Lone pair of N9 is involve in aromaticity. N9 के एकाकी युग्म ऐरोमैटिकता में सम्मिलित है।

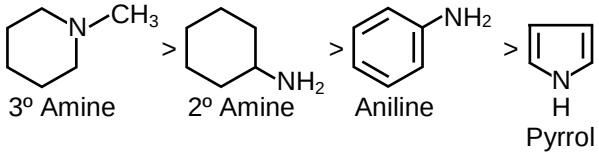
5. Among the following compounds, the increasing order of their basic strength is :
[JEE(Main) 2017 Online (09-04-17), 4/120]

निम्न यौगिको में इनकी क्षारीय सामर्थ्य का बढता हुआ क्रम है? **[JEE(Main) 2017 Online (09-04-17), 4/120]**

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

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

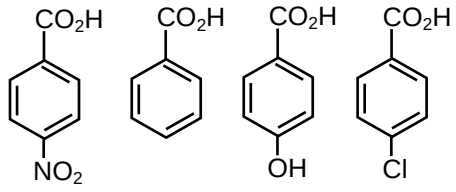
(3) (II) < (I) < (III) < (IV) (4*) (II) < (I) < (IV) < (III)

Sol. 

3º Amine > 2º Amine > Aniline > Pyrrol

6. The increasing order of the acidity of the following carboxylic acids is : **[JEE(Main) 2018 Online (15-04-18), 4/120]**

निम्न कार्बोक्सिलिक अम्लों की अम्लीयता का बढता क्रम है : **[JEE(Main) 2018 Online (15-04-18), 4/120]**

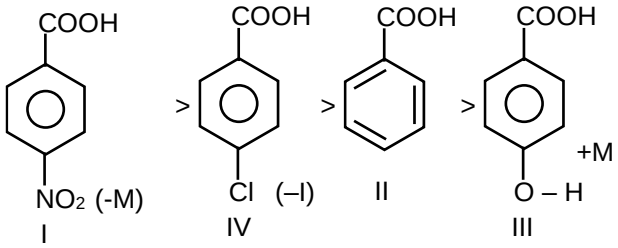


I II III IV

(1) I < III < II < IV (2) IV < II < III < I (3) II < IV < III < I (4*) III < II < IV < I

Sol. Order of acidity

अम्लीयता का क्रम



I IV II III

7. Which amongst the following is the strongest acid ? **[JEE(Main) 2019 Online (09-01-19), 4/120]**

निम्न में से कौनसा प्रबलतम अम्ल है ? **[JEE(Main) 2019 Online (09-01-19), 4/120]**

(1) $CHBr_3$ (2) $CHCl_3$ (3) CHI_3 (4*) $CH(CN)_3$

Sol. The conjugate base of $CH(CN)_3$ is $\bar{C}(CN)_3$ and in $\bar{C}(CN)_3$ the negative charge is extensively delocalized.

$CH(CN)_3$ का संयुग्मी क्षार $\bar{C}(CN)_3$ का ऋणावेश अत्यधिक विस्थानीकरण के कारण स्थायी है।

8. The correct decreasing order for acid strength is : **[JEE(Main) 2019 Online (09-01-19), 4/120]**

अम्ल सामर्थ्य के लिए सही घटता क्रम है : **[JEE(Main) 2019 Online (09-01-19), 4/120]**

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

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

(3*) $NO_2CH_2COOH > NCCH_2COOH > FCH_2COOH > ClCH_2COOH$

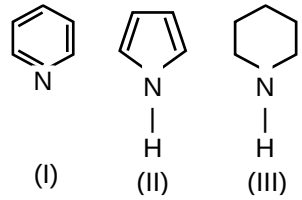
(4) $NO_2CH_2COOH > FCH_2COOH > CNCH_2COOH > ClCH_2COOH$

Sol. Greater the –I effect, greater will be the acidity**.**

अधिक **–I** प्रभाव, अधिक अम्लीय।

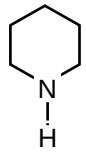
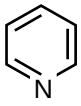
9. Arrange the following amines in the decreasing order of basicity : **[JEE(Main) 2019 Online (09-01-19), 4/120]**

क्षारकता के घटते क्रम में निम्न ऐमीनों को व्यवस्थित कीजिए : **[JEE(Main) 2019 Online (09-01-19), 4/120]**

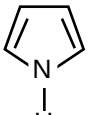


(I) (II) (III)

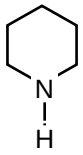
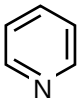
(1) I > III > II (2*) III > I > II (3) III > II > I (4) I > II > III

Sol. In  the lone pair is localized in sp^3 hybrid orbital, in  the lone pair is localized in sp^2

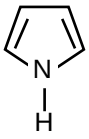
(R) (P)

hybrid orbital, and in  the lone pair electron is delocalized in aromaticity.

(Q)

हल  इलेक्ट्रॉन युग्म sp^3 संकर कक्षक में स्थानीय है,  इलेक्ट्रॉन युग्म sp^2 संकर कक्षक में स्थानीय है,

(R) (P)

 का इलेक्ट्रॉन युग्म एरौमेटिक वलय में विस्थानीकृत है।

(Q)

10. The increasing basicity order of the following compounds is:

[JEE(Main) 2019 Online (09-01-19), 4/120]

निम्नलिखित यौगिकों में क्षारकता का बढ़ता क्रम हैः **[JEE(Main) 2019 Online (09-01-19), 4/120]**

(A) $CH_3CH_2NH_2$ (B) $CH_3CH_2\underset{\displaystyle CH_2CH_3}{\underset{|}{N}}H$ (C) $H_3C-\underset{\displaystyle CH_3}{\underset{|}{N}}-CH_3$ (D) $Ph-\underset{\displaystyle CH_3}{\underset{|}{N}}-H$

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

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

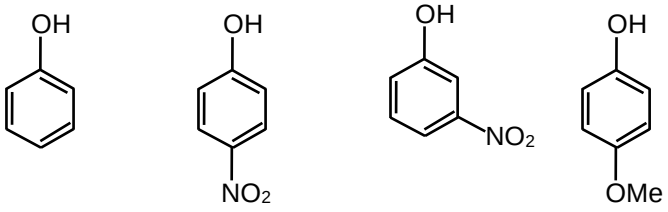
Sol. Basic strength order is क्षारीय सामर्थ्यता का क्रम है

$$CH_3CH_2\underset{\displaystyle CH_2CH_3}{\underset{|}{N}}H > CH_3CH_2NH_2 > CH_3-\underset{\displaystyle CH_3}{\underset{|}{N}}-CH_3 > Ph-\underset{\displaystyle CH_3}{\underset{|}{N}}-H$$

11. The increasing order of the pK_a values of the following compounds is :

[JEE(Main) 2019 Online (10-01-19), 4/120]

निम्न यौगिकों के pK_a का बढ़ता हुआ क्रम है, **[JEE(Main) 2019 Online (10-01-19), 4/120]**



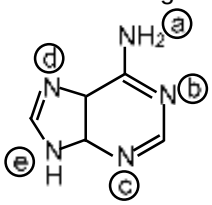
A B C D

(1) C < B < A < D (2) B < C < D < A (3*) B < C < A < D (4) D < A < C < B

Sol. Electron withdrawing group increases acidic strength and Electron releasing group decreases acidic strength.

इलेक्ट्रॉन ग्राही समूह अम्लीयता बढ़ाता है और इलेक्ट्रॉन दाता समूह अम्लीयता कम करता है।

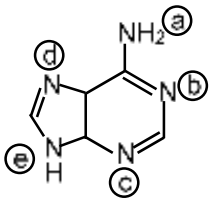
12. In the following compound the favourable site/s for protonation is /are :



[JEE(Main) 2019 Online (11-01-19), 4/120]

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

निम्न यौगिक में, प्रोटनीकरण के लिए अनुकूल स्थल है/हैं : **[JEE(Main) 2019 Online (11-01-19), 4/120]**



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

Sol. Lone pair of electons in 'a' and 'e' are in delocalisation.

'a' और 'e' के एकाकी युग्म इलेक्ट्रॉन विस्थानिकृत है।

13. The correct order of acid strength of compounds CH≡CH, CH_3–C≡CH and CH_2=CH_2 is as follows : **[JEE(Main) 2019 Online (12-01-19), 4/120]**

CH≡CH, CH_3–C≡CH तथा CH_2=CH_2 यौगिकों के अम्लीय सामर्थ्य का सही क्रम है: **[JEE(Main) 2019 Online (12-01-19), 4/120]**

(1) CH_3–C≡CH > CH≡CH > CH_2=CH_2 (2) CH_3–C≡CH > CH_2 =CH_2 > HC≡CH

(3*) HC≡CH > CH_3 –C≡CH > CH_2 = CH_2 (4) CH ≡CH > CH_2 =CH_2 > CH_3–C≡CH

Sol. Acidic strength $\propto$ Stability of conjugate base

E.N. $\rightarrow$ sp carbon > sp^2 carbon > sp^3 carbon

Sol. अम्लीय सामर्थ्य $\propto$ संयुग्मी क्षार का स्थायित्व

विद्युतऋणता $\rightarrow$ sp कार्बन > sp^2 कार्बन > sp^3 कार्बन

Additional Problems for Self Practice (APSP)

This Section is not meant for classroom discussion. It is being given to promote self-study and self testing amongst the Resonance students.

PART - I : PRACTICE TEST-1 (IIT-JEE (MAIN Pattern))

Max. Marks: 100 **Max. Time : 1 Hour**

Important Instructions:

A. General :

1. The test paper is of **1** hour duration.
2. The Test Paper consists of **25** questions and each questions carries **4** Marks. Test Paper consists of **Two** Sections.

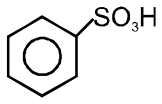
B. Test Paper Format and its Marking Scheme:

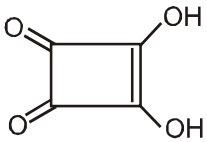
1. Section-1 contains **20** multiple choice questions. Each question has four choices (1), (2), (3) and (4) out of which **ONE** is correct. For each question in Section-1, you will be awarded 4 marks if you give the corresponding to the correct answer and zero mark if no given answers. In all other cases, minus one **(–1)** mark will be awarded.
2. Section-2 contains **5** questions. The answer to each of the question is a **Numerical Value**. For each question in Section-2, you will be awarded 4 marks if you give the corresponding to the correct answer and zero mark if no given answers. No negative marks will be answered for incorrect answer in this section. In this section answer to each question is **NUMERICAL VALUE** with two digit integer and decimal upto two digit. If the numerical value has more than two decimal places **truncate/round-off** the value to **TWO** decimal placed.

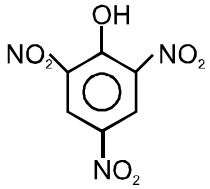
SECTION-1

This section contains **20** multiple choice questions. Each questions has four choices (1), (2), (3) and (4) out of which Only **ONE** option is correct.

1. Which of the following would produce effervesence with sodium bicarbonate ?

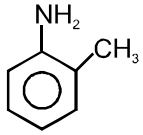
(1) 

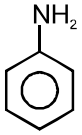
(2) 

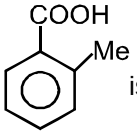
(3) 

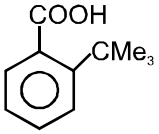
(4) All of these

2. Select correct statement from the following :

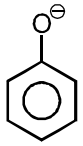
(1) 

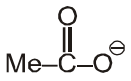
is more basic than 

(2) 

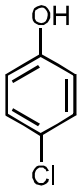
is more acidic than 

(3) HC≡CH is more acidic than NH_3

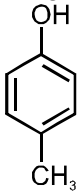
(4) 

is more stable than 

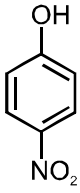
3. Arrange the following compounds in order of decreasing acidity.



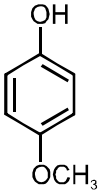
(i)



(ii)



(iii)

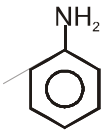


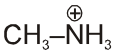
(iv)

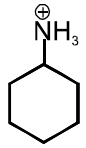
(1) (i) > (ii) > (iii) > (iv) (2) (iii) > (i) > (ii) > (iv) (3) (iv) > (iii) > (i) > (ii) (4) (ii) > (iv) > (i) > (iii)

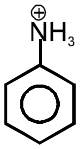
4. The order of decreasing basicity in the four halide ions is :
(1) $I^- > Br^- > Cl^- > F^-$ (2) $Cl^- > Br^- > I^- > F^-$ (3) $F^- > Cl^- > Br^- > I^-$ (4) $Cl^- > F^- > Br^- > I^-$

5. Correct order of acidic strength :


(i)

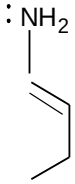

(ii)

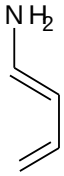

(iii)

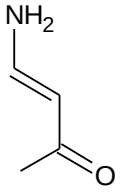

(iv)

(1) (iv) > (i) > (ii) > (iii) (2) (iv) > (iii) > (ii) > (i) (3) (iv) > (ii) > (iii) > (i) (4) (ii) > (iv) > (i) > (iii)

6. Which of the following is **incorrect** about the given molecules

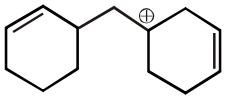
(a) 

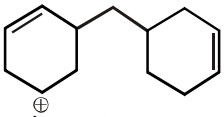
(b) 

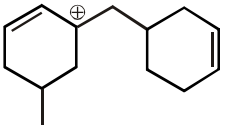
(c) 

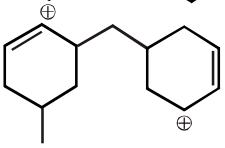
(1) The correct order of basic strength (K_b) is : a > b > c
(2) The correct order of C–N bond length is : a > b > c
(3) The correct C=C bond length order is : a > b > c
(4) The correct pK_b order is : c > b > a

7. Which of the following is the most stablized carbocation ?

(1) 

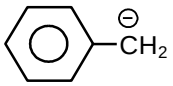
(2) 

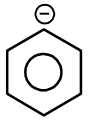
(3) 

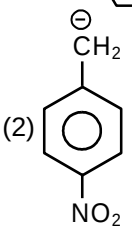
(4) 

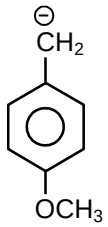
8. Which one among the following is the least basic:
(1) $\overset{\ominus}{C}H_3$ (2) $\overset{\ominus}{N}H_2$ (3) $\overset{\ominus}{O}H$ (4) $\overset{\ominus}{F}$

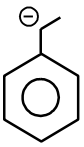
9. Which is most basic in aqueous solution ?
(1) CH_3NH_2 (2) $(CH_3)_2NH$ (3) $(CH_3)_3N$ (4) $Ph–NH_2$

10. Which is less basic than benzyl  carbanion?

(1) 

(2) 

(3) 

(4) 

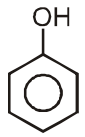
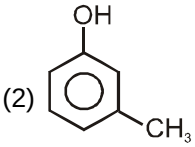
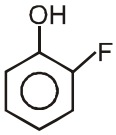
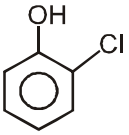
11. The correct order of decreasing acid strength of trichloroacetic acid (A), trifluoroacetic acid (B), acetic acid (C) and formic acid (D) is :
(1) B > A > D > C (2) B > D > C > A (3) A > B > C > D (4) A > C > B > D

12. Base strength is in the order of
(i) $\overset{-}{C}H_3CH_2$ (ii) $H_2C{=}\overset{\ominus}{C}H$ and (iii) $H{-}C{\equiv}\overset{\ominus}{C}$
(1) (ii) > (i) > (iii) (2) (iii) > (iii) > (i) (3) (i) > (iii) > (ii) (4) (i) > (ii) > (iii)

13. Pyridine is less basic than triethylamine because :

(1) Pyridine has aromatic character
(2) Nitrogen in pyridine is sp^2 hybridised
(3) Pyridine is a cyclic system
(4) In pyridine, lone pair of nitrogen is delocalised

14. Which of the following phenol has lowest pK_a ?

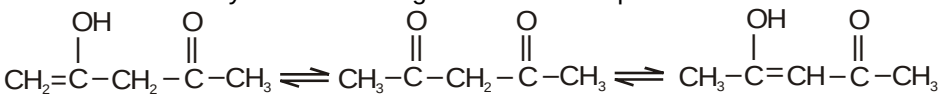
(1) 
(2) 
(3) 
(4) 

15. Which is most basic among the followings ?

(1) Ph-NH_2
(2) NH_3
(3) CH_3–NH_2
(4) C_2H_5–CN

16. **Assertion :** The pK_a of acetic acid is lower than that of phenol.
Reason : Phenoxide ion is more resonance stabilised.
(1) If both assertion and reason are true and reason is a correct explanation of assertion.
(2) If both assertion and reason are true but reason is not a correct explanation of assertion.
(3) If assertion is true but reason is false.
(4) If assertion and reason both are false.

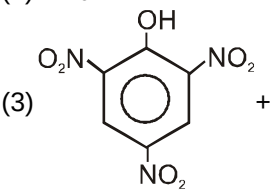
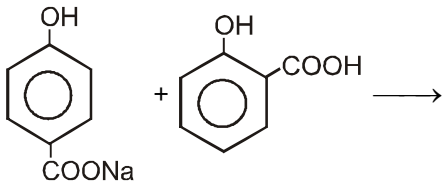
17. The order of stability of the following tautomeric compounds is :



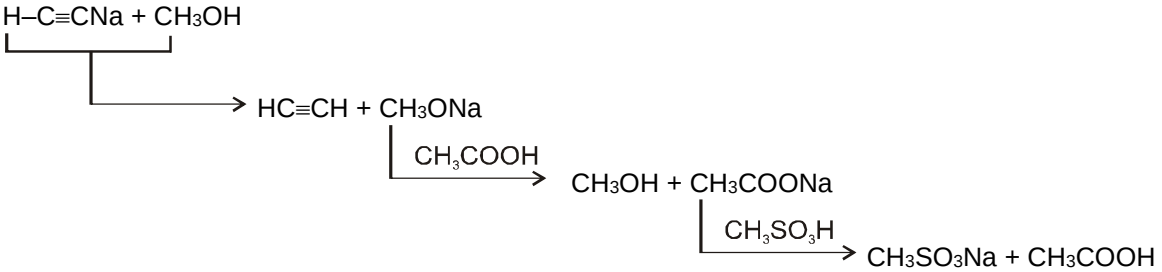
I II III

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

18. The feasible reaction is :

(1) $CH_3COOH + NaCl \longrightarrow$
(2) $C_6H_5COOH + KBr \longrightarrow$
(3)  $+ KHSO_4 \longrightarrow$
(4)  $\longrightarrow$

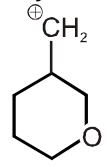
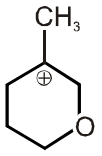
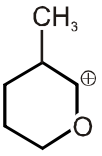
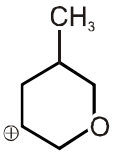
19. Observe the following reaction sequence.



Which is correct acidic strength order :

(1) HC ≡ CH > CH_3COOH > CH_3SO_3H
(2) CH_3SO_3H > CH_3COOH > HC ≡ CH
(3) CH_3SO_3H > HC ≡ CH > CH_3COOH
(4) CH_3COOH > CH_3SO_3H > HC ≡ CH

20. Identify the most stable carbocation among the following :

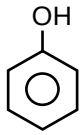
(1) 
(2) 
(3) 
(4) 

SECTION-2

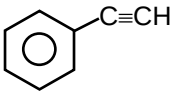
This section contains **5** questions. Each question, when worked out will result in **Numerical Value**.

21. Consider the following compounds :

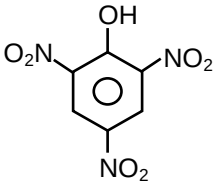
(i)



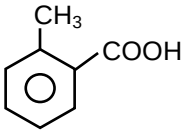
(ii)



(iii)

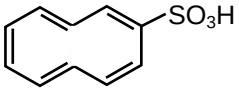


(iv)



(v)

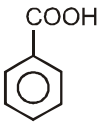
(vi)

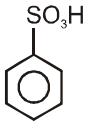


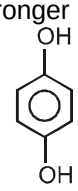
(vii)

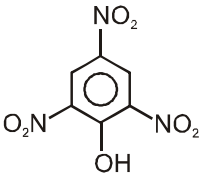
Give the value of (b + c) – a :
a = number of nonaromatic compounds
b = number of compounds which can evolve CO_2 gas on reaction with $NaHCO_3$
c = number of compounds which are more acidic than benzoic acid

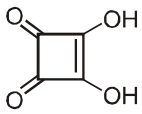
22. Find the total number of acidic compounds which are stronger acids than H_2CO_3.







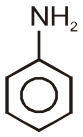




HCl

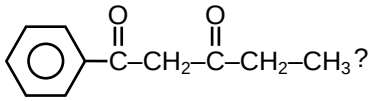
$CH_3C{\equiv}CH$

HCOOH

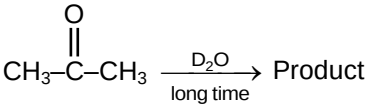


23. How many of the following is/are less acidic than formic acid ?

(i) Ph–OH	(ii) Ph–COOH	(iii) CH_3–SO_3H	(iv) H_2CO_3
(v) CH_3–OH	(vi) Picric acid	(vii) Cl–CH_2CH_2COOH	(viii) Ph–NH_2

24. How many total enolic forms (only structural) are possible for  ?

25. How many hydrogen's will be replaced by deuterium of the given compound if D_2O is allowed to react with the compound for long time.



Practice Test-1 (IIT-JEE (Main Pattern))

OBJECTIVE RESPONSE SHEET (ORS)

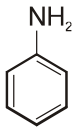
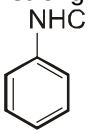
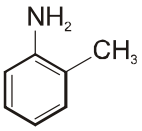
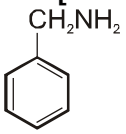
Que.	1	2	3	4	5	6	7	8	9	10
Ans.										
Que.	11	12	13	14	15	16	17	18	19	20
Ans.										
Que.	21	22	23	24	25					
Ans.										

PART - II : JEE (MAIN) / AIEEE OFFLINE PROBLEMS (PREVIOUS YEARS)

1. The correct order of increasing basic nature for the bases NH_3, CH_3NH_2 and $(CH_3)_2NH$ is: **[AIEEE-2003, 3/225]**

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

2. Which of the following is the strongest base? **[AIEEE-2004, 3/225]**

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

3. Consider the acidity of the carboxylic acids: **[AIEEE-2004, 3/225]**

(i) PhCOOH (ii) o-$NO_2C_6H_4COOH$ (iii) p-$NO_2C_6H_4COOH$ (iv) m-$NO_2C_6H_4COOH$
(1) i > ii > iii > iv (2) ii > iii > iv > i (3) iii > ii > iv > i (4) ii > iv > iii > i

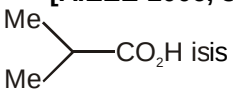
4. Among the following acid which has the lowest pK_a value ? **[AIEEE-2005, 3/225]**

(1) CH_3CH_2COOH (2) $(CH_3)_2CH–COOH$ (3) HCOOH (4) CH_3COOH

5. Amongst the following the most basic compound is **[AIEEE-2005, 3/225]**

(1) p-Nitroaniline (2) Acetanilide (3) Aniline (4) Benzylamine

6. The correct order of increasing acid strength of the compounds. **[AIEEE-2006, 3/165]**

(a) CH_3CO_2H (b) $MeOCH_2CO_2H$ (c) CF_3CO_2H (d) 

(1) b < d < a < c (2) d < a < c < b (3) d < a < b < c (4) a < d < c < b

7. Which one of the following is the strongest base in aqueous solution? **[AIEEE-2007, 3/120]**

(1) Dimethylamine (2) Methylamine (3) Trimethylamine (4) Aniline

8. The correct order of increasing basicity of the given conjugate bases (R = CH_3) is: **[AIEEE-2010, 4/144]**

(1) $R\overline{C}O\overline{O} < HC \equiv \overline{C} < \overline{R} < \overline{N}H_2$ (2) $\overline{R} < HC \equiv \overline{C} < R\overline{C}O\overline{O} < \overline{N}H_2$
(3) $R\overline{C}O\overline{O} < \overline{N}H_2 < HC \equiv \overline{C} < \overline{R}$ (4) $R\overline{C}O\overline{O} < HC \equiv \overline{C} < \overline{N}H_2 < \overline{R}$

9. The strongest acid amongst the following compounds is : **[AIEEE-2011, 4/120]**

(1) CH_3COOH (2) HCOOH
(3) $CH_3CH_2CH(Cl)CO_2H$ (4) $ClCH_2CH_2CH_2COOH$

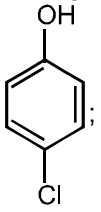
10. Identify the compound that exhibits tautomerism. **[AIEEE-2011, 4/120]**

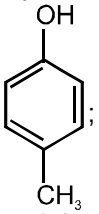
(1) 2-Butene (2) Lactic acid (3) 2-Pentanone (4) Phenol

11. The correct order of acid strength of the following compounds: **[AIEEE-2011, 4/120]**

(A) Phenol (B) p-Cresol (C) m-Nitrophenol (D) p-Nitrophenol
is :
(1) D > C > A > B (2) B > D > A > C (3) A > B > D > C (4) C > B > A > D

12. Arrange the following compounds in order of decreasing acidity : **[JEE(Main)-2013, 4/120]**


(I)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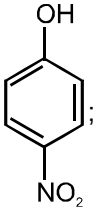
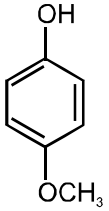

(III)

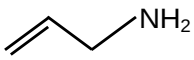
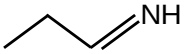
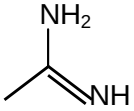
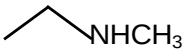

(IV)

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

13. Considering the basic strength of amines in aqueous solution, which one has the smallest pK_b value? **[JEE(Main)-2014, 4/120]**

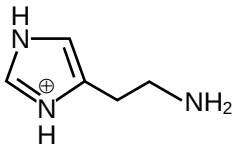
(1) $(CH_3)_2NH$ (2) CH_3NH_2 (3) $(CH_3)_3N$ (4) $C_6H_5NH_2$

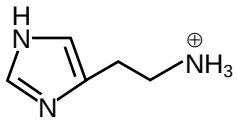
14. The increasing order of basicity of the following compounds is : **[JEE(Main)-2018, 4/120]**

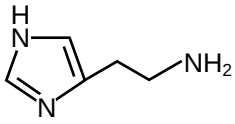
(a)  (b)  (c)  (d) 

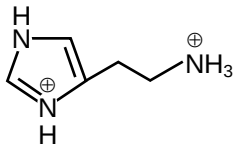
(1) (b) < (a) < (d) < (c) (2) (d) < (b) < (a) < (c)
(3) (a) < (b) < (c) < (d) (4) (b) < (a) < (c) < (d)

15. The predominant form of histamine present in human blood is (pK_a, Histidine = 6.0) **[JEE(Main)-2018, 4/120]**

(1) 

(2) 

(3) 

(4) 

PART- III : NATIONAL STANDARD EXAMINATION IN CHEMISTRY (NSEC) STAGE–I

1. Which of the following is the strongest acid ? **[NSEC-2000]**
(A) 3,5-dinitrophenol (B) 2,4-dinitrophenol (C) phenol (D) 2,4,6-trinitrophenol

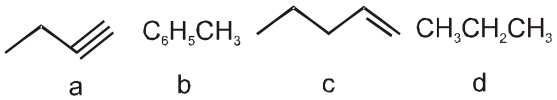
2. Which of the following is the strongest base ? **[NSEC-2000]**
(A) $HC\equiv C^-$ (B) $CH_2 = CH^-$ (C) $CH_3CH_2^-$ (D) NH_2^-

3. Which of the following orders is true regarding the acidic nature of phenol ? **[NSEC-2001]**
(A) phenol > o-cresol < o-nitrophenol (B) phenol < o-cresol < o-nitrophenol
(C) phenol > o-cresol > o-nitrophenol (D) phenol < o-cresol > o-nitrophenol

4. Which of the following order is expected to be correct ? **[NSEC-2001]**
(A) $pK_a(ClCH_2COOH) > pK_a(CH_3COOH) < pK_a(CH_3CH_2COOH)$
(B) $pK_a(ClCH_2COOH) < pK_a(CH_3COOH) < pK_a(CH_3CH_2COOH)$
(C) $pK_a(ClCH_2COOH) > pK_a(CH_3COOH) > pK_a(CH_3CH_2COOH)$
(D) $pK_a(ClCH_2COOH) < pK_a(CH_3COOH) > pK_a(CH_3CH_2COOH)$

5. Which of the following compounds is the most acidic ? **[NSEC-2002]**
(A) HCO_2H (B) CH_3CO_2H (C) $CH_3CH_2CO_2H$ (D) CCl_3CO_2H

6. Out of the four pK_a values 3.75, 9.89, 15.54 and 19.30, the highest pK_a value corresponds to **[NSEC-2003]**
(A) acetone (B) formic acid (C) phenol (D) methanol.

7. 

The correct order of acidic character in the above compounds is **[NSEC-2003]**

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

8. The weakest base among the following is **[NSEC-2004]**

(A) $C_6H_5SO_3^-$ (B) $C_2H_5O^-$ (C) $C_6H_5O^-$ (D) $CH_3–CH=CH–CH_2–O^-$

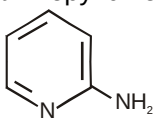
9. $\underset{(i)}{CH_3COOH}$ $\underset{(ii)}{HCOOH}$ $\underset{(iii)}{CH_2ClCOOH}$ $\underset{(iv)}{PhCOOH}$

The order of acidity in the given series of compounds is **[NSEC-2004]**

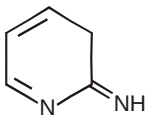
(A) (iv) < (ii) < (i) < (iii) (B) (i) < (ii) < (iii) < (iv)

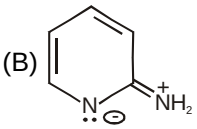
(C) (i) < (ii) < (iv) < (iii) (D) (i) < (iv) < (ii) < (iii)

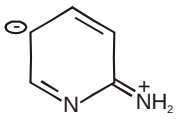
10. The proper tautomeric structure for 2-aminopyridine (X) is **[NSEC-2004]**

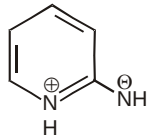


(X)

(A) 

(B) 

(C) 

(D) 

11. The correct order of acidity for the following compound is **[NSEC-2005]**

(1) Benzoic acid > phenol > p-nitrobenzoic acid > m-nitrobenzoic acid.

(2) phenol > p-nitrobenzoic acid > m-nitrobenzoic acid > benzoic acid.

(3) p-nitrobenzoic acid > m-nitrobenzoic acid > benzoic acid > phenol.

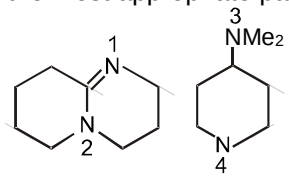
(4) m-nitrobenzoic acid > p-nitrobenzoic acid > benzoic acid > phenol.

12. Identify the group in which the order of basicity is not correct ? **[NSEC-2005]**

(A) $OH^- > H_2O > H_3O^+$ (B) $S^{2-} > HS^- > H_2S$

(C) $NH_3 > OH^- > H_2O$ (D) $Cl^- > Br > I^-$

13. Choose the most appropriate pair of nitrogens that gets protonated in the following structures.



(A) 1 and 3 (B) 2 and 4 (C) 1 and 4 (D) 2 and 3.

14. As the base changes from RNH_2 to R_2NH, to R_3N the basicity **[NSEC-2006]**

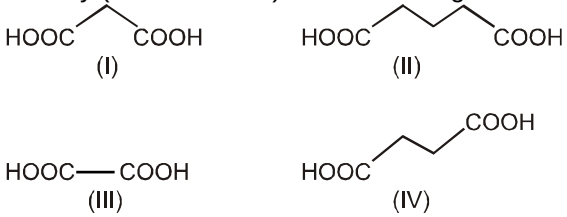
(A) $R_2NH > R_3N > RNH_2$ (B) $RNH_2 > R_3N > R_2NH$

(C) $RNH_2 > R_2NH > R_3N$ (D) $R_3N > RNH_2 > R_2NH$.

15. The most acidic of the following substances is **[NSEC-2006]**

(A) aniline (B) p-nitrophenol (C) phenol (D) acetaldehyde.

16. Indicate the correct of acidity (first ionization) in the following dicarboxylic acids : **[NSEC-2007]**



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

17. The correct order of acidity of the C-H proton is – **[NSEC-2007]**

(A) acetylene > ethylene > ethane (B) ethylene > ethylene > ethane

(C) ethane > ethylene > acetylene (D) acetylene > ethane >.ethylene

18. Salicylic acid is a stronger acid than p-hydroxybenzoic acid due to **[NSEC-2008]**

(A) Steric hindracne (B) Hydrogen bonding

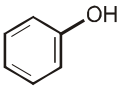
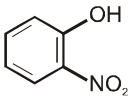
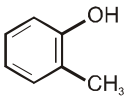
(C) Mesomeric effect (D) Solvation energy

19. Which one of the following compounds can be deprotonated by OH fastest ? **[NSEC-2008]**

(A) HCOOH, $pK_a = 3.8$ (B) H_2S, $pK_a = 7.0$

(C) Toluene, $pK_a = 41$ (D) CH_3NH_2, $pK_a = 40$

20. The most acidic among the following compound is : **[NSEC-2009]**

(A) $Cl–CH_2–CH_2–OH$ (B)  (C)  (D) 

21. Keto and enol forms of a compound are related to each other as **[NSEC-2010]**

(A) Resonance structures (B) Conformations

(C) Configurational isomers (D) Constitutional isomers

22. The correct order of acidity of the following compounds is : **[NSEC-2010]**

(I) CH_3COOH (II) $ClCH_2COOH$ (III) O_2NCH_2COOH (IV) $HOCH_2COOH$

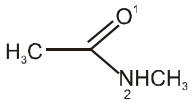
(A) IV > II > III > I (B) I > IV > II > III (C) II > III > I > IV (D) III > II > IV > I

23. The order of acidities of the H-atoms underlined in the following compounds is in the order – **[NSEC-2011]**

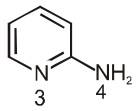
(I) Ph–C<u>H</u>$_2$–CH_3 (II) Ph–C≡C<u>H</u> (III) Ph–CH=C<u>H</u>$_2$ (IV) 

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

24. The preferred sites of protonation in the following compounds are **[NSEC-2012]**



I



II

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

25. Acetone and propen-2-ol are **[NSEC-2013]**

(A) enantiomers (B) keto-enol tautomers

(C) diastereoisomers (D) meso compounds

26. Which of the following does not have an active methylene group ? **[NSEC-2013]**

(A) $CH_3CH_2NO_2$ (B) $CH_3COCH_2COCH_3$

(C) $PhCOCH_2CN$ (D) $CH_3CH_2NH_2$

27. Which of the following phenols is most soluble in aqueous sodium bicarbonate ? **[NSEC-2013]**

(A) 2,4-dihydroxyacetophenone (B) p-cyanophenol

(C) 3,4-dicyanophenol (D) 2,4,6-tricyanophenol

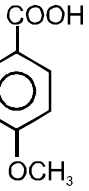
28. The order of basicity is **[NSEC-2014]**

$(I)\ Ph-CONH_2$ $(II)\ Ph-NH_2$

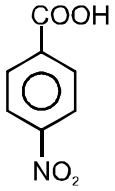
$(III)\ Ph-CH_2-NH_2$ $(IV)\ p-OCH_3Ph-NH_2$

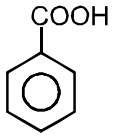
(A) $II > IV > I > III$ (B) $III > II > IV > I$ (C) $III > IV > II > I$ (D) I>II>IV>III

29. The pKa values of the acids A to D are found to be 4.19, 3.41, 4.46 and 4.76. The acid having pKa of 3.41 is **[NSEC-2014]**

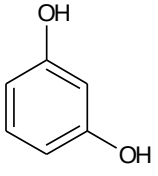
(A) 

(B) CH_3COOH

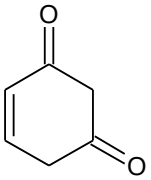
(C) 

(D) 

30. At normal temperature, X and Y are **[NSEC-2014]**



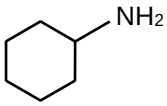
X

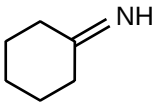


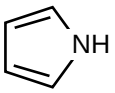
Y

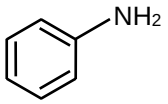
(A) resonance structures
(B) tautomers
(C) functional isomers
(D) positional isomers

31. The order of basicity of the following compounds is **[NSEC-2015]**

(I) 

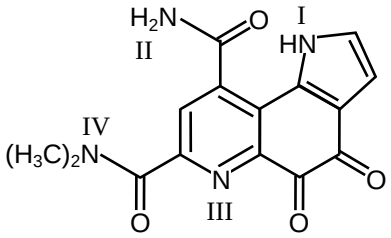
(II) 

(III) 

(IV) 

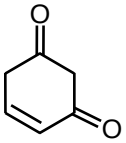
(A) I > II > IV > III (B) IV > II > I > II (C) III > II > I > IV (D) I > II > III > IV

32. The most basic nitrogen in the following compound is **[NSEC-2017]**

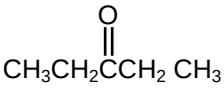


(A) I (B) II (C) III (D) IV

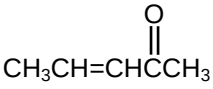
33. The order of enol content in the following molecules is **[NSEC-2017]**



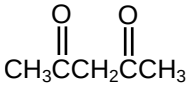
(a)



(b)



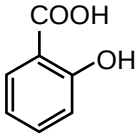
(c)



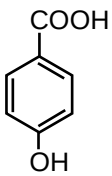
(d)

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

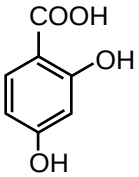
34. The order of pK_a values of the following acids is **[NSEC-2018]**



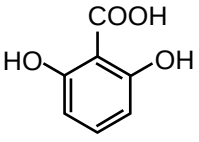
(I)



(II)



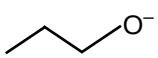
(III)



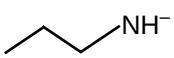
(IV)

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

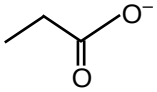
35. The correct order of basicity of the following species is **[NSEC-2018]**



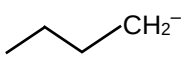
I



II



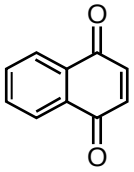
III



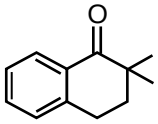
IV

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

36. The molecules that can exhibit tautomerism are **[NSEC-2018]**



(I)



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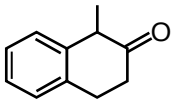
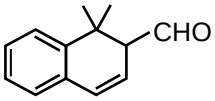


(III)



(IV)

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

PART - III : PRACTICE TEST-2 (IIT-JEE (ADVANCED Pattern))

Max. Time : 1 Hr. **Max. Marks : 45**

Important Instructions :

A. General :

1. The test is of 1 hour duration.
2. The Test Booklet consists of 15 questions. The maximum marks are 45.

B. Question Paper Format :

3. Each part consists of five sections.
4. Section-1 contains 6 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE is correct.
5. Section-2 contains 5 multiple choice questions. Each question has four choices (A), (B), (C) and (D) out of which ONE OR MORE THAN ONE are correct.
6. Section-3 contains 3 questions. The answer to each of the questions is a numerical value, ranging from 0 to 9 (both inclusive).
8. Section-4 contains 1 multiple choice questions. Question has two lists (list-1 : P, Q, R and S; List-2 : 1, 2, 3 and 4). The options for the correct match are provided as (A), (B), (C) and (D) out of which ONLY ONE is correct.

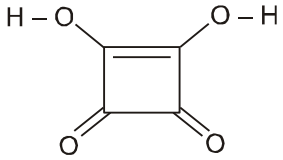
C. Marking Scheme :

9. For each question in Section 1, 4 and 5 you will be awarded 3 marks if you darken the bubble corresponding to the correct answer and zero mark if no bubble is darkened. In all other cases, minus one (–1) mark will be awarded.
10. For each question in Section 2, you will be awarded 3 marks. If you darken all the bubble(s) corresponding to the correct answer(s) and zero mark. If no bubbles are darkened. No negative marks will be answered for incorrect answer in this section.
11. For each question in Section 3, you will be awarded 3 marks if you darken only the bubble corresponding to the correct answer and zero mark if no bubble is darkened. No negative marks will be awarded for incorrect answer in this section.

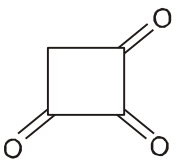
SECTION-1 : (Only One option correct Type)

This section contains 6 multiple choice questions. Each questions has four choices (A), (B), (C) and (D) out of which Only ONE option is correct.

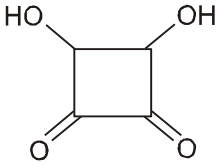
1. The correct pK_a order of the following acids is :



I



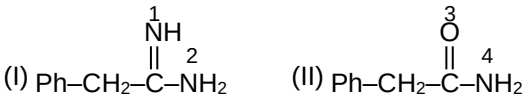
II



III

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

2. The preferred sites of protonation in the following compounds are



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

3. In which pairs first compound is stronger acid than the second ?

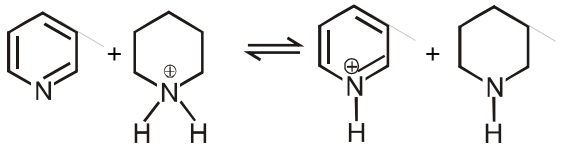
(A) Adipic acid, succinic acid (B) Fumaric acid, maleic acid

(C) Pthalic acid, terepthalic acid (D) Benzoic acid, Picric acid

4. Among the following reaction which favours forward reaction ?

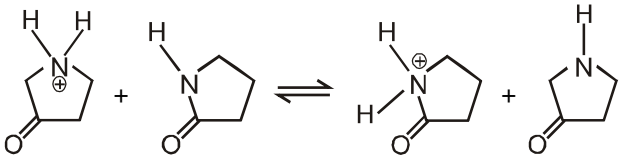
(A) $EtOH + PhO^{\ominus} \rightleftharpoons EtO^{\ominus} + PhOH$

(B)

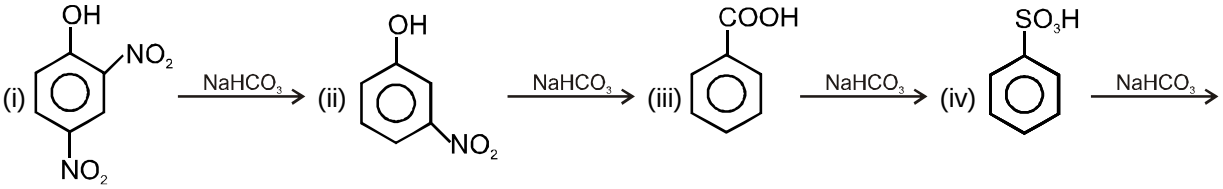


(C) $CH_3\text{–}\overset{\ominus}{C}H_2 + CH_3\text{–}NH_2 \rightleftharpoons CH_3\text{–}CH_3 + CH_3\overset{\ominus}{N}H$

(D)

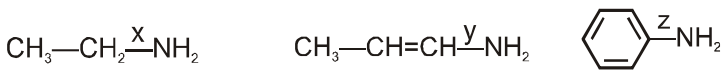


5. Which of the following reactions is/are feasible :



(A) (i) & (ii) (B) (ii), (iii) & (iv) (C) (i), (ii) & (iv) (D) (i), (iii) & (iv)

6. Compare the bond lengths and select the correct option :



(A) x = y = z (B) x > y > z (C) x < y < z (D) x > y = z

Section-2 : (One or More than one options correct Type)

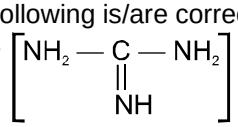
This section contains 6 multipole choice questions. Each questions has four choices (A), (B), (C) and (D) out of which ONE or MORE THAN ONE are correct.

7. Which of the following compounds will show tautomerism ?

(A) 2,2- Dimethylpropanal (B) 2,2-Dimethyl-1 nitropropane

(C) Acetyl Acetone (D) Benzophenone

8. Which of the following is/are correct statement/statements ?

(A) Guanidine  is more basic than pyridine because conjugate acid of guanidine has three equal contributing resonating structure.

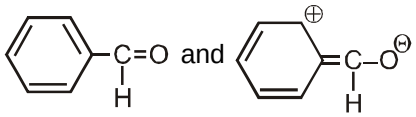
(B) Diethylamine is stronger base than triethylamine in aqueous medium.

(C) Ortho-methyl aniline is weaker base than para-methyl aniline.

(D) 2,4,6-Trinitro-N,N-dimethyl aniline is stronger base than 2,4,6-Trinitro aniline.

9. The tautomeric pairs are

(A) $Me_2C{=}NOH$ and $Me_2CH{-}N{=}O$ (B) $CH_2{=}CH{-}NHCH_3$ and $CH_3{-}CH{=}N{-}CH_3$

(C)  (D) $CH_2{=}CH{-}\underset{\displaystyle OH}{\underset{|}{CH}}{-}CH_3$ and $CH_3{-}CH_2{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}CH_3$

10. In which compounds (II) is more basic than (I)

(A) $(C_2H_5)_3N$ &  (I) (II)

(B) $H_2N{-}\underset{\displaystyle O}{\underset{\|}{C}}{-}NH_2$ & $H_2N{-}\underset{\displaystyle NH}{\underset{\|}{C}}{-}NH_2$ (I) (II)

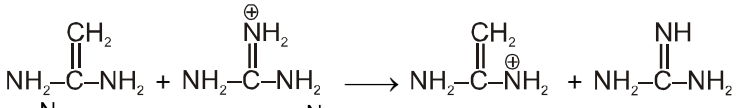
(C) $C_2H_5{-}NH{-}C_2H_5$ &  (I) (II)

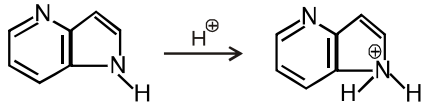
(D) CH_3NH_2 & $(CH_3)_2NH$ (I) (II)

11. Which of the following reactions is/are not feasible :

(A) $CH_3COONa + HCOOH \longrightarrow CH_3COOH + HCOONa$

(B) $CH_3COONa + Ph{-}OH \longrightarrow CH_3COOH + PhONa$

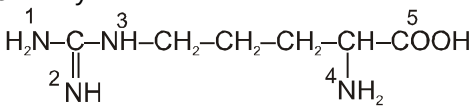
(C) 

(D) 

Section-3: (One Numerical Value Correct Type.)

This section contains 3 questions. Each question, when worked out will result in one numerical value from 0 to 9 (both inclusive)

12. In the given molecule the sites undergoes deprotonation and protonation most readily respectively are x & y then x + y = ?



13. How many of the following compounds will accept $H^{\oplus}$ from ammonium ion.

Pyridine, Aniline, Pyrrole, Triphenyl amine,
Benzyl amine, Methyl amine, Di-methyl amine, Tri-methyl amine

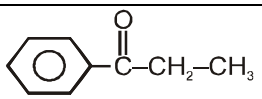
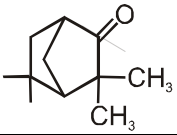
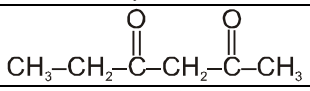
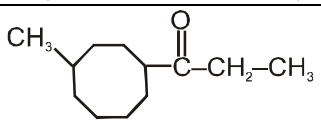
14. How many of the following compounds react with $NaHCO_3$ and liberate $CO_2(g)$

1. Salicylic acid	2. Pthalic acid	3. Picric acid	4. Resorcinol
5. Carbolic acid	6. Aspirin	7. Anisol	8. Tarteric acid

SECTION-4 : Matching List Type (Only One options correct)

This section contains 1 questions, each having two matching lists. Choices for the correct combination of elements from List-I and List-II are given as options (A), (B), (C) and (D) out of which one is correct

15. Match each List-I with List-II and select the correct answer using the code given below the lists.

	Column-I		**Column-II**
P		**1**	Zero enolizable H-atom
Q		**2**	7-enolizable H-atom
R		**3**	2-enolizable H-atom
S		**4**	3-enolizable H-atom

Code :

	P	Q	R	S		P	Q	R	S
(A)	3	1	2	4	(B)	1	2	4	3
(C)	2	1	3	4	(D)	3	2	1	4

Practice Test-2 ((IIT-JEE (ADVANCED Pattern))

OBJECTIVE RESPONSE SHEET (ORS)

Que.	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**
Ans.										
Que.	**11**	**12**	**13**	**14**	**15**					
Ans.										

APSP Answers

PART - I

1.	(4)	**2.**	(3)	**3.**	(2)	**4.**	(3)	**5.**	(3)
6.	(3)	**7.**	(3)	**8.**	(4)	**9.**	(2)	**10.**	(2)
11.	(1)	**12.**	(4)	**13.**	(2)	**14.**	(4)	**15.**	(3)
16.	(3)	**17.**	(1)	**18.**	(4)	**19.**	(2)	**20.**	(3)
21.	5.0	**22.**	6.0	**23.**	6	**24.**	03.00	**25.**	06

PART- II

1.	(3)	**2.**	(4)	**3.**	(2)	**4.**	(3)	**5.**	(4)
6.	(3)	**7.**	(1)	**8.**	(4)	**9.**	(3)	**10.**	(3)
11.	(1)	**12.**	(3)	**13.**	(1)	**14.**	(1)	**15.**	(2)

PART- III

1.	(D)	**2.**	(C)	**3.**	(A)	**4.**	(B)	**5.**	(D)
6.	(A)	**7.**	(A)	**8.**	(A)	**9.**	(D)	**10.**	(A)
11.	(C)	**12.**	(C)	**13.**	(C)	**14.**	(A)	**15.**	(B)
16.	(C)	**17.**	(A)	**18.**	(B)	**19.**	(A)	**20.**	(C)
21.	(D)	**22.**	(D)	**23.**	(A)	**24.**	(A)	**25.**	(B)
26.	(D)	**27.**	(D)	**28.**	(C)	**29.**	(C)	**30.**	(B)
31.	(A)	**32.**	(C)	**33.**	(A)	**34.**	(D)	**35.**	(B)
36.	(C)								

PART- IV

1.	(C)	**2.**	(A)	**3.**	(C)	**4.**	(C)	**5.**	(D)
6.	(B)	**7.**	(BC)	**8.**	(ABCD)	**9.**	(AB)	**10.**	(ABCD)
11.	(BCD)	**12.**	7	**13.**	4 (v, vi, vii, viii)	**14.**	5 (1,2,3,6,8)		
15.	(A)								

PART - I

1. All acids which are stronger than carbonic acid will produces effervesence with sodium bicarbonate.

2. Self explanatory.

3. Electron withdrawing group increase acidic strength and electron relasing group decrease acidic strength.

5. An acid with weaker conjugate base is stronger.

6._ The polarity of N–H bond will be maximum on the N-atom which is most electron deficient.

8. Lone pair electrons present on more electronegative atom is less basic.

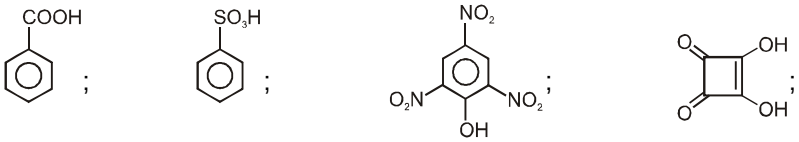
9. Secondary amine is most basic in aqueous solution among aliphatic amines.

11. CF_3–COOH > CCl_3–COOH > HCOOH > CH_3COOH (K_a order)

17. Acetyl acetone is liquid and exist mainly as III due to intramolecular H-bonding and the correct answer is III > II > I.
However in aquous medium, the correct answer is II > III > I.

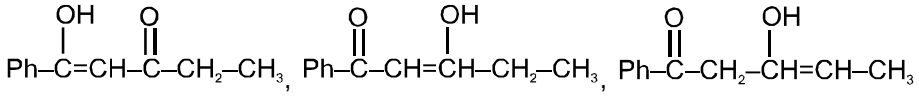
18. Salicylic acid is more acidic than p-hydroxy benzoic acid.

21. a = 3
b = 4
c = 4

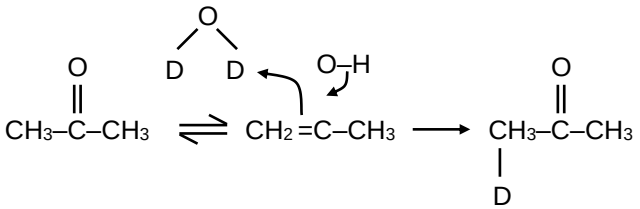
22. 

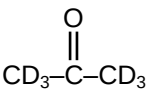
HCl & HCOOH are stronger acids than H_2CO_3.

23. Following are less acidic than formic acid
(i) Ph–OH (ii) Ph–COOH (iv) H_2CO_3
(v) CH_3–OH (vii) Cl–CH_2CH_2COOH (viii) Ph–NH_2

24. 

25. Enolisation occurs in presence of D_2O and new C–D bonds are formed instead of –CH bonds on C–D bonds are stronger than –C–H bonds but breaking occurs of –C–H bond during enolisation.

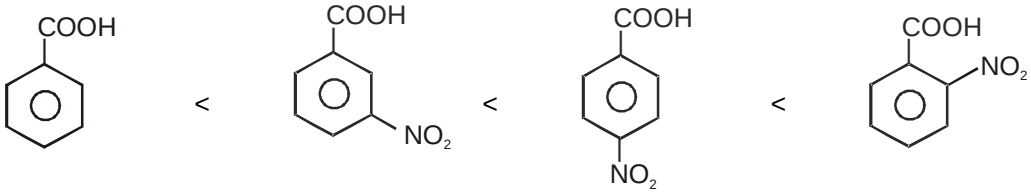


Like this way all H's are displaced by deuterium on  is formed.

PART – II

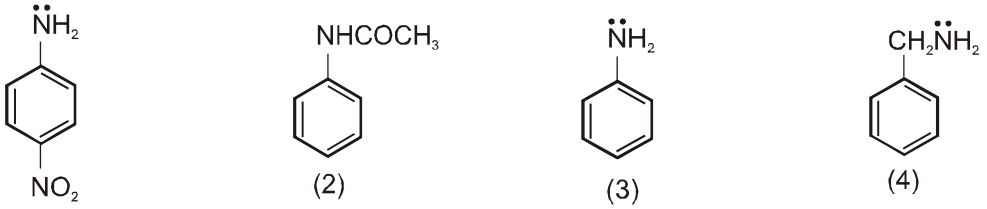
1. Except the amines containing tertiary butyl group, all lower aliphatic amines are stronger bases than ammonia because of + I (inductive). The alkyl groups, which are electron releasing groups, increase the electron density around the nitrogen there by increasing the availability of the lone pair of electrons to proton or lewis acids and making the amine more basic.
Thus the relative strength is in order $(CH_3)_2$ NH > CH_3NH_2 > NH_3.

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

3. 

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

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



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

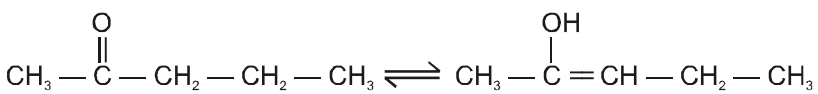
6. Effect of substituent on the acid strength of aliphatic acids.
(i) Acidity decreases as the +I – effect of the alkyl group increases.
(ii) Acidity decreases as the –I – effect decreases.
(iii) On the basis of given information the relative order of increasing acid strength of the given compounds:
$(CH_3)_2$ COOH < CH_3 COOH < CH_3 OCH_2COOH < CF_3COOH

7. The increasing order of basicity of the given compounds is
$(CH_3)_2NH$ > CH_3NH_2 > $(CH_3)_3N$ > $C_6H_5NH_2$
Due to the +I effect of alkyl groups the electron density on nitrogen increases and thus the availability of the lone pair of electrons to proton increases and hence the basicity of amines also increases. So aliphatic amines are more basic than aniline.
In case of tertiary amine $(CH_3)_3$ N, the covering of alkyl groups over nitrogen atom from all sides makes the approach and bonding by a proton relatively difficult, hence the basicity decreases. Electron withdrawing (C_6H_5–) groups decreases electron density on nitrogen atom and thereby decreasing basicity.

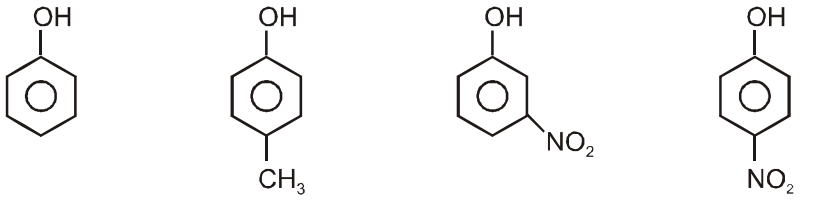
8. Basicity $\frac{1}{\text{Electroneg ativity}}$ (In period)

If lone pair of electron takes part in conjugation then availability of lone pair of electron decrease and basic strength decrease.

9. α-chlorobutyric acid is more stronger acid than others due to – I effect of Cl.

10. 

11.

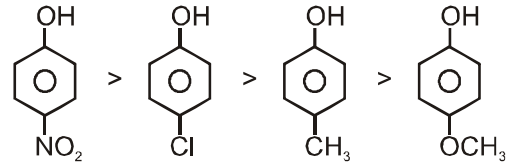


HC, + I – I – M, – I

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

Therefore acidity order is : D > C > A > B.

12.



(–m, –I) (–I) (+I, + HC) (+m)

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

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

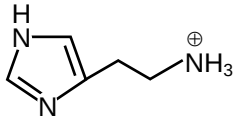
order of K_b : $(CH_3)_2\ddot{N}H > CH_3\ddot{N}H_2 > (CH_3)_3\ddot{N} > C_6H_5\ddot{N}H_2$

As we know $pK_b = -\log K_b$

so $(CH_3)_2\ddot{N}H$ will have smallest pK_b value.

14. Imidine is more basic than 2º amine followed by 1º amine.

15. The pH of blood is approx 7.0, therefore the acids with pK_a less than 7 will loose H^+.



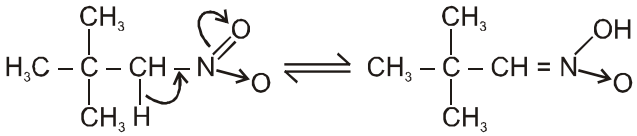
PART - IV

1. On the basis of stability of conjugate base due to electronic effects.

2. Protonation at site 1 and 3 is supported by resonance stabilization.

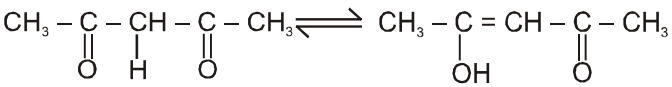
3. (C) Phthalic acid is stronger acid due to intramolecular hydrogen bonding.

7. (B)



2,2-dimethyl-1-nitropropane

(C)



Acetylacetone

8. All statements are correct.

9. (A,B) Nitroso $\rightleftharpoons$ oxime (Tautomer)

Imine $\rightleftharpoons$ enamine (Tautomer).

12. 5 is deprotanated since it is most acidic acid, 2 is protonated since it is most basic (guanidinic N).

x = 5, y =2 so x + y = 7