

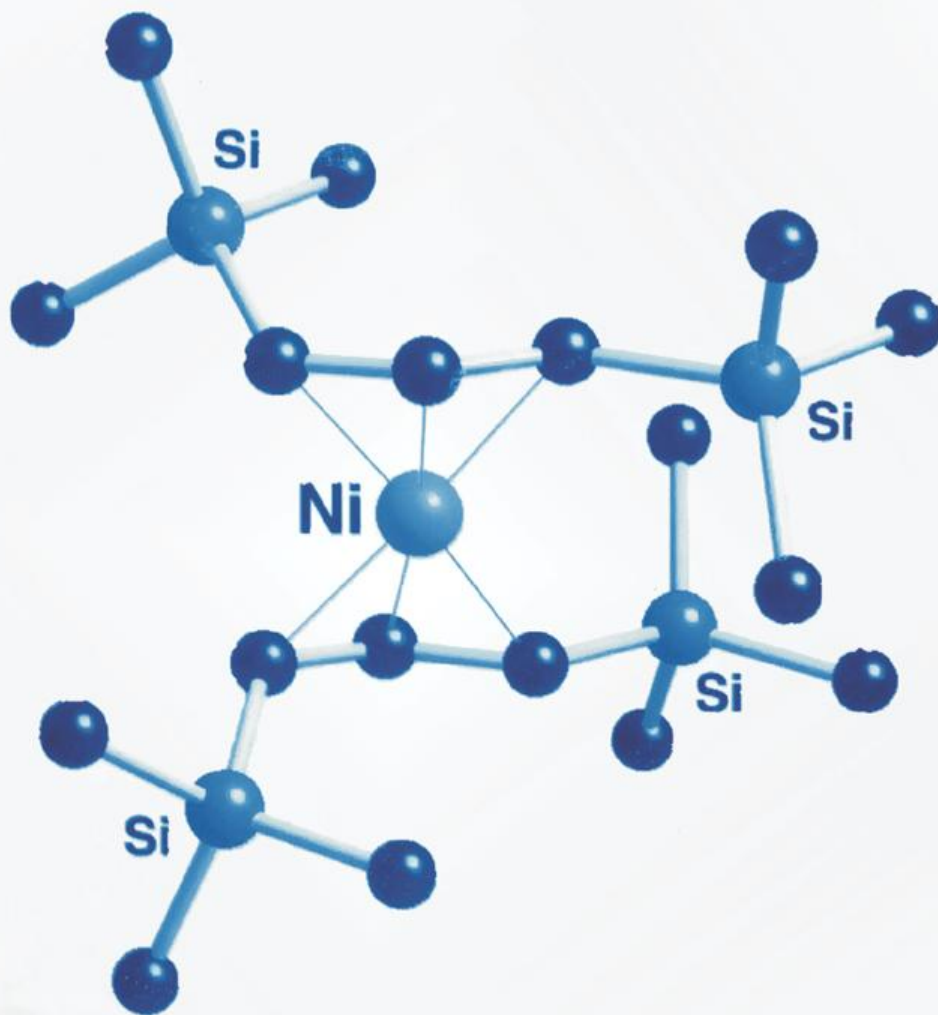
CHEMISTRY



Resonance
Educating for better tomorrow

Distance Learning Programmes Division (DLPD)

JEE (Main)



Electronic Effects and Applications

Part A : GOC- I

Electron displacement in organic compounds :

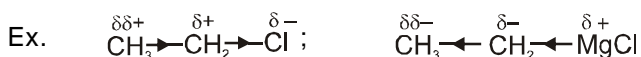
The electron displacement in an organic molecule may take place under the influence of an atom or a substituent group or in the presence of an appropriate attacking reagent.

Types of electronic displacement

- | | | |
|---------------------|---|---------------------|
| 1. Inductive effect | 2. Resonance | 3. Mesomeric effect |
| 4. Hyperconjugation | 5. Electromeric effect (temporary effect) | |

1. Inductive effect :

When a covalent bond is formed between the two atoms of different electronegativity then sigma bond pair of electrons are shifted towards more electronegative atom as a result dipole is created between two atoms. Due to this dipole, sigma bonded electrons in the carbon chain becomes polarised. Such polarisation of σ bond caused by the polarisation of adjacent σ bond is referred to as the **inductive effect**.



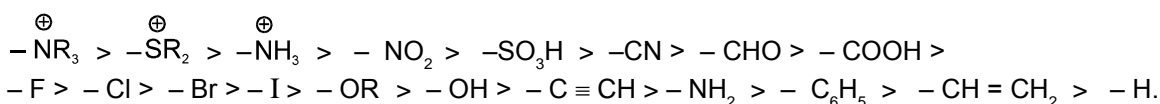
- Note :** (i) It is a permanent effect (ii) It is distance dependent
 (iii) It is operated through σ bond not through π -bond (iv) It is negligible after three carbon atom
 (v) C-H bond is the reference of inductive effect i.e. polarity of C-H bond is considered to be negligible.

Inductive effects are of two types :

(i) -I effect :

The atom or group which withdraws electron clouds is known as -I group and effect is called -I effect.

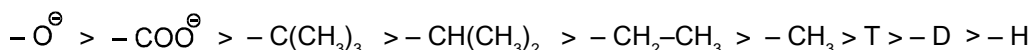
Decreasing order of -I effect :



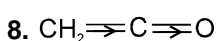
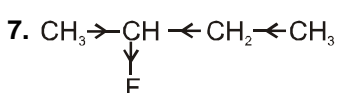
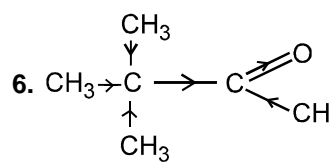
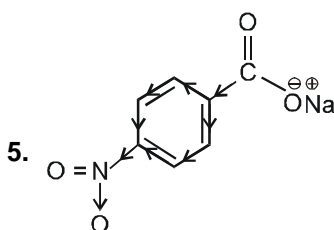
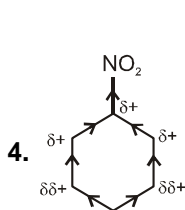
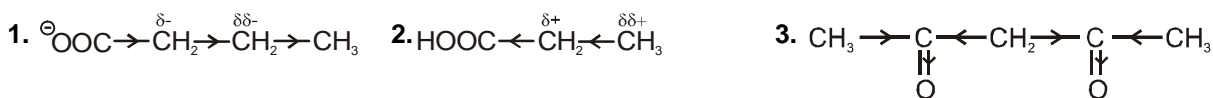
(ii) +I effect :

The group which releases or donates electron clouds is known as +I group & effect is called +I effect.

Decreasing order of +I effect :



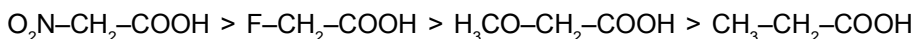
Direction of electron displacements



Applications of Inductive effect :

(i) Acidic strength :

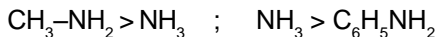
– I effect \propto Acidic strength (presence of – I groups increases acidic character)



Since NO_2 has strong – I effect, its influence will make corresponding acid strongest.

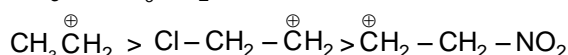
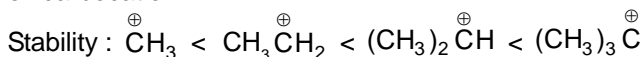
(ii) Basic strength :

+ I effect \propto Basic strength (presence of + I groups increases basic character)



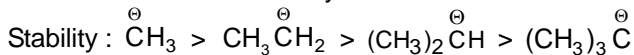
(iii) Stability of carbocations :

Carbocations are electron deficient species and they are stabilised by + I effect and destabilised by – I effect. Because + I effect tends to decrease the positive charge and – I effect tends to increase the positive charge on carbocation



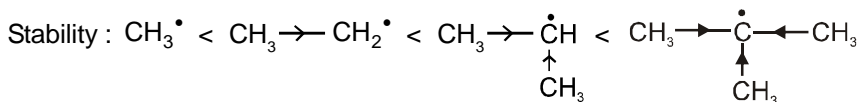
(iv) Stability of carbanion :

Carbanions are stabilised by – I effect and destabilised by + I effect.



(v) Stability of carbon free radical :

Carbon free radicals are stabilised by + I effect.

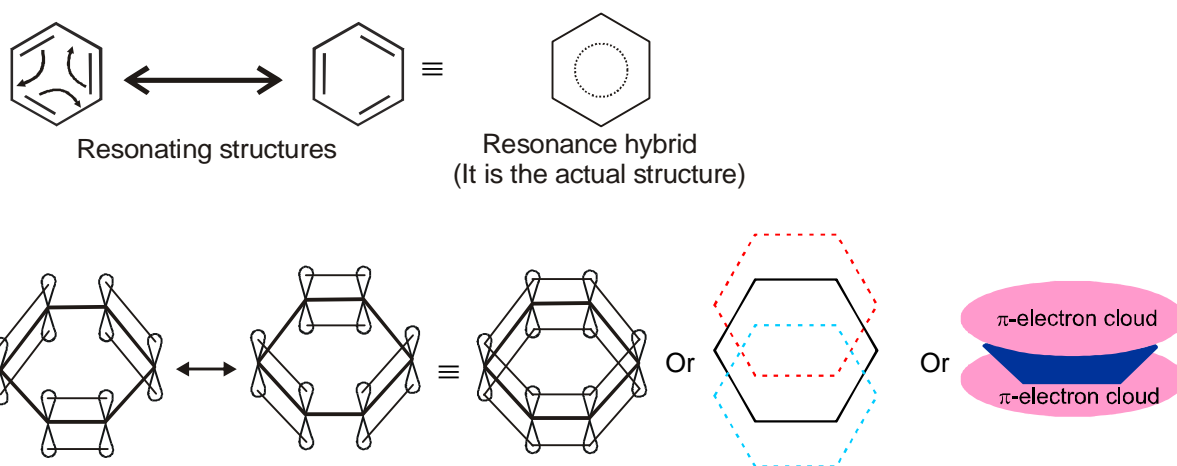


(vi) Dipole moment : Greater I effect results in greater dipole moment.



2. Resonance Effect :

It is a phenomenon in which a particular compound can be written in two or more structures with identical position of atoms. These lewis structures are called resonating structure or canonical structure or contributing structures.



The resonance structures are hypothetical and individually do not represent any real molecule. But they all contribute to a real structure which is called resonance hybrid.

The resonance hybrid is more stable than any resonating structure.

The most stable resonating structure contribute maximum to the resonance hybrid and least stable resonating structure contribute minimum to resonance hybrid.

Resonance energy :

The P.E. difference between the most stable resonating structure and resonance hybrid is called resonance energy. The stability of molecule is directly proportional to resonance energy.

Conditions for resonance :

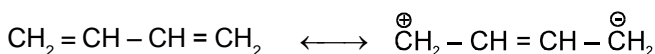
1. All atoms participating in resonance must be sp or sp² hybridised.
2. The parallel p-orbitals overlap to each other.
3. Molecule should have conjugated system (parallel p-orbitals system is called conjugate system)

Types of Conjugation :

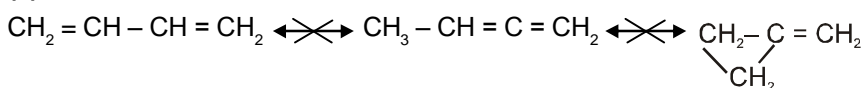
1. Conjugation between C = C and C = C ($\text{CH}_2 = \text{CH} \rightleftharpoons \text{CH} = \dot{\text{C}}\text{H}_2 \longleftrightarrow \overset{\oplus}{\text{C}}\text{H}_2 - \text{CH} = \text{CH} - \overset{\ominus}{\text{C}}\text{H}_2$)
2. Conjugation between +ve charge and C = C ($\text{CH}_2 = \text{CH} - \overset{\oplus}{\text{C}}\text{H}_2 \longleftrightarrow \overset{\oplus}{\text{C}}\text{H}_2 - \text{CH} = \text{CH}_2$)
3. Conjugation between lone pair and C = C ($:\ddot{\text{Cl}} - \text{CH} = \text{CH}_2 \longleftrightarrow \overset{\oplus}{\text{Cl}} = \text{CH} - \overset{\ominus}{\text{C}}\text{H}_2$)
4. Conjugation between odd electron and C = C ($\text{CH}_2 = \text{CH} - \dot{\text{C}}\text{H}_2 \longleftrightarrow \dot{\text{C}}\text{H}_2 - \text{CH} = \text{CH}_2$)
5. Conjugation between negative charge and C = C ($\text{CH}_2 = \text{CH} - \overset{\ominus}{\text{C}}\text{H}_2 \longleftrightarrow \overset{\ominus}{\text{C}}\text{H}_2 - \text{CH} = \text{CH}_2$)

Rules for writing resonating structure :

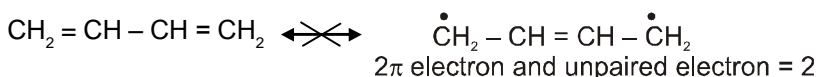
(i) In resonating structure only p-orbitals electron are shifted, σ bond electron are not involved in resonance, therefore the σ bond skeleton will remain same in two resonating structures.



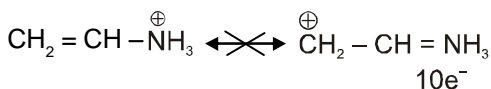
(ii) The movement of atoms are not allowed.



(iii) The no. of paired e⁻ are same and no. of unpaired electron are same in two resonating structures.

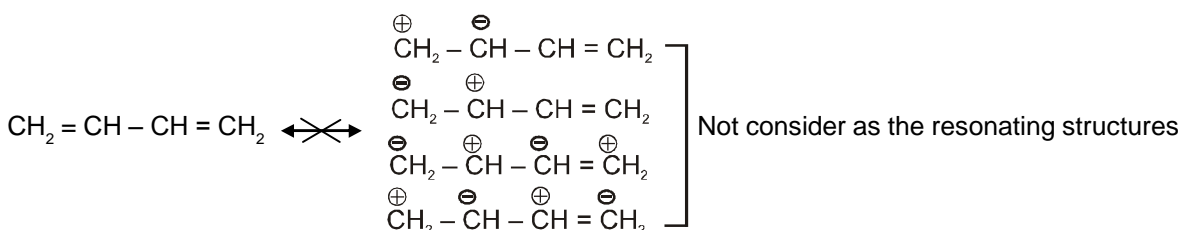


(iv) The octet rule is not violated (for second period element).

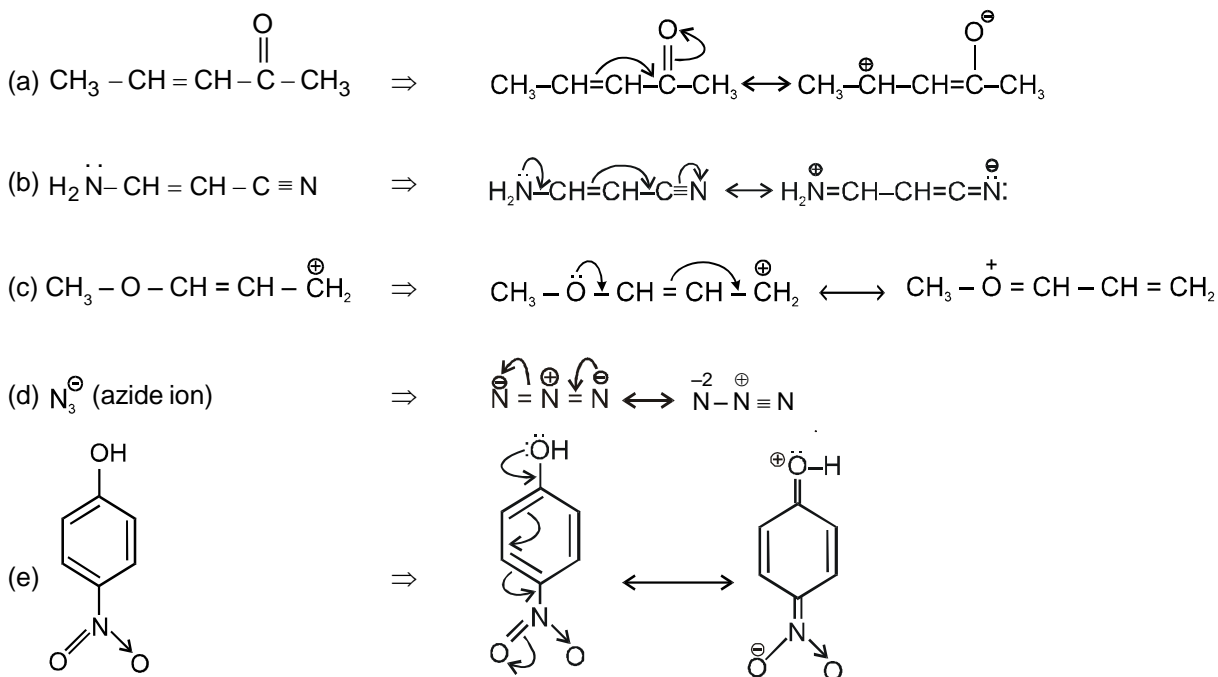


(v) High energy structures are rejected as resonating structure and their contribution to the resonance hybrid is negligible.

Opposite charges on adjacent atoms and similar charges on adjacent atoms are cases of high energy. These are not accepted as resonating structures.

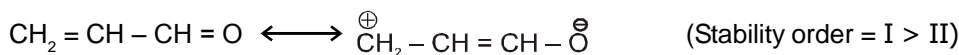


Examples : Resonating structures for the following molecules are :



Rules for stability of resonating structure :

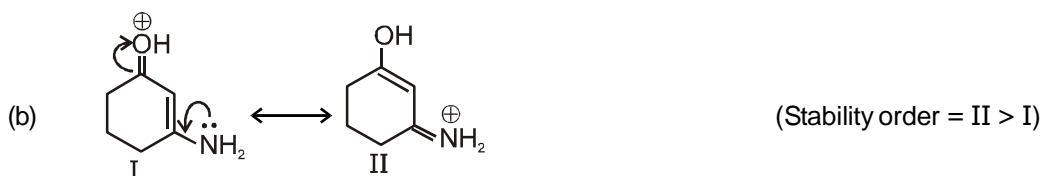
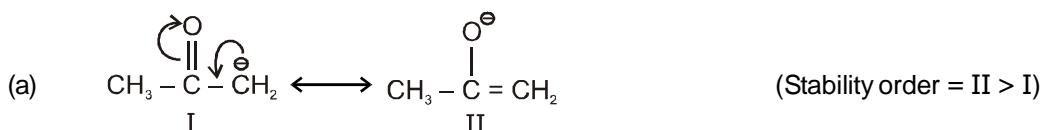
(i) The resonating structure without any charge separation is more stable.



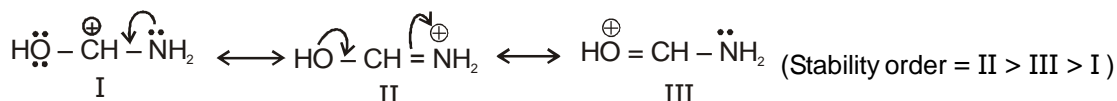
(ii) The resonating structure with more no. of π bonds is more stable and structure with complete octet of each atom is more stable.



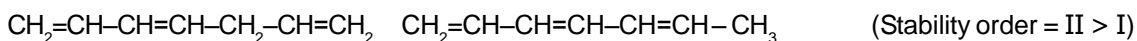
(iii) Negative charge on more electronegative atom and positive charge on less electronegative atom are more stable.



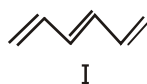
Note : If the rule of electronegativity and rule of octet are contradictory to each other then priority is given to the octet rule.



(iv) Between two different compounds more conjugated is more stable (provided nature of bonding is same).



(v) In two compounds if one is aromatic and another is non aromatic and conjugation is equal in both the compounds then aromatic compound is more stable (nature of bonding is same)



I

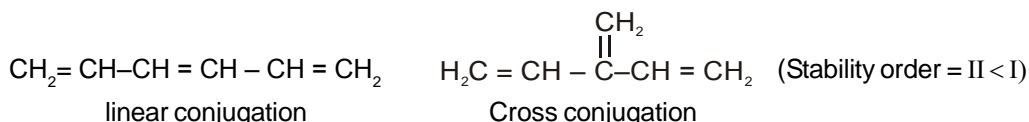


II (Aromatic)

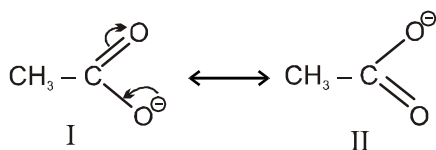
(Stability order = I < II)

(vi) Structure with linear conjugation is more stable than cross conjugation (nature of bonding is same).

Cross conjugation : If two groups are in conjugation with a particular group but not conjugated with each other then the system is called cross conjugation.



Note : Equivalent resonance structures make equal contributions to the hybrid and a system described by them has a large resonance stabilization.



I

II

(Stability order : I = II)

3. Mesomeric effect :

Mesomeric effect is defined as permanent effect of π electron shifting from multiple bond to atom or from multiple bond to single bond or from lone pair to single bond.

This effect mainly operates in conjugated system of double bond. So that this effect is also known as conjugate effect and **distance independent**.

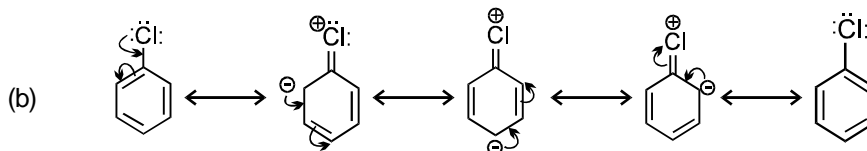
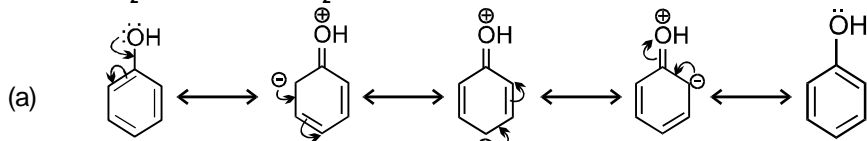
Types of Mesomeric effect :

(i) + m effect (ii) - m effect

(i) + m group (Electron releasing group) :

A group, first atom of which bears -ve charge or lone pair always shows +m effect. Due to +m effect the electron density of benzene ring is increased particularly on ortho and para positions.

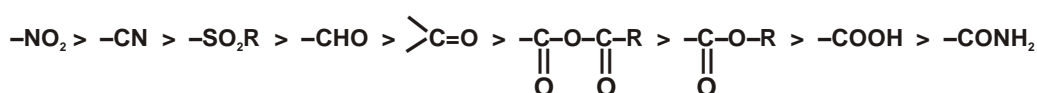
Relative order of +m group :

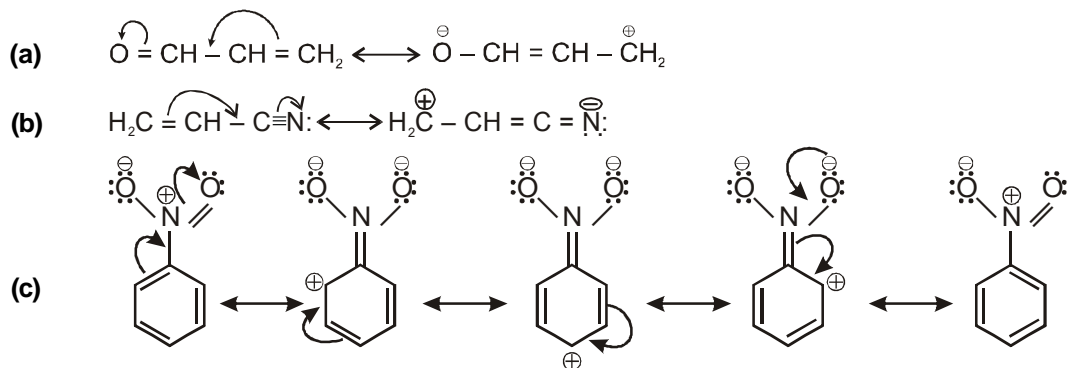


(ii) - m group (Electron withdrawing group) :

A group that contains double bond or triple bond between hetero atoms will show -m effect. Due to -m the electron density on benzene ring is decreased particularly on ortho and para positions.

Relative order of -m group :





4. Hyperconjugation :

When a sigma C–H bond of sp^3 hybridised carbon is in conjugation with π -bond (p-orbital), half filled p-orbital or vacant p-orbital, then the bond pair e^- of sigma C–H bond overlap with adjacent p-orbital. This phenomenon is called hyperconjugation. It may take place in alkene, alkynes, carbocations and carbon free radicals.

Like resonance hyperconjugation is also a stabilising effect but **the effect of resonance is more dominating than hyperconjugation**, since in resonance only p-orbital overlap while in hyperconjugation σ molecular orbitals overlap with p- molecular orbital.

* Hyperconjugation is also called **no bond resonance or Baker Nathan Effect**.

Number of hyperconjugative structure = Number of α -hydrogen atoms at sp^3 hybridised α -carbon atoms.

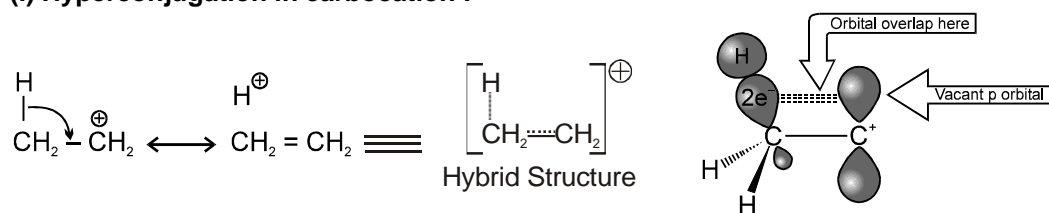
* **Condition** : sp^3 hybrid C–H or C–D must be present adjacent to the $\text{C}^+/\text{C}^\cdot/\text{C}=\text{C}/\text{C}\equiv\text{C}$.

Important points :

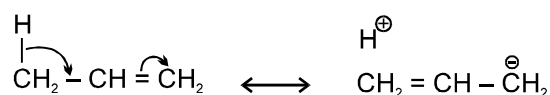
- (i) It is distance independent. (ii) Not applicable at carbanion.
 (iii) Hybridisation of atoms remains unchanged. (iv) It is a permanent effect.

Structure	Number of α -hydrogens	Structure	Number of α -hydrogens
$\text{CH}_3-\text{CH}=\text{CH}_2$	3	$\text{H}_3\text{C}-\overset{\oplus}{\text{C}}-\text{CH}_3$	9
$\text{CH}_3-\text{CH}_2-\text{CH}=\text{CH}_2$	2	$\begin{array}{c} \text{CH}_3 \\ \\ \text{H}_3\text{C}-\overset{\oplus}{\text{C}}-\text{CH}_3 \\ \\ \text{CH}_3 \end{array}$	9
$\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3$	6		
$\text{CH}_3-\overset{\oplus}{\text{C}}\text{H}_2$	3		

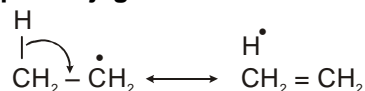
(i) Hyperconjugation in carbocation :



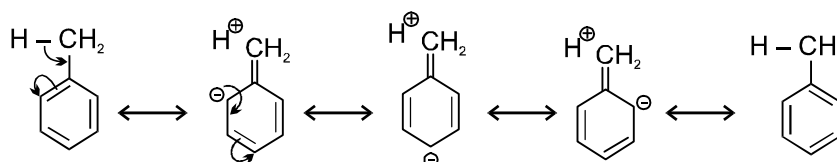
(ii) Hyperconjugation in alkene :



(iii) Hyperconjugation in radical :



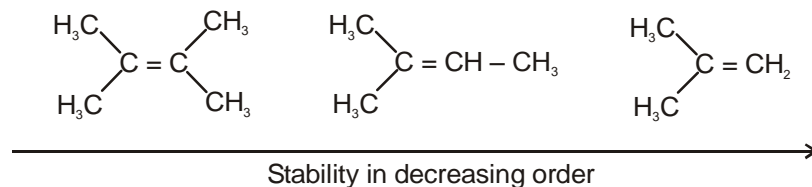
(iv) Hyperconjugation in toluene :



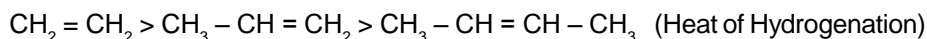
Applications of Hyperconjugation effect :

(i) **Stability of Alkenes** : Hyperconjugation explains the stability of certain alkenes over other alkenes.

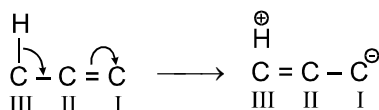
Stability of alkenes \propto no. of hyperconjugative structures $\propto \frac{1}{\Delta H_{\text{Hydrogenation}}}$



(ii) **Heat of hydrogenation** : Greater the number of α hydrogen atoms, greater will be stability of alkene. Thus greater extent of hyperconjugation results lower value of heat of hydrogenation ($\Delta H_{\text{hydrogenation}}$)



(iii) **Bond Length** : Bond length is also affected by hyperconjugation

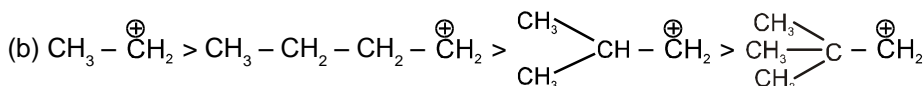
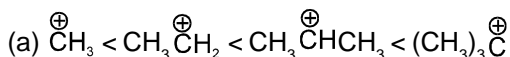


(a) Bond length of C(II) – C(III) bond is less than expected

(b) Bond length of C(II) – C(I) bond is more than expected

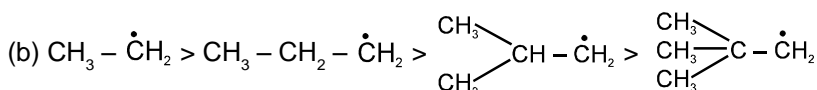
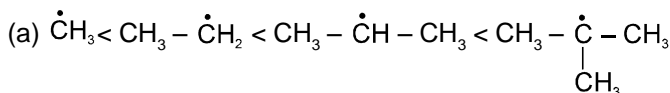
(c) C – H bond is longer than expected

(iv) **Stability of carbocation** : Greater number of ' α ' hydrogen atoms, greater will be stability of carbocations.



(due to resultant of inductive effect and hyperconjugation)

(v) **Stability of free radical** : More the number of α -hydrogen atoms, more will be stability of carbon free radical



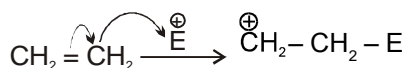
(due to resultant of inductive effect and hyperconjugation)

5. Electromeric effects :

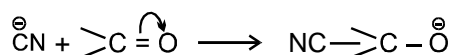
It is a temporary effect. It is defined as the complete transfer of a shared pair of π -electrons to one of the atoms joined by a multiple bond on the demand of an attacking reagent. The organic compound having a multiple bond (double or triple bond) show this effect in the presence of an attacking reagent only. It is represented by E and the shifting of the electrons is shown by a curved arrow.

There are two types of electromeric effect.

(i) **+E effect** : In this effect π -electron of the multiple bond transferred to that atom to which the reagent gets attached.



(ii) **– E effect** : In this effect the π -electron of the multiple bond transferred to that atom to which the attacking reagent does not get attached.



When inductive and electromeric effects operate in opposite directions then the electromeric effect dominates.

6. Aromatic Character : [The Huckel $4n + 2$ rule]

Aromatic compounds have characteristic smell, have extra stability and burn with sooty flame.

Based on the properties of aromatic compounds there are four criteria about the π -system.




(i) Complete conjugated system (all atoms must be sp^2 or sp hybridised).

(ii) Cyclic.

(iii) Planar.

(iv) Huckel rule $(4n + 2) \pi$ electrons in the cyclic conjugated π -system. Where $n =$ an integer $0, 1, 2, 3, \dots$

Comparison between aromatic, anti aromatic and non-aromatic compounds.

Characteristics	Aromatic compounds (A)	Anti Aromatic compounds (B)	Non-Aromatic compounds (C)
Example			
1. Structure	Cyclic, planar all atoms of ring sp^2 hybridised	Cyclic, planar all atoms of ring sp^2 hybridised	Cyclic or acyclic planar, or non planar sp or sp^2 or sp^3
2. No. of πe^- s in the ring	$(4n+2)\pi e^-$ (Huckle's rule)	$(4n)\pi e^-$	Any no. of πe^- s
3. MOT	Unpaired e^- s in B.M.O.	Some πe^- s in non-bonding M.O.	B.M.O. / Non-bonding M.O.
4. Overlapping	Favourable over lapping of p orbital	Unfavourable over lapping of p orbital	Simple overlapping like alkenes
5. Resonance energy (R.E.)	Very high R.E. $> 20-25$ kcal/mol	Zero	4-8 kcal/mol like alkenes
6. Stability	Have extra stability due to close conjugation of πe^- s	Unstable not-exist at room temperature	Normal stability like a conjugated system
7. Characteristic Reactions	Electrophilic substitution Reaction	Dimerisation reaction to attain stability	Electrophilic addition reaction like alkenes

Stability of compounds = Aromatic compound $>$ Non-Aromatic compound $>$ Anti-Aromatic compound

Part B : GOC- II

7. Reaction Intermediates :

A covalent bond can get cleaved either by : (i) Homolytic cleavage or (ii) Heterolytic cleavage

(i) Homolytic bond dissociation : A bond dissociation in which a bond pair electron is equally distributed to the bonding atoms.



a homolytic bond dissociation generates radicals.

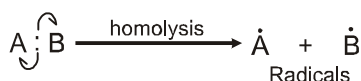
(ii) Heterolytic bond dissociation : A bond dissociation in which a bond pair electron is shifted to one atom only.



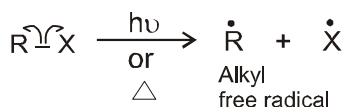
A heterolytic bond dissociation always generate a cation and an anion.

(A) Free Radicals :

Homolysis of covalent bond results into free radical intermediates possess the unpaired electrons.



It is generated in presence of Sun light, peroxide or High temperature



- (i) It is Neutral species with odd e^-
- (ii) It is paramagnetic in nature due to odd e^-
- (iii) No rearrangement is observed generally.
- (iv) Carbon atom having odd electron is in sp^2 hybridised state and 7 e^- in its valence shell.
- (v) Usually O_2 is used as inhibitor
- (vi) Any reaction if it is carried out in the presence of sunlight, peroxide or high temperature it generally proceeds via free radical intermediate.

Stability of free radical: It is stabilised by resonance, hyperconjugation and + I groups.

stability order $(C_6H_5)_3 C^\bullet > (C_6H_5)_2 \dot{C}H > C_6H_5 \dot{C}H_2 > CH_2 = \dot{C}H - CH_2 > 3^\circ > 2^\circ > 1^\circ > \dot{C}H_3$

(B) Carbocation :

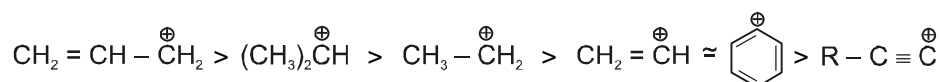
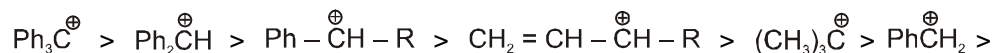
A carbon intermediate which contain three bond pair & a positive charge on it is called carbocation. It is a six electron having electrodeficient, diamagnetic species and rearrangement can be possible if stability increases.

Hybridisation	Example
sp^2	$\overset{\oplus}{C}H_3, CH_3 - \overset{\oplus}{C}H_2$
sp	$H_2C = \overset{\oplus}{C}H, HC \equiv \overset{\oplus}{C}$

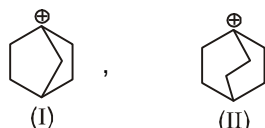
Stability of carbocations : Followings factors increases the stability of carbocations

- (i) + m effect (ii) Resonance stabilization (iii) Hyperconjugation (iv) + I effect

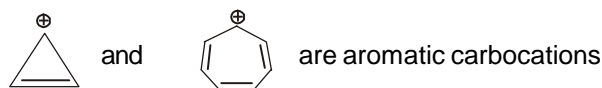
General stability order :



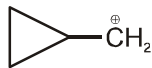
Note : (1) The carbocation is not possible at following bridge head positions I and II



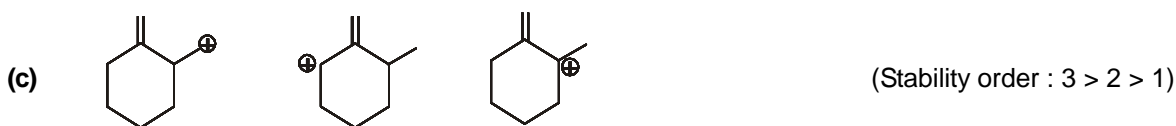
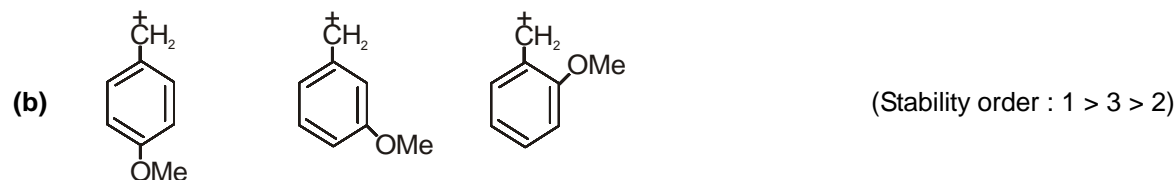
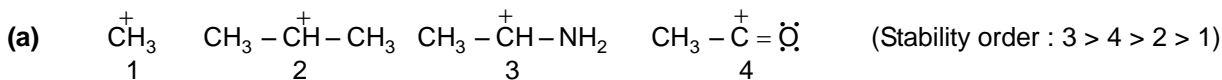
(2) Carbocations showing aromatic behaviour are exceptionally more stable



(3) Cyclopropylmethylcarbonium ion is also more stable due to σ bond overlapping with empty p-orbital.



Examples of stability order :



(C) Carbanion :

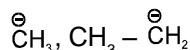
A carbon intermediate which contains three bond pairs and a negative charge on it, is called carbanion.

Hybridisation : Carbanion carbon is in sp^3 hybridised state if it is linked to sp^3 hybridised carbon or hydrogen atom, whereas it will be in sp^2 hybridised state if it is linked to sp^2 hybridised C-atom due to resonance.

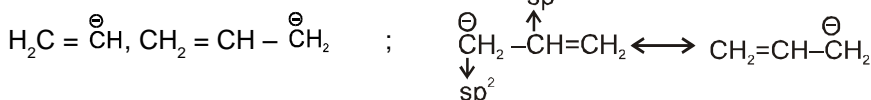
Hybridisation

Example

sp^3



sp^2



sp



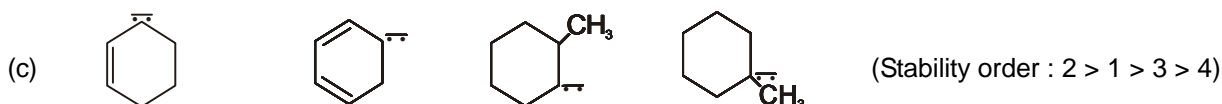
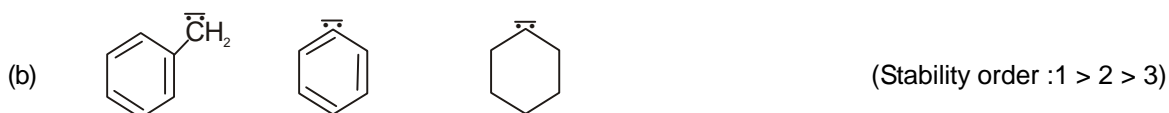
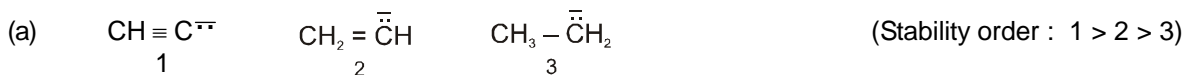
- Note :** (i) Carbanion carbon is in sp^3 , sp^2 and sp hybridised state.
 (ii) No rearrangement takes place.
 (iii) It is diamagnetic ($8e^-$) in nature.

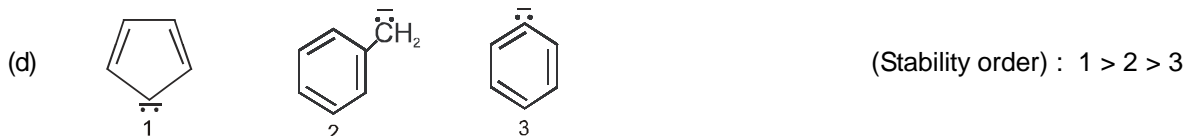
Stability of Carbanion : Following factors increase the stability of carbanions.

- (i) – M effect (ii) Delocalisation of charge (iii) – I effect

Note : If α -position of a carbanion has a functional group which contains multiple bond ($\text{C} = \text{C}$, $\text{C} = \text{O}$, $\text{C} \equiv \text{N}$, NO_2 etc) then carbanions are stabilised by resonance.

Example of stability order :

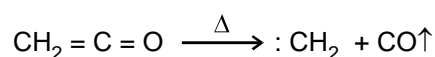
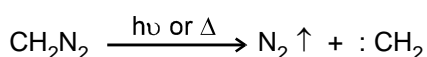
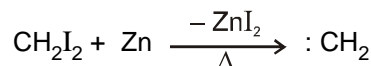
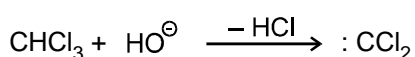



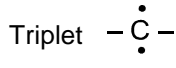


(D) Carbenes (Divalent Carbon intermediates) :

Definition : There is a group of intermediates in which carbon forms only two bonds. These neutral divalent carbon species are called carbenes. Most carbenes are highly unstable that are capable of only fleeting existence. Soon after carbenes are formed, they usually react with another molecules.

Methods of preparation of carbene :



Types of carbene	Singlet 	Triplet 
Shape	Bent	Linear
Hybridisation	sp^2	sp
Nature of reaction	stereospecific	None
State	Excited state	Ground state
Magnetic	Diamagnetic	Paramagnetic
Nature	Paired electrons	Diradical

(E) Nitrenes

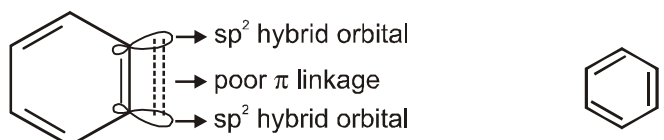
The nitrogen analog of carbenes are nitrenes. They are very much reactive since in them octet of N is incomplete.

In nitrenes only one valency of N is satisfied.



(F) Benzyne

The benzene ring has one extra C – C π bond in benzyne



Clearly, we can see that the newly formed π bond cannot enter in resonance with other π orbitals of ring. since it is in perpendicular plane.

It is also important to note that hybridisation of each carbon involved in 'Benzynic bond' is sp^2 since the overlap between these sp^2 hybrid orbitals is not so much effective.

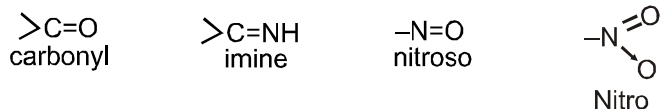
8. Tautomerism :

Definition :

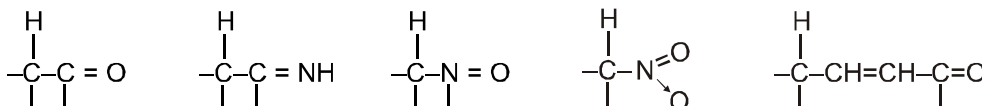
Tautomerism is a phenomenon by which a single compound exists in two or more readily interconvertible structures that differ in the relative positions of at least one atomic nucleus, generally hydrogen. These two isomers remain in dynamic equilibrium, can be isolated and also give different lab test.

Conditions :

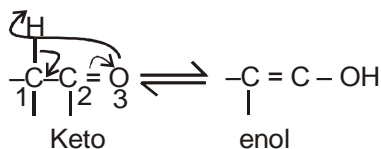
1. Usually present in the following functional groups



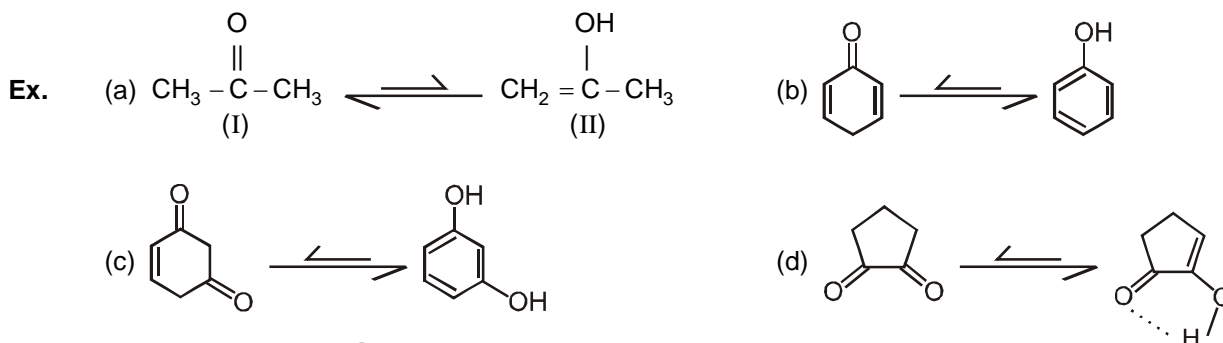
2. Basic need for its existence is attachment of these groups with the sp^3 hybridised C-atom having atleast one hydrogen atom as –



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 :



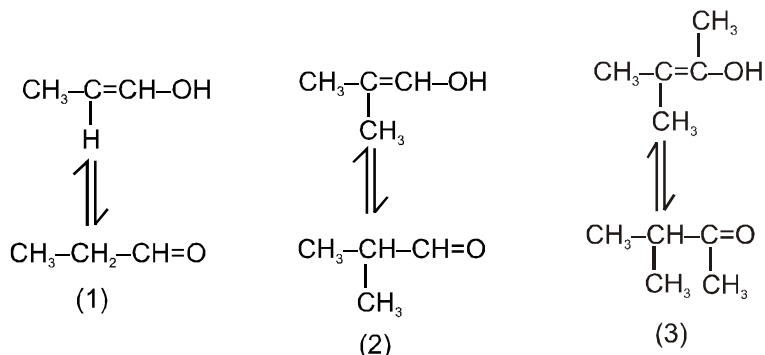
These two forms (remain in equilibrium) are called tautomers of each other. The interconvertibility of tautomers is a chemical reaction which involves making and breaking of bonds.



% Enol content in the carbonyl compounds :

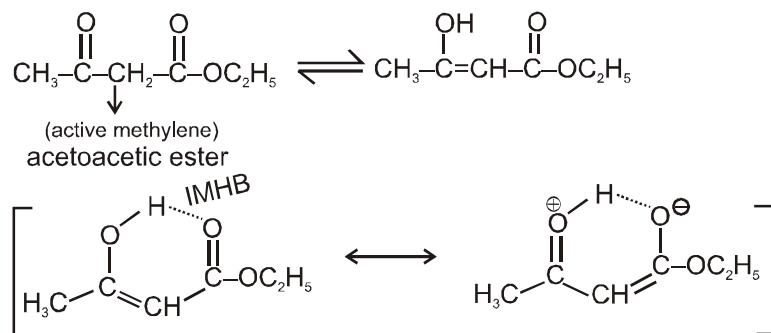
(i) For monocarbonyl generally it is very less.

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



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

(iii) 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.

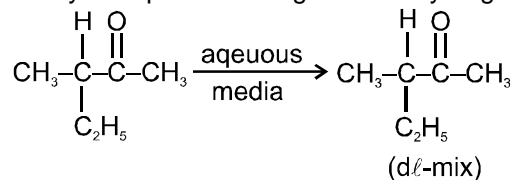


(iv) If active methylene group is more acidic then enol content will be more.

For example in acetyl acetone ($\text{CH}_3-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_2-\overset{\text{O}}{\parallel}{\text{C}}-\text{CH}_3$) enolic content is 75–76% while it is 7–8% in acetoacetic ester because ester group shows less electron withdrawing nature than keto group.

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

(vi) A carbonyl compound having chiral α -hydrogen atom racemizes in aqueous solution.



9. Acidic Strength :

Definitions :

(1) **Arrhenius Acid** : The compounds which furnish H^+ ion in aqueous solution are called Arrhenius acids.

Ex. H_2SO_4 , HNO_3 , HCl , HClO_4 etc.

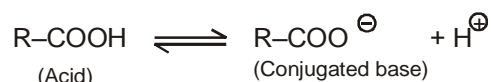
(2) **Bronsted Acids** : The species, which are proton (H^+ ion) donors, are called Bronsted acids.

Ex. NH_4^+ , H_3O^+ , etc. All Arrhenius acids are Bronsted acids.

(3) **Lewis Acids** : The lone pair acceptors are known as Lewis acids. They have vacant p or d orbitals.

Ex. BX_3 , AlX_3 , ZnX_2 etc.

Scale for Measurement of Acid Strength :



$$K_a = \frac{[\text{RCOO}^\ominus][\text{H}^\oplus]}{[\text{RCOOH}]} \quad \text{Where } K_a \rightarrow \text{acid dissociation constant.}$$

A strong acid is defined as the acid which furnish more number of H^+ ion in aqueous solution

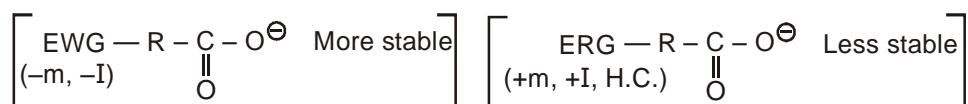
So, a stronger acid has higher value of K_a , or it has lower value of $\text{p}K_a$.

$\text{p}K_a = -\log K_a$ (More K_a or less $\text{p}K_a$ i.e. more acidic compound)

Note : A stronger acid has more stable conjugate base.

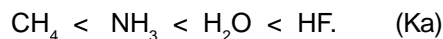
Factors affecting stability of conjugate base/anion :

Presence of EWG in the alkyl ($-\text{R}$) part of the acid increases stability of anion, and hence increases acidic strength.



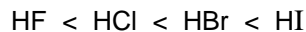
(A) Acid Strength of Hydrides in periodic table :

(1) Along the period from left to right : As electronegativity increase, $K_a \uparrow$

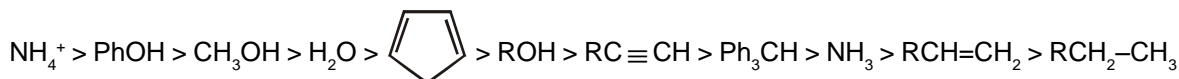
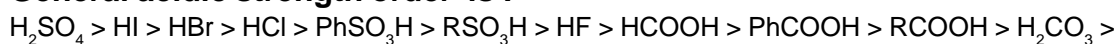


Conjugate base/Anion : $\ominus\text{CH}_3 < \ominus\text{NH}_2 < \ominus\text{OH} < \ominus\text{F}$ (stability)

(2) Along the group from top to bottom : As size of anion increases, $K_a \uparrow$

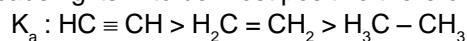


General acidic strength order is :



(B) Relative acidity of hydrocarbons :

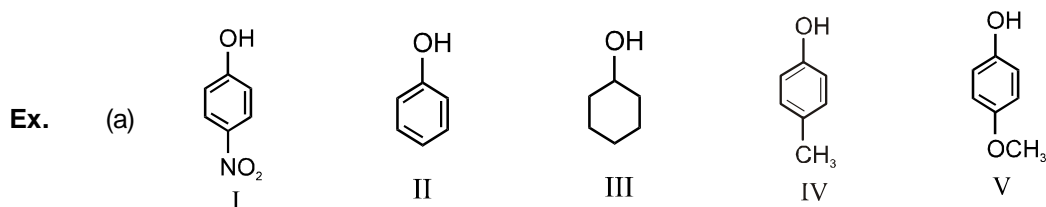
Being most electronegative the sp hybridised carbon atom of ethyne polarizes its C–H bond to the greatest extent causing its H to be most positive therefore ethyne is most acidic hydrocarbon.



(C) 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.

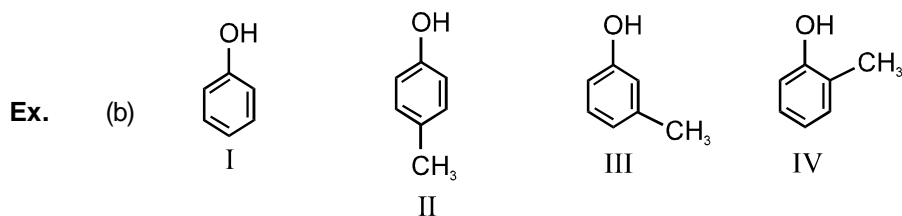


Ans. acid strength order : I > II > IV > V > III

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,

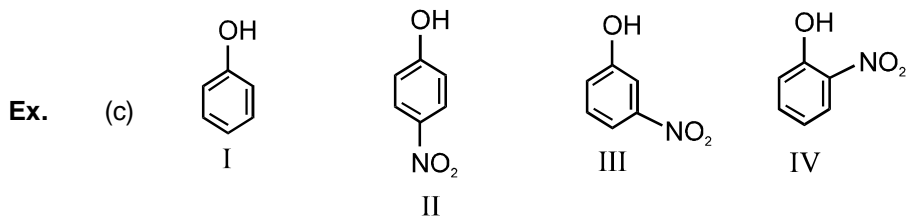
Step 3. Amongst cresol and methoxyphenol, methoxyphenol has +m effect of – OCH₃ which increases e[–] density hence decrease acidic strength



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

Sol. **Step 1 :** Notice that CH₃ have + I effect so all methylphenols (cresols) are less acidic than phenol (I).

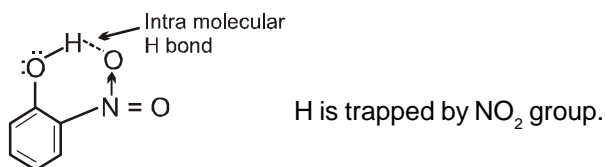
Step 2 : Now amongst cresols p- and o- CH₃ are increasing the e[–] density due to their hyper conjugation but ortho isomer has viable + I effect also, which will help in destabilising phenoxide ion therefore o- is least acidic. Since at meta position only + I works it as least e[–] density amongst the cresol.



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

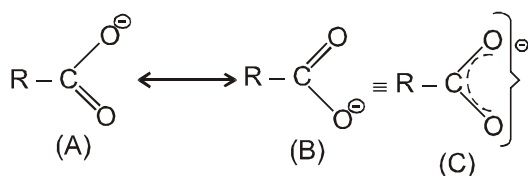
Sol. **Step 1.** In nitrophenols – I effect of NO_2 will help to increase acidic strength hence phenol is least acidic amongst all nitrophenols

Step 2. Only –I effect is applicable in meta nitrophenol so 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 nitrophenol because of intramolecular H-bond.



(D) Acidity of carboxylic acids :

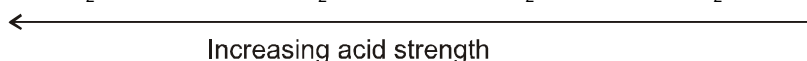
Conjugate base of carboxylic acid exists as two equivalent canonical structures (A) and (B). This ion is resonance stabilised and resonance hybrid structure is (C).



Electron withdrawing group (–M, –I effect) **increases** acidic nature.

Electron releasing group (+M, +I effect) **decreases** acidic nature.

Ex. (a) $\text{F}-\text{CH}_2-\text{COOH} > \text{Cl}-\text{CH}_2\text{COOH} > \text{Br}-\text{CH}_2\text{COOH} > \text{I}-\text{CH}_2\text{COOH}$

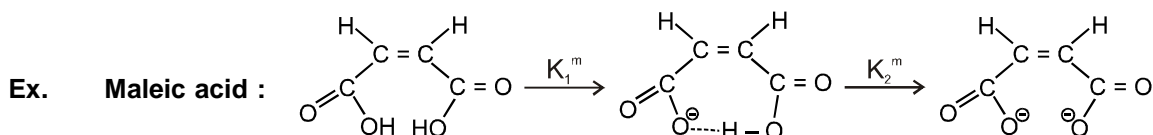


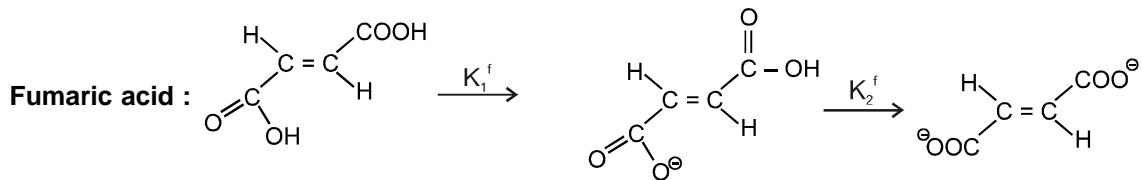
(b) $\text{Cl}-\underset{\text{Cl}}{\underset{\text{Cl}}{\text{C}}}-\text{COOH} > \text{Cl}-\underset{\text{Cl}}{\text{CH}}-\text{COOH} > \text{Cl}-\text{CH}_2\text{COOH} > \text{CH}_3\text{COOH}$

(c) $\text{HCOOH} > \text{CH}_3\text{COOH} > \text{CH}_3-\text{CH}_2-\text{COOH}$

(d) $\text{C}_6\text{H}_4(\text{COOH})_2 > \text{C}_6\text{H}_4(\text{COOH})_2 > \text{C}_6\text{H}_4(\text{COOH})_2$

Comparison between two geometrical isomers





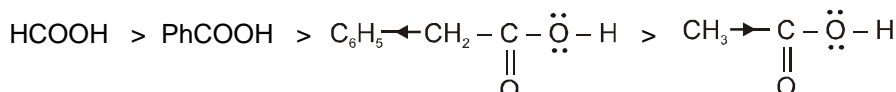
Now $K_1^m > K_1^f$

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 $-\text{COO}^\ominus$ groups faces each other and makes system unstable. In fumarate ion this repulsion is less.

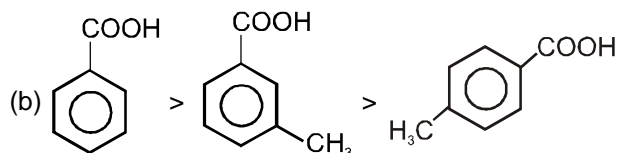
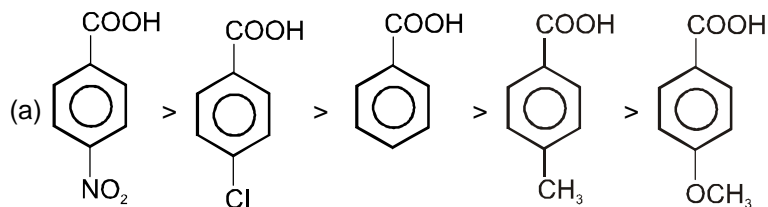
Acidic strength of substituted benzoic acid :

(i) Formic acid is more acidic than benzoic acid while phenyl acetic acid is more acidic than acetic acid.

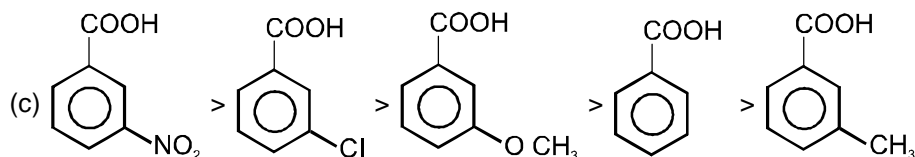


(ii) Electron withdrawing group attached to benzene ring will increase the acidic strength while electron releasing group decreases acidic strength.

(iii) If electron donating group present at para position than it is always less acidic than benzoic acid and also it is less acidic than meta substituted benzoic acid.

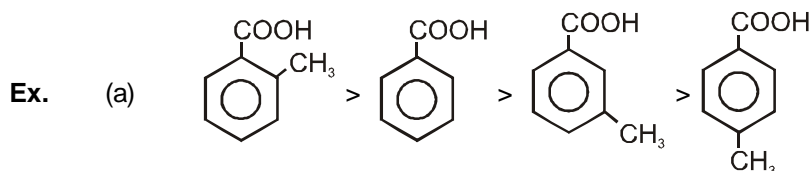


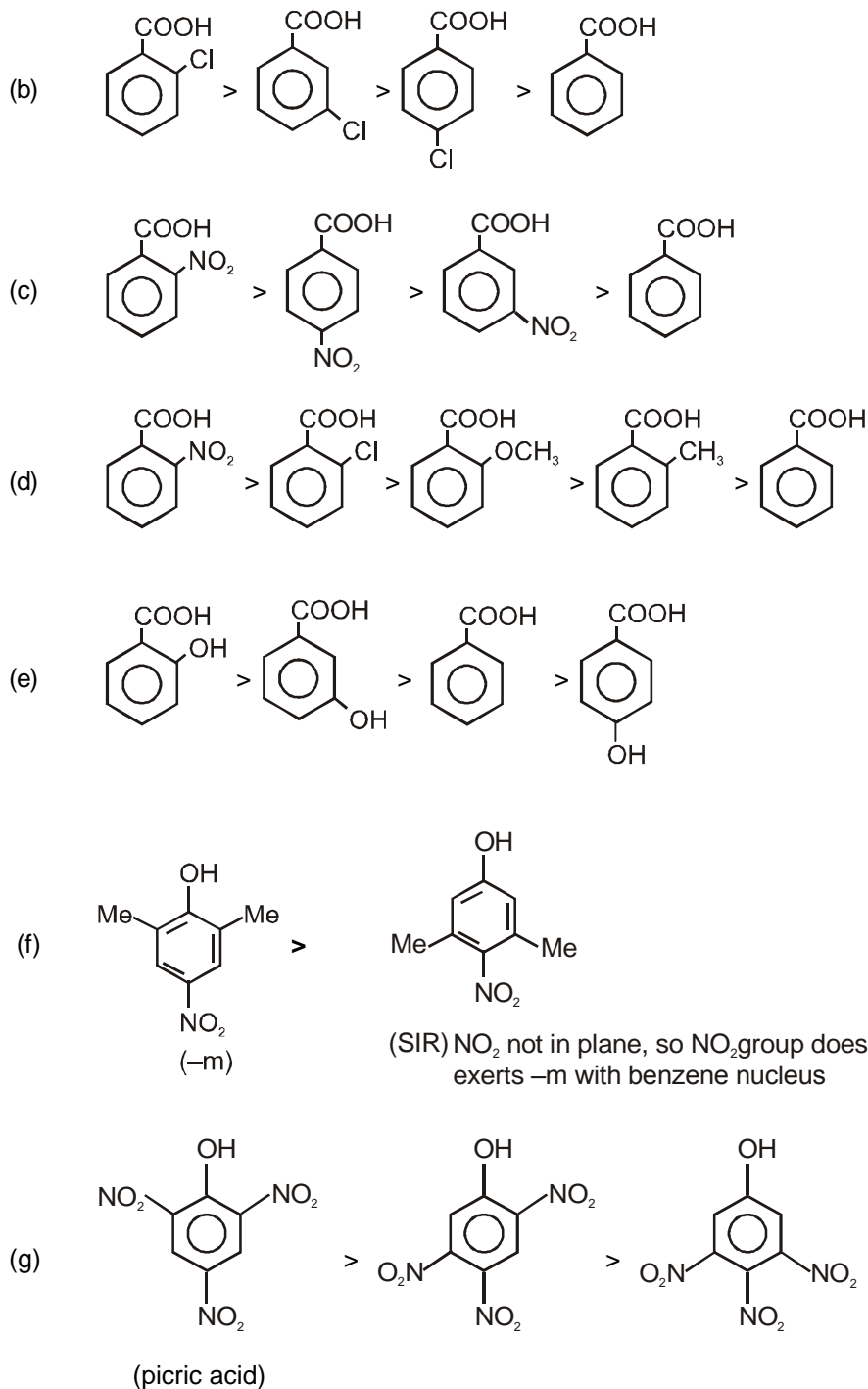
(v) On the other hand if e^- withdrawing group is present at meta position then it is more acidic than benzoic acid.



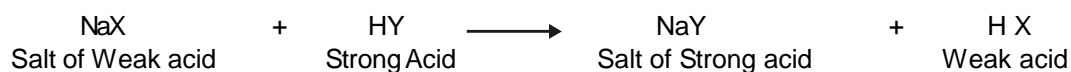
Ortho effect :

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.





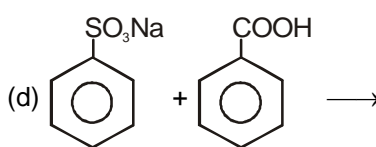
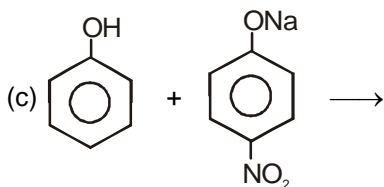
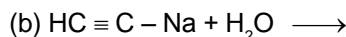
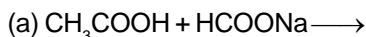
(E) Reaction of Acids with salts :



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.

- (a) $2 \text{NaCl} + \text{H}_2\text{SO}_4 \longrightarrow \text{Na}_2\text{SO}_4 + 2\text{HCl}$ (feasible)
- (b) $\text{Na}_2\text{SO}_4 + 2\text{HCl} \longrightarrow$ No reaction
- (c) $\text{CH}_3\text{COONa} + \text{CH}_3\text{SO}_3\text{H} \longrightarrow \text{CH}_3\text{COOH} + \text{CH}_3\text{SO}_3\text{Na}$ (feasible)
- (d) $\text{CH}_3\text{COONa} + \text{PhOH} \longrightarrow \text{PhONa} + \text{CH}_3\text{COOH}$ (not feasible)

Que. Which of the following reaction is possible ?



Ans. (a) Not possible (reverse is possible) (b) Possible (c) Not possible (d) Not possible

10. Basic strength

Definitions:

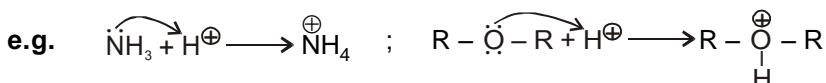
(a) Arrhenius base : Those compound which furnishes OH^\ominus ions in aqueous solutions are known as Arrhenius base.

e.g. NaOH , KOH , $\text{Ca}(\text{OH})_2$ etc.

(b) Bronsted base: Proton (H^\oplus ion) acceptor.

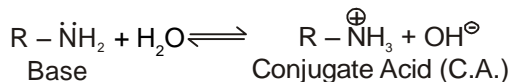
e.g. NH_3 , $\text{R}\ddot{\text{N}}\text{H}_2$, $\text{R}_2\ddot{\text{N}}\text{H}$, $\text{R}_3\ddot{\text{N}}$, $\text{H}_2\ddot{\text{O}}$, $\text{R}\ddot{\text{O}}\text{H}$, $\text{R}-\ddot{\text{O}}-\text{R}$

(c) Lewis base: e^- pair donor to H^\oplus ion.



Basicity/Basic Strength (K_b) : It is the tendency to accept H^\oplus ion.

In aq. solution:-

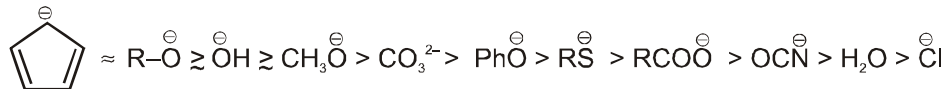
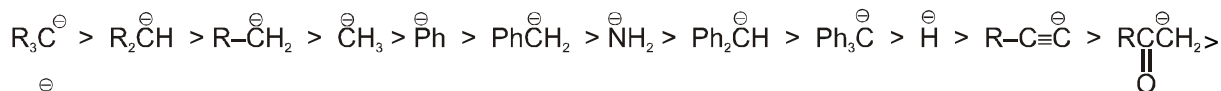


$$K_b = \frac{[\text{RNH}_3^\oplus][\text{OH}^\ominus]}{[\text{RNH}_2]} \quad \text{[where } K_b = \text{Base dissociation constant].}$$

$$\text{p}K_b = -\log K_b$$

Note : A stronger base always has a weaker conjugate acid and vice versa.

General basicity order :



(A) Basic Strength in periodic table:-

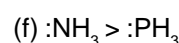
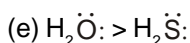
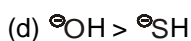
(i) From left to right in a period, Electron Negativity of elements increases so, $K_b \downarrow$

(ii) From top to bottom in a group, size increases so, $K_b \downarrow$

Basic strength order is :

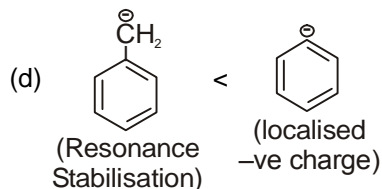


CH_3^\ominus is strongest base in periodic table.



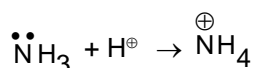
(B) Carbanion Bases (:C^\ominus):

- (a) $\text{CH}_3 - \overset{\ominus}{\text{C}}\text{H}_2 > \text{CH}_2 = \overset{\ominus}{\text{C}}\text{H} > \text{CH} \equiv \overset{\ominus}{\text{C}}$ (E.N. \uparrow , $K_b \downarrow$)
(b) $\text{CH}_3 - \text{CH}_2 - \overset{\ominus}{\text{C}}\text{H}_2 \gg \text{CH}_2 = \text{CH} - \overset{\ominus}{\text{C}}\text{H}_2$ (delocalised lone pair is less basic)
(c) $\text{CH}_2 = \text{CH} - \overset{\ominus}{\text{C}}\text{H}_2 > \text{CH}_3 - \overset{\ominus}{\text{C}}(\text{O}) - \text{CH}_2$ (better resonance due to $-ve$ charge on 'O')

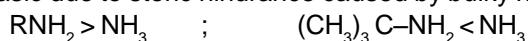


(C) Basic strength of aliphatic nitrogenous base :

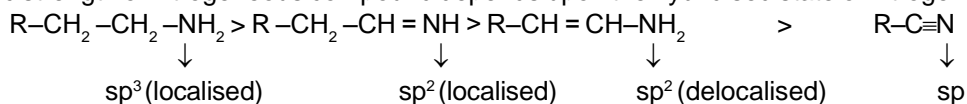
In nitrogenous compound basic strength is due to presence of lone pair of electrons at nitrogen atom which accept the proton



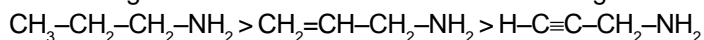
Note : (1) Usually 1° amine is more basic than ammonia but if alkyl part of 1° amine is tertiary butyl then NH_3 is more basic due to steric hindrance caused by bulky nature of tertiary butyl group



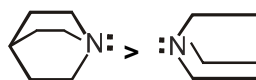
(2) Basic strength of nitrogenous compound depends upon the hybridised state of nitrogen



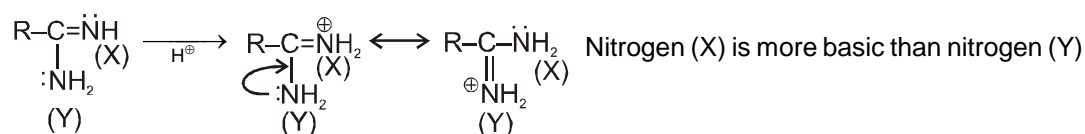
(3) More electronegative atom will decrease the basic strength



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



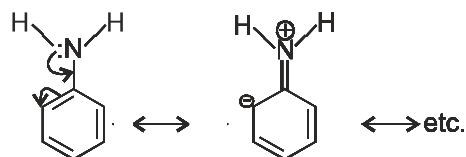
(5) Amidines are more basic in nature because their conjugate acid are more stable due to resonance.



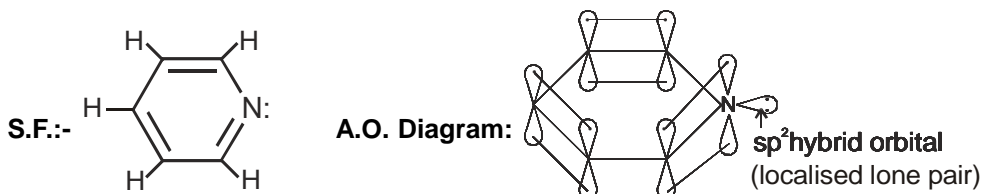
(D) Basic Strength of Aromatic Amines and substituted Anilines :

(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

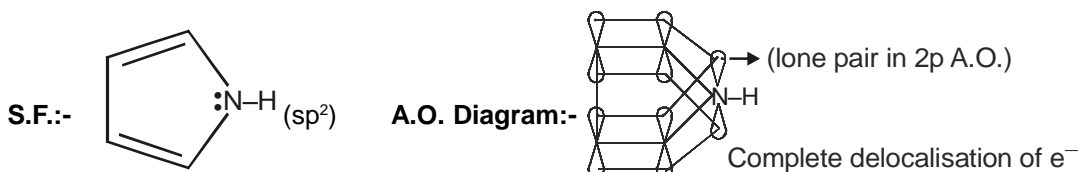


(b) Pyridine (C₅H₅N) : 6- π electrons, aromatic

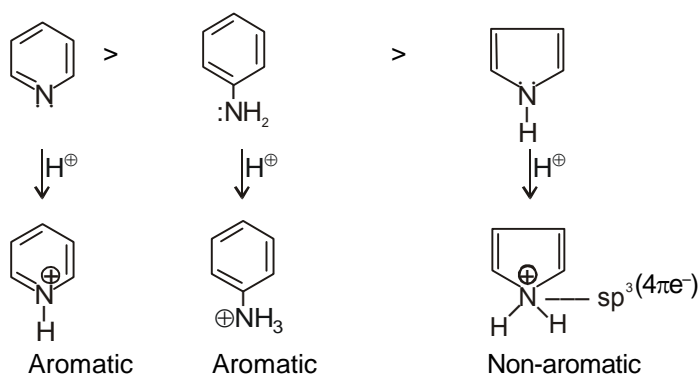


Lone pair of N in pyridine is localised so it is more basic than aniline.

(c) Pyrrole (C₄H₅N): 6- π electrons, aromatic



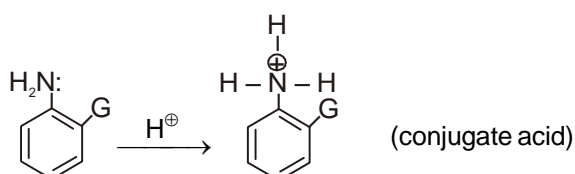
Lone pair of N in pyrrole is delocalised in the aromaticity so it is very less basic than aniline.



(d) 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) :

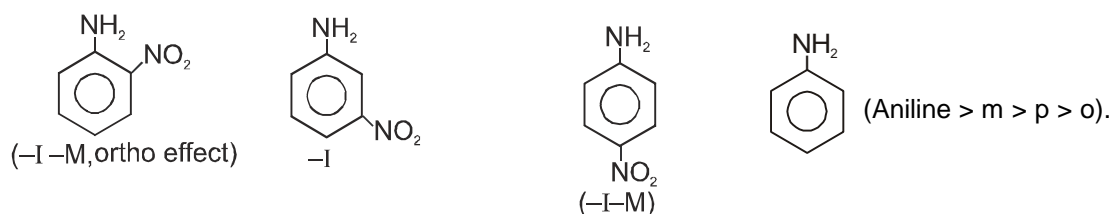


(i) Ortho-substituted anilines are mostly weaker bases than aniline itself.

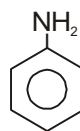
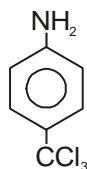
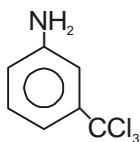
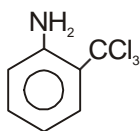
(ii) Ortho-substituent causes steric hinderance to solvation in the product (conjugate acid i.e. cation).

(iii) The small groups like -NH₂ or -OH do not experience (SIR) due to small size.

Ex. (a) G = (-M, -I); NO₂



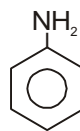
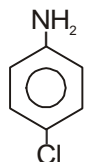
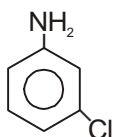
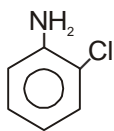
(b) $G = (-I)$; CCl_3



(Aniline > p > m > o).

Only $(-I)$ decides the order.

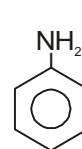
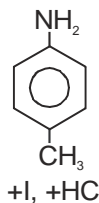
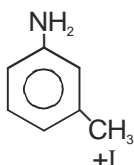
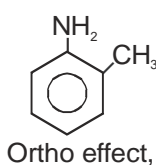
(c) $G = (-I > +m)$; Cl



(Aniline > p > m > o)

Only $(-I)$ decides the order.

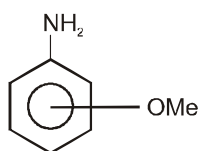
(d) $G = (+I, \text{HC})$; If $R = -\text{CH}_3$ (Toluidines)



(p > m > Aniline > o)

(HC \rightarrow more dominating)

(e) $G = (+m > -I)$;



(K_b order : p > Aniline > o > m)

(E) Solvent Effect in bases :

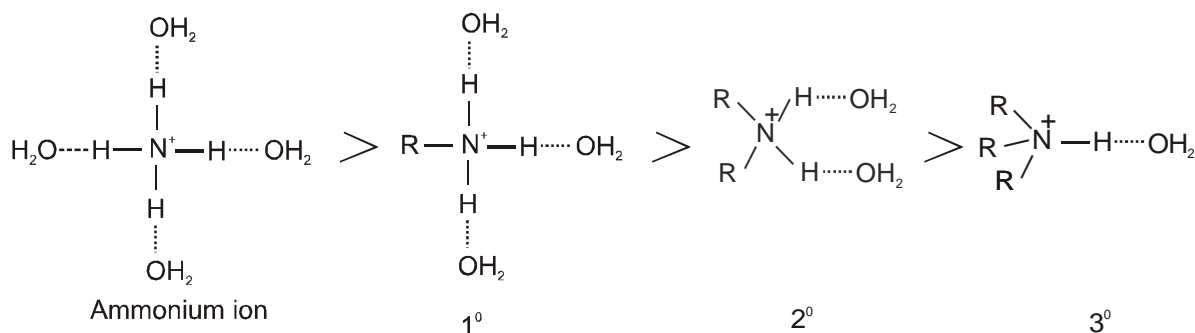
The trend is not regular in the aqueous state as evident by their pK_b values given in Table.

Name of amine	pK_b	Name of amine	pK_b
Methanamine	3.38	N,N-Diethylethanamine	3.25
N-Methylmethanamine	3.27	Bebzenamine	9.38
N, N-Dimethylmethanamine	4.22	Phenylmethanamine	4.70
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:



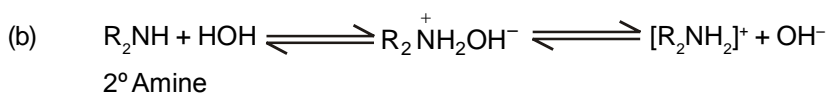
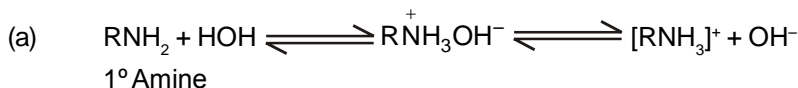
Greater is the stability of the substituted ammonium cation, stronger should be the corresponding amine as a base.

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.



(F) Reaction of Bases :

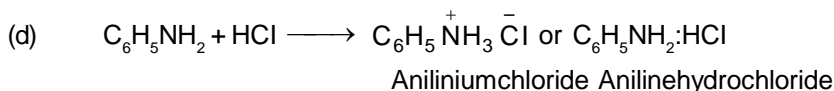
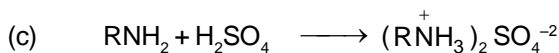
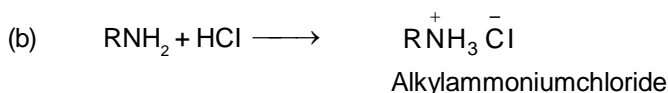
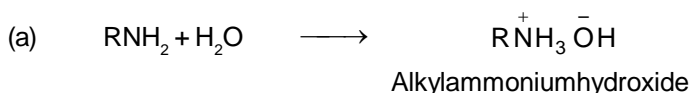
(1) Nature of aqueous solution : Amines combine with water to form alkyl ammonium hydroxides. This gives hydroxide ions in solution, thus the aqueous solution of amines is basic in nature.



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

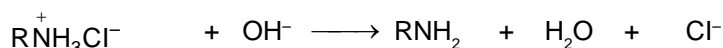


(ii) Aliphatic and aromatic amines form salt because of their basic nature:



Salts of amines are ionic compounds and hence water soluble.

The amine salts react with base to give free amines as –



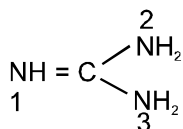
(Soluble in water)

Board Level Exercise

Type (I) : Very Short Answer Type Questions :

[01 Mark Each]

1. What is a homolytic cleavage? The homolytic fission of C–C bond in ethane produces :
2. What is a carbocation?
3. What are free radical reactions?
4. The central carbon atom of a free radical, carbocation and carbanion containing electrons in outermost shell respectively.
5. Which nitrogen is protonated readily in the guanidine ?

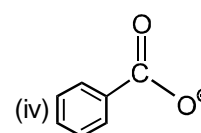
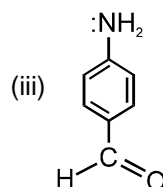
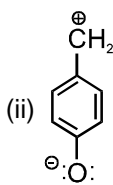
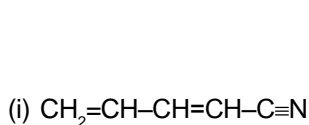


6. The correct order for basicity of halide ions is :
7. The correct K_a order of the following compounds is :
 (I) ClCH_2COOH (II) CH_3COOH (III) $\text{ClCH}_2\text{CH}_2\text{COOH}$ (IV) $(\text{CH}_3)_2\text{CHCOOH}$
8. $\text{CH}_2 = \text{CH}^-$ is more basic than $\text{HC} \equiv \text{C}^-$. Explain ?

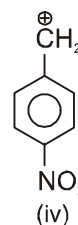
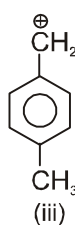
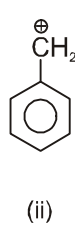
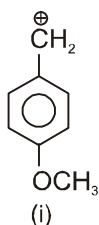
Type (II) : Short Answer Type Questions :

[02 Marks Each]

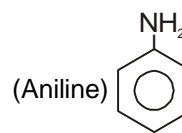
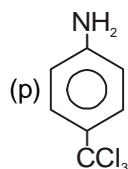
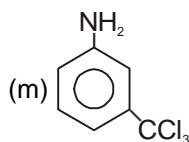
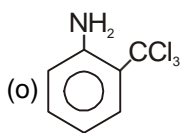
9. Explain why alkyl groups act as electron donors when attached to a π -system.
10. Which has highest percentage of enol content in the solution phase. Write the structure of enol of that compound.
 (a) Acetone (b) Acetophenone (c) Acetic acid (d) Acetyl acetone
11. Phenols are more acidic than alcohols. Explain?
12. Write a stable resonating structure for each of the following compounds :



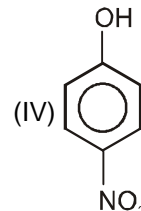
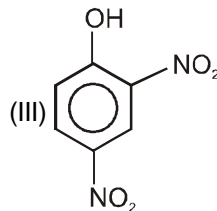
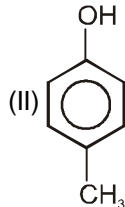
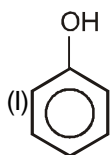
13. Draw all the hyperconjugating structures of toluene.
14. The basic strength of aliphatic amines in solution is in the order sec. > ter. > primary. While in gaseous phase the order is ter. > sec. > primary amine. Explain ?
15. Which of the following will show tautomerism.
 (P) $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CHO}$ (Q) $\text{Ph} - \text{C}(=\text{O}) - \text{Ph}$ (R) $\text{D}_3\text{C} - \text{C}(=\text{O}) - \text{CD}_3$ (S) $\text{CH}_2 = \text{CH} - \text{OH}$
16. Relative stabilities of the following carbocation will be in order.



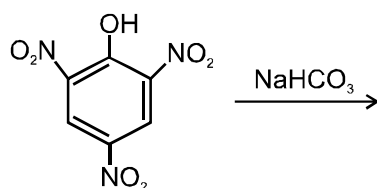
17. Select the basic strength order of following molecules ?



18. Strength of acidity is in order :

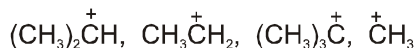


19.



The products of above reaction will be:

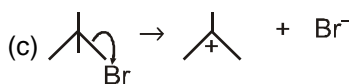
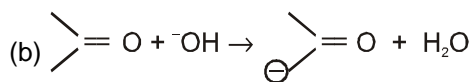
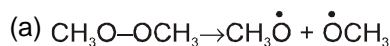
20. Arrange the following carbocations in increasing order of their stability with reason.



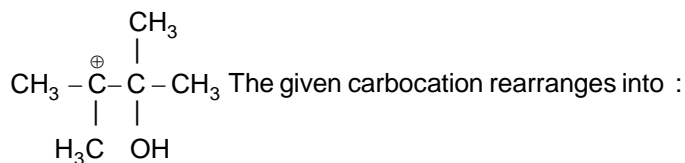
Type (III) : Long Answer Type Questions:

[03 Mark Each]

21. For the following bond cleavages, use curved-arrows to show the electron flow and classify each as homolysis or heterolysis. Identify reactive intermediate produced as free radical, carbocation and carbanion.



22.



23.

Cyclohexa-2,5-dien-1-one exists mainly in enol form. Which factor accounts for the stability of its enol form?

Type (IV) : Very Long Answer Type Questions:

[05 Mark Each]

24. Draw all the resonating structures of the following compounds :

(a) Benzene

(b) Naphthalene

(c) Anthracene

(d) Phenanthrene

Exercise # 1

PART - I : OBJECTIVE QUESTIONS

Part - I (GOC-I)

Section (A) : Inductive effect :

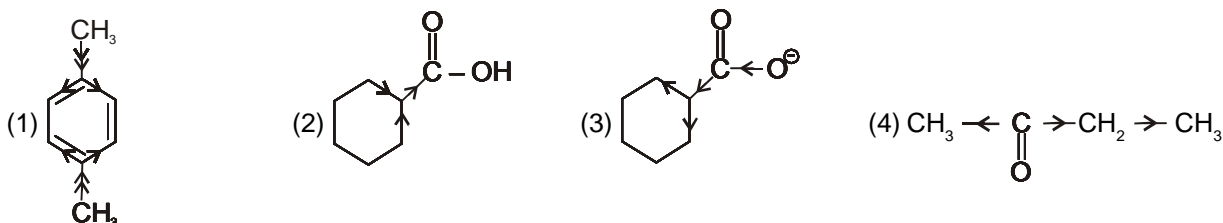
A-1. Inductive effect involves :

- (1) delocalisation of σ -electrons
(2) delocalisation of π -electrons
(3) displacement of σ -electrons
(4) displacement of π -electrons

A-2. Which statement is correct regarding Inductive effect ?

- (1) Electron displacement along a carbon chain and develops partial charges on atoms.
(2) Complete transfer of one of the shared pair of electrons to one of the atom joined by a double bond.
(3) Implies transfer of lone pair of electron from more electronegative atom to the less electronegative atom.
(4) I effect increases with increase in the distance.

A-3. Which of the following has incorrect direction of Inductive effect.



A-4. Which of the following alkyl group has the maximum +I effect ?

- (1) $(\text{CH}_3)_2\text{CH}-$ (2) $(\text{CH}_3)_3\text{C}-$ (3) CH_3CH_2- (4) CH_3-

A-5. Decreasing -I effect of given groups is :

- (i) CN (ii) NO_2 (iii) NH_2 (iv) Cl
(1) $\text{iii} > \text{ii} > \text{i} > \text{iv}$ (2) $\text{ii} > \text{iii} > \text{iv} > \text{i}$ (3) $\text{iii} > \text{ii} > \text{iv} > \text{i}$ (4) $\text{ii} > \text{i} > \text{iv} > \text{iii}$

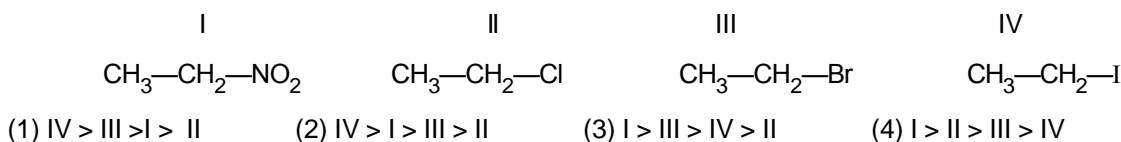
A-6. Which is the correct order of inductive effect ?

- (1) $-\text{NH}_2 > -\text{OR} > -\text{F}$ (2) $-\text{F} > -\text{OR} > -\text{NH}_2$
(3) $-\text{NH}_2 > -\text{F} > -\text{OR}$ (4) $-\text{OR} > -\text{F} > -\text{NH}_2$

A-7. Which of the following statement is correct?

- (1) +I group stabilises the carbocation. (2) +I group stabilises the carbon free radical
(3) -I group stabilises the carbanion (4) all of these

A-8. Arrange following compounds in decreasing order of their dipole moment.



Section (B) : Resonance

B-1. Resonance effect involves :

- (1) Delocalization of π -electrons along a conjugated system.
(2) Delocalization of lone pair along a conjugated system.
(3) Delocalization of negative charge along a conjugated system.
(4) All are correct.

B-2. Resonance structures of a molecule do not have :

- (1) Identical bonding (2) Identical arrangement of atoms
(3) The same number of paired electrons (4) Nearly the same energy content

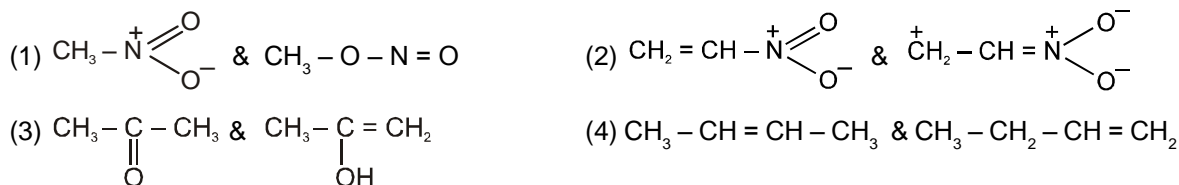
- B-3.** In which of the following delocalisation of π -electron is possible.
 (1) $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CHO}$ (2) $\text{CH}_2=\text{CH}-\text{CH}=\text{O}$ (3) $\text{CH}_3-\underset{\text{OH}}{\text{CH}}-\text{CH}_3$ (4) $\text{CH}_2=\text{CH}-\text{CH}_2-\text{CH}=\text{CH}_2$

- B-4.** Which of the following compound show resonance ?




- B-5.** In which compound delocalisation is not possible :
 (1) 2-butene (2) 1,3-Butadiene (3) 1,3,5-hexatriene (4) Benzene

- B-6.** Which of the following pairs are resonating structures.



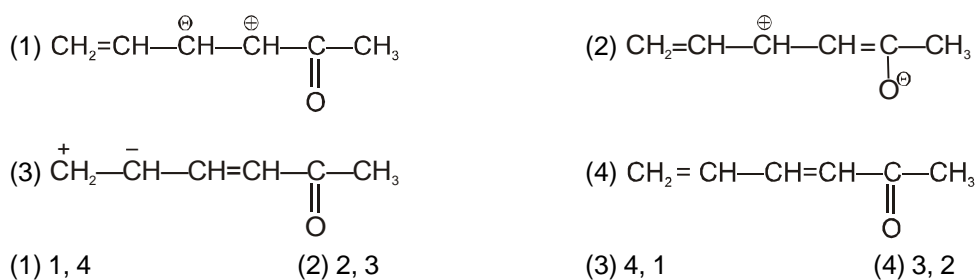
- B-7.** Stability of $\overset{+}{\text{C}}\text{H}_2-\text{CH}=\text{CH}_2$ can be explained by :
 (1) Inductive effect (2) Electromeric effect
 (3) Resonance (4) Polar effect

- B-8.** How many equally stable resonating structures are possible for  (tropylium cation) ?
 (1) 2 (2) 4 (3) 5 (4) 7

- B-9.** Which of the following is not acceptable resonating structure of Buta-1, 2, 3-triene.



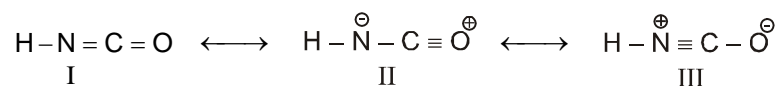
- B-10.** The least and most stable resonating structure respectively are :



- B-11.** Which will be the least stable resonating structure :



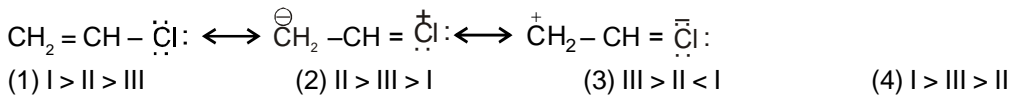
- B-12.** HNCO (isocyanic acid) has following resonating structures :



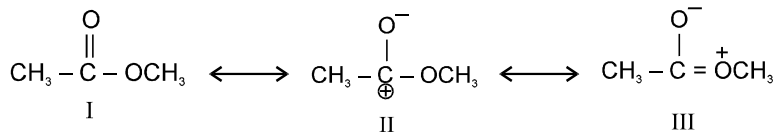
The order of stability is :

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

B-13. The decreasing order of stability of the following resonating structures is :



B-14. Which of the following resonating structure will contribute minimum to resonance hybrid?

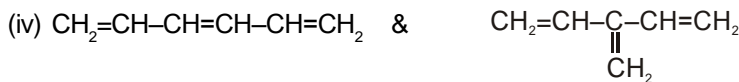
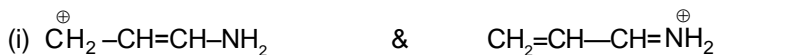


- (1) I (2) II
 (3) III (4) All structures contribute equally

B-15. In each of the following pairs of ions which ion is more stable :

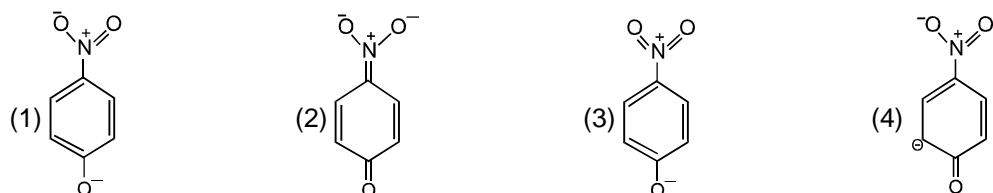
(x)

(y)



- (1) x y y y (2) y x y x
 (3) x x x x (4) y x y y

B-16. The most unlikely representation of resonance structures of p-nitrophenoxide ion is:



Section (C) : Mesomeric effect

C-1. Mesomeric effect involves the delocalisation of :

- (1) protons (2) sigma electrons (3) π electrons (4) none of these

C-2. Arrange the following groups in order of decreasing $-m$ effect.

- (i) NO_2 (ii) COOH (iii) CN (iv) CHO
 (1) i > iii > ii > iv (2) i > ii > iii > iv (3) i > iii > iv > ii (4) iv > iii > ii > i

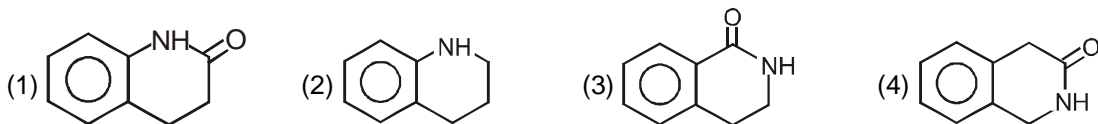
C-3. Arrange the following groups in order of decreasing $+m$ effect.

- (i) $-\overset{\ominus}{\text{O}}$ (ii) $-\text{NH}_2$ (iii) $-\text{OH}$ (iv) $-\text{NHCOCH}_3$
 (1) i > ii > iii > iv (2) iv > iii > ii > i (3) i > iii > ii > iv (4) i > iv > iii > ii

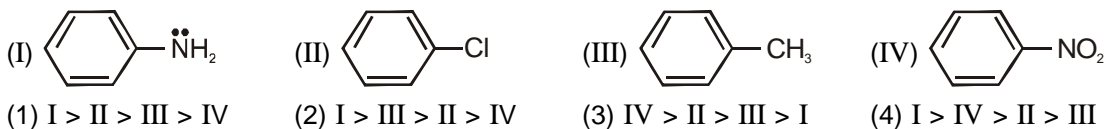
C-4. In which of the following molecule, the mesomeric effect is present ?



C-5. In which of the following molecule, the mesomeric effect is not with the benzene nucleus ?



C-6. Electron density order in the benzene nucleus is



C-7. Rank the following compounds in order of decreasing electron density in the benzene nucleus.

- (I) Chlorobenzene (II) 4-nitrochlorobenzene
 (III) 2, 4-dinitrochlorobenzene (IV) 2, 4, 6-trinitrochlorobenzene
 (1) I > II > III > IV (2) I > III > II > IV (3) III > I > IV > II (4) IV > III > II > I

Section (D) : Hyperconjugation effect

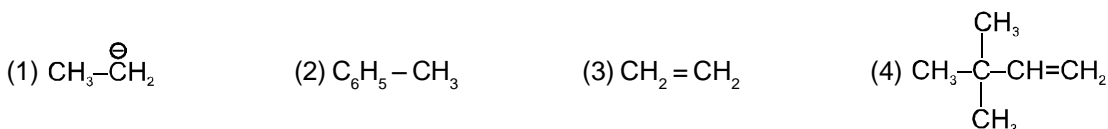
D-1. Hyperconjugation effect involves :

- (1) Delocalization of lone pair into an adjacent π -bond.
 (2) Delocalization of π -electrons into an adjacent double bond.
 (3) delocalization of σ -electrons into an adjacent π -bond.
 (4) All are true.

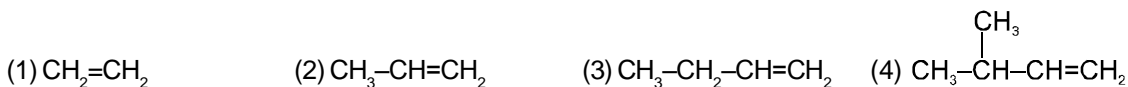
D-2. Which of the following group has the maximum hyperconjugation effect ?

- (1) CH_3- (2) CH_3CH_2- (3) $(\text{CH}_3)_2\text{CH}-$ (4) $(\text{CH}_3)_3\text{C}-$

D-3. Hyperconjugation is possible in which of the following species ?



D-4. Which of the following alkenes will show maximum number of hyperconjugation forms ?



D-5. Which of the following cannot exhibit hyperconjugation ?



D-6. The C-C bond length in propene is little shorter (1.49 \AA) than the C-C bond length (1.54 \AA) in ethane.

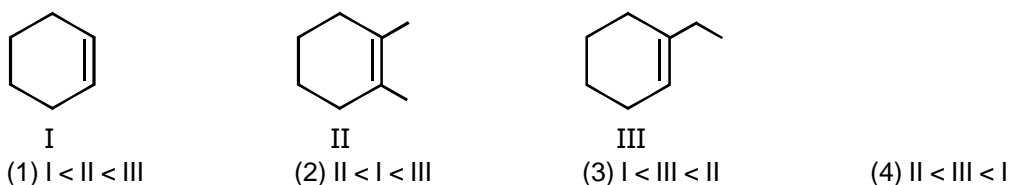
This is due to

- (1) +I effect of CH_3 (2) Mesomeric effect (3) Resonance effect (4) Hyperconjugation effect

D-7. Among the following alkenes the order of decreasing stability is :

- (I) 1-butene (II) cis-2-butene (III) trans-2-butene
 (1) II > I > III (2) III > I > II (3) I > II > III (4) III > II > I

D-8. Arrange in the stability order of following :



Section (E) : Aromaticity

E-1. Point out the wrong statement in relation to the structure of benzene

- (1) It is aromatic compound.
- (2) The C - C bond distance in benzene is uniformly 1.397 Å
- (3) It is a resonance hybrid of a number of canonical forms
- (4) It has three delocalised - molecular orbitals

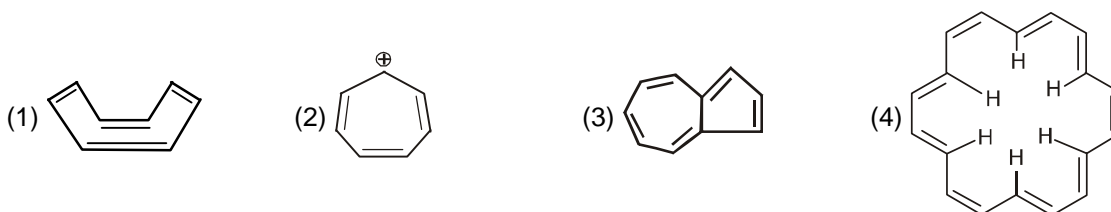
E-2. Which of the following compound is an Aromatic in nature.



E-3. Which of the following ion is an Aromatic in nature.

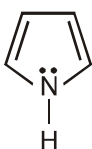


E-4. Which of the following compound is not Aromatic in nature.



E-5. Which of the following molecules have all C-C bonds are of equal length?



E-6. The hybridisation of nitrogen in  (pyrrole) is :

- (1) sp^3 (2) sp^2 (3) sp (4) Can't be predicted

E-7. In the compound C_6H_5Z which of the following set of groups is predominately ortho/para directing ?

- (1) $Z = -NO_2, -Cl, -OH$ (2) $Z = -OMe, -CN, -NH_2$
(3) $Z = -NHCOCH_3, -Cl, -COOH$ (4) $Z = -NHCOCH_3, -CH_3, -OH$

Part - II (GOC-II)

Section (F) : Carbon free radicals & carbocations :

F-1. Heterolysis of a carbon -carbon bond gives :

- (1) Carbanion (2) Carbocation
(3) Both carbanion and carbocation (4) Free radical

F-2. In CH_3CH_2OH , the bond that undergoes heterolytic cleavage most readily is :

- (1) C—C (2) C—O (3) C—H (4) O—H

F-3. The geometry of a methyl carbocation and methyl carbanion is likely to be respectively :

- (1) Octahedral & linear (2) Tetrahedral & planar
(3) Planar & tetrahedral (4) Linear & tetrahedral

F-4. The stability of given free radicals in decreasing order is :

- (i) $\text{CH}_3-\dot{\text{C}}\text{H}_2$ (ii) $\text{CH}_3-\dot{\text{C}}\text{H}-\text{CH}_3$ (iii) $\text{CH}_3-\overset{\cdot}{\underset{\text{CH}_3}{\text{C}}}-\text{CH}_3$ (iv) $\dot{\text{C}}\text{H}_3$
- (1) iii > iv > i > ii (2) i > ii > iii > iv (3) iii > ii > iv > i (4) iii > ii > i > iv

F-5. Stability of carbocations can be explained on the basis of ?

- (1) Inductive effect (2) Hyperconjugative effect
 (3) Resonance effect (4) All the three

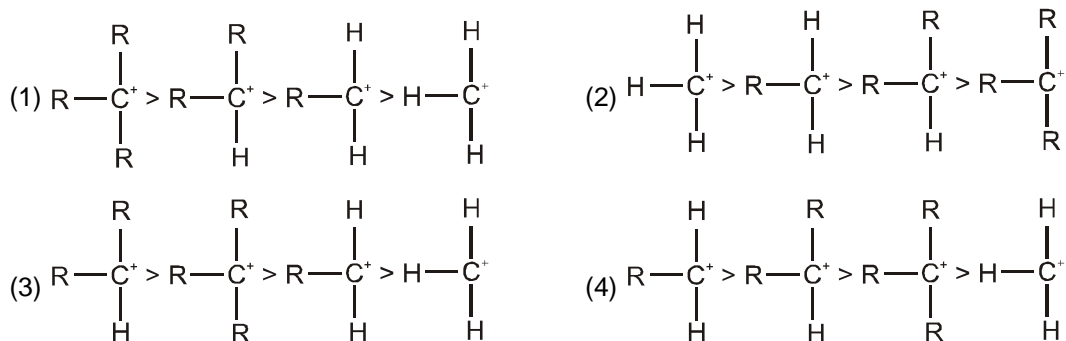
F-6. Which one is a 1° carbocation ?

- (1) $\text{CH}_3\overset{+}{\text{C}}\text{H}_2$ (2) $\text{CH}_3\overset{+}{\text{C}}\text{H}-\text{C}_2\text{H}_5$ (3) $(\text{CH}_3)_2\overset{+}{\text{C}}\text{H}$ (4) $(\text{CH}_3)_3\overset{+}{\text{C}}$

F-7. The most stable carbocation is :



F-8. The decreasing order of stability of alkyl carbonium ion is in the order of : (R = C₂H₅)



F-9. Which of the following represents the correct order of stability of carbocations ?

- (1) $(\text{CH}_3)_3\overset{+}{\text{C}} > \text{CH}_2=\text{CH}\overset{+}{\text{C}}\text{H}_2 > \text{C}_6\text{H}_5\overset{+}{\text{C}}\text{H}_2 > (\text{CH}_3)_2\overset{+}{\text{C}}\text{H}$
 (2) $(\text{CH}_3)_3\overset{+}{\text{C}} > \text{C}_6\text{H}_5\overset{+}{\text{C}}\text{H}_2 > (\text{CH}_3)_2\overset{+}{\text{C}}\text{H} > \text{CH}_2=\text{CH}-\overset{+}{\text{C}}\text{H}_2$
 (3) $\text{CH}_2=\text{CH}-\overset{+}{\text{C}}\text{H}_2 > \text{C}_6\text{H}_5\overset{+}{\text{C}}\text{H}_2 > (\text{CH}_3)_3\overset{+}{\text{C}} > (\text{CH}_3)_2\overset{+}{\text{C}}\text{H}$
 (4) $(\text{CH}_3)_3\overset{+}{\text{C}} > \text{C}_6\text{H}_5\overset{+}{\text{C}}\text{H}_2 > \text{CH}_2=\text{CH}-\overset{+}{\text{C}}\text{H}_2 > (\text{CH}_3)_2\overset{+}{\text{C}}\text{H}$


F-10. Which of the following statement is correct ?

- (1) Allyl carbocation ($\text{H}_2\text{C}=\text{CH}-\overset{+}{\text{C}}\text{H}_2$) is more stable than propyl carbocation.
 (2) Ethyl carbocation is more stable than allyl carbocation.
 (3) Vinyl carbocation is more stable than ethyl carbocation.
 (4) Benzyl carbocation is more stable than cyclopropyl methyl carbocation.

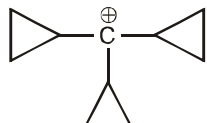

F-11. Which of the following shows the correct order of stability -

- (1) $\text{CH}_3\overset{+}{\text{O}}\text{CHCH}_3 < \text{CH}_3\overset{+}{\text{O}}\text{CH}_2 < \text{CH}_3\overset{\oplus}{\text{C}}\text{HCH}_3 < \text{CH}_3\overset{+}{\text{C}}\text{H}_2$
 (2) $\text{CH}_3\overset{\oplus}{\text{C}}\text{HCH}_3 < \text{CH}_3\overset{+}{\text{C}}\text{H}_2 < \text{CH}_3\overset{+}{\text{O}}\text{CHCH}_3 < \text{CH}_3\overset{+}{\text{O}}\text{CH}_2$
 (3) $\text{CH}_3\overset{+}{\text{C}}\text{H}_2 < \text{CH}_3\overset{\oplus}{\text{C}}\text{HCH}_3 < \text{CH}_3\overset{+}{\text{O}}\text{CH}_2 < \text{CH}_3\overset{+}{\text{O}}\text{CHCH}_3$
 (4) $\text{CH}_3\overset{+}{\text{O}}\text{CH}_2 < \text{CH}_3\overset{+}{\text{O}}\text{CHCH}_3 < \text{CH}_3\overset{+}{\text{C}}\text{H}_2 < \text{CH}_3\overset{\oplus}{\text{C}}\text{HCH}_3$

F-12. Decreasing order of stability of given carbocations is as :

- (i)  (ii) $\text{CH}_2=\text{CH}-\overset{\oplus}{\text{C}}\text{H}_2$ (iii) $\text{C}_6\text{H}_5-\overset{\oplus}{\text{C}}\text{H}_2$ (iv) $\text{CH}_3-\overset{\oplus}{\text{C}}\text{H}-\text{CH}_3$
 (1) $\text{iii} > \text{ii} > \text{iv} > \text{i}$ (2) $\text{i} > \text{iii} > \text{iv} > \text{ii}$ (3) $\text{i} > \text{iii} > \text{ii} > \text{iv}$ (4) $\text{iii} > \text{ii} > \text{i} > \text{iv}$

F-13. Which one of the following carbocations is most stable ?

- (1)  (2) $\text{C}_6\text{H}_5-\overset{\oplus}{\text{C}}\text{H}_2$ (3)  (4) $\text{CH}_3-\overset{\oplus}{\text{C}}\text{H}-\text{CH}_3$

F-14. Which of the following shows the correct order of decreasing stability ?

- (1) $\text{CH}_3-\text{C}_6\text{H}_4-\overset{\oplus}{\text{C}}\text{H}_2 > \text{CH}_3\text{O}-\text{C}_6\text{H}_4-\overset{\oplus}{\text{C}}\text{H}_2 > \text{C}_6\text{H}_5-\overset{\oplus}{\text{C}}\text{H}_2 > \text{CH}_3-\overset{\oplus}{\text{C}}\text{H}_2$
 (2) $\text{CH}_3\text{O}-\text{C}_6\text{H}_4-\overset{\oplus}{\text{C}}\text{H}_2 > \text{CH}_3-\text{C}_6\text{H}_4-\overset{\oplus}{\text{C}}\text{H}_2 > \text{C}_6\text{H}_5-\overset{\oplus}{\text{C}}\text{H}_2 > \text{CH}_3-\overset{\oplus}{\text{C}}\text{H}_2$
 (3) $\text{C}_6\text{H}_5-\overset{\oplus}{\text{C}}\text{H}_2 > \text{CH}_3\text{O}-\text{C}_6\text{H}_4-\overset{\oplus}{\text{C}}\text{H}_2 > \text{CH}_3-\text{C}_6\text{H}_4-\overset{\oplus}{\text{C}}\text{H}_2 > \text{CH}_3-\overset{\oplus}{\text{C}}\text{H}_2$
 (4) $\text{CH}_3\text{O}-\text{C}_6\text{H}_4-\overset{\oplus}{\text{C}}\text{H}_2 > \text{C}_6\text{H}_5-\overset{\oplus}{\text{C}}\text{H}_2 > \text{CH}_3-\overset{\oplus}{\text{C}}\text{H}_2 > \text{CH}_3-\text{C}_6\text{H}_4-\overset{\oplus}{\text{C}}\text{H}_2$

Section (G) : Carbanions:

G-1. Which of the following intermediates have the complete octet around the carbon atom ?

- (1) Carbonium ion (2) Carbanion (3) Free radical (4) Carbene

G-2. Which of the following is the least stable carbanion ?

- (1) $\text{HC}\equiv\text{C}^-$ (2) $(\text{C}_6\text{H}_5)_3\text{C}^-$ (3) $(\text{CH}_3)_3\text{C}^-$ (4) CH_3^-

G-3. Arrange the following carbanions in decreasing order of stability :

- (i) $\text{CH}_3-\text{CH}_2-\overset{\ominus}{\text{C}}\text{H}_2$ (ii) $\text{CH}_2=\text{CH}-\overset{\ominus}{\text{C}}\text{H}_2$ (iii) $\text{CH}_2=\text{CH}-\text{CH}=\text{CH}-\overset{\ominus}{\text{C}}\text{H}_2$
 (1) $\text{(i)} > \text{(ii)} > \text{(iii)}$ (2) $\text{(ii)} > \text{(iii)} > \text{(i)}$ (3) $\text{(iii)} > \text{(ii)} > \text{(i)}$ (4) $\text{(ii)} > \text{(i)} > \text{(iii)}$


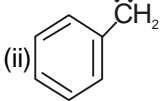
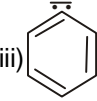
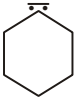
G-4. Arrange the following carbanions in decreasing order of stability :

- (i) $\text{CH}_2=\text{CH}-\overset{\ominus}{\text{C}}\text{H}_2$ (ii) $\text{CH}_3-\overset{\ominus}{\text{C}}(\text{O})-\text{CH}_2$ (iii) $\text{CH}_3-\overset{\ominus}{\text{C}}(\text{O})-\text{CH}-\overset{\ominus}{\text{C}}(\text{O})-\text{CH}_3$
 (1) $\text{(i)} > \text{(ii)} > \text{(iii)}$ (2) $\text{(ii)} > \text{(iii)} > \text{(i)}$ (3) $\text{(iii)} > \text{(ii)} > \text{(i)}$ (4) $\text{(ii)} > \text{(i)} > \text{(iii)}$

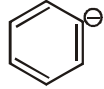
G-5. Arrange the following carbanions in decreasing order of stability :

- (i) $\text{CH}\equiv\text{C}^-$ (ii) $\text{CH}_2=\overset{\ominus}{\text{C}}\text{H}$ (iii) $\text{CH}_3-\overset{\ominus}{\text{C}}\text{H}_2$
 (1) $\text{(i)} > \text{(ii)} > \text{(iii)}$ (2) $\text{(ii)} > \text{(iii)} > \text{(i)}$ (3) $\text{(iii)} > \text{(ii)} > \text{(i)}$ (4) $\text{(ii)} > \text{(i)} > \text{(iii)}$

G-6. Arrange the following carbanions in decreasing order of stability :

- (i)  (ii)  (iii)  (iv) 
 (1) $\text{(i)} > \text{(ii)} > \text{(iii)} > \text{(iv)}$ (2) $\text{(ii)} > \text{(iii)} > \text{(i)} > \text{(iv)}$ (3) $\text{(iii)} > \text{(iv)} > \text{(ii)} > \text{(i)}$ (4) $\text{(iv)} > \text{(ii)} > \text{(i)} > \text{(iii)}$

G-7. The stability order of the following carbanions is : (R = CH_3)

- (i) $\text{RC}\equiv\text{C}^-$ (ii)  (iii) $\text{R}_2\text{C}=\overset{\ominus}{\text{C}}\text{H}$ (iv) $\text{R}_3\text{C}-\overset{\ominus}{\text{C}}\text{H}_2$
 (1) $\text{(i)} > \text{(ii)} > \text{(iii)} > \text{(iv)}$ (2) $\text{(ii)} > \text{(iii)} > \text{(iv)} > \text{(i)}$ (3) $\text{(iv)} > \text{(ii)} > \text{(iii)} > \text{(i)}$ (4) $\text{(i)} > \text{(iii)} > \text{(ii)} > \text{(iv)}$

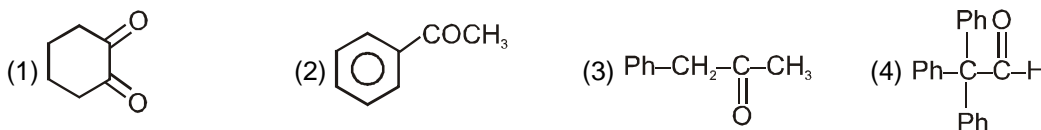
G-8 Arrange the following carbanions in decreasing order of stability :



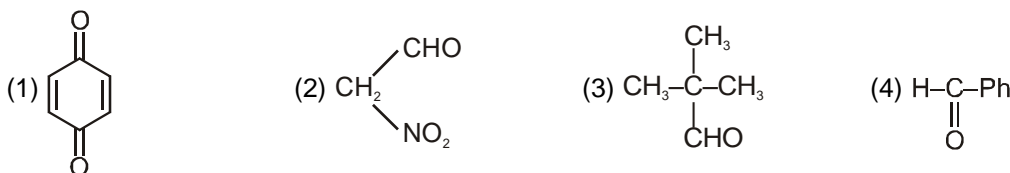
- (1) III > I > IV > II (2) III > II > I > IV (3) I > III > II > IV (4) III > I > II > IV

Section (H) : Tautomerism :

H-1 Which of the following does not show tautomerism ?



H-2. Which of the following can show tautomerism ?

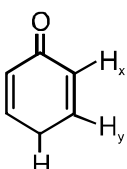


H-3. Tautomerism will be exhibited by :

- (1) $(\text{CH}_3)_2\text{NH}$ (2) $(\text{CH}_3)_3\text{CNO}$ (3) R_3CNO_2 (4) RCH_2NO_2

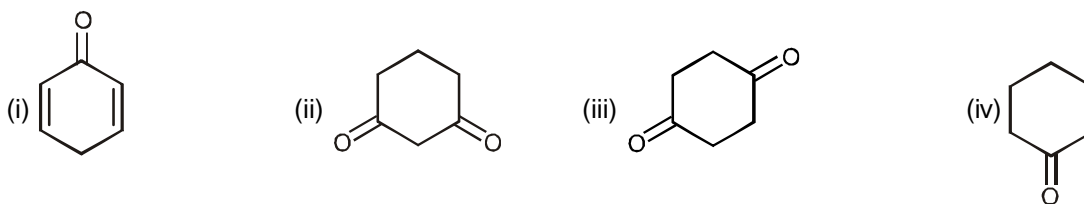
H-4. The enolic form of acetone contains :

- (1) 9 σ bonds, 1 π bond and 2 lone pairs (2) 8 σ bond, 2 π bond and 2 lone pairs
(3) 10 σ bond, 1 π bond and 1 lone pair (4) 9 σ bond, 2 π bond and 1 lone pair

H-5. Molecule  can be enolised by which hydrogen ?

- (1) x-H (2) y-H (3) z-H (4) None of these

H-6. Among the following in decreasing order of percentage enol content ?



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

H-7. Enol content is highest in :



Section (I) : Acidic strength :

I-1. Incorrect statement for acidic strength (K_a) is :

- (1) + I, + M effect increases then K_a will be decreases.
- (2) - I, - M effect increases then K_a will be increases.
- (3) stability of conjugated base increases then K_a will be increases.
- (4) hyperconjugation increases then K_a will be increases.

I-2. Which of the following K_a values, represents the strongest acid ?

- (1) 10^{-4}
- (2) 10^{-8}
- (3) 10^{-5}
- (4) 10^{-2}

I-3. Among the following the strongest acid is :

- (1) $\text{HC} \equiv \text{CH}$
- (2) C_6H_6
- (3) C_2H_6
- (4) CH_3OH

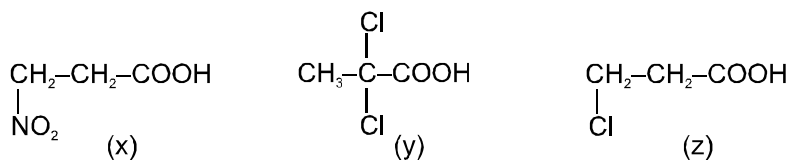
I-4. For which carboxylic acid, the pKa value is the lowest :

- (1) $\text{CH}_3\text{-CH}_2\text{-COOH}$
- (2) $\text{CH} \equiv \text{C-COOH}$
- (3) $\text{CH}_3\text{-CH}_2\text{-CH}_2\text{COOH}$
- (4) $\text{CH}_2=\text{CH-COOH}$

I-5. Strongest acid among the following is :

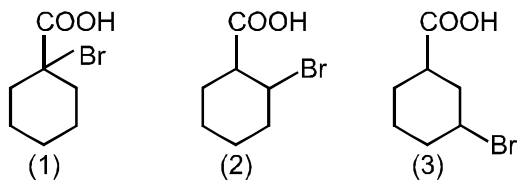
- (1) CF_3COOH
- (2) CCl_3COOH
- (3) CBr_3COOH
- (4) CH_3COOH

I-6. What is the correct order of acidic strength in following compounds ?



- (1) $x > y > z$
- (2) $y > x > z$
- (3) $x > z > y$
- (4) $z > y > x$

I-7. What is the correct order of acidic strength in following compounds ?



- (1) $1 > 3 > 2$
- (2) $1 > 2 > 3$
- (3) $3 > 2 > 1$
- (4) $3 > 1 > 2$

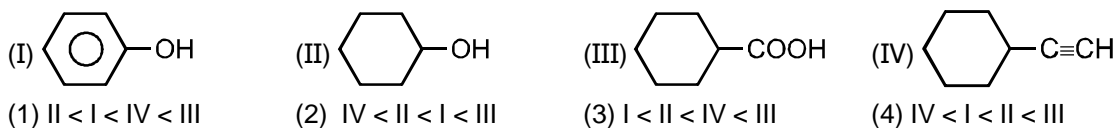
I-8. Which of the following option shows the correct order of decreasing acidity :

- (1) $\text{PhCO}_2\text{H} > \text{PhSO}_3\text{H} > \text{PhCH}_2\text{OH} > \text{PhOH}$
- (2) $\text{PhSO}_3\text{H} > \text{PhOH} > \text{PhCH}_2\text{OH} > \text{PhCH}_2\text{OH}$
- (3) $\text{PhCO}_2\text{H} > \text{PhOH} > \text{PhCH}_2\text{OH} > \text{PhSO}_3\text{H}$
- (4) $\text{PhSO}_3\text{H} > \text{PhCO}_2\text{H} > \text{PhOH} > \text{PhCH}_2\text{OH}$

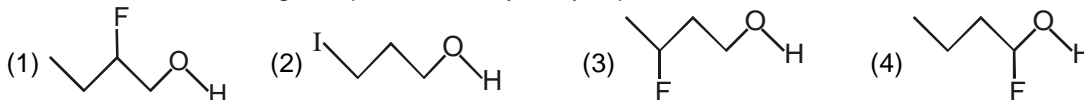
I-9. The correct order of relative acidic strength of phenol, ethyl alcohol and water is-

- (1) Phenol > Water > Ethyl alcohol
- (2) Ethyl alcohol > Water > Phenol
- (3) Ethyl alcohol > Phenol > Water
- (4) Water > Phenol > Ethyl alcohol

I-10. Give the correct order of increasing acidity of the following compounds -



I-11. In which of the following compounds the hydroxylic proton is the most acidic ?



I-12. Which of the following alcohol is the strongest acid ?

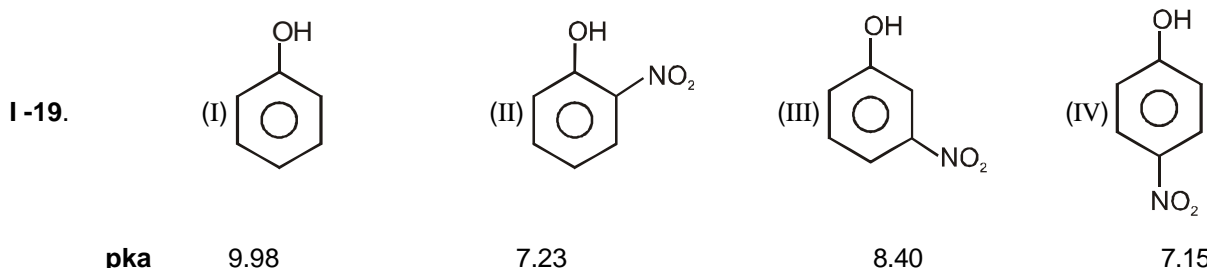
- (1) CH_3OH
- (2) $\text{CH}_3\text{CH}_2\text{OH}$
- (3) $(\text{CH}_3)_2\text{CHCH}_2\text{OH}$
- (4) $(\text{CH}_3)_3\text{COH}$

- I-13. Which one of the following carboxylic acid is most acidic in character :
 (1) o-methyl benzoic acid (2) m-methyl benzoic acid
 (3) p-methyl benzoic acid (4) Benzoic acid
- I-14. Arrange the following in the increasing order of acidity ?
 (i) Benzoic acid (ii) p-methoxybenzoic acid (iii) o-methoxybenzoic acid
 (1) (i) < (ii) < (iii) (2) (iii) < (i) < (ii) (3) (ii) < (i) < (iii) (4) (iii) < (ii) < (i).
- I-15. Which of the following is a polybasic acid :
 (1) Acetic acid (2) Benzoic acid (3) Salicylic acid (4) Oxalic acid



The reason for higher K_{a_1} value of oxalic acid (I) as compared to that of malonic acid (II) is :

- (1) The anion formed after the removal of first H^{\oplus} of oxalic acid (I) is more stable due to stronger $-I$ effect of $-\text{COOH}$ present at close distance
 (2) The anion formed after the removal of first H^{\oplus} of oxalic acid (I) is less stable due to $+I$ effect of $-\text{COOH}$ group.
 (3) The anion formed on removal of first H^{\oplus} of malonic acid is more stable than that of oxalic acid due to $-m$ effect of other $-\text{COOH}$ group.
 (4) Oxalic acid is more acidic than malonic acid due to its lesser molecular weight.
- I-17. The ionisation constant of phenol is higher than that of ethanol because
 (1) phenoxide ion is bulkier than ethoxide
 (2) phenoxide ion is stronger base than ethoxide
 (3) phenoxide ion is stabilised through delocalisation
 (4) phenoxide ion is less stable than ethoxide
- I-18. Phenol is less acidic than :
 (1) p-nitrophenol (2) ethanol (3) cresol (4) benzyl alcohol



Mark True and False statements related to the variation in pKa values given for the compounds mentioned above ?

S_1 : III is more acidic than I due to $-I$ effect of $-\text{NO}_2$ group.

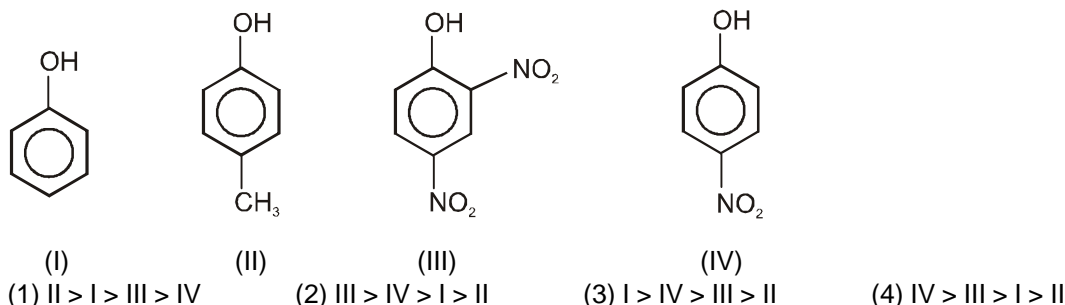
S_2 : due to H-bonding in II, it is slightly less acidic than IV.

S_3 : due to presence of $-m$ effect II & IV are more acidic than that of III.

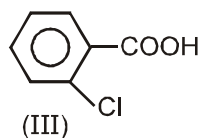
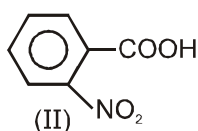
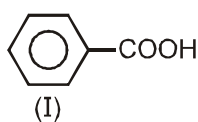
S_4 : Mesomeric effect of $-\text{NO}_2$ group is not operative in case of III with respect to OH group.

- (1) TTTT (2) TFTF (3) FTFT (4) FFTT

- I-20. Strength of acidity is in order :



I-21. Increasing value of dissociation constant K_a of



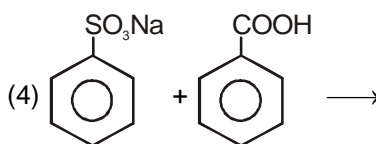
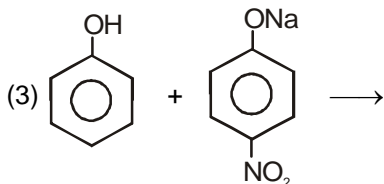
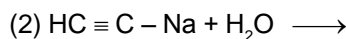
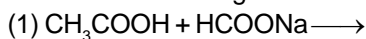
(1) I < II < III

(2) II < III < I

(3) III < II < I

(4) I < III < II .

I-22. Which of the following reactions is/are feasible ?



Section (J) : Basic strength :

J-1. The basic character of amines can be explained :

(1) Only in terms of Lowry-Bronsted concept.

(2) Only in terms of Lewis concept.

(3) Both in terms of Arrhenius and Lewis concepts.

(4) Both in terms of Lewis and Lowry-Bronsted concepts.

J-2. Which has the highest $\text{p}K_b$ value ?

(1) R_3N

(2) R_2NH

(3) RNH_2

(4) NH_3

J-3. Amines are more basic than :

(1) Alcohols

(2) Ethers

(3) Ester

(4) All of these

J-4. Which of the following shows the correct order of decreasing basicity in gas phase ?

(1) $(\text{CH}_3)_3\text{N} > (\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > \text{NH}_3$

(2) $(\text{CH}_3)_2\text{NH} > (\text{CH}_3)_3\text{N} > \text{CH}_3\text{NH}_2 > \text{NH}_3$

(3) $(\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_3\text{N} > \text{NH}_3$

(4) $(\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > \text{NH}_3 > (\text{CH}_3)_3\text{N}$

J-5. Which of the following shows the correct order of decreasing basicity in aqueous medium ?

(1) $(\text{CH}_3)_3\text{N} > (\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > \text{NH}_3$

(2) $(\text{CH}_3)_2\text{NH} > (\text{CH}_3)_3\text{N} > \text{CH}_3\text{NH}_2 > \text{NH}_3$

(3) $(\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > (\text{CH}_3)_3\text{N} > \text{NH}_3$

(4) $(\text{CH}_3)_2\text{NH} > \text{CH}_3\text{NH}_2 > \text{NH}_3 > (\text{CH}_3)_3\text{N}$

J-6. Which of the following shows the correct order of decreasing basicity in aqueous medium ?

(1) $(\text{C}_2\text{H}_5)_3\text{N} > (\text{C}_2\text{H}_5)_2\text{NH} > \text{C}_2\text{H}_5\text{NH}_2 > \text{NH}_3$

(2) $(\text{C}_2\text{H}_5)_2\text{NH} > (\text{C}_2\text{H}_5)_3\text{N} > \text{C}_2\text{H}_5\text{NH}_2 > \text{NH}_3$

(3) $(\text{C}_2\text{H}_5)_2\text{NH} > \text{C}_2\text{H}_5\text{NH}_2 > (\text{C}_2\text{H}_5)_3\text{N} > \text{NH}_3$

(4) $(\text{C}_2\text{H}_5)_2\text{NH} > \text{C}_2\text{H}_5\text{NH}_2 > \text{NH}_3 > (\text{C}_2\text{H}_5)_3\text{N}$

J-7. The correct basic strength order of following anions is :

(1) $\text{CH}_3\text{-CH}_2^- > \text{NH}_2^- > \text{CH}_2=\text{CH}^- > \text{CH}\equiv\text{C}^- > \text{HO}^- > \text{F}^-$

(2) $\text{NH}_2^- > \text{CH}_3\text{-CH}_2^- > \text{CH}_2=\text{CH}^- > \text{CH}\equiv\text{C}^- > \text{F}^- > \text{HO}^-$

(3) $\text{CH}_3\text{-CH}_2^- > \text{CH}_2=\text{CH}^- > \text{NH}_2^- > \text{CH}\equiv\text{C}^- > \text{HO}^- > \text{F}^-$

(4) $\text{F}^- > \text{HO}^- > \text{CH}\equiv\text{C}^- > \text{CH}_2=\text{CH}^- > \text{NH}_2^- > \text{CH}_3\text{-CH}_2^-$

J-8. Arrange basicity of the given compounds in decreasing order :

(i) $\text{CH}_3\text{-CH}_2\text{-NH}_2$

(ii) $\text{CH}_2=\text{CH-NH}_2$

(iii) $\text{CH}\equiv\text{C-NH}_2$

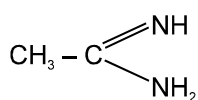
(1) i > ii > iii

(2) i > iii > ii

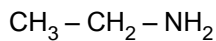
(3) iii > ii > i

(4) ii > iii > i

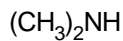
J-9. Write the basicity order of the following :



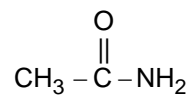
(I)



(II)



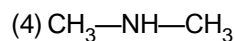
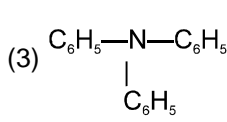
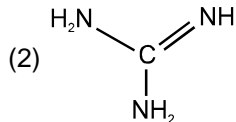
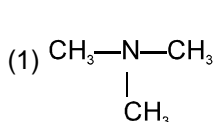
(III)



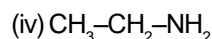
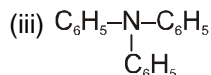
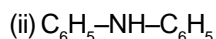
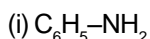
(IV)

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

J-10. The strongest base is :

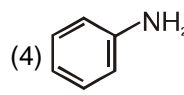
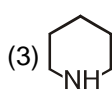
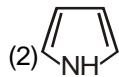
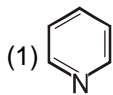


J-11. Decreasing order of basicity is :

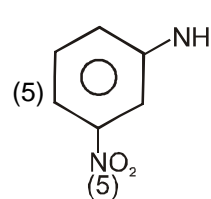
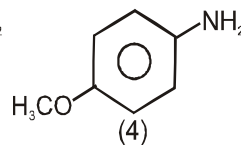
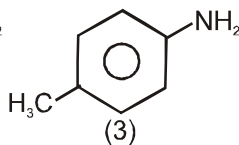
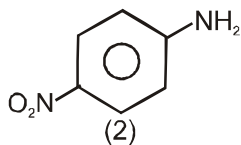
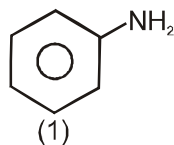


- (1) i > ii > iii > iv (2) iv > i > ii > iii (3) iii > ii > i > iv (4) iv > iii > ii > i

J-12. The strongest base among the following is :

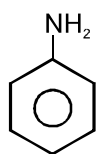


J-13. The correct order of increasing basic nature of the following bases is :

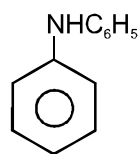


- (1) 2 < 5 < 1 < 3 < 4 (2) 5 < 2 < 1 < 3 < 4 (3) 2 < 5 < 1 < 4 < 3 (4) 5 < 2 < 1 < 4 < 3

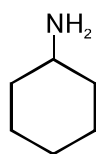
J-14. Arrange the following in increasing order of pH value :



I



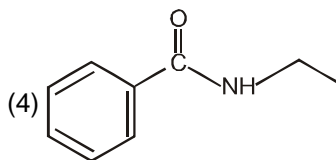
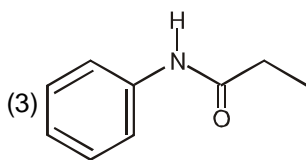
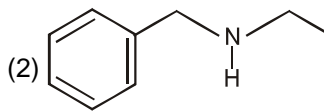
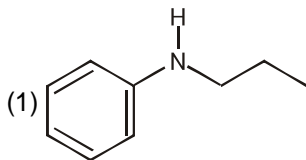
II



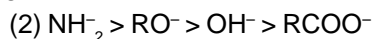
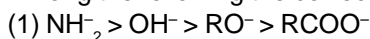
III

- (1) II < I < III (2) III < I < II (3) III < II < I (4) II < III < I

J-15. Which one of the following compound is most basic ?



J-16. Among the following the correct order of basicity is:



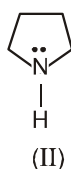
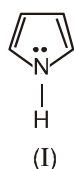
PART - II : ASSERTION / REASONING

DIRECTIONS :

Each question has 5 choices (1), (2), (3), (4) and (5) out of which ONLY ONE is correct.

- (1) Statement-1 is True, Statement-2 is True; Statement-2 is a correct explanation for Statement-1.
(2) Statement-1 is True, Statement-2 is True; Statement-2 is NOT a correct explanation for Statement-1.
(3) Statement-1 is True, Statement-2 is False.
(4) Statement-1 is False, Statement-2 is True.
(5) Both Statements are False.

- Statement-1** : The acidity of alcohols follows the order $1^\circ > 2^\circ > 3^\circ$.
Statement-2 : The + I effect of alkyl groups ($3^\circ > 2^\circ > 1^\circ$) favours the dissociation of O–H group.
- Statement-1** : p-Nitrophenol is stronger acid than o-nitrophenol.
Statement-2 : Intramolecular hydrogen bonding makes ortho-isomer weaker acid than para-isomer.
- Statement-1** : Phenol and benzoic acid can be distinguished by NaOH.
Statement-2 : Benzoic acid is weaker acid than phenol
- Statement-1** : Heterolytic fission involves the breaking of a covalent bond in such a way that both the electrons of the shared pair are carried away by one of the atoms.
Statement-2 : Heterolytic fission occurs readily in polar covalent bonds.
- Statement-1** : Tertiary carbocations are generally formed more easily than primary carbocations.
Statement-2 : Hyperconjugation as well as inductive effect due to additional alkyl group stabilize tertiary carbocations.
- Statement-1** : Allyl free radical is more stable than simple alkyl free radical.
Statement-2 : The allyl free radical is stabilized by resonance.
- Statement-1** : The K_a value of acetic acid is lower than that of phenol.
Statement-2 : Phenoxide ion is more resonance stabilized than acetate ion.
- Statement-1** : The resonating structure of acylium ion, $R - C \equiv \overset{+}{O}$ is more stable than $R - \overset{+}{C} = \ddot{O}:$.
Statement-2 : The octet of all atoms is complete in $R - C \equiv \overset{+}{O}$
- Statement-1** : Amines are more basic than amides.
Statement-2 : Nitrogen is less electronegative than oxygen. So it is better electron donor.
- Statement-1** : pK_{a1} of fumaric acid is more than maleic acid.
Statement-2 : Conjugate base of fumaric acid is stabilised by intramolecular H-bonding.
- Statement-1** : Salicylic acid is much stronger than its m-, p-isomers and benzoic acid itself.
Statement-2 : It is due to steric inhibition to resonance of –OH group to –COOH.
- Statement-1** : Ortho substituted benzoic acids are stronger acid than benzoic acid.
Statement-2 : Ortho substituent tends to prevent coplanarity of –COOH with ring. Thus resonance is diminished which increases acidic strength (ortho effect)
- Statement-1** : Carbon–oxygen bonds are of equal length in acetate ion.
Statement-2 : Bond length decreases with the multiplicity of bond between two atoms.
- Statement-1** : Pyrrolidine (II) is more basic than pyrrole (I)



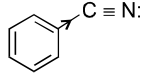
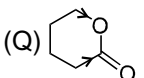
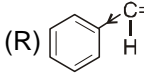
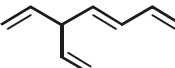
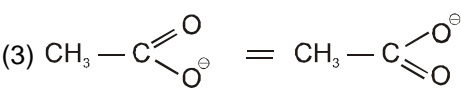
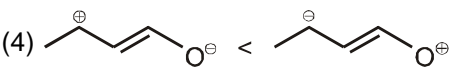
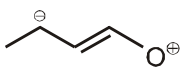
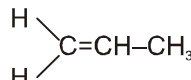
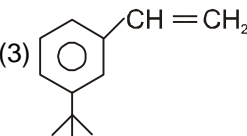
Statement-2 : Protonated pyrrole has delocalisation of positive charge in aromatic ring.

Exercise # 2

PART - I : OBJECTIVE QUESTIONS

Part - I (GOC-I)

Single choice type

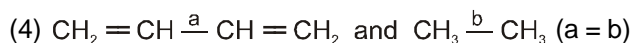
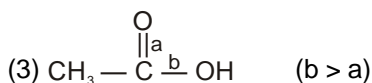
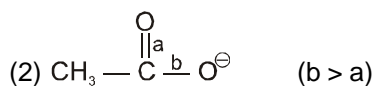
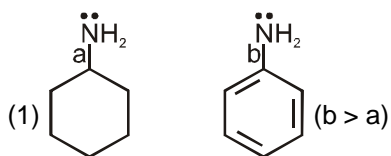
- Which of the following cases have correct direction of I effect ?
 (P)  (Q)  (R)  (S) $\text{CH}_3\text{CH}_2 \rightarrow \text{MgBr}$ (T) $\text{CH}_3\text{CH}_2 \leftarrow \text{Na}$
 (1) PQS (2) PQR (3) PST (4) PQT
- Which of the following is the strongest - I group :
 (1) $-\overset{+}{\text{N}}(\text{CH}_3)_3$ (2) $-\overset{+}{\text{NH}}_3$ (3) $-\overset{+}{\text{S}}(\text{CH}_3)_2$ (4) $-\text{F}$
- Which of the following statement is not true about the resonance contributing structures to a resonance hybrid ?
 (1) Contributing structures contribute to the resonance hybrid in proportion of their energies.
 (2) Number of unpaired electrons remain same in the resonating structures.
 (3) Contributing structures represent hypothetical molecules having no real existence.
 (4) Contributing structures are less stable than the resonance hybrid.
- In  how many π bonds are in resonance ?
 (1) 4 (2) 2 (3) 3 (4) None
- Which of the following resonance structures does not represent the correct stability order :
 (1) $\text{CH}_3 - \text{CH}_2 - \overset{\oplus}{\text{C}}\text{H} - \overset{\ominus}{\text{O}}\text{CH}_3 < \text{CH}_3 - \text{CH}_2 - \text{CH} = \overset{\oplus}{\text{O}}\text{CH}_3$
 (2) $\text{CH}_2 = \text{CH} - \overset{\oplus}{\text{C}}\text{H} - \overset{\oplus}{\text{N}}\text{H}_2 > \overset{\oplus}{\text{C}}\text{H}_2 - \text{CH} = \text{CH} - \overset{\oplus}{\text{N}}\text{H}_2$
 (3)  = $\text{CH}_3 - \overset{\ominus}{\text{O}}\text{C} = \overset{\oplus}{\text{O}}$
 (4)  < 
- Which of the following series contains atoms/groups having only -m (mesomeric) effect ?
 (1) COR, OR, COOR (2) Cl, CHO, NH_2 (3) NO_2 , CN, SO_3H (4) OH, NR_2 , SR
- Which of the following group can exert both + m and - I effect ?
 (1) $-\text{CHO}$ (2) $-\text{NO}_2$ (3) $-\text{Cl}$ (4) $-\text{CH}_3$
- Hyper conjugation is possible in :
 (1)  (2) $\text{CH}_3 - \overset{\oplus}{\text{C}}\text{H}_2$ (3)  (4) $|\text{C} - \text{CH} = \text{CH} - \text{C}|$
- Which of the following compounds has inductive, mesomeric and hyperconjugative effect ?
 (1) CH_3Cl (2) $\text{CH}_3 - \text{CH} = \text{CH}_2$
 (3) $\text{CH}_3 - \text{CH} = \text{CH} - \overset{\text{O}}{\parallel}{\text{C}} - \text{CH}_3$ (4) $\text{CH}_2 = \text{CH} - \text{CH} = \text{CH}_2$

10. Which among the following statements are true with respect to electronic displacement in a covalent bond?
 (a) Inductive effect operates through π -bond
 (b) Resonance effect operates through σ -bond
 (c) Inductive effect operates through σ -bond
 (d) Resonance effect operates through π -bond
 (e) Hyperconjugation involves C-H sigma bond electrons
 (1) a and c (2) b and c (3) b and d (4) c, d and e

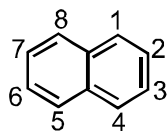
11. Carbon-carbon double bond length will be maximum in which of the following compound ?
 (1) $\text{CH}_3-\text{CH}=\text{CH}_2$ (2) $\text{CH}_3-\text{CH}=\text{CH}-\text{CH}_3$
 (3) $\begin{array}{c} \text{CH}_3-\text{C}=\text{C}-\text{CH}_3 \\ | \quad | \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$ (4) $\text{CH}_2=\text{CH}_2$

12. Consider the following three halides :
 (i) $\text{CH}_3-\text{CH}_2-\text{Cl}$ (ii) $\text{CH}_2=\text{CH}-\text{Cl}$ (iii) $\text{C}_6\text{H}_5-\text{Cl}$
 Arrange C-Cl bond length of these compounds in decreasing order :
 (1) $i > ii > iii$ (2) $i > iii > ii$ (3) $iii > ii > i$ (4) $ii > iii > i$

13. Which of the following is correct about bond length :

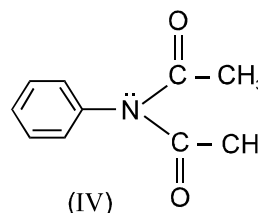
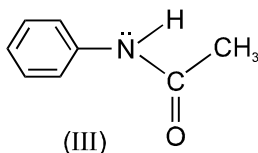
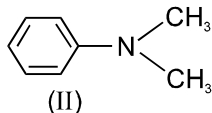
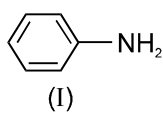


14. Which of the following is correct about the following compound



(Naphthalene)

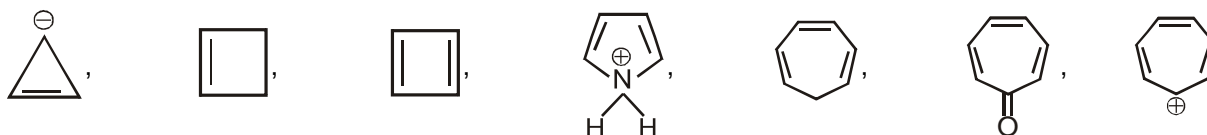
- (1) All the C-C bond length are same
 (2) C_1-C_2 bond length is shorter than C_2-C_3 bond length
 (3) C_1-C_2 bond length is greater than C_2-C_3 bond length
 (4) All the C-C bond length are equal to C-C bond length of benzene
15. The correct order of +m effect of 'N' containing functional group on benzene ring, amongst the given compounds is :



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

16. Aromatic compounds burn with sooty flame because :
 (1) They contain a ring structure of carbon atoms.
 (2) They contain a relatively high percentage of hydrogen.
 (3) They resist reaction with oxygen of air.
 (4) They contain a relatively high percentage of carbon.

17. How many species out of the following are aromatic ?



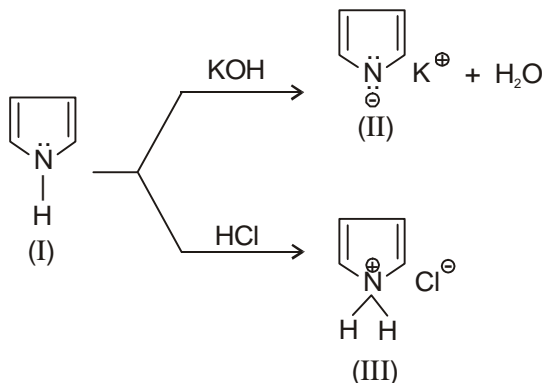
(1) 2

(2) 4

(3) 6

(4) 5

18. What is true about the following reactions



(1) I is nonaromatic

(2) II is nonaromatic

(3) III is antiaromatic

(4) Out of I, II and III only III compound is nonaromatic

Part - II (GOC- II)

19. Heterolysis of propane will yield :

(1) CH_3 and C_2H_5 radicals

(2) CH_3^- and CH_3CH_2^+ ions

(3) CH_3^+ and CH_3CH_2^- ions

(4) CH_3^+ and CH_3CH_2^+ ions

20. Among the following, the paramagnetic species is :

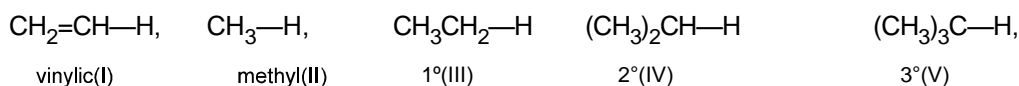
(1) Free radical

(2) Carbonium ion

(3) Carbanion

(4) All the three

21. Reactivity of C—H bond (abstraction of H)

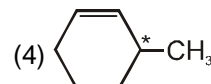
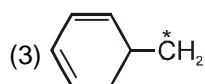


(1) $\text{II} < \text{III} < \text{I} < \text{IV} < \text{V}$ (2) $\text{I} > \text{II} > \text{III} > \text{IV} > \text{V}$ (3) $\text{I} < \text{II} < \text{III} < \text{IV} < \text{V}$ (4) $\text{I} < \text{II} < \text{IV} < \text{III} < \text{V}$

22. Maximum stability will be in which of the following free radicals ?

(1) $\text{H}_2\text{C}=\dot{\text{C}}\text{H}$

(2) $\text{H}_2\text{C}=\text{CH}-\dot{\text{C}}\text{H}_2$



23. Which allylic carbocation is the most stable carbocation ?

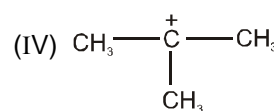
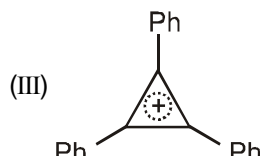
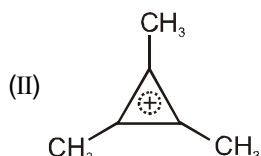
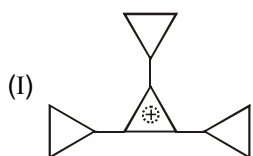
(1) $\text{CH}_3-\text{CH}=\text{CH}-\text{C}^+\text{H}_2$

(2) $\text{CH}_2=\text{CH}-\text{C}^+\text{H}_2$

(3) $\text{C}_6\text{H}_5-\text{CH}=\text{CH}-\text{C}^+(\text{CH}_3)_2$

(4) All have same stability

24. The correct order of stability of following carbocation is :



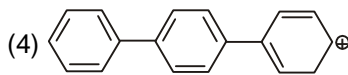
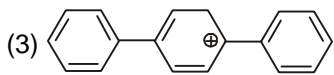
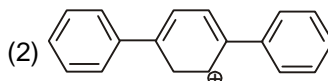
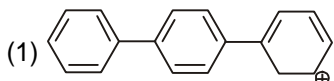
(1) (III) > (II) > (I) > (IV)

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

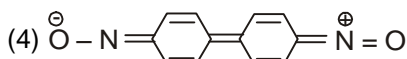
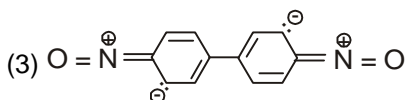
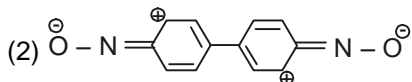
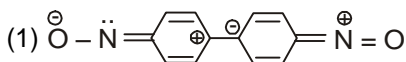
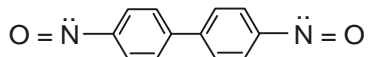
(3) (I) > (III) > (IV) > (II)

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

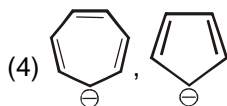
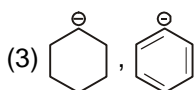
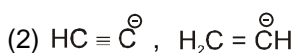
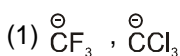
25. The most stable carbocation is



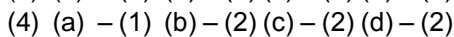
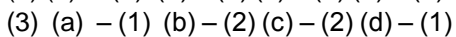
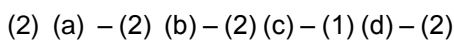
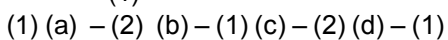
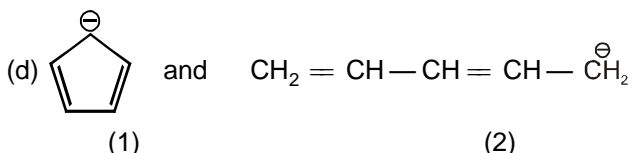
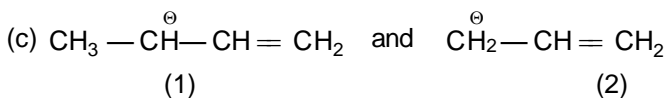
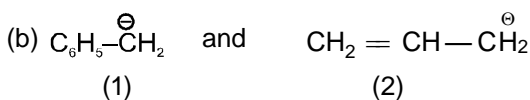
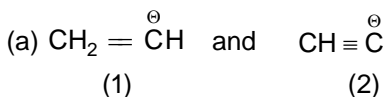
26. The most stable resonating structure of following compound is



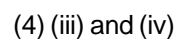
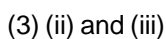
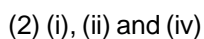
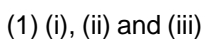
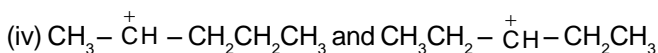
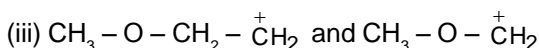
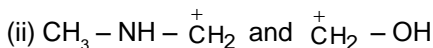
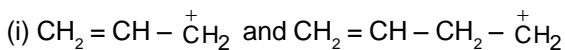
27. In which of the pair of carbanion first is more stable than second ?



28. In each of the following pairs of ions which ion is more stable :



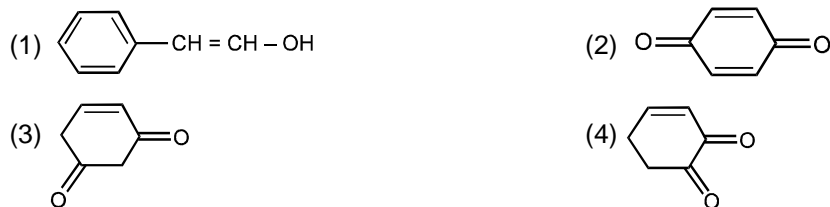
29. In which of the following pairs of carbocations, the first carbocation is more stable than the second ?



30. Which of the following compounds is the most basic in aqueous medium ?



31. Tautomerism does not exhibited by :



32. Which among the following compounds will give maximum enol content in solution :

- (1) 3-hexanone (2) 2, 4-hexanedione
(3) 2, 5-hexanedione (4) 2, 3-hexanedione

33. Which of the following would be expected to be easily dissociate in water ?

- (1) $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{COOH}$ (2) $\text{CH}_3\text{CCl}_2\text{CH}_2\text{COOH}$
(3) $\text{CH}_3\text{CH}_2\text{CCl}_2\text{COOH}$ (4) $\text{CH}_3\text{CH}_2\text{CHClCOOH}$

34. Which of the following substituents will decrease the acidity of phenol -

- (1) $-\text{NO}_2$ (2) $-\text{CN}$ (3) $-\text{CH}_3$ (4) $-\text{CHO}$

35. Select the compound having maximum pKa

- (1) Phenol (2) Ethyl alcohol (3) Formic acid (4) Cyanoacetic acid

36. Which of the following is weaker acid ?

- (1) $\text{CH}_3\text{CHF}\text{COOH}$ (2) $\text{FCH}_2\text{CH}_2\text{COOH}$ (3) $\text{BrCH}_2\text{CH}_2\text{COOH}$ (4) $\text{CH}_3\text{CHBr}\text{COOH}$

37. Among the following which is least acidic ?

- (1) p-Nitrophenol (2) p-Chlorophenol (3) Phenol (4) o-Cresol

38. Find the strongest acid among the following compounds is :

- (1) $\text{HOOC}-(\text{CH}_2)_2-\text{COOH}$ (2) $\text{H}_3\text{N}^\oplus-(\text{CH}_2)_2-\text{COOH}$
(3) $\text{F}-(\text{CH}_2)_2-\text{COOH}$ (4) $\text{CH}_3-(\text{CH}_2)_2-\text{COOH}$

39. The increasing order of acidity of α , β and γ - chlorobutyric acids is :

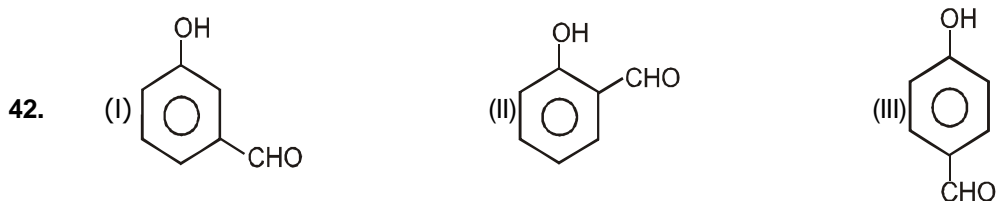
- (1) $\alpha < \beta < \gamma$ (2) $\beta < \gamma < \alpha$ (3) $\gamma < \alpha < \beta$ (4) $\gamma < \beta < \alpha$

40. Arrange Increasing order of K_a value of following dibasic acids :

- (I) oxalic acid, (II) succinic acid, (III) malonic acid, (IV) adipic acid
(1) III < II < I < IV (2) II < III < I < IV (3) IV < II < III < I (4) II < I < III < IV

41. The strongest acid amongst the following is :

- (1) o-nitrobenzoic acid (2) p-nitrobenzoic acid
(3) m-nitrobenzoic acid (4) Benzoic acid



Arrange above phenol in increasing order of $\text{p}K_a$ value

- (1) I < II < III (2) III < I < II (3) III < II < I (4) I < III < II

43. Which of the following compounds when dissolved in water, gives a solution with pH less than seven ?

- (1) CH_3COCH_3 (2) $\text{C}_6\text{H}_5\text{OH}$ (3) $\text{C}_6\text{H}_5\text{NH}_2$ (4) $\text{C}_2\text{H}_5\text{OH}$

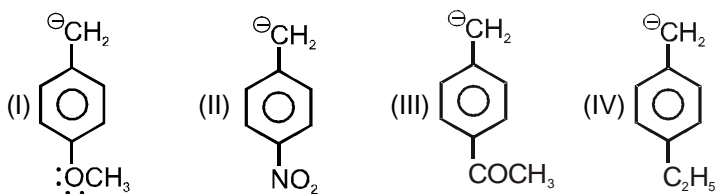
44. Arrange the following compounds in Decreasing order of their pK_b value ?
 $CH_2=CHCH_2NH_2$, $CH_3CH_2CH_2NH_2$, $CH\equiv CCH_2NH_2$
 I II III
 (1) I > II > III (2) III > I > II (3) III > II > I (4) I > III > II

45. Which is the correct order of increasing basicity ?
 (1) $CH_3CH_2CH_3 < CH_3CH_2SH < CH_3CH_2OH < CH_3CH_2NH_2$
 (2) $CH_3CH_2CH_3 < CH_3CH_2OH < CH_3CH_2SH < CH_3CH_2NH_2$
 (3) $CH_3CH_2NH_2 < CH_3CH_2SH < CH_3CH_2OH < CH_3CH_2CH_3$
 (4) $CH_3CH_2CH_3 < CH_3CH_2OH < CH_3CH_2NH_2 < CH_3CH_2SH$

46. Which of the following correctly shows the order of decreasing basicity -
 (1) Aniline > o-nitroaniline > p-nitroaniline > m-nitroaniline
 (2) Aniline > p-nitroaniline > o-nitroaniline > m-nitroaniline
 (3) Aniline > m-nitroaniline > p-nitroaniline > o-nitroaniline
 (4) o-Nitroaniline > p-nitroaniline > aniline > m-nitroaniline

47. Increasing pK_b values of o-, m- and p-toluidine is
 (1) p < m < o (2) o < m < p (3) p < o < m (4) m < o < p

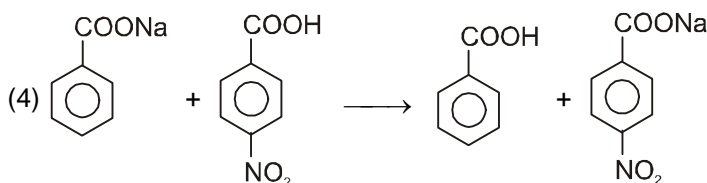
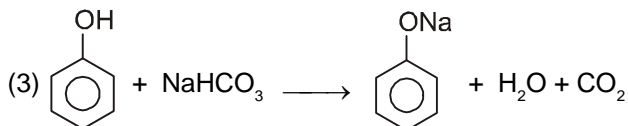
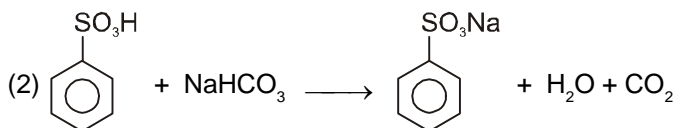
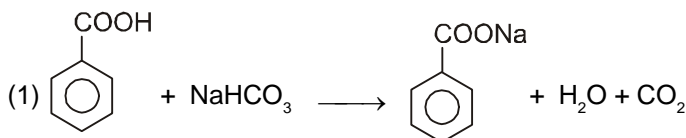
48. Select the correct basicity order for



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

49. The pK_a and pK_b values of some bases are given below. Which represents the weakest base :
 (1) $pK_b = 9.40$ (2) $pK_a = 11.12$ (3) $pK_a = 3.0$ (4) $pK_b = 3.32$

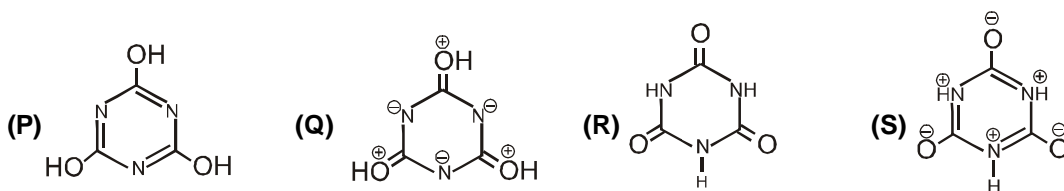
50. Which of the following reactions is not feasible ?



More than one choice type

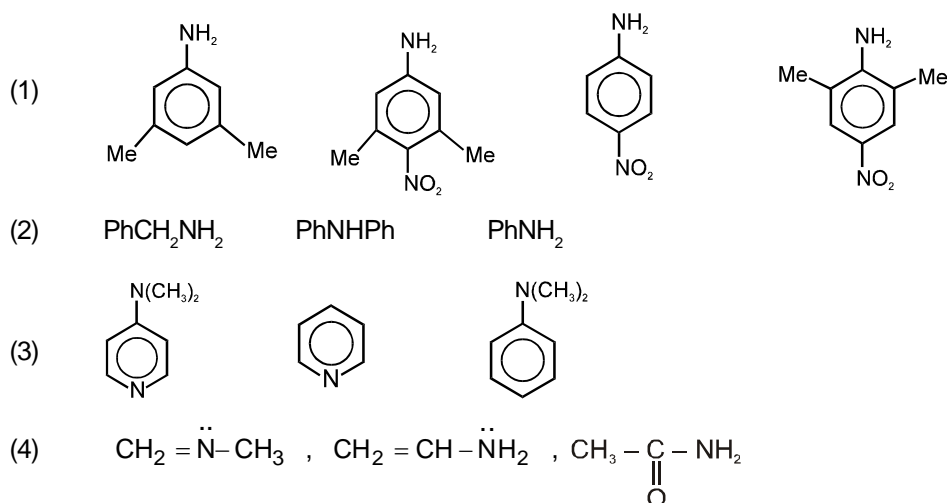
51. Monocarbonyl compounds exist predominantly in keto form because :
 (1) Carbonyl group has resonance stability (2) $>C=O$ bond has high bond energy
 (3) Keto form exhibits intramolecular H-bond. (4) Keto form exhibits strong acidic character

52.* The **correct** statement(s) concerning the structures P,Q,R & S is/are

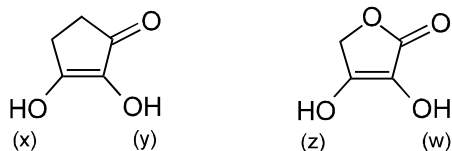


- (1) Q & S are not resonating structures
 (2) R & S are resonating structures
 (3) P & R are tautomers
 (4) P & Q are resonating structures

53. Which of the following compounds arranged in their decreasing order of basic strength (K_b) ?



54. Compare the acidity of four hydrogen atoms x, y, z and w.



- (1) x is more acidic than z
 (2) y is more acidic than x
 (3) z is more acidic than w
 (4) x is most acidic and w is least acidic amongst the four hydrogen atoms.

PART - II : COMPREHENSION

Comprehension # 1

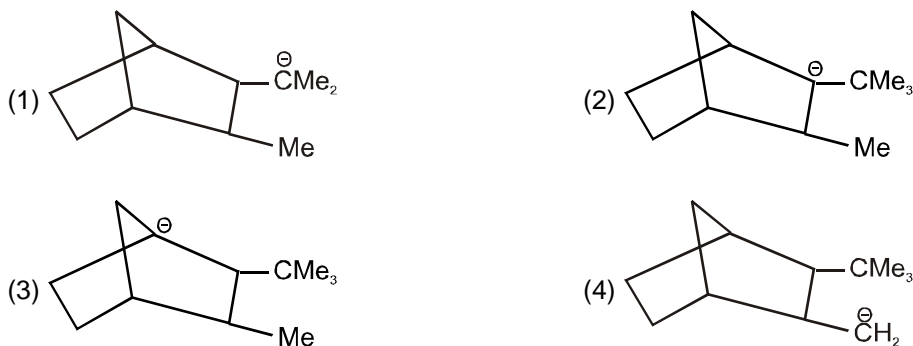
Reaction intermediates : Reaction intermediates are short lived species and are highly reactive. They are formed by heterolytic and homolytic bond fission. There are various types of reaction intermediates in which the most important are carbocation, carbanion and free radical.

Carbocation is an organic species in which carbon have positive charge and six electrons in its outermost shell. The stability of carbocation can be increased by positive inductive effect, hyperconjugation and delocalisation. If α -atom with respect to carbocation has one or more lone pair of electrons then lone pair of electron strongly stabilises the carbocation due to octet completion.

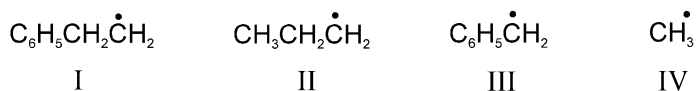
Species in which carbon have negative charge is called carbanion. Carbanion carries three bond pairs and one lone pair. The stability of carbanion can be increased by negative inductive effect, negative mesomeric effect and delocalisation.

Free radical is a species which have seven electrons in its outermost shell. The stability of free radical can be increased by hyperconjugation and delocalisation.

1. Which of the following is the most stable carbanion intermediate ?

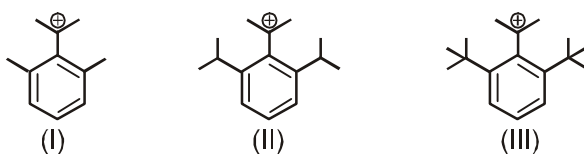


2. The stability order of following free radicals is :



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

3. The stability order of following carbocations is



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

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 substituent. ERG substituents, such as $-\text{CH}_3$, $-\text{NH}_2$ and $-\text{OCH}_3$ increases the basicity and EWG substituents, such as $-\text{Cl}$, $-\text{NO}_2$ and $-\text{CN}$ decreases basicity. While sp^2 -hybridized nitrogen atom in pyridine is less basic than the sp^3 -hybridized nitrogen in an alkylamine.

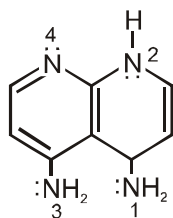
4. Select the correct order of K_b .

(1) $\text{CH}_3\text{NH}_2 > \text{NaOH}$ (2) p-Methyl aniline > p-Chloroaniline > p-Amino acetophenone
 (3) Pyridine > $\text{CH}_3-\ddot{\text{N}}\text{H}-\text{CH}_3$ (4) p-Bromoaniline > p-Nitroaniline > p-Amino benzaldehyde

5. pK_b order of the following compound is :

(I) NH_2OH (II) NH_2NH_2 (III) NH_3 (IV) H_2O
 (1) IV > I > II > III (2) III > II > I > IV (3) I > IV > II > III (4) III > I > II > IV

6. The correct basicity order of various atoms is :

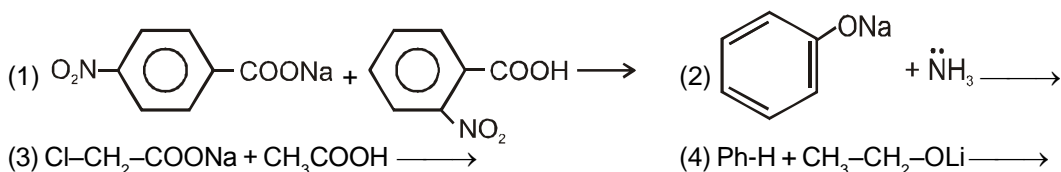


(1) 1 < 2 < 3 < 4 (2) 2 < 4 < 3 < 1 (3) 3 < 2 < 1 < 4 (4) 3 < 2 < 4 < 1

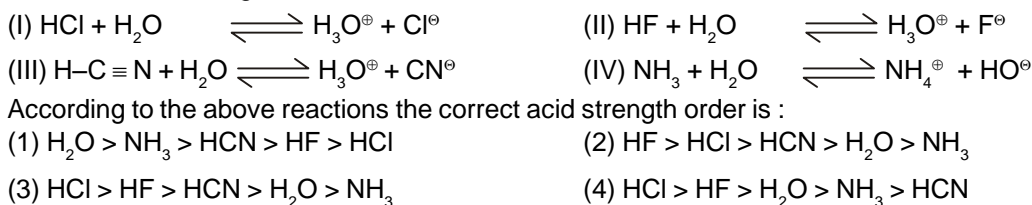
Comprehension # 3

A stronger acid displaces the weaker acid from any 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.

7. Which of the following reaction is feasible ?



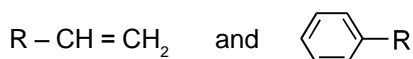
8. Observe the following reaction



Exercise # 3

PART - I : AIEEE PROBLEMS (LAST 10 YEARS)

1. In the following benzyl/allyl system



(R is alkyl group)

decreasing order of inductive effect is :

[AIEEE-2002]

- (1) $(\text{CH}_3)_3\text{C-} > (\text{CH}_3)_2\text{CH-} > \text{CH}_3\text{CH}_2\text{-}$ (2) $\text{CH}_3\text{CH}_2\text{-} > (\text{CH}_3)_2\text{CH-} > (\text{CH}_3)_3\text{C-}$
 (3) $(\text{CH}_3)_2\text{CH-} > \text{CH}_3\text{CH}_2\text{-} > (\text{CH}_3)_3\text{C-}$ (4) $(\text{CH}_3)_3\text{C-} > \text{CH}_3\text{CH}_2\text{-} > (\text{CH}_3)_2\text{CH-}$

2. In the anion HCOO^- the two carbon-oxygen bonds are found to be of equal length. What is the reason for it?

- (1) electronic orbitals of carbon atom are hybridised
 (2) the C=O bond is weaker than the C-O bond
 (3) the anion HCOO^- has two equivalent resonating structures
 (4) the anion is obtained by removal of a proton from the acid molecule.

[AIEEE 2003]

3. The correct order of increasing basic nature for the bases NH_3 , CH_3NH_2 and $(\text{CH}_3)_2\text{NH}$ is :

[AIEEE-2003]

- (1) $\text{CH}_3\text{NH}_2 < \text{NH}_3 < (\text{CH}_3)_2\text{NH}$ (2) $(\text{CH}_3)_2\text{NH} < \text{NH}_3 < \text{CH}_3\text{NH}_2$
 (3) $\text{NH}_3 < \text{CH}_3\text{NH}_2 < (\text{CH}_3)_2\text{NH}$ (4) $\text{CH}_3\text{NH}_2 < (\text{CH}_3)_2\text{NH} < \text{NH}_3$

4. Which of the following is the strongest base?

[AIEEE 2004]



5. Consider the acidity of the carboxylic acids:

[AIEEE 2004]

- (i) PhCOOH (ii) $\text{o-NO}_2\text{C}_6\text{H}_4\text{COOH}$ (iii) $\text{p-NO}_2\text{C}_6\text{H}_4\text{COOH}$ (iv) $\text{m-NO}_2\text{C}_6\text{H}_4\text{COOH}$
 (1) $\text{i} > \text{ii} > \text{iii} > \text{iv}$ (2) $\text{ii} > \text{iii} > \text{iv} > \text{i}$ (3) $\text{iii} > \text{ii} > \text{iv} > \text{i}$ (4) $\text{ii} > \text{iv} > \text{iii} > \text{i}$

6. Among the following acid which has the lowest pK_a value ?

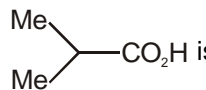
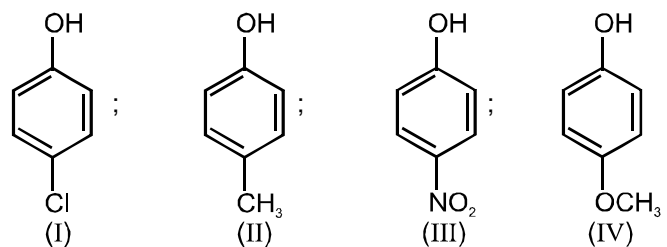
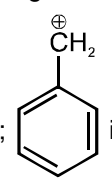
[AIEEE-2005]

- (1) $\text{CH}_3\text{CH}_2\text{COOH}$ (2) $(\text{CH}_3)_2\text{CH-COOH}$ (3) HCOOH (4) CH_3COOH

7. Amongst the following the most basic compound is

[AIEEE-2005]

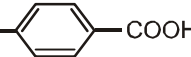
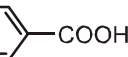
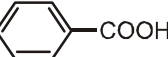
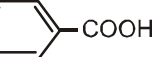
- (1) p-Nitroaniline (2) Acetanilide (3) Aniline (4) Benzylamine

8. The increasing order of stability of the following free radicals is : [AIEEE 2006]
- (1) $(\text{CH}_3)_2\dot{\text{C}}\text{H} < (\text{CH}_3)_3\dot{\text{C}} < (\text{C}_6\text{H}_5)_2\dot{\text{C}}\text{H} < (\text{C}_6\text{H}_5)_3\dot{\text{C}}$
 (2) $(\text{C}_6\text{H}_5)_2\dot{\text{C}} < (\text{C}_6\text{H}_5)_2\dot{\text{C}}\text{H} < (\text{CH}_3)_3\dot{\text{C}} < (\text{CH}_3)_2\dot{\text{C}}\text{H}$
 (3) $(\text{C}_6\text{H}_5)_2\dot{\text{C}}\text{H} < (\text{C}_6\text{H}_5)_3\dot{\text{C}}\text{H} < (\text{CH}_3)_3\dot{\text{C}} < (\text{CH}_3)_2\dot{\text{C}}\text{H}$
 (4) $(\text{CH}_3)_2\dot{\text{C}}\text{H} < (\text{CH}_3)_3\dot{\text{C}} < (\text{C}_6\text{H}_5)_3\dot{\text{C}} < (\text{C}_6\text{H}_5)_2\dot{\text{C}}\text{H}$
9. The correct order of increasing acid strength of the compounds [AIEEE 2006]
- (a) $\text{CH}_3\text{CO}_2\text{H}$ (b) $\text{MeOCH}_2\text{CO}_2\text{H}$ (c) $\text{CF}_3\text{CO}_2\text{H}$ (d)  is
- (1) $b < d < a < c$ (2) $d < a < c < b$ (3) $d < a < b < c$ (4) $a < d < c < b$
10. Which one of the following is the strongest base in aqueous solution? [AIEEE 2007]
- (1) Dimethylamine (2) Methylamine (3) Trimethylamine (4) Aniline
11. Arrange the carbanions, $(\text{CH}_3)_3\bar{\text{C}}$, $\bar{\text{C}}\text{Cl}_3$, $(\text{CH}_3)_2\bar{\text{C}}\text{H}$, $\text{C}_6\text{H}_5\bar{\text{C}}\text{H}_2$ in order of their decreasing stability : [AIEEE-2009, 4/144]
- (1) $(\text{CH}_3)_2\bar{\text{C}}\text{H} > \bar{\text{C}}\text{Cl}_3 > \text{C}_6\text{H}_5\bar{\text{C}}\text{H}_2 > (\text{CH}_3)_3\bar{\text{C}}$ (2) $\bar{\text{C}}\text{Cl}_3 > \text{C}_6\text{H}_5\bar{\text{C}}\text{H}_2 > (\text{CH}_3)_2\bar{\text{C}}\text{H} > (\text{CH}_3)_3\bar{\text{C}}$
 (3) $(\text{CH}_3)_3\bar{\text{C}} > (\text{CH}_3)_2\bar{\text{C}}\text{H} > \text{C}_6\text{H}_5\bar{\text{C}}\text{H}_2 > \bar{\text{C}}\text{Cl}_3$ (4) $\text{C}_6\text{H}_5\bar{\text{C}}\text{H}_2 > \bar{\text{C}}\text{Cl}_3 > (\text{CH}_3)_3\bar{\text{C}} > (\text{CH}_3)_2\bar{\text{C}}\text{H}$
12. The correct order of increasing basicity of the given conjugate bases ($\text{R} = \text{CH}_3$) is : [AIEEE-2010, 4/144]
- (1) $\text{RCOO}^- < \text{HC} \equiv \bar{\text{C}} < \bar{\text{R}} < \bar{\text{N}}\text{H}_2$ (2) $\bar{\text{R}} < \text{HC} \equiv \bar{\text{C}} < \text{RCOO}^- < \bar{\text{N}}\text{H}_2$
 (3) $\text{RCOO}^- < \bar{\text{N}}\text{H}_2 < \text{HC} \equiv \bar{\text{C}} < \bar{\text{R}}$ (4) $\text{RCOO}^- < \text{HC} \equiv \bar{\text{C}} < \bar{\text{N}}\text{H}_2 < \bar{\text{R}}$
13. The strongest acid amongst the following compounds is : [AIEEE-2011]
- (1) CH_3COOH (2) HCOOH
 (3) $\text{CH}_3\text{CH}_2\text{CH}(\text{Cl})\text{CO}_2\text{H}$ (4) $\text{ClCH}_2\text{CH}_2\text{CH}_2\text{COOH}$
14. Identify the compound that exhibits tautomerism. [AIEEE-2011, 4/120]
- (1) 2-Butene (2) Lactic acid (3) 2-Pentanone (4) Phenol
15. The correct order of acid strength of the following compounds: [AIEEE-2011]
- (A) Phenol (B) p-Cresol (C) m-Nitrophenol (D) p-Nitrophenol
- is :
- (1) $\text{D} > \text{C} > \text{A} > \text{B}$ (2) $\text{B} > \text{D} > \text{A} > \text{C}$ (3) $\text{A} > \text{B} > \text{D} > \text{C}$ (4) $\text{C} > \text{B} > \text{A} > \text{D}$
16. Arrange the following compounds in order of decreasing acidity : [JEE(Mains)-2013]
- 
- (1) $\text{II} > \text{IV} > \text{I} > \text{III}$ (2) $\text{I} > \text{II} > \text{III} > \text{IV}$ (3) $\text{III} > \text{I} > \text{II} > \text{IV}$ (4) $\text{IV} > \text{III} > \text{I} > \text{II}$
17. The order of stability of the following carbocations : [JEE(Mains)-2013]
- $\text{CH}_2=\text{CH}-\text{CH}_2^+$ (I) ; $\text{CH}_3-\text{CH}_2-\text{CH}_2^+$ (II) ;  (III) is :
- (1) $\text{III} > \text{II} > \text{I}$ (2) $\text{II} > \text{III} > \text{I}$ (3) $\text{I} > \text{II} > \text{III}$ (4) $\text{III} > \text{I} > \text{II}$

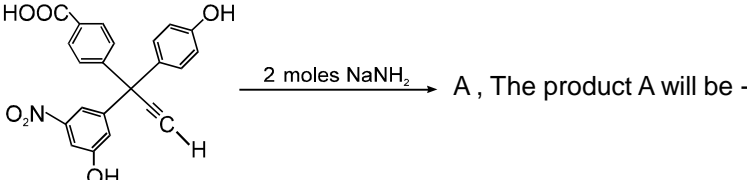
PART - II : IIT-JEE PROBLEMS (LAST 10 YEARS)

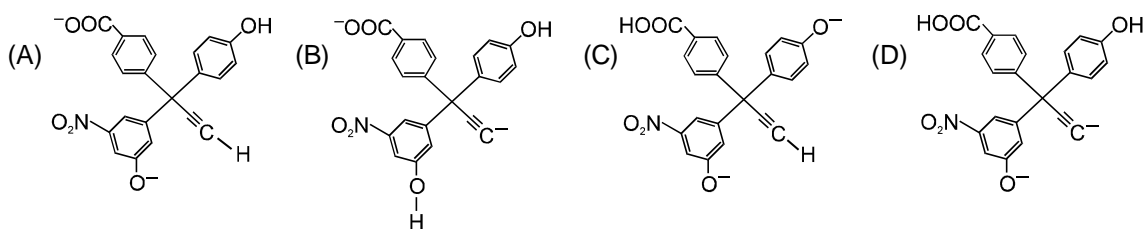
* Marked Questions are more than one correct options.

1. Which of the following acid has the lowest value of acid dissociation constant : [JEE-02(S), 3/90]
 (A) $\text{CH}_3\text{CHF}\text{COOH}$ (B) $\text{FCH}_2\text{CH}_2\text{COOH}$ (C) $\text{BrCH}_2\text{CH}_2\text{COOH}$ (D) $\text{CH}_3\text{CHBr}\text{COOH}$
2. Match the K_a values : [JEE-03(M), 2/60]

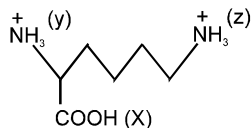
Compounds	K_a
(a) Benzoic acid	(i) 3.3×10^{-5}
(b) 	(ii) 6.3×10^{-5}
(c) 	(iii) 30.6×10^{-5}
(d) 	(iv) 6.4×10^{-5}
(e) 	(v) 4.2×10^{-5}

3. Write resonating structure of the compound $\text{H}_3\text{C}-\text{C}(\text{OH})=\text{CH}-\text{CH}_2$. [JEE-03(S), 2/60]

4.  A, The product A will be - [JEE-03(S), 3/84]



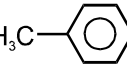
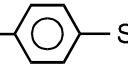
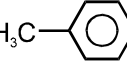
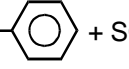
5. What is the acidity order of x, y & z ? [JEE-04(S), 3/84]



- (A) $x > y > z$ (B) $x > z > y$ (C) $y > z > x$ (D) $z > y > x$

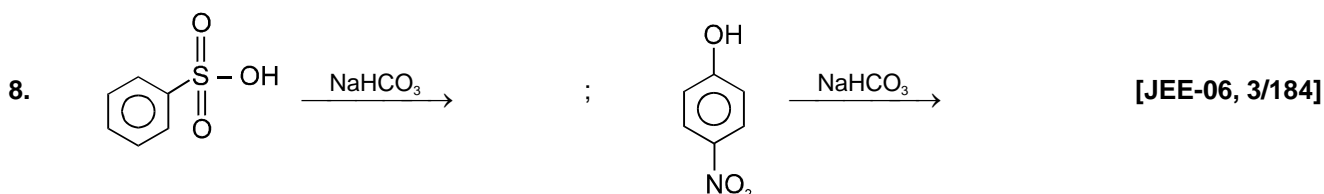


The products will be :

- (A)  + CH_3COONa (B)  + CH_3COOH
 (C)  + CH_3COOH (D)  + SO_3

7. Which will be the least stable resonating structure : [JEE-05(S), 3/84]

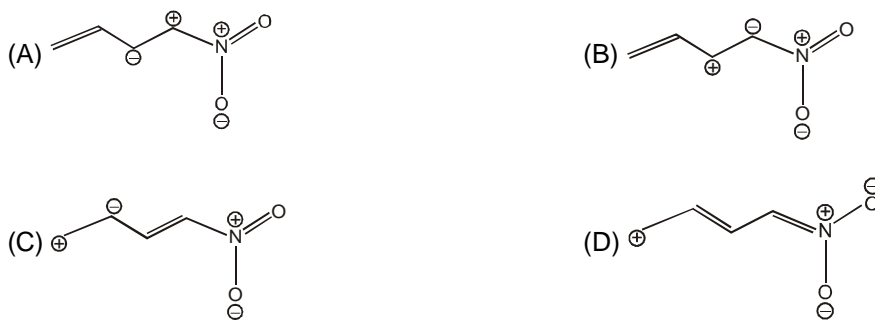
- (A) $\text{CH}_2 = \text{CH} - \overset{\oplus}{\text{C}}\text{H} - \overset{\ominus}{\text{C}}\text{H} - \text{O} - \text{CH}_3$ (B) $\overset{\ominus}{\text{C}}\text{H}_2 - \overset{\oplus}{\text{C}}\text{H} - \text{CH} = \text{CH} - \text{OCH}_3$
 (C) $\overset{\ominus}{\text{C}}\text{H}_2 - \text{CH} = \text{CH} - \text{CH} = \overset{\oplus}{\text{O}} - \text{CH}_3$ (D) $\text{CH}_2 = \text{CH} - \overset{\ominus}{\text{C}}\text{H} - \text{CH} = \overset{\oplus}{\text{O}} - \text{CH}_3$



Benzenesulphonic acid and para nitrophenol react with NaHCO_3 separately. The gases produced are respectively.

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

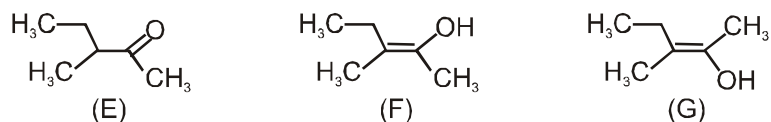
9. Among the following, the least stable resonating structure is : [JEE-07, 3/162]



10. Hyperconjugation involves overlap of the following orbitals : JEE-08, 3/163]

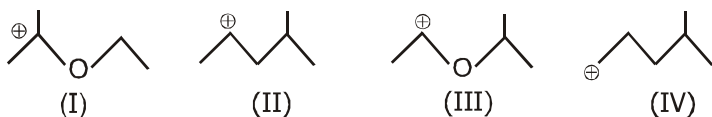
- (A) $\sigma - \sigma$ (B) $\sigma - p$ (C) $p - p$ (D) $\pi - \pi$

11.* The correct statement(s) concerning the structures E, F and G is (are) : [JEE-08, 4/163]



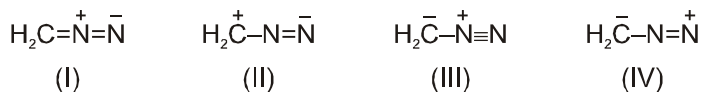
- (A) E, F, and G are resonating structures (B) E, F and E, G are tautomers
 (C) F and G are geometrical isomers (D) F and G are diastereomers

12. The correct stability order for the following species is : [JEE-08, 3/163]



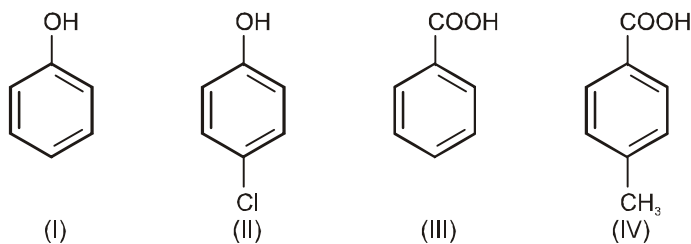
- (A) (II) > (IV) > (I) > (III) (B) (I) > (II) > (III) > (IV)
 (C) (II) > (I) > (IV) > (III) (D) (I) > (III) > (II) > (IV)

13. The correct stability order of the following resonating structures is : [JEE-09, 3/160]



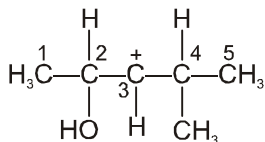
- (A) (I) > (II) > (IV) > (III) (B) (I) > (III) > (II) > (IV) (C) (II) > (I) > (III) > (IV) (D) (III) > (I) > (IV) > (II)

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



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

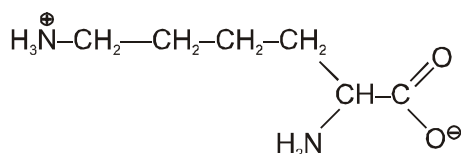
15. In the following carbocation; H/CH₃ that is most likely to migrate to the positively charged carbon is



[JEE-09, 3/160]

- (A) CH₃ at C-4 (B) H at C-4 (C) CH₃ at C-2 (D) H at C-2

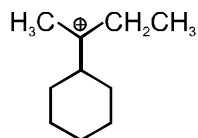
16. The total number of basic groups in the following form of lysine is : [JEE-10, 3/163]



17. 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

18. The total number of contributing structures showing hyperconjugation (involving C-H bonds) for the following carbocation is [JEE-11, 4/180]



19. The carboxyl functional group (-COOH) is present in [JEE-12, 3/136]

- (A) picric acid (B) barbituric acid (C) ascorbic acid (D) aspirin

PART - III : CBSE PROBLEMS

- Account alkyl amines are stronger bases than aryl amine. [CBSE 1999, 1997]
- For an amine RNH_2 write the expression for K_b to indicate its base strength. [CBSE 2000]
- Account for the following : [CBSE 2000]
 - Phenol has a smaller dipole moment than methanol.
 - Phenols do not give protonation reactions readily but alcohols are easily protonated.
- What is meant by "acidity constant, K_a " ? How is it expressed ? [CBSE 2001, 1997]
- Why is it that phenol is acidic and hexanol is neutral towards a solution of NaOH ? [CBSE-2001, 1999]
- Account for chloroacetic acids has lower $\text{p}K_a$ than acetic acid. [CBSE-2005]
- Explain the observed K_b order : [CBSE-2006]
 $\text{Et}_2\text{NH} > \text{Et}_3\text{N} > \text{EtNH}_2$ in aqueous solution.
- Give reasons for the following : [CBSE-2006]
Ortho-nitrophenol is more acidic than ortho-methoxyphenol.
- How would you account for the following: [CBSE 2007]
 - Phenols are much more acidic than alcohols.
 - The boiling points of ethers are much lower than those of the alcohols of comparable molar masses.
- Arrange the following compounds in an increasing order of their acid strengths: [CBSE 2008]
 $(\text{CH}_3)_2\text{CHCOOH}$, $\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{COOH}$, $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{COOH}$
- Account for the following observations: [CBSE 2008]
 - $\text{p}K_b$ for aniline is more than that for methylamine.
 - Methylamine solution in water reacts with ferric chloride solution to give a precipitate of ferric hydroxide.
- Why is an alkylamine more basic than ammonia? [CBSE 2009]
- In the following cases rearrange the compounds as directed : [CBSE 2010]
 - In an increasing order of basic strength : $\text{C}_6\text{H}_5\text{NH}_2$, $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$, $(\text{C}_2\text{H}_5)_2\text{NH}$ and CH_3NH_2
 - In a decreasing order of basic strength : Aniline, p-nitroaniline and p-toluidine
 - In an increasing order of $\text{p}K_b$ values : $\text{C}_2\text{H}_5\text{NH}_2$, $\text{C}_6\text{H}_5\text{NHCH}_3$, $(\text{C}_2\text{H}_5)_2\text{NH}$ and $\text{C}_6\text{H}_5\text{NH}_2$
- Rearrange the following in an increasing order of their basic strengths : [CBSE 2011, 1 M]
 $\text{C}_6\text{H}_5\text{NH}_2$, $\text{C}_6\text{H}_5\text{N}(\text{CH}_3)_2$, $(\text{C}_6\text{H}_5)_2\text{NH}$ and CH_3NH_2
- Arrange the following compounds in an increasing order of their property as indicated : [CBSE 2012, 2 M]
 - Benzoic acid, 3, 4-Dinitrobenzoic acid, 4-Methoxybenzoic acid (acid strength)
 - $\text{CH}_3\text{CH}_2\text{CH}(\text{Br})\text{COOH}$, $\text{CH}_3\text{CH}(\text{Br})\text{CH}_2\text{COOH}$, $(\text{CH}_3)_2\text{CHCOOH}$ (acid strength)
- Arrange the following in the decreasing order of their basic strength in aqueous solutions : [CBSE 2012, 1 M]
 CH_3NH_2 , $(\text{CH}_3)_2\text{NH}$, $(\text{CH}_3)_3\text{N}$ and NH_3