

General Organic Chemistry

1.1 Introduction:

Organic reaction involve the breaking and making of covalent bonds. The breaking and making of covalent bonds usually occurs in several discrete steps before transformation into product. The detailed sequential description of all steps of the transformation into products is called the mechanism of a reaction.

Complete information regarding all the steps is seldom obtained. However, a good deal of data can be gathered from the following

- study of kinetics of the reactions
- isolation of intermediate, if isolable.
- study of reactions in the presence of other similar substrate.
- study of the isotopically labelled atom in the reactants.
- trapping of free radicals
- crossover experiments
- stereochemical aspects etc.

Reaction mechanism containing following tools



(i) Reactant :

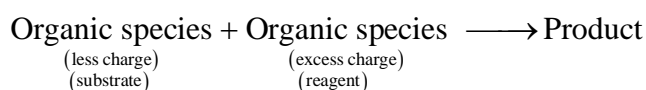
Reactant are classified into substrate and reagent

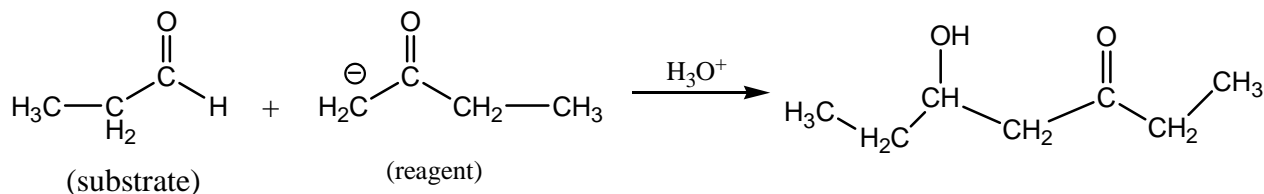
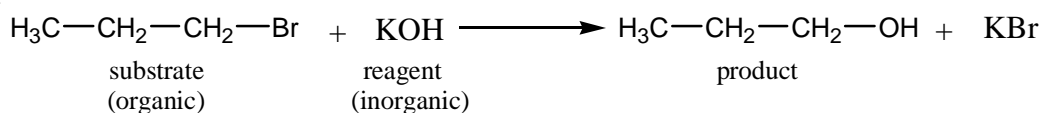
- substrate \Rightarrow species at which reagent attack.
- Reagent \Rightarrow attacking species (more reactive species)

Case-I: If reaction occurs between organic and inorganic species, organic species act as substrate and inorganic species act as reagent.

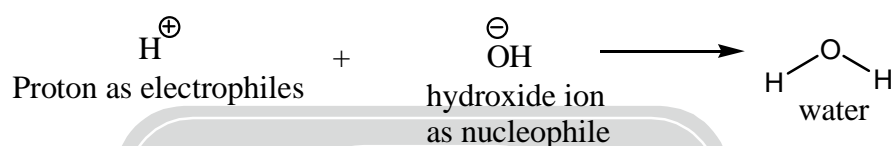


Case-II: If reaction takes place between organic species then higher charge species act as reagent, other species act as substrate.



Example:**1.2. Electrophiles :**

(Electron loving species) electrophiles are electrons-deficient species and tend to attack the substrate at a site of high electron density. They may be neutral species as exemplified by Lewis acid (such as BF_3 , AlCl_3 , ZnCl_2), carbene and carbocations.

**Classification of electrophiles:**

(a) Species having positive charge

Example : H^+ , R^+ , Cl^+ , NO^+ , NO_2^+ , $\text{C}_6\text{H}_5-\text{N}_2^+$, $\text{CH}_3-\text{C}^+=\text{O}$ etc.

(b) Neutral species having vacant p-orbitals

Example : BF_3 , BCl_3 , BBr_3 , carbene, etc.

(c) Species having vacant d-orbital

Example : FeCl_3 , FeCl_2 etc.

(d) Species having low lying σ -antibonding molecular orbital.

Example : Br_2 , Cl_2 , I_2 etc.

(e) π -bonding molecule:



(f) Element in their atomic state :

Example : O, S etc.

1.3. Nucleophiles:

(Nucleus-loving species) Nucleophiles are electron donor species. Nucleophilic reagents tend to attack the electron deficient species (electrophiles).

Classification of Nucleophiles:

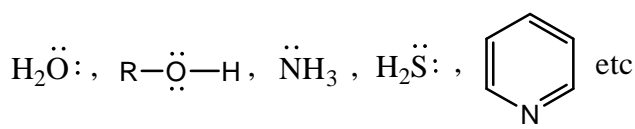
(a) Negative charge species:

OH^- , OR^- , SH^- , SR^- , R^- , Cl^- , Br^- , I^- etc

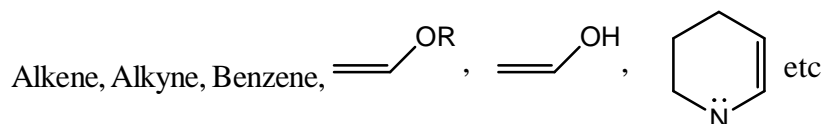
(b) Organometallic reagent:

$\text{R}^- \text{MgX}$, $\text{R}^- \text{Li}$, $\text{R}_2^- \text{CuLi}$, $\text{R}_2^- \text{Cd}$, $\text{R}_2^- \text{Zn}$ etc

(c) Lone pair containing species:



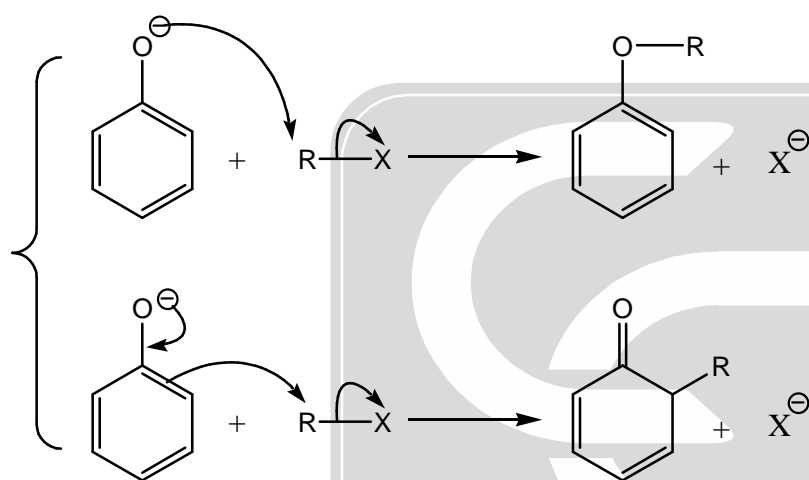
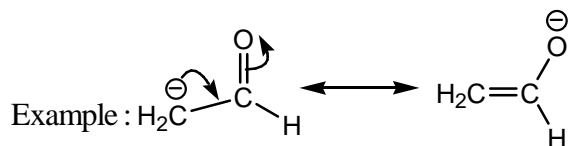
(d) π -bonded molecules:



Note: Some species behave as the electrophiles as well as nucleophiles

Example : Br_2 , Cl_2 , I_2 , etc.

Ambidentated nucleophile : Those nucleophile which possess more than one site for E^+ attack but at the same time only one side is used to form bond with electrophile. It is called ambidentated nucleophile, such type of ambidentated nucleophile are regioselective.

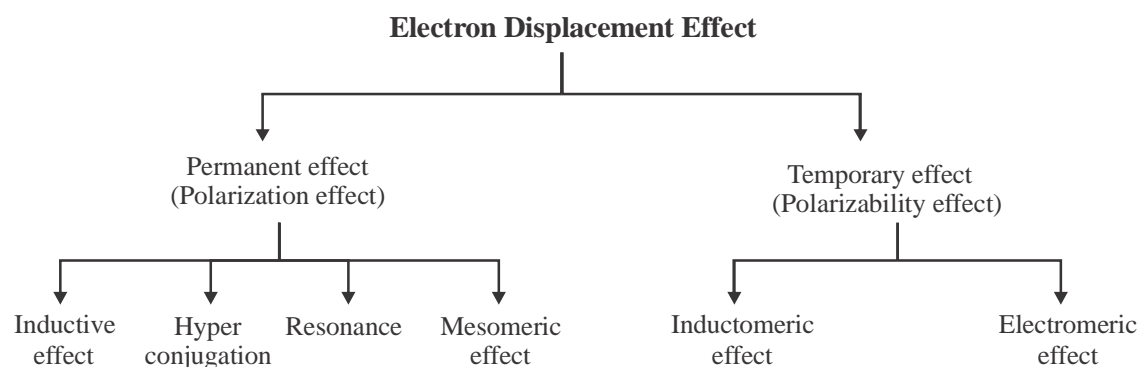


Note: $-, \cdot\cdot, \cdot, =, \equiv, +$
Decreasing order of nucleophilicity
[Electronegativity \propto % of s-character]

Note : Electron Displacement Effects:

Effect occurring due to displacement of electron in organic compound is called *Electron Displacement Effect* or electron delocalisation effect.

Electron displacement effect is of mainly two types.

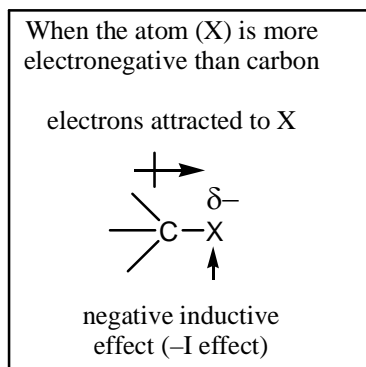


Other Effect:

(a) Steric inhibition of resonance (b) Ortho effect.

1.4. Inductive effects:

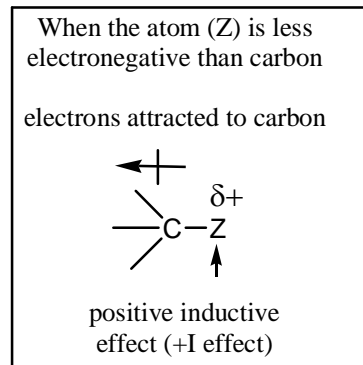
In a covalent bond between two different atoms, the electrons in the σ – bond are not shared equally. The electrons are attracted towards the most electronegative atom. An arrow drawn above the line representing the covalently bonded electrons shifts towards higher electronegative atom can show this. Electrons are pulled in the direction of the arrow.

**-I groups**

X=Br, Cl, NO₂, OH, OR, SH,
SR, NH₂, NHR, NR₂, CN, CO₂H,
CHO, COR

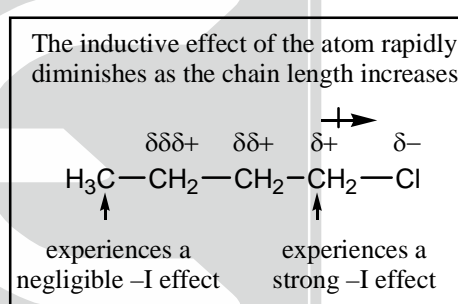
The more electronegative the atom(X),
the stronger the -I effect

Pauling electronegativity scale	
K = 0.8	I = 2.5
C = 2.5	Br = 2.8
N = 3.0	Cl = 3.0
O = 3.5	F = 4.0
Higher the value, more electronegative will be atom	

**+I groups**

Z=R(alkyl or aryl),
metals (e.g. Li or Mg)

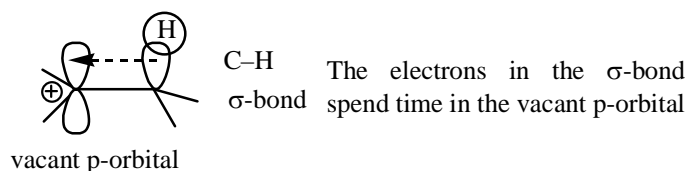
The more electropositive the atom (Z),
the stronger the +I effect.



The overall polarity of a molecule is determined by the individual bond polarities, formal charges and lone pair contributions, and this can be measured by the dipole moment (μ). Higher the dipole moment (measured in debyes (D)), more polar will be compound.

1.5. Hyperconjugation:

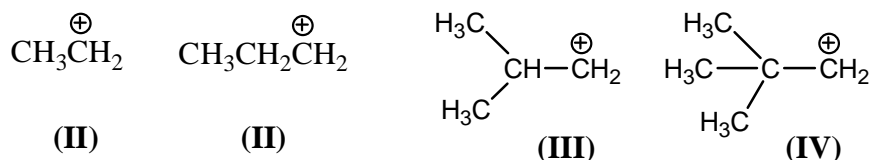
A σ – bond can stabilise a neighbouring carbocation (or positively charged carbon) by donating electrons to the vacant p-orbital. The positive charge is delocalised or ‘spread out’, and this stabilising effect is known as “no-bond resonance”.

**Points to Remember :**

Number of α hydrogen \propto number of hyperconjugating structure \propto stability

$$\propto \frac{1}{\text{Heat of hydrogenation}} \propto \text{Polarity} \propto \text{dipole moment} \propto \frac{1}{\text{bond length}}$$

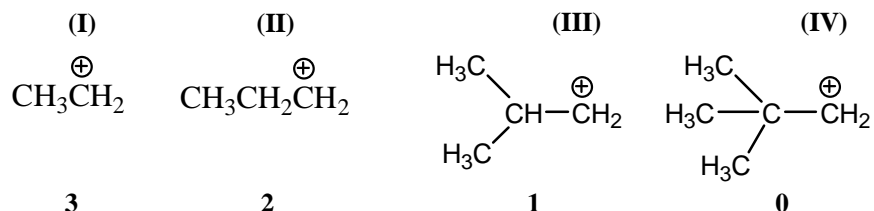
Problem : The correct order for the stability among following compound is



(a) I > II > III > IV (b) I > III > IV > II (c) IV > III > II > I (d) IV > III > I > II

Soln. Number of α hydrogen \propto stability.

Thus,

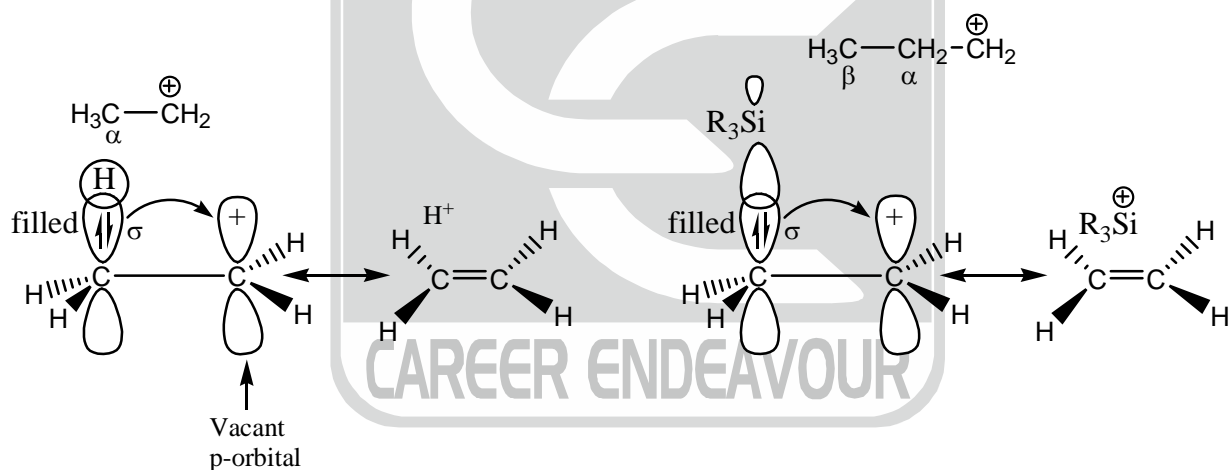


Hence, option (a) is correct.

Types of hyperconjugation:

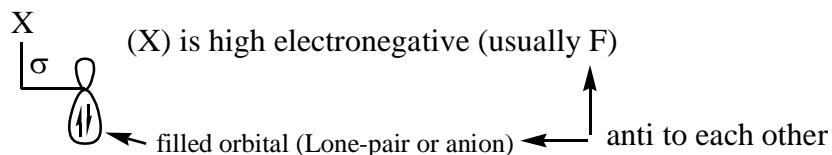
(i) Positive-Hyperconjugation (Separation of positive charge moiety)

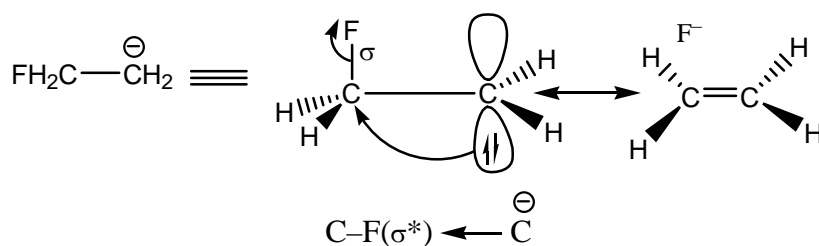
Example: (For the stabilization of electron deficient species)



(ii) Negative-Hyperconjugation (separation of negative charge moiety)

(For the stabilization of electron rich species)

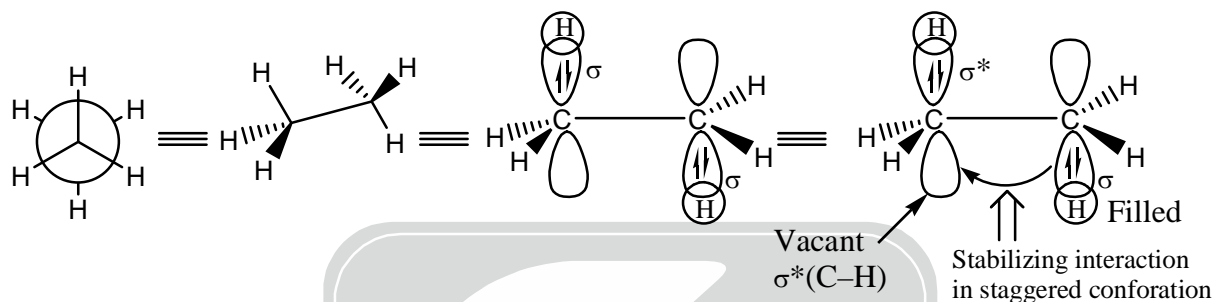


Example :

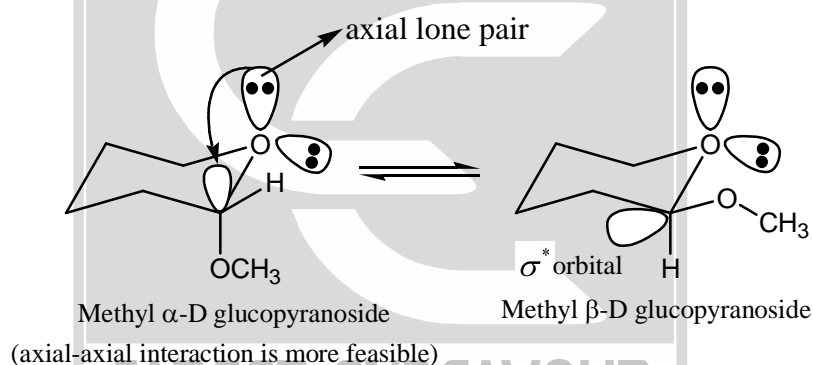
Note: CF_3 group attached to carbanion/aromatic ring shows negative-hyperconjugation.

(iii) Neutral-Hyperconjugation (In Alkanes)

The staggered conformation of ethane is due to steric as well as this hyperconjugation factor.

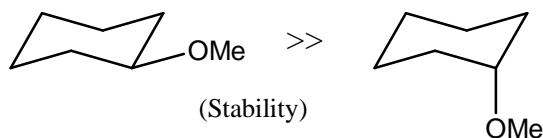


Problem : Which is more stable methyl α -D glucopyranoside or methyl β -D glucopyranoside.



There is stabilising interaction i.e. hyperconjugation between the unshared pair on the hetero atom and σ^* orbital for the axial C–X bond in the case of α anomer. thus it is more stable as compared to its β analogue in which there is no such interaction.

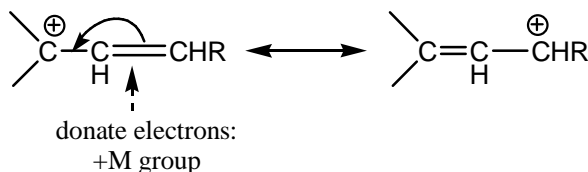
Note : If oxygen is replaced by carbon, there is no such stability interaction as like as above. Thus, stability can only be decided on steric ground. Thus stability order for such species will be

**1.6. Mesomeric effects:**

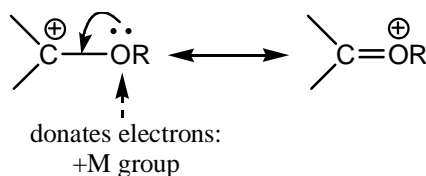
Whilst inductive effects pull electrons through the σ – bond framework, electrons can also move through the π – bond network. A π – bond can stabilise a negative charge, a positive charge, a lone pair of electrons or an adjacent bond by resonance (i.e. delocalisation or ‘spreading out’ of the electrons). Curly arrows are used to represent the movement of π or non-bonding electrons to give different resonance forms. It is only the electrons, not the nuclei, that move in the resonance forms and a double-headed arrow is used to show their relationship.

(a) Positive mesomeric effect:

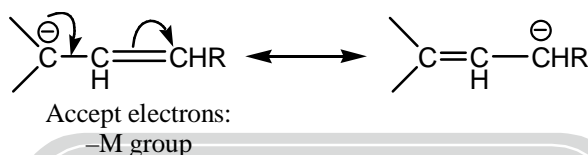
- When a π -system donate electrons, the π -system has a positive mesomeric effect (+M effect).



- When a lone pair of electrons is donated, the group donating the electrons has a positive mesomeric effect.

**(b) Negative mesomeric effect:**

- When a π -system accepts electrons, the π -system has a negative mesomeric effect (-M effect).



The actual structures of the cations or anions lie somewhere between the two resonance forms. All resonance forms must have the same overall charge and obey the same rules of valency.

-M groups generally contain an electronegative atom(s) and/or a π -bond(s):

CHO, C(O)R, CO₂H, CO₂Me, NO₂, aromatic groups, alkenes etc.

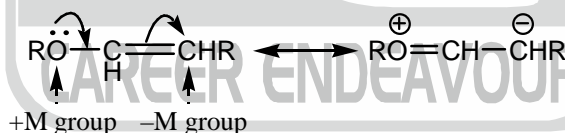
+M groups generally contain atleast a lone pair of electrons or a π -bond(s):

$:\ddot{\text{Cl}}:$, $:\ddot{\text{Br}}:$, $\ddot{\text{O}}\text{H}$, $\ddot{\text{O}}\text{R}$, $\ddot{\text{S}}\text{H}$, $\ddot{\text{N}}\text{H}_2$, $\ddot{\text{N}}\text{HR}$, $\ddot{\text{N}}\text{R}_2$, aromatic, alkenes etc.

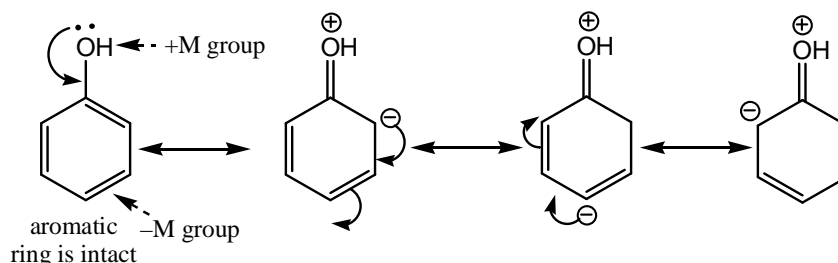
Aromatic (or aryl) groups and alkenes can be both +M or -M effect.

In neutral compounds, there will always be a +M and -M groups(s):

One group donates (+M) the electrons and the other group(s) accepts the electrons(-M).



All resonance forms are not of the same energy. In phenol, for example, the resonance form which the intact aromatic benzene ring is expected to predominate.



As a rule of thumb, the more resonance structures an anion, cation or neutral π -system can have, the more stable it is.

Inductive versus mesomeric effects:

Mesomeric effects are generally stronger than inductive effects. A +M group is likely to stabilise a cation more effectively than a +I group.

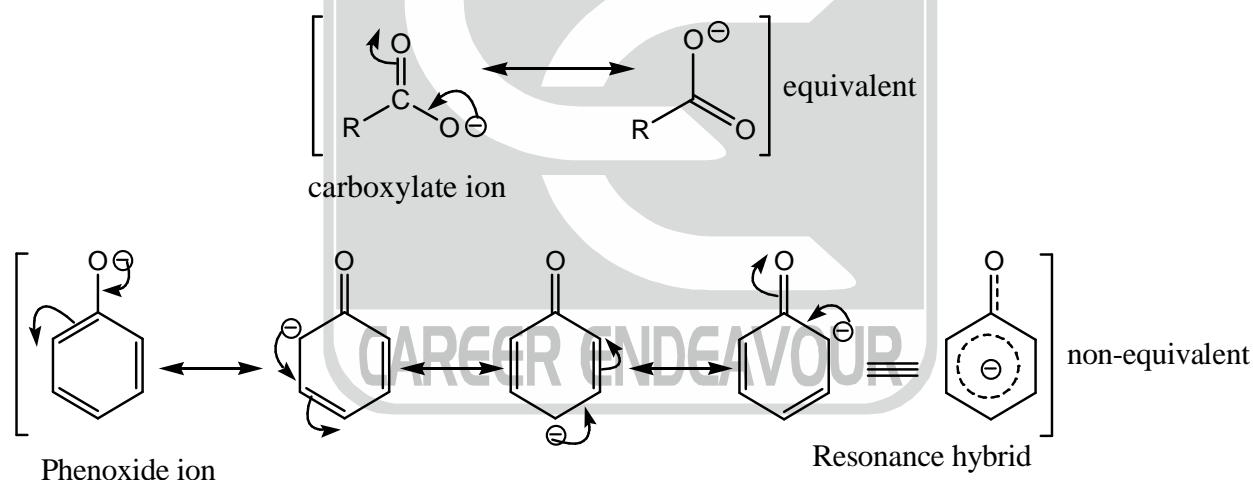
Mesomeric effects can be effective over much longer distances than inductive effects, provided that conjugation is present (i.e. alternating single and double bonds). Whereas inductive effects are determined by distance, mesomeric effects are determined by the relative positions of +M and -M groups in a molecule.

1.7. Resonance:

The different structure of a compound divided by different methods of pairing electrons in a fixed atomic skeleton are called resonance of canonical structure. The actual structure of the compound is then a combination of these structure and hence the compound is called a resonance hybrid. A hybrid is more stable than any one of the contributing structures. The contributing resonance structure are shown by double-headed arrows (\leftrightarrow) indicating that the real structures involves both way of pairing electrons.

Key point about resonance:

- Resonating structure/contributing structure/canonical structure are imaginary hypothetical, while resonance hybrid is the true structure.
- Resonance involve the delocalization of lone pair and π -electrons.
- Resonance is the intramolecular process.
- Resonance must follow the Lewis octate rule, i.e. C-atom, N-atom never pentavalent and O-atom never tetravalent.
- In the resonating structure arrangement of atoms remain same, there should be different only in relative arrangement of electrons.
- Resonance stabilisation is greatest, when there are equivalent resonating structure.



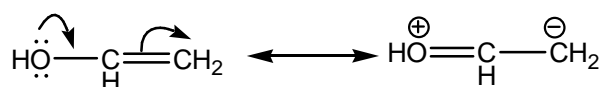
- The energy difference in between resonance hybrid and most stable resonating structure is called resonance energy
- Resonance work only at ortho and para position with equal intensity, it never work at meta position.
- The atoms, that are participating in resonance, should be in one plane.

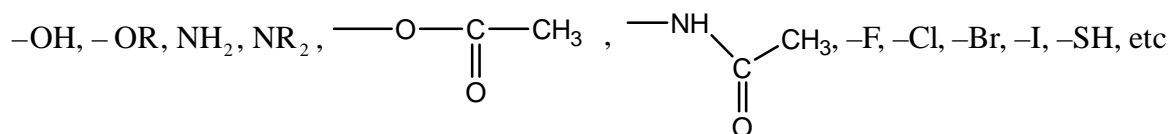
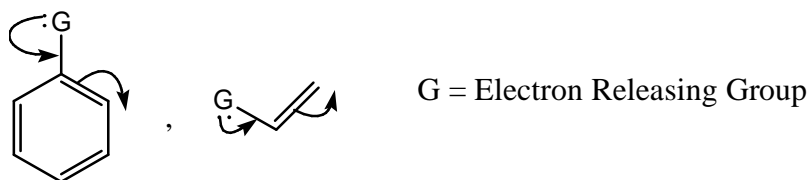
Classification of Resonance:

(A) +R effect (B) -R effect

(A) +R effect (Electron releasing effect):

Lone pair of electron containing atom attached with conjugation.



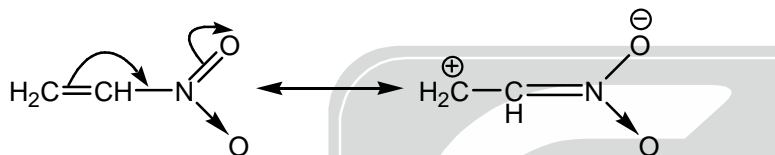
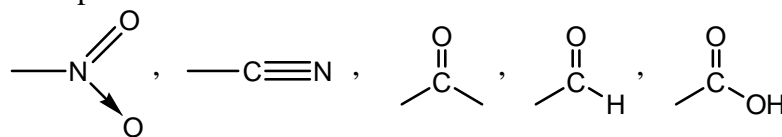


(B) –R effect (Electron withdrawing effect):

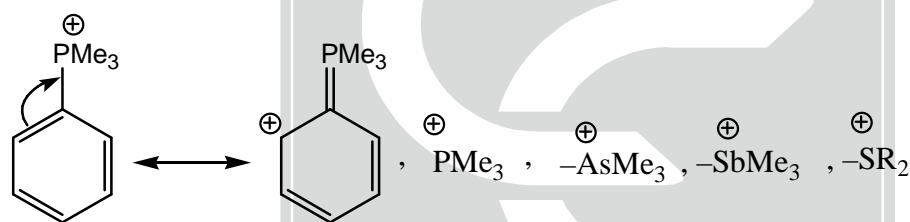
Electronegative atom attached with multiple bond containing compound

(a) Electron withdrawing resonance effect

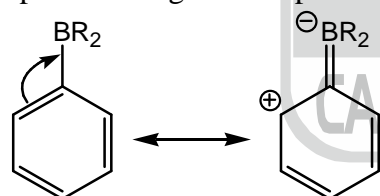
Example :



(b) Species having Vacant d-orbitals



(c) Species having vacant -p- orbitals:

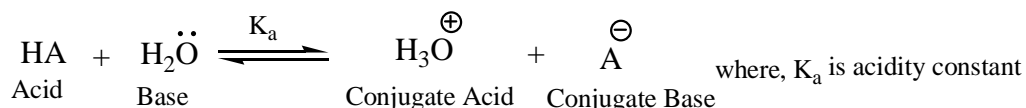


1.8. Application of inductive effect, hyperconjugation and mesomeric effect:

Acidity and basicity:

Acids: An acid is a substance that donates a proton (Bronsted-Lowry). Acidic compounds have low pK_a values and are good proton donors, as the anions (or conjugate bases), formed on the deprotonation, are relatively stable.

In water:



The more stable the conjugate base the stronger the acid

$$K_a = \frac{[\text{H}_3\text{O}^{\oplus}][\text{A}^{\ominus}]}{[\text{HA}]}$$

As H_2O is in excess

$$\text{pK}_a = -\log_{10} K_a$$

The higher the value of K_a , the lower the pK_a value and the more acidic is HA

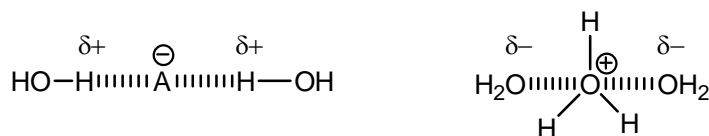
The pK_a -value equals the pH of the acid when it is half dissociated. At pH above the pK_a the acid exists predominantly as the conjugate base in water. At pH below the pK_a , it exists predominantly as HA.

pH = 0 (strongly acidic)

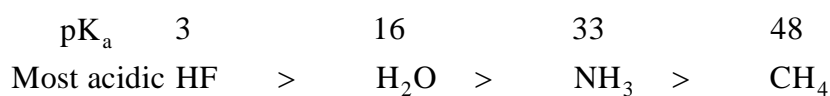
pH = 7 (neutral)

pH = 14 (strongly basic)

The pK_a -values are influenced by the solvent. Polar solvents will stabilise cations and/or anions by solvation, in which the charge is delocalised over the solvent (e.g. by hydrogen-bonding in water).



The more electronegative the atom bearing the negative charge, the more stable the conjugate base (which is negatively charged).



increasing electronegativity

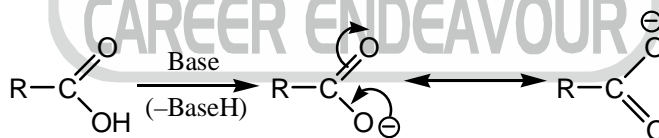
Therefore, F[⊖] is more stable than H₃C[⊖].

The conjugate base can also be stabilised by -I and -M groups which can delocalise the negative charge. (The more spread out the negative charge, the more stable it is)

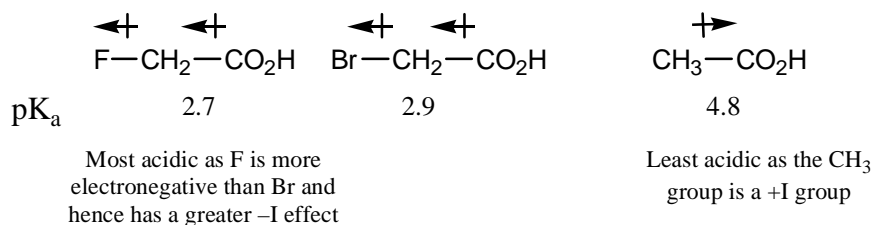
-I and -M groups therefore lower the pK_a , while
+I and +M groups raise the pK_a

(a) Inductive effects and carboxylic acids:

The carboxylate anion is formed on deprotonation of carboxylic acids. The anion is stabilised by resonance (i.e. the charge is spread over both oxygen atoms) but can also be stabilised by the R group if this has a -I effect.



The greater the -I effect, the more stable the carboxylate anion and the more acidic is carboxylic acid.

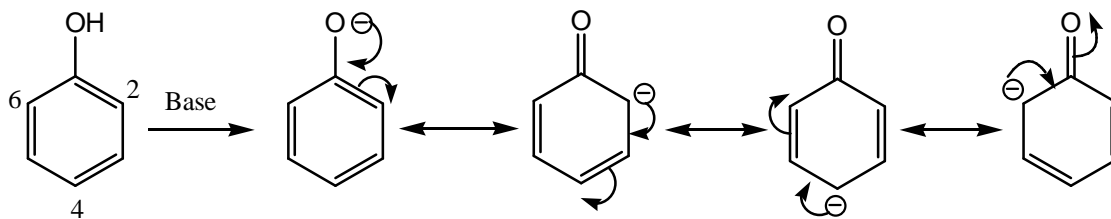


(b) Inductive and mesomeric effects and phenols:

Mesomeric effects can also stabilise positive and negative charges.

The negative charge needs to be on adjacent carbon atom for a -M group to stabilise it
The positive charge needs to be on adjacent carbon atom for a +M group to stabilise it

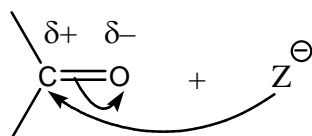
On deprotonation of phenol the phenoxide anion is formed. This is stabilised by delocalisation of the negative charge at the 2-, 4- and 6-positions of the benzene ring.



Temporary Effect :

(a) Electromeric Effect :

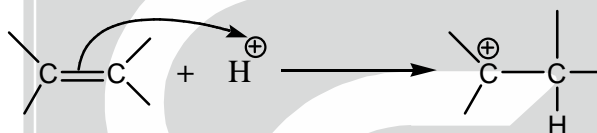
- Temporary effect.
- Takes place between two atoms joined by a multiple bond
- Occurs at requirement of attacking reagent.



Instantaneous shift of electron pair of carbonyl group towards oxygen.

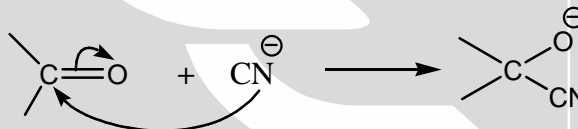
It is of two types.

(1) +E effect : Transition of electron towards the attacking reagent.



(2) -E effect :

Transition of electron away from attacking reagent.



(b) Inductomeric Effect ;

- Temporary effect.
- Takes place in sigma bonded system
- In presence of attacking reagent, transition of a electron cloud takes place more readily.

Example :

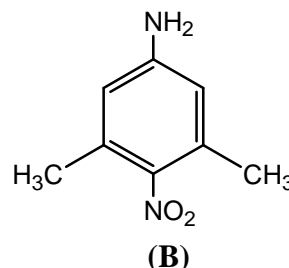
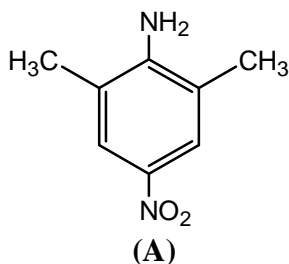


In presence of base B, movement of sigma electron takes place faster.

(3) Other Effect :

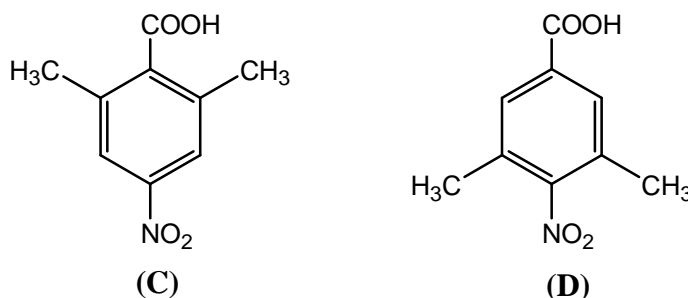
(a) Effect of inertia/steric inhibition of resonance:

Resonance ability of an atom is lost if it loses planarity with the other part of the conjugated system due to steric crowding by bulky group at adjacent positions.



The above two compounds A and B have everything identical except position of the two methyl group. It is expected that A should be stronger base than B due to closeness of two electron donating methyl groups to -NH_2 . The fact is opposite to this. In compound B, -NO_2 is surrounded by two bulky methyl group and they sterically repel the -NO_2 group. In order to minimize the steric repulsion by the two adjacent methyl groups, the nitro group loses planarity with the benzene ring. So, now -NO_2 due to lack of planarity with ring, not able to resonate. This is known as steric inhibition of resonance. Thus in B, -NO_2 is not decreasing basic strength by resonance. In A, -NO_2 lies in the plane of the ring, it is in resonance with the ring, decreases basic strength of -NH_2 by resonance, hence weaker base.

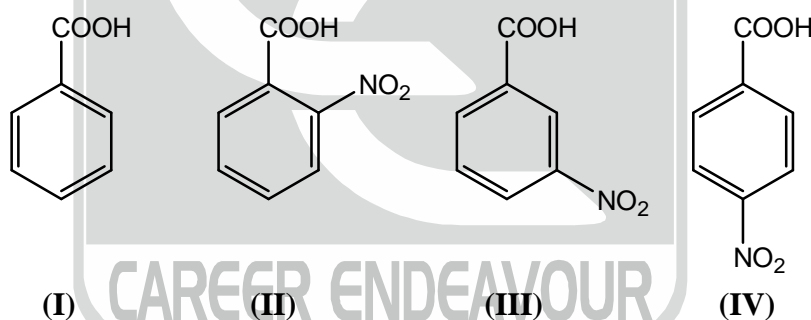
Similarly we can explain the acidic strength of C and D



C is stronger acid inspite of closeness of two electron donating methyl groups to -COOH .

(b) Ortho effect: If any electron withdrawing group present on ortho position of the benzoic acid. It always increases acidic nature of acid because this group increases outer resonance of the ring toward acidic nature. Similarly if any group present on ortho position of aniline, it decreases basic nature. This effect is known as ortho effect.

Problem : The correct order of acidity among the following compound I-IV is



(a) $\text{II} > \text{III} > \text{IV} > \text{I}$ (b) $\text{IV} > \text{II} > \text{III} > \text{I}$ (c) $\text{II} > \text{IV} > \text{III} > \text{I}$ (d) $\text{IV} > \text{III} > \text{II} > \text{I}$

Soln. Because of ortho effect o-nitro benzoic acid is most acidic followed by para and meta.

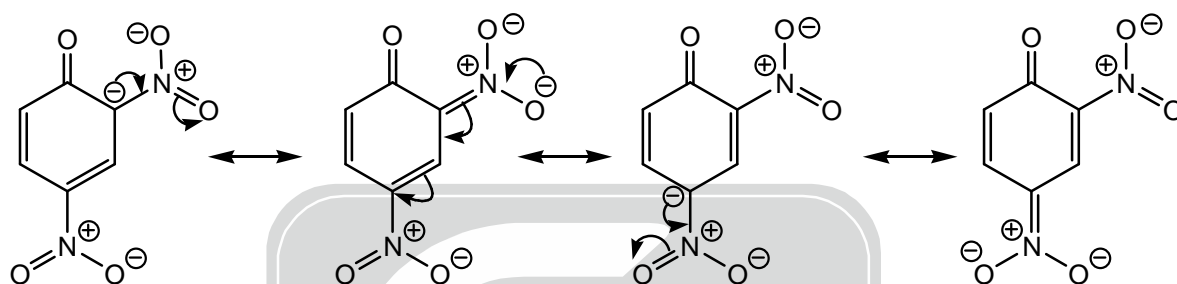
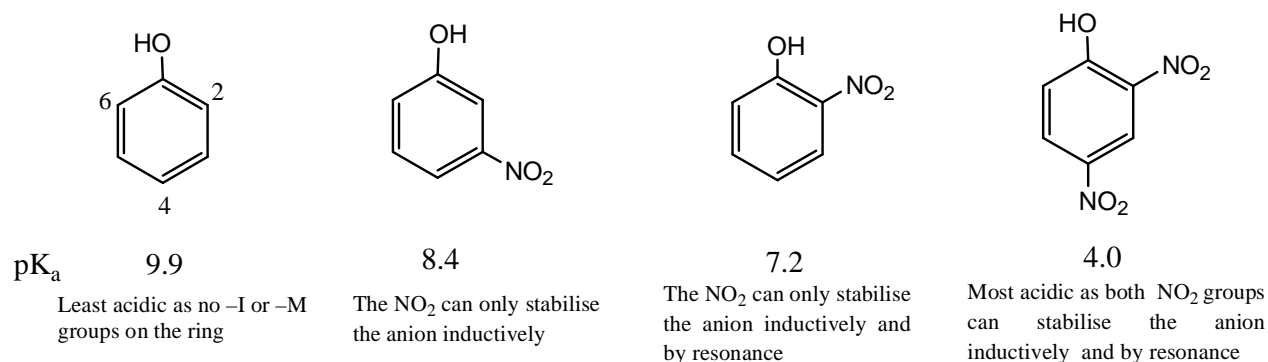
Thus order will be $\text{II} > \text{IV} > \text{III} > \text{I}$.

Hence, option (c) is correct.

Keynotes in Organic Chemistry:

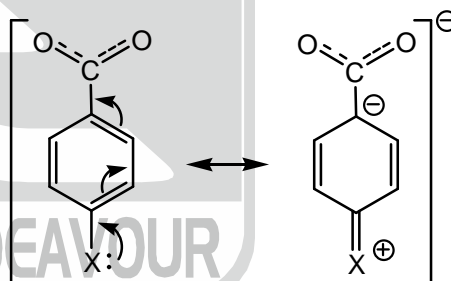
- If -M groups are introduced at 2-, 4- and/or 6-positions, the anion can be further stabilised by delocalisation through the π -system, as the negative charge can be spread onto the -M group. We can use double-headed curly arrows to show this process.
- If -M groups are introduced at the 3- and/or 5-positions, the anion can not be stabilised by delocalisation, as the negative charge cannot be spread onto the -M group. There is no way of using curly arrows to delocalise the charge onto the -M groups.
- If -I groups are introduced on the benzene ring, the effect will depend on their distance from the negative charge. The closer the -I group is to the negative charge, the greater will be the stabilising effect. The order of -I stabilisation is therefore 2-position $>$ 3-position $>$ 4-position.
- The -M effects are much stronger than -I effects.

Example: The NO_2 group is strongly electron-withdrawing; $-I$ and $-M$.

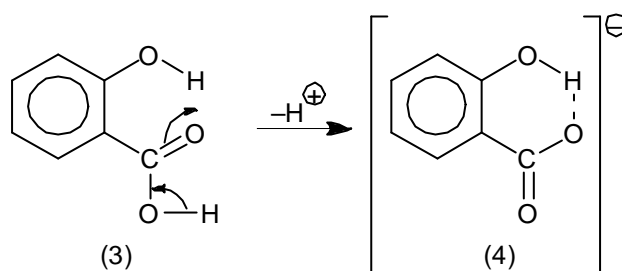


The presence of groups such as OH , OMe , or halogen an electron-withdrawing inductive effect, but an electron-donating mesomeric effect when in the o - and p - positions, may, however, cause the p -substituted acids to be weaker than the m - and, on occasion, weaker even than the unsubstituted acid itself, e.g. p -hydroxybenzoic acid:

	pK_a of $\text{XC}_6\text{H}_4\text{CO}_2\text{H}$			
H	Cl	Br	OMe	OH
o -4.20	2.94	2.85	4.90	2.98
m -4.20	3.83	3.81	4.09	4.08
p -4.20	3.99	4.00	4.47	4.58



It will be noticed that this compensating effect becomes more pronounced in going $\text{Cl} \approx \text{Br} \rightarrow \text{OH}$, i.e. in increasing order of readiness with which the atom attached to the nucleus will part with its electron pairs. The behaviour of o -substituted acids is, as seen above, often anomalous. Their strength is sometimes found to be considerably greater than expected due to direct interaction between the adjacent groups. Thus intramolecular hydrogen bonding stabilises the anion (4) from o -hydroxybenzoic (salicylic) acid (3) by delocalising its charge, an advantage not shared by its m - and p -isomers, nor by o -methoxy benzoic acid:



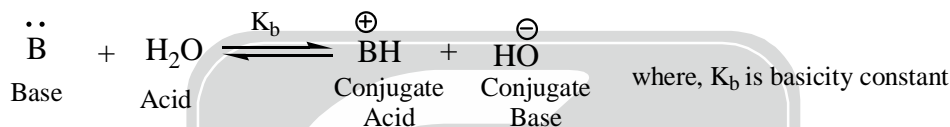
Intramolecular hydrogen bonding can, of course, operate in the undissociated acid as well as in the anion, but it is likely to be considerably more effective in the latter than in the former - with consequent relative stabilisation - because the negative charge on oxygen in the anion will lead to stronger hydrogen bonding. The effect is even more pronounced where hydrogen bonding can occur with hydroxyl groups in both *o*-position, and 2, 6-dihydroxybenzoic acid is found to have $pK_a = 1.30$.

Dicarboxylic Acids:

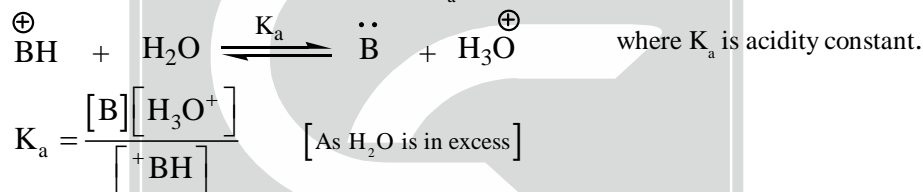
Acid	pKa Value	Acid	pKa Value
HCO ₂ H	3.77	HO ₂ CCO ₂ H	1.23
CH ₃ CO ₂ H	4.76	HO ₂ CCH ₂ CO ₂ H	2.83
CH ₃ CH ₂ CO ₂ H	4.88	HO ₂ CCH ₂ CH ₂ CO ₂ H	4.19
C ₆ H ₅ CO ₂ H	4.17	HO ₂ CC ₆ H ₄ CO ₂ H	<i>o</i> - 2.98; <i>m</i> - 3.46; <i>p</i> - 3.51

Bases: A base is a substance that accepts a proton (Bronsted-Lowry). Basic compounds have high pK_a -values and are good proton acceptors, as the cations (or conjugate acids), formed on protonation, are relatively stable.

In water:



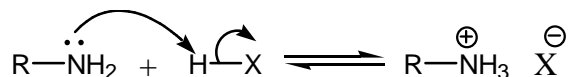
The strength of bases are usually described by the K_a - and pK_a -values of the conjugate acid.



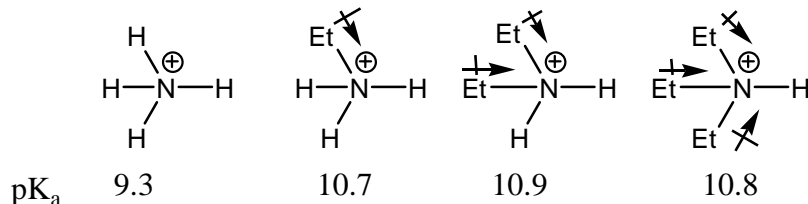
- If B is a strong base, then BH[⊕] will be relatively stable and not easily deprotonated. BH[⊕] will therefore have a high pK_a -value
- If B is a weak base, then BH[⊕] will be relatively unstable and easily deprotonated. BH[⊕] will therefore have a low pK_a -value.

The cation can be stabilised by +I and +M groups, which can delocalise the positive charge. (The more 'spread out' the positive charge, the more stable it is).

(c) Inductive effects and aliphatic (or alkyl) amines: On protonation of amines, ammonium salts are formed.



The greater the +I effect of the R group, the greater the electron density at nitrogen and the more basic the amine. The greater the +I effect, the more stable the ammonium cation and the more basic the amine.



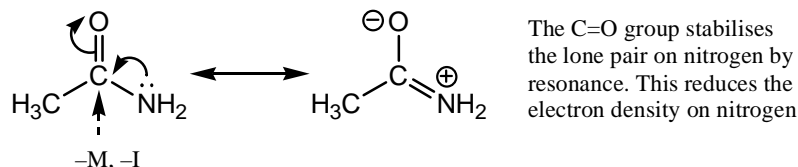
The pK_a -values should increase steadily as more +I alkyl groups are introduced on nitrogen. However, the pK_a -values are determined in water, and the more hydrogen atoms on the positively charged nitrogen, the greater the extent of hydrogen-bonding between water and the cation. This solvation leads to the stabilisation of the cations containing N-H bonds.

In organic solvents (which can not solvate the cation) or in gas phase, the order of pK_a s is expected to be as follows:



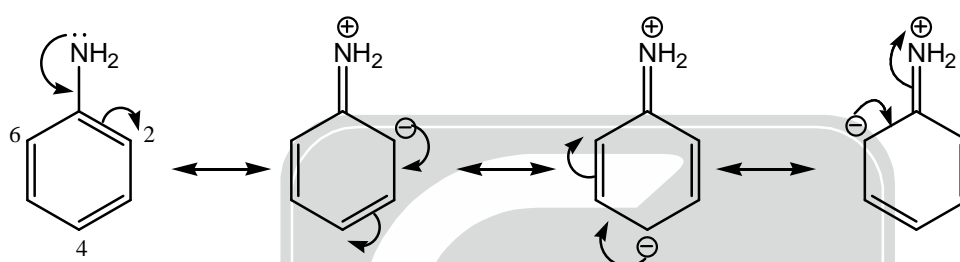
The presence of $-I$ and/or $-M$ groups on nitrogen reduces the basicity, and hence, for example, amides are poor bases.

Ethanamide has a pK_a of -0.5 .

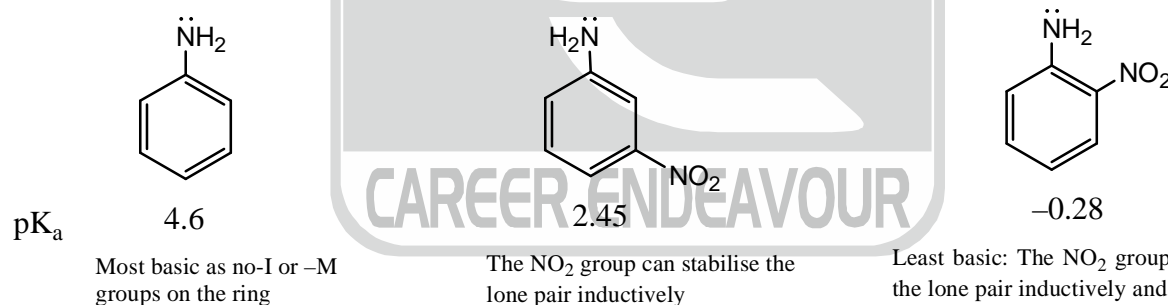


(d) Mesomeric effects and aryl (or aromatic) amines:

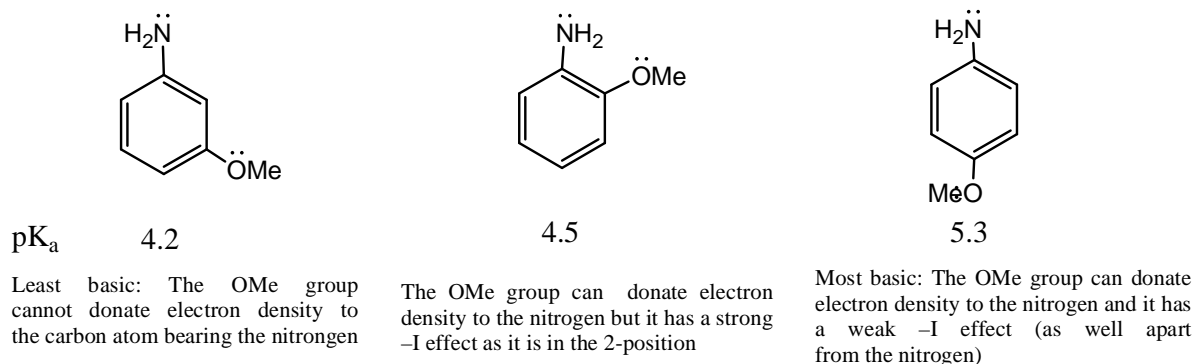
The lone pair of electrons on the nitrogen atom of aminobenzene (or aniline) can be stabilised by the delocalisation of the electrons onto the 2-, 4- and 6-positions of the benzene ring. Aromatic amines are therefore less basic than aliphatic amines.



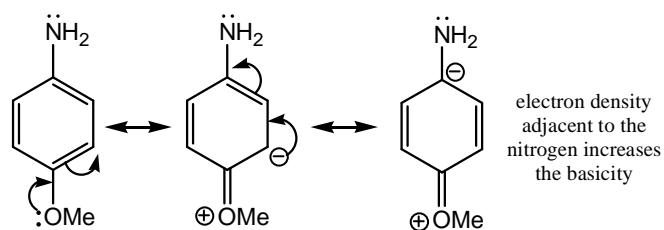
- If $-M$ groups are introduced at the 2-, 4- and/or 6-positions (but not at the 3- or 5-position), the anion can be further stabilised by delocalisation, as the negative charge can be spread onto the $-M$ group. This reduces the basicity of the amine.
- If $-I$ groups are introduced on the benzene ring, the order of $-I$ stabilisation is 2-position $>$ 3-position $>$ 4-position. This reduces the basicity of the amine.



- If $+M$ group (e.g. OMe) are introduced at the 2-, 4- or 6-position of aminobenzene, then the basicity is increased. This is because the $+M$ group donates electron density to the carbon atom bearing the amine group.

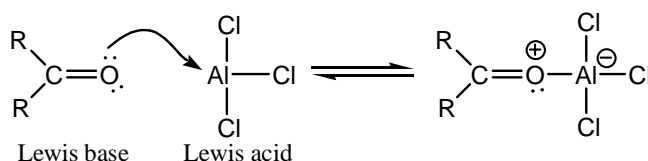


Curly arrows can be used to show the delocalisation of electrons onto the carbon atom bearing the nitrogen.



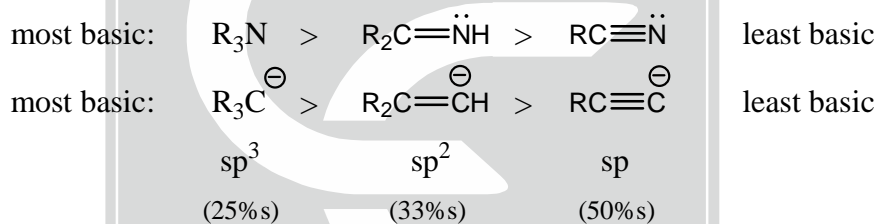
(e) Lewis acids and base:

- A Lewis acid is any substance that accepts an electron pair in forming a coordinate bond. Examples include H^+ , BF_3 , AlCl_3 , TiCl_4 , ZnCl_2 and SnCl_4 . They have unfilled valence shells and hence can accept electron pairs.
- A Lewis base is any substance that donates an electron pair in forming a coordinate bond. Examples include H_2O , ROH , RCHO , R_2CO , R_3N and R_2S . They all have a lone pair(s) of electrons on the hetero atom (O, N or S)

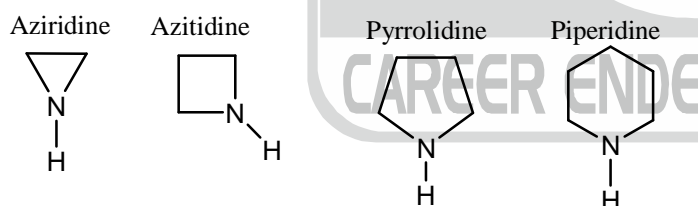


(f) Basicity and hybridisation:

The greater the 's' character of an orbital, the lower is energy the electrons and the more tightly the electrons are held to the nucleus. The electrons in an sp -orbital are therefore less available for protonation than those in an sp^2 - or sp^3 -hybrid orbital and hence the compounds are less basic.



Exceptional example:

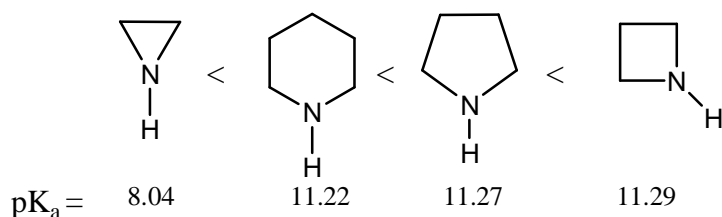


Outer bond angle decreases \longrightarrow

s-character decreases \longrightarrow

Basicity increases \longrightarrow (In gas phase)

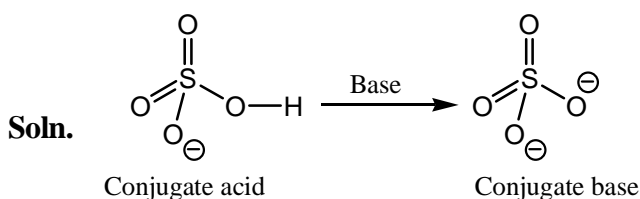
Note: In aqueous solution phase, the basicity trend is opposite except aziridine due to very high s-character (Banana bond)



JNUEE Previous Years Question with Solutions

1. The conjugate base for the acid HSO_4^- is [JNU 2003]

- (a) H_2SO_4 (b) NaOH (c) SO_4^{2-} (d) H_2SO_3



Correct option is (c)

2. Which of the following molecules / ions can act as a Lewis base?

- (a) BF_3 (b) NH_3 (c) H^+ (d) Cu^{++} [JNU 2003]

Soln. Lewis Base \Rightarrow Lone pair Donor

$\text{BF}_3 \Rightarrow$ Lewis acid

$\ddot{\text{N}}\text{H}_3 \Rightarrow$ Lewis base

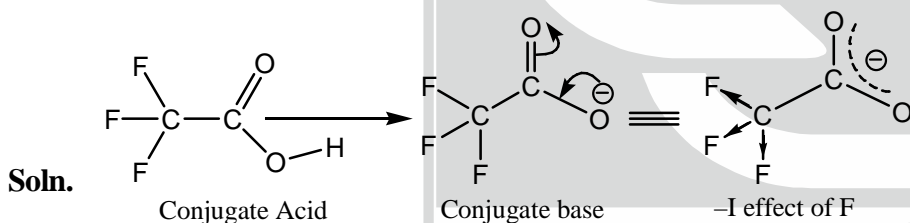
$\text{H}^+ \Rightarrow$ Lewis acid

$\text{Cu}^{++} \Rightarrow$ Lewis acid

Correct option is (b)

3. Which of the following acids is strongest acid?

- (a) $\text{Cl}_2\text{CH.COOH}$ (b) ClF_2CCOOH (c) F_3CCOOH (d) CH_3COOH [JNU 2004]



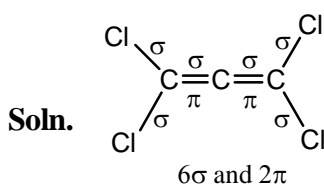
Acidity increases with increase the stability of conjugate base

Here, conjugate base stabilised through formation of equivalent ion pair and strong -I effect of F.

Correct option is (c)

4. $\text{Cl}_2\text{C}=\text{C}=\text{CCl}_2$ has total number of σ and π bonds as given in [JNU 2004]

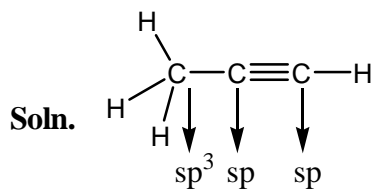
- (a) 6σ and 2π (b) 4σ and 4π (c) 5σ and 3π (d) 2σ and 6π



Correct option is (a)

5. The hybridized state of carbons in $\text{CH}_3-\text{C}\equiv\text{CH}$ is [JNU 2004]

- (a) sp^3 and sp (b) sp^2 and sp (c) sp (d) sp^2

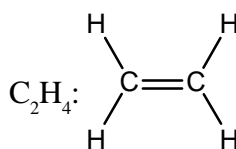
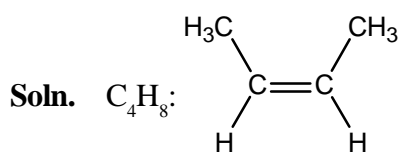


Correct option is (a)

6. In which pair of hydrocarbons does each compound contain only one double bond pair molecule?

[JNU 2005]

- (a) C_2H_2 and C_2H_6 (b) C_2H_2 and C_3H_6 (c) C_4H_8 and C_2H_4 (d) C_6H_6 and C_7H_8



Correct option is (c)

7. Which of the following has highest stability?

[JNU 2006]

- (a) HCl (b) HBr (c) HF (d) HI

Soln. Size order = $I > Br > Cl > F$

Hydrogen has small size, better interaction with smaller size atom F

Correct option is (c)

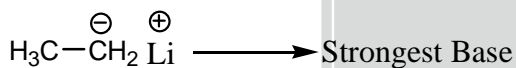
8. Which of the following is the strongest base?

[JNU 2006]

- (a) CH_3ONa (c) NaOH (c) $CH_3 \cdot COONa$ (d) $CH_3 \cdot CH_2 \cdot Li$

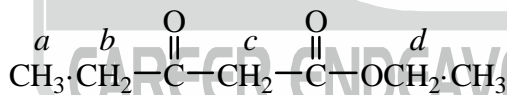
Soln. **Basicity:** Availability of negative charge (or lone pair) for donation. Lone pair of electrons on more electronegative elements are poor donor.

Left to right in periods – Size decreases with polarization decreases, donation power decreases.



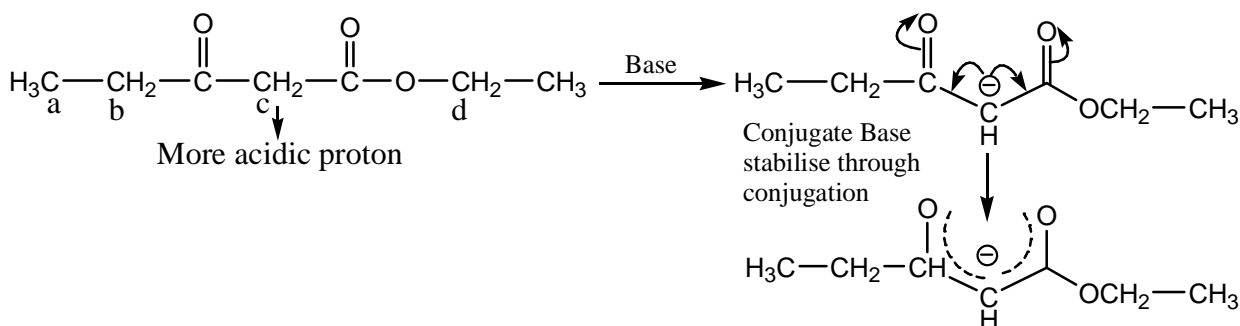
9. Which hydrogen atoms in the following ester are more acidic?

[JNU 2006]



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

Soln. Acidity \propto stability of conjugate base.

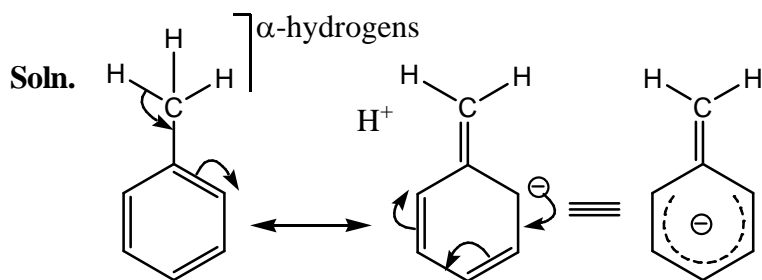


Correct option is (c)

10. The electron releasing effect of methyl group attached to aromatic nucleus can be explained by

- (a) inductive effect (b) lone pair of electron
(c) electronegativity (d) hyperconjugation

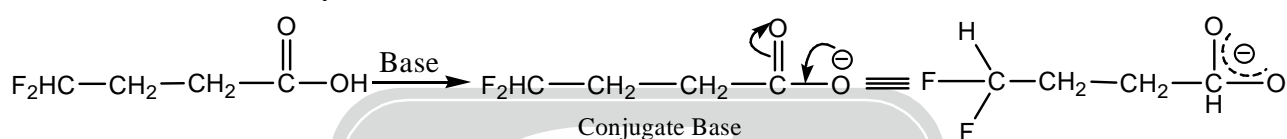
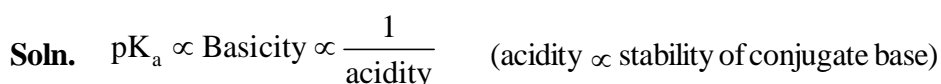
[JNU 2006]



Benzene ring activate through the hyperconjugation.

Correct option is (d)

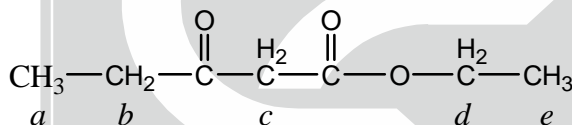
11. Which of the following carboxylic acids will have highest pK_a value? [JNU 2006]
- (a) $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CF}_2 \cdot \text{COOH}$ (b) $\text{CH}_3 \cdot \text{CF}_2 \cdot \text{CH}_2 \cdot \text{COOH}$
 (c) $\text{CHF}_2 \cdot \text{CH}_2 \cdot \text{CH}_2 \cdot \text{COOH}$ (d) $\text{CH}_3 \cdot \text{CH}_2 \cdot \text{CHF} \cdot \text{COOH}$



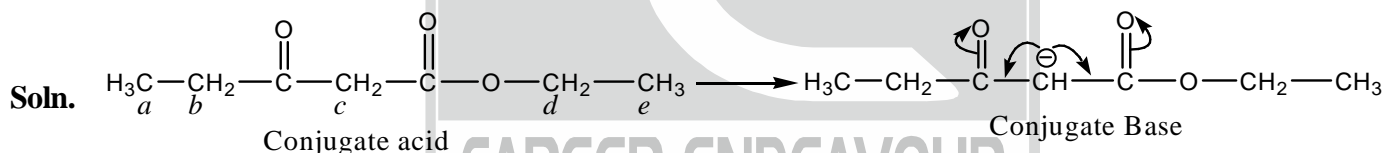
Inductive effect is a distance dependent effect. Conjugate base stabilised with electron withdrawing group. So, (c) is least acidic with highest pK_a value.

Correct option is (c)

12. Which hydrogen atoms in the following ester are most acidic? [JNU 2007]



- (a) a, e (b) b (c) c (d) d

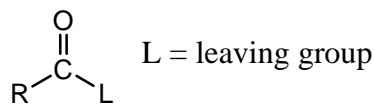


Negative charge (conjugate base) stabilised through conjugation (cross conjugation). Proton will be more acidic.

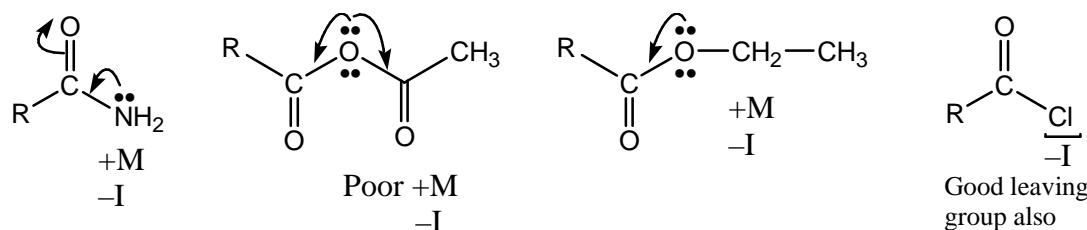
Correct option is (c)

13. Rate of hydrolysis of RCOL is maximum when L is [JNU 2010]
- (a) NH_2 (b) OCOCH_3 (c) OCH_2CH_3 (d) Cl

Soln. Rate of hydrolysis:

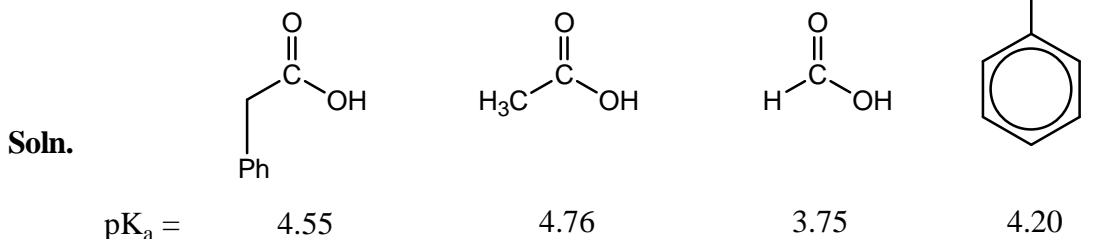


Rate of hydrolysis depends upon electrophilicity as well as leaving tendency. Which group having better leaving tendency, they enhance the rate of hydrolysis.



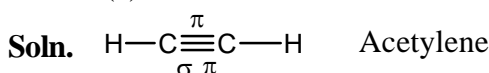
Correct option is (d)

14. Which of the following acids has the lowest pK_a value? [JNU 2010]
 (a) Phenyl acetic acid (b) Acetic acid (c) Formic acid (d) Benzoic acid



Correct option is (c)

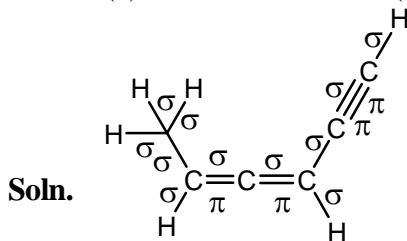
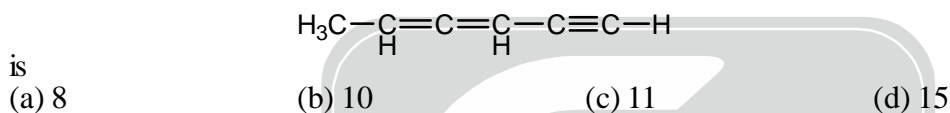
15. The triple bond of acetylene is made up of [JNU 2011]
 (a) three σ bonds (b) one σ bond and two π bonds
 (c) three π bonds (d) two s bonds and one p bond



Two π bond and one σ bond.

Correct option is (b)

16. The number of sigma bonds present in the compound [JNU 2012]

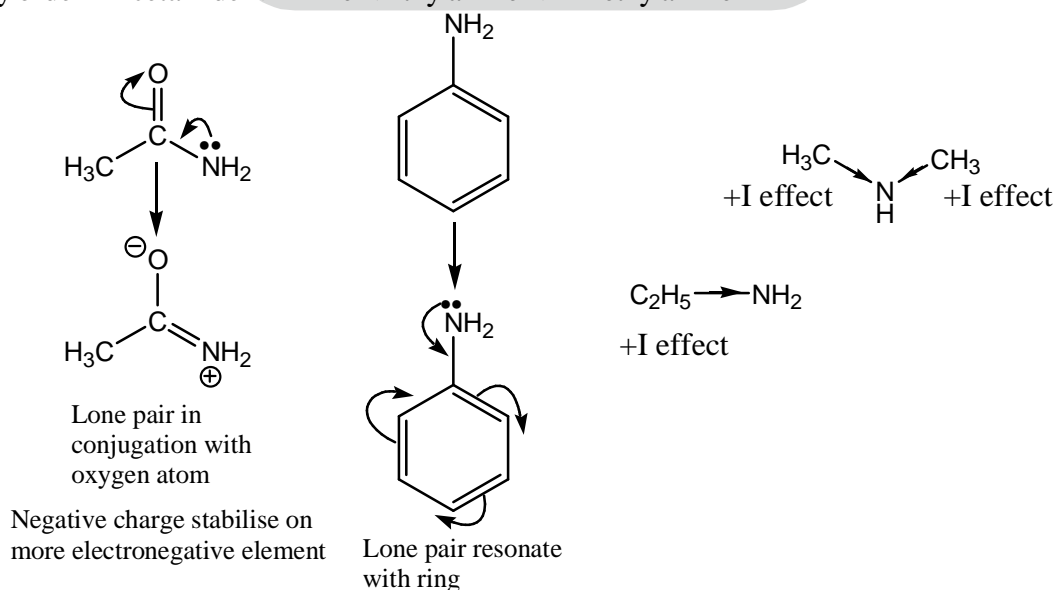


Total sigma bond = 11

17. Choose from the following the appropriate alternative in which the compounds are arranged in the increasing order of their basicity (least to most basic). [JNU 2012]

- (a) Aniline < Acetamide < Ethylamine < Dimethylamine
 (b) Acetamide < Aniline < Ethylamine < Dimethylamine
 (c) Dimethylamine < Ethylamine < Acetamide < Aniline
 (d) Ethylamine < dimethylamine < Aniline < Acetamide

Soln. Basicity order = Acetamide < Aniline < Ethylamine < Dimethylamine



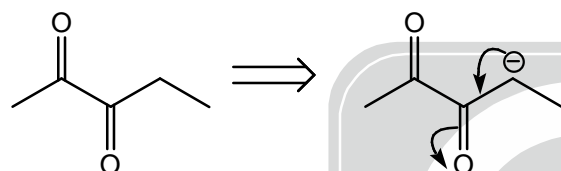
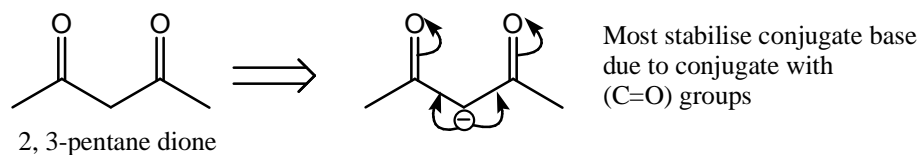
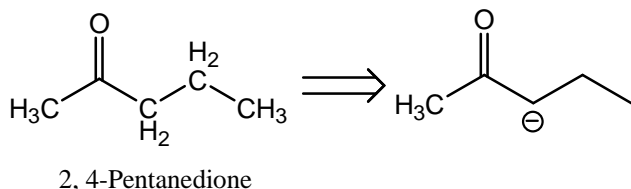
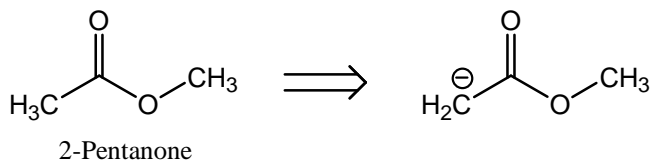
Correct option is (b)

18. Which of the following compounds has most acidic hydrogens? [JNU 2012]

- (a) Methyl acetate (b) 2-Pentanone (c) 2, 4-Pentane dione (d) 2, 3-Pentane dione

Soln. **Conjugate Acid** **Conjugate Base**

Methyl acetate



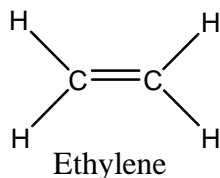
Most stabilise conjugate base with most acidic proton.

Correct option is (c)

19. Which of the following molecules has the lowest bond length between two carbons? [JNU 2013]

- (a) Ethane (b) Cyclohexane (c) Benzene (d) Ethylene

Soln.



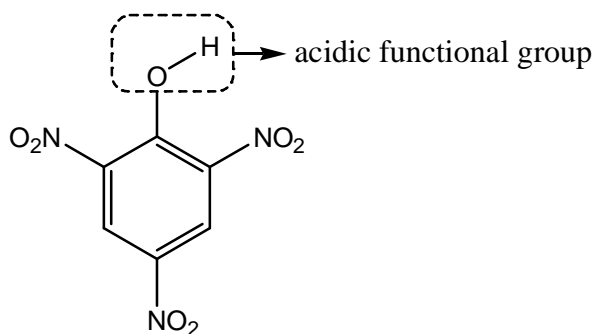
In ethylene pure localized double bond character present. So, double bond has short bond length as compare to single bond.

Correct option is (d)

21. The acidic functional group present in picric acid is [JNU 2015]

- (a) $-\text{SO}_3\text{H}$ (b) $-\text{COOH}$ (c) $-\text{OH}$ (d) None of these

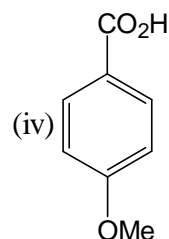
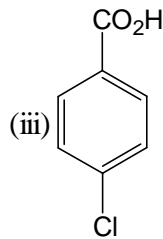
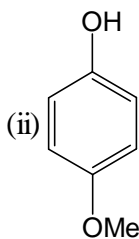
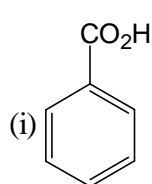
Soln. Picric acid: 2, 4, 6-trinitrophenol.



Correct option is (c)

22. Arrange the following compounds in the increasing order of acidity :

[JNU 2015]



(a) (ii) < (iv) < (i) < (iii)

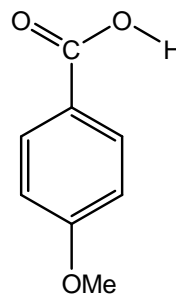
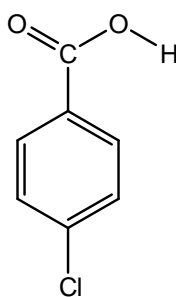
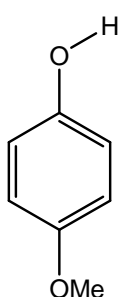
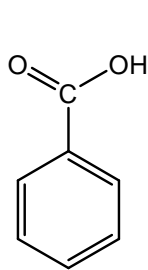
(b) (ii) < (i) < (iii) < (iv)

(c) (ii) < (iii) < (i) < (iv)

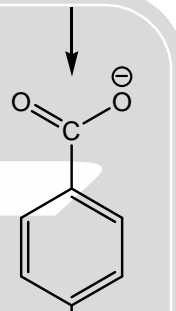
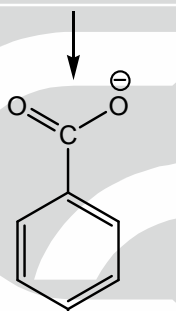
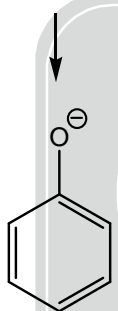
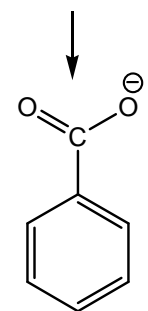
(d) (ii) < (i) < (iv) < (iii)

Soln.

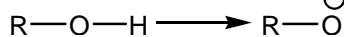
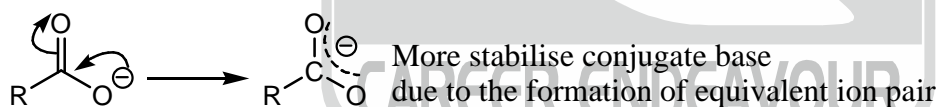
C.A.



C.B.



(OMe) → ERG (Cl) → EWG (OMe) → EWG



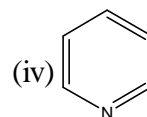
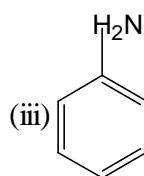
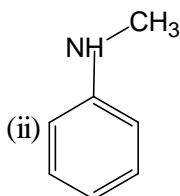
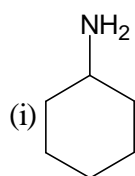
Electron withdrawing group stabilise the conjugate base with increases acidic character. ERG destabilise conjugate base with acidic character.

Correct order of acidity : III > I > IV > II

Correct option is (a)

23. Arrange the following compounds in the increasing order of basicity :

[JNU 2015]



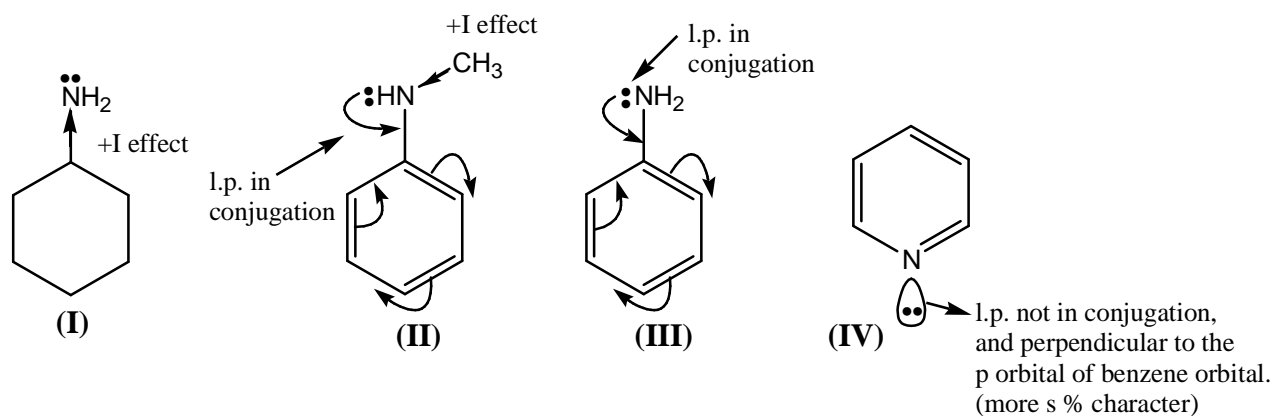
(a) (iii) < (iv) < (ii) < (i)

(b) (iv) < (iii) < (ii) < (i)

(c) (iv) < (iii) < (i) < (ii)

(d) (iii) < (ii) < (iv) < (i)

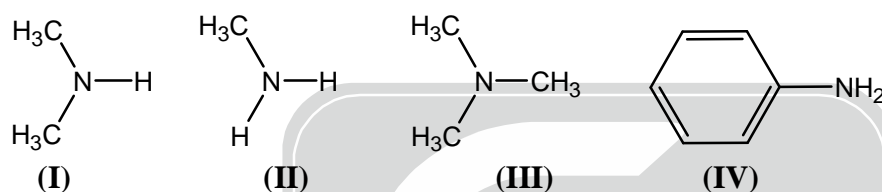
Soln. Basicity ∝ availability of electron pair for donation.



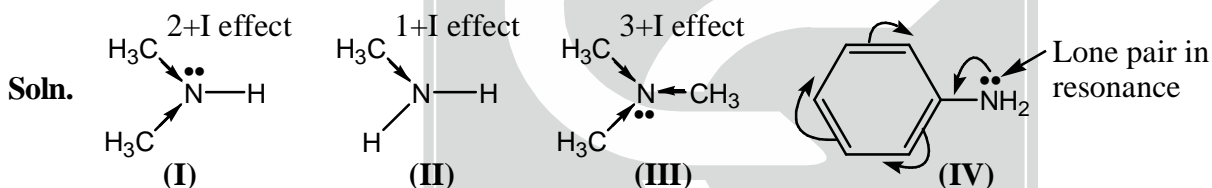
Correct order of basicity : I > IV > II > III

Correct option is (d)

24. Arrange the following compounds according to decreasing order of basic strength [JNU 2019]



- (a) II > I > III > IV (b) I > II > III > IV (c) III > I > II > IV (d) III > II > I > IV

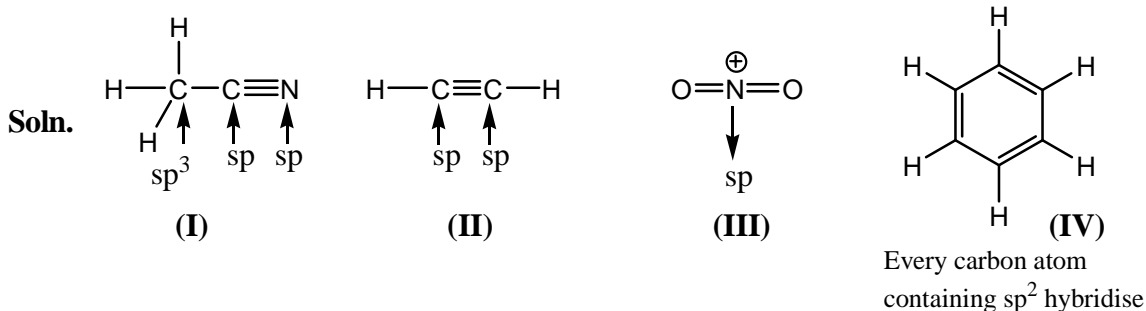


Correct order of basicity: III > I > II > IV

Correct option is (c)

25. Identify the molecule(s) in which sp hybridized atoms are not present [JNU 2019]

- (I) CH_3CN (II) C_2H_2 (III) $^+\text{NO}_2^-$ (IV) C_6H_6
 (a) I only (b) IV only (c) III and IV (d) I, III and IV

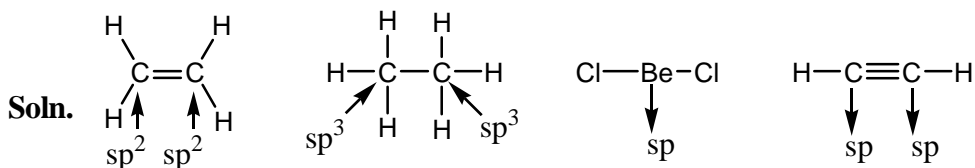


Correct option is (b)

HCU Previous Years Question with Solution

1. Which of the following has sp power of 2 hybridisation? [HCU 2011]

- (a) C_2H_4 (b) C_2H_6 (c) $BeCl_2$ (d) C_2H_2



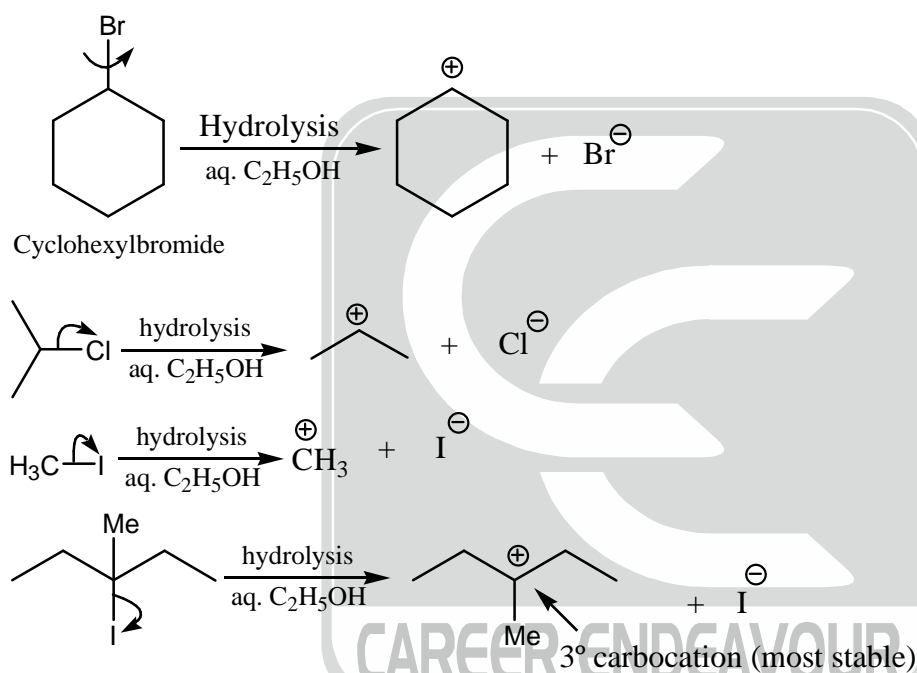
Correct option is (a)

2. Which compound undergoes solvolysis in aqueous ethanol most rapidly? [HCU 2014]

[Remember: solvolysis refers to ionization of the molecule aided by the solvent.]

- (a) cyclohexyl bromide (b) isopropyl chloride (c) methyl iodide (d) 3-iodo-3-methylpentane

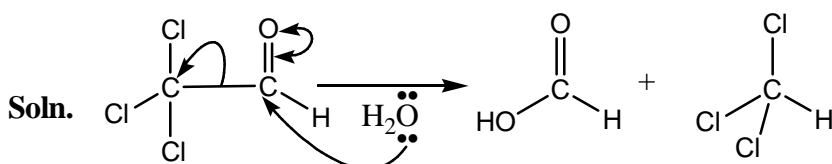
Soln. (Rate of solvolysis \propto stability of carbocation)



Correct option is (d)

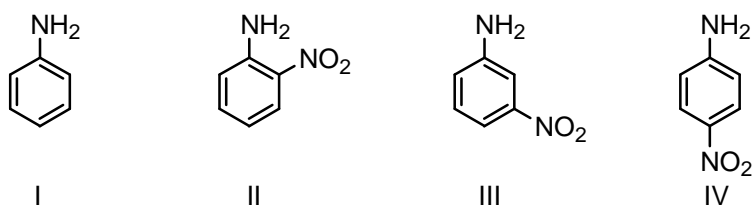
3. Which of the following will react with water? [HCU 2015]

- (a) $CHCl_3$ (b) CCl_3CHO (c) CCl_4 (d) $ClCH_2CH_2Cl$



Correct option is (b)

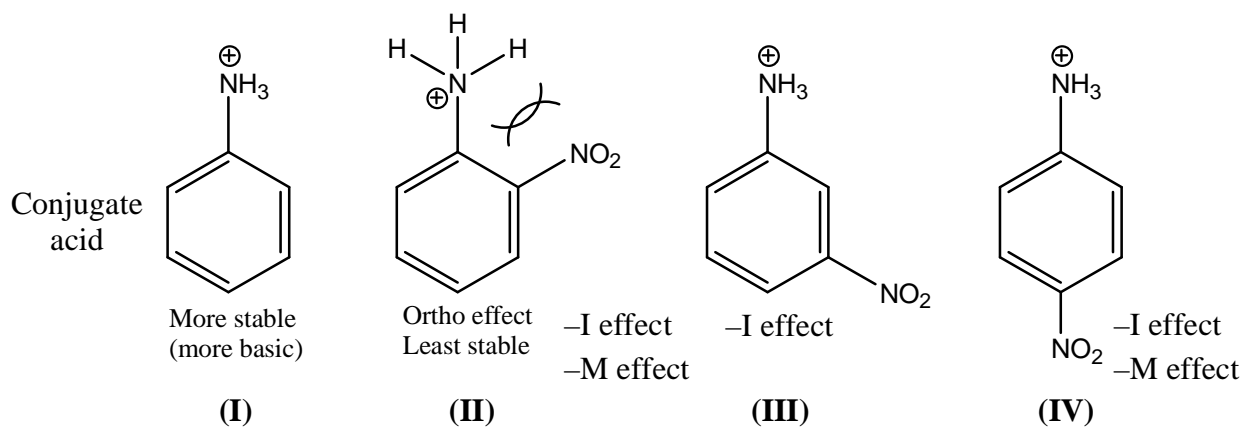
4. Among the following given compounds [HCU 2015]



The decreasing order of their basicity is :

- (a) I > IV > III > II (b) I > III > IV > II (c) II > IV > III > I (d) I > II > III > IV

Soln.



Order of basicity : I > III > IV > II

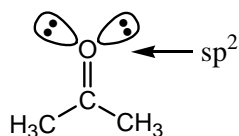
Correct option is (b)



TIFR Previous Years Question with Solution

1. What is the hybridization of oxygen in CH_3COCH_3 [TIFR 2010]
 (a) sp^3 (b) sp^2 (c) sp (d) All of these

Soln.



Hybridisation = steric number = lone pair + number of surrounding species or sigma bonds.

Correct option is (b)

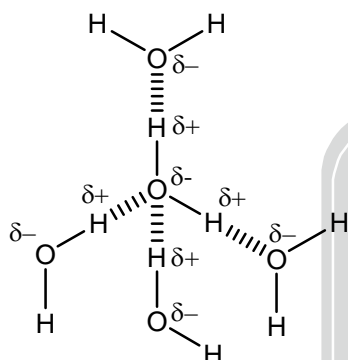
2. The general formula of single-ring cyclo alkane is [TIFR 2014]
 (a) $\text{C}_n\text{H}_{2n+2}$ (b) $\text{C}_n\text{H}_{2n-2}$ (c) C_nH_{2n} (d) C_nH_n

Soln. General formula of single-ring cycloalkane is $(\text{C}_n\text{H}_{2n})$.

Correct option is (c)

3. The maximum number of hydrogen bonds that can be formed by a water molecule is [TIFR 2014]
 (a) 2 (b) 3 (c) 4 (d) 6

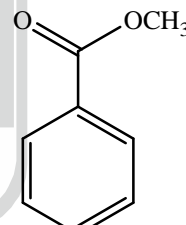
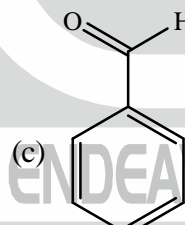
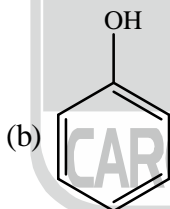
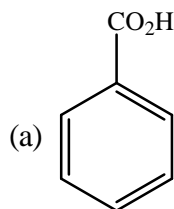
Soln.



Number of hydrogen bonds formed by water molecules are 4

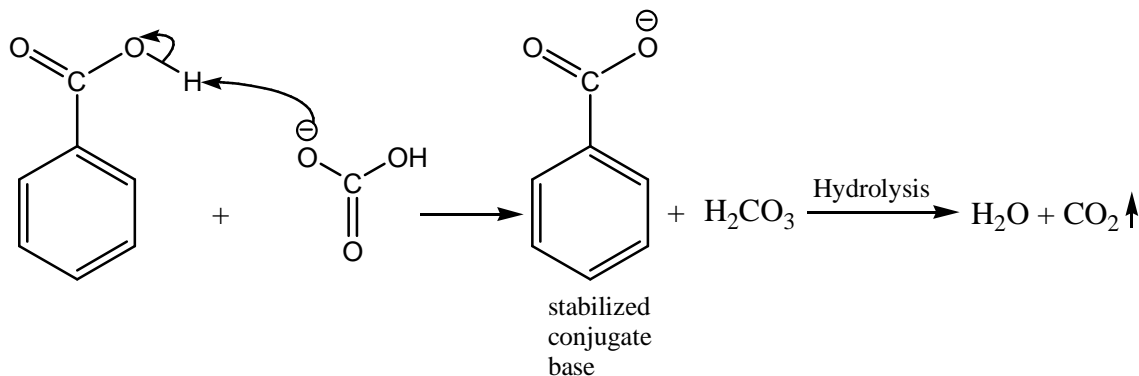
Correct option is (c)

4. The compound that liberates CO_2 on treatment with aqueous sodium bicarbonate solution is:



[TIFR 2014]

Soln. Strong acid + NaHCO_3 (weak base) \longrightarrow CO_2 (gas)
 Weak acid + NaHCO_3 (weak base) \longrightarrow no reaction, no CO_2



Correct option is (a)

5. Which of the following compounds would you expect to be most soluble in water ?

- (a) $\text{CH}_3 - \text{CH}_2 - \text{OH}$
 (b) $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{OH}$
 (c) $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{OH}$
 (d) $\text{CH}_3 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{CH}_2 - \text{OH}$

[TIFR-2015]

Soln. Number of carbon atoms in alcohol increases with decreases solubility in water. Lowest carbon atom contain alkyl alcohol are most soluble in water.

Correct option is (a)

6. Which one of the following is correct order of basic strength?

[TIFR 2016]

- (a) $\text{CN}^- > \text{HCO}_4^- > \text{ClO}_4^- > \text{HS}^-$ (b) $\text{CN}^- > \text{HS}^- > \text{HCO}_3^- > \text{ClO}_4^-$
 (c) $\text{CN}^- > \text{HCO}_3^- > \text{HS}^- > \text{ClO}_4^-$ (d) $\text{HS}^- > \text{CN}^- > \text{HCO}_3^- > \text{ClO}_4^-$

Soln. Basic strength increases with increase the availability of electron for donation

Basicity order = $\text{HS}^- > \text{CN}^- > \text{HCO}_3^- > \text{ClO}_4^-$

Correct option is (d)

7. Between ethanol, ethylamine and ethanethiol, which is the most nucleophilic :

- (a) ethanol (b) ethylamine (c) ethanethiol
 (d) Both ethylamine and ethanethiol are equally nucleophilic

[TIFR-2017]

Soln. $\text{C}_2\text{H}_5\text{OH}$ ethanol

$\text{C}_2\text{H}_5\text{NH}_2$ ethylamine

$\text{C}_2\text{H}_5\text{SH}$ ethanethiol

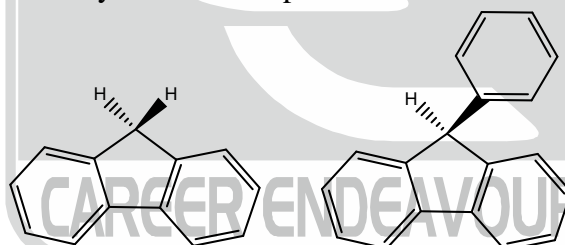
Nucleophilic character increases, when we move top to down in a group.

Ethanethiol is the most nucleophilic in nature.

Correct option is (c)

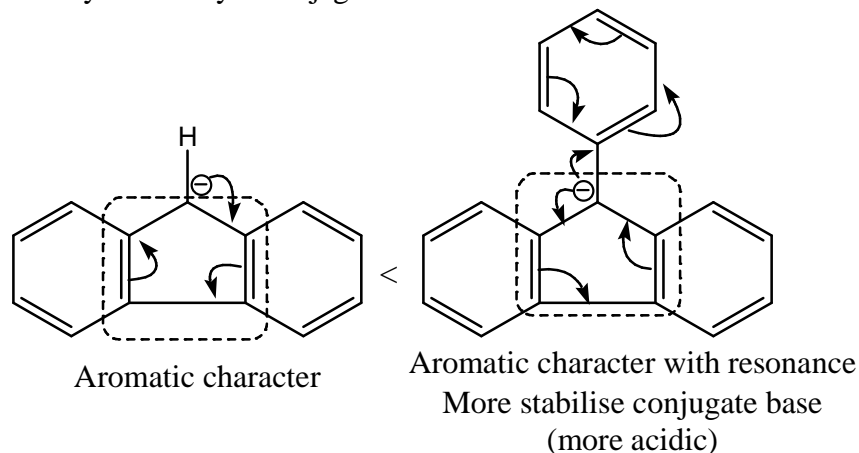
8. What is the correct order of acidity for these compounds?

[TIFR-2017]



- (a) (a) < (b) (b) (a) = (b) (c) (a) > (b) (d) It depends on the pH

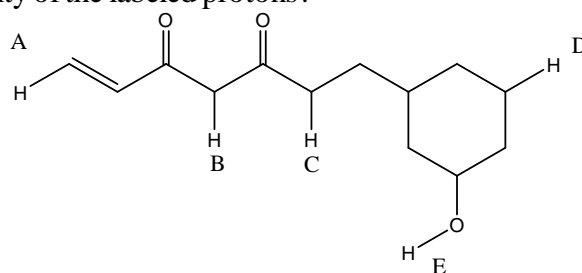
Soln. Acidity \propto stability of conjugate base



Correct option is (a)

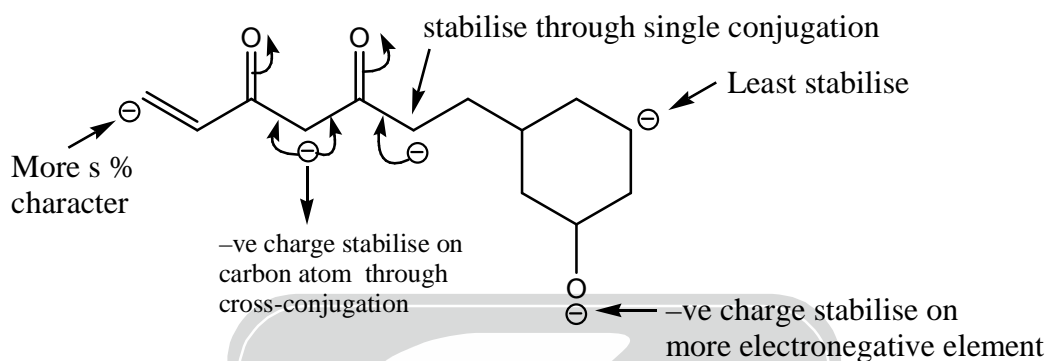
9. What is the order of acidity of the labeled protons?

[TIFR-2018]



- (a) $A > B > C > D > E$ (b) $C > E > D > A > B$
 (c) $E > B > C > A > D$ (d) $D > E > B > A > C$

Soln. More stabilise the conjugate base, more will be acidic.



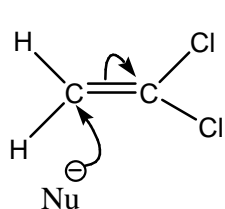
So, order of stability = $E > B > C > A > D$

Correct option is (c)

10. Nucleophilic attack will be most facile on

[TIFR-2018]

- (a) $\text{CH}_2 = \text{CF}_2$ (b) $\text{CH}_2 = \text{CCl}_2$ (c) $\text{CF}_2 = \text{CF}_2$ (d) $\text{CH}_2 = \text{CH}_2$



Soln.

-ve charge stabilise due to conjugation of -ve charge with vacant d-orbitals of chlorine atoms.

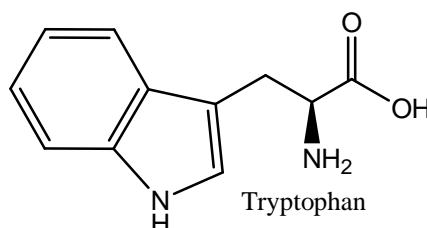
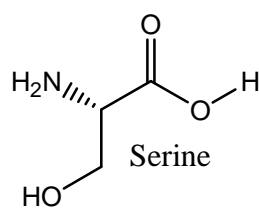
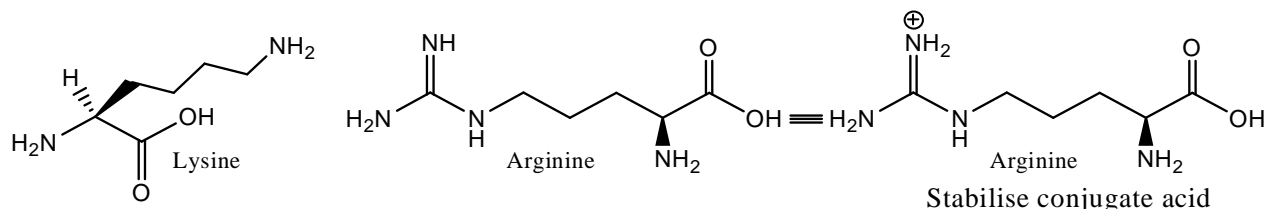
Correct option is (b)

11. The most basic naturally occurring amino acid is :

[TIFR-2018]

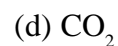
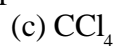
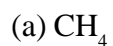
- (a) lysine (b) arginine (c) serine (d) tryptophan

Soln. Arginine is the most basic in nature among the following



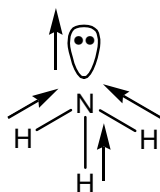
Correct option is (b)

12. Which of the following molecules will have a dipole moment?



[TIFR 2019]

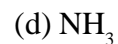
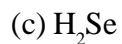
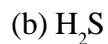
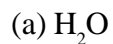
Soln.



More dipole moment

Correct option is (b)

13. Which compound is most acidic?



[TIFR 2019]

Soln. Top to down in a group.

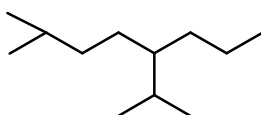
$\text{H}-\text{Se}^- > \text{H}-\text{S}^- > \text{H}-\text{O}^-$ stability of C.B.

Correct option is (c)

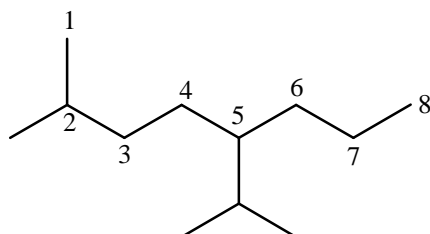


JNUEE Previous Years Question with solution (Nomenclature)

1. Which of the following represents most appropriate IUPAC name for the following compound?



- (a) 5-isopropyl-2-methyloctane
 (b) 1, 1-dimethyl-4-isopropyl heptane [JNU 2005]
 (c) 5-(1-methylethyl)-2-methyloctane
 (d) 1, 3-diisopropyl hexane



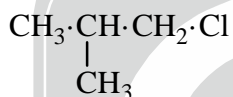
Soln.

IUPAC Name: 5-(1-methylethyl)-2-methyloctane

Correct option is (c)

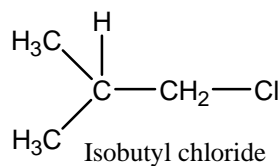
2. Select the correct name of the compound whose structure is

[JNU 2006]



- (a) Butyl chloride (b) Sec. butyl chloride (c) Isobutyl chloride (d) Tert. butyl chloride

Soln.

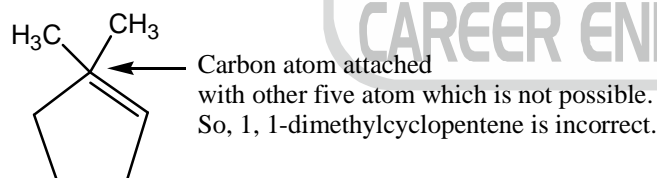


3. Which of the following names is incorrect?

[JNU 2007]

- (a) 1-Butene (b) Trans-2-butene
 (c) Cyclohexene (d) 1, 1-Dimethylcyclopentene

Soln.



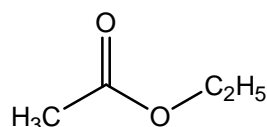
Correct option is (d)

4. IUPAC name for $\text{CH}_3\text{COOC}_2\text{H}_5$ will be

[JNU 2008]

- (a) ethyl acetate (b) ethyl ethanoate (c) methyl propanoate (d) methyl ethanoate

Soln.



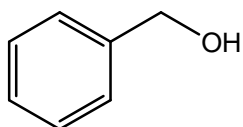
Ethyl ethanoate

Correct option is (b)

5. Structure of phenylcarbinol is [JNU 2009]

- (a) C_6H_5OH (b) $C_6H_5CH_2OH$ (c) C_6H_5CO (d) C_3H_7OH

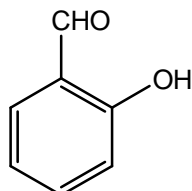
Soln. Phenyl carbinol



Correct option is (b)

6. What is the IUPAC name of salicylaldehyde? [JNU 2009]

- (a) 2-hydroxybenzaldehyde (b) 2-hydroxyphenylaldehyde
(c) 3-hydroxybenzaldehyde (d) 4-hydroxybenzaldehyde



Soln.

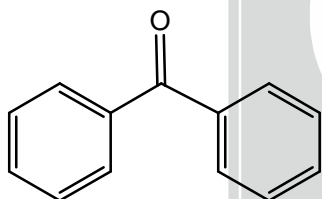
2-hydroxybenzaldehyde

Correct option is (a)

7. Molecular formula of benzophenone is [JNU 2009]

- (a) $C_6H_5COC_6H_5$ (b) C_6H_5CO (c) $C_6H_5COCH_3$ (d) $C_6H_5CH_2CHO$

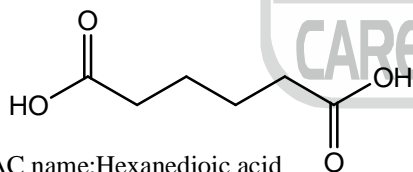
Soln. Molecular formula of benzophenone



Correct option is (a)

8. What is the IUPAC name of the adipic acid? [JNU 2009]

- (a) hexanedioic acid (b) Butanedioic acid (c) Propanedioic acid (d) Heptanedioic acid



Soln.

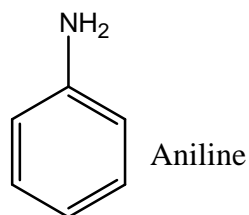
IUPAC name: Hexanedioic acid

Common name: Adipic acid

Correct option is (a)

9. Aniline is an [JNU 2010]

- (a) aromatic carboxylic acid (b) aromatic amine
(c) aliphatic amine (d) aliphatic carboxylic acid



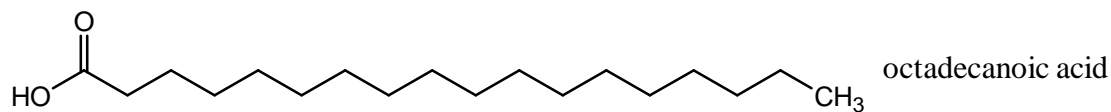
Soln.

Aromatic amine

Correct option is (b)

10. IUPAC name of stearic acid is [JNU 2010]
 (a) hexadecanoic acid (b) octadecanoic acid
 (c) cis-9, 12-octadecadienoic acid (d) cis-9-octadecanoic acid

Soln. Stearic acid



Correct option is (b)

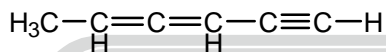
11. The triple bond of acetylene is made up of [JNU 2011]
 (a) three σ bonds (b) one σ bond and two π bonds
 (c) three π bonds (d) two s bonds and one p bond

Soln. $\text{H}-\overset{\pi}{\underset{\sigma}{\text{C}}}\equiv\overset{\pi}{\text{C}}-\text{H}$ Acetylene

Two π bond and one σ bond.

Correct option is (b)

12. The number of sigma bonds present in the compound [JNU 2012]



is

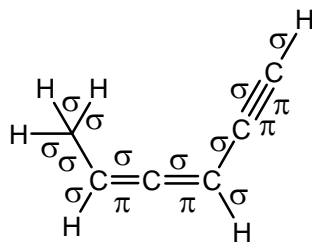
(a) 8

(b) 10

(c) 11

(d) 15

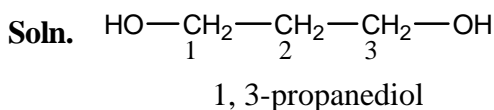
Soln.



Total sigma bond = 11

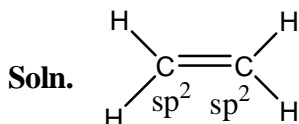
HCU Previous Years Question with Solution (Nomenclature)

1. The IUPAC name of the compound with chemical formula given as [HCU 2011]
 $\text{HO}-\text{CH}_2-\text{CH}_2-\text{CH}_2-\text{OH}$ is
 (a) 1,2,3-Propanediol (b) 1,2,3,-Ethanediol (c) 1,3-Propanediol (d) 1,2,3-Propanetriol



Correct option is (c)

2. Which of the following has sp power of 2 hybridisation? [HCU 2011]
 (a) C_2H_4 (b) C_2H_6 (c) BeCl_2 (d) C_2H_2



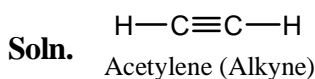
Correct option is (d)

3. Generically chemical compounds are given IUPAC names. The acronym, IUPAC stands for [HCU 2015]
 (a) International Union of Pure and Applied Chemistry
 (b) International Unicode for Paramedical and Analytical Compounds
 (c) Indian Union for Public and Administrative Code
 (d) Indian Unicode for Public and Applied Chemistry

Soln. IUPAC – international union of pure and applied chemistry.

Correct option is (a)

4. Acetylene is categorized under one of the following classes [HCU 2015]
 (a) Alkane series (b) Saturated hydrocarbons
 (c) Alkyne series (d) Olefin series



Correct option is (c)

