CLASS XII
SAMPLE PAPER
CHEMISTRY

Q1.In what kind of defect density of crystal increases. 1
Q2.Define the maximum boiling point azeotrope. 1
Q3.Write the product of electrolysis of $AgNO_3$ by using silver electrode. 1
Q4.Define the elementary reaction. 1
Q5.Define the gel, or dialysis. 1
Q6.Define the term pyro metallurgy. 1
Q7. Why ICl is more reactive than I_2? 1
Q8. Why enthalpy of atomization of transition metals are generally high? 1
Q9.R of 1 molar common salt solution filled in a cylindrical container having length 10 cm and radius 4 cm is 500 ohm find the conductivity of solution. 2
Q10.Define the pseudo first order reaction ,write the unit of K. 2
Q11.Write the difference between physisorption and chemisorptions. 2
Q12.A reaction is first order w.r.t. A and second order with respect to B. 1.Write the differential rate equation .2.How is the rate of reaction affected if concentration of B is increases three time . 2
Q13.Discuss the contact process of preparation of sulphuric acid . 2
Q14.What is lanthanide contraction ? 2
Q.15.What are the properties of a d-block elements which make them a good catalyst? 2
Q.16.1.Sulphur in vapour state exhibit paramagnetic behavior. Explain. 2
2.N_2 is least reactive at room temperature .explain.
Q.17.1.Why does PCl_3 fume in moisture.? 3
2. write the isoelectronic neutral species of ClO^{-1} .
3.Write the increasing order of bod dissociation enthalpy of F_2,Cl_2,Br_2,I_2.
Q.18.How do you account for reducing nature of H_3PO_2 on the basis of its structure? 3
Q19.Silver crystallizes in F.c.c. ,if edge length is 4.07×10^{-8} cm and density is 10.5 g/cm^3 calculate the Atomic mass of silver. 3
Q20.Explain the following term .1.ferromagnetism 2. Tetrahedral void 3. Frankel defect . 3
Q21.H_2S is toxic gas with rotten egg like smell, is used for qualitative analysis .if the solubility of H_2S in water at STP is 0.195 m ,calculate the Henry law consant. 3
Q22.Define the Raoult's law .C_7H_{16} (heptanes) and octane form an ideal solution .At 373 K , the vapour pressures of two liquid components are 105.2 kPa and 46.8 kPa respectively.What will be the vapour pressure of the mixture of 26.0 g of heptanes and 35 g of octane.? 3

Q23.The time required for 10% completion of a first order reaction at 298 K is equal to that required for its 25% completion at 308 K.If the value of A is 4×10^{10} /s .Calculate k at 318 K and Ea. 3

Q24.Discuss the following terms.1.slectivity 2.hydrophillic sol 3.peptization. 3

Q25.1.Draw the structure of SF_4,BrF_3. 1x 3
2.Cu + HNO_3 (conc) ----→ ?
3.What happens H_3PO_3 is heated?

Q26.Define the conductivity .$E^\circ_{Al^{+3}/Al}$= – 1.66 V and for $E^\circ_{Ni^{2+}/Ni}$ = – 0.25 V .Write the cell (1+1+3)
reaction and find the E.M.F. of the cell.($[Al^{+3}]$ =0.001 mol/L, $[Ni^{2+}]$ = 0.05 mol/L)

or

Discuss the molar conductivity ,show the graphical variation of molarconductivity with dilution.Calculate the cell potetential E cell of following cell.
$E^\circ_{Cu^{+2}/Cu}$= 0.34 V $E^\circ_{Ag^{+1}/Ag}$= +0.80 V and ($[Cu^{+2}]$ =0.01 mol/L, $[Ag^{1+}]$ = 0.001 mol/L)

Q27. (a) Discuss the chemistry involved in Brown ring test for nitrate ion. Give equations also. 2

(b) Complete the following equations: 3
(i) $P_4 + SOCl_2$ ---------------→
(ii) $4\ AgNO_3 + 2H_2O + H_3PO_4$ -------------→
(iii) $NaCl + MnO_2 + H_2SO_4$ -----------------→

OR

(a) Account For the Following: 3
(i) H_3PO_2 act as monobasic acid.
(ii) Interhalogen compounds are more reactive than halogens
(iii) Bond dissociation energy of F_2 is smaller than Cl_2.
(b) Discuss the quantitative method for estimating O_3 gas. 2

Q28. **(i)** What are interstitial compounds? Why are such compounds well known for transition metals? 1
(ii) How is the variability in oxidation states of transition metals different from that of the non transition metals? Illustrate with examples. 1
(iii) Describe the preparation of potassium dichromate from iron chromite ore. What is the effect of increasing pH on a solution of potassium dichromate? 2+1

OR

(i) Account for the following 1 x 3

(a) Sc, the first member of first transition series doesn't exhibit variable oxidation state.Account for the following

(b) Transition metals have a strong tendency to form complexes.

(c) Zirconium (atomic no 40) and hafnium (atomic no 72) exhibit similar properties.

(ii) How does acidified solution of potassium dichromate react with (a) $FeSO_4$ and (b) H_2S?

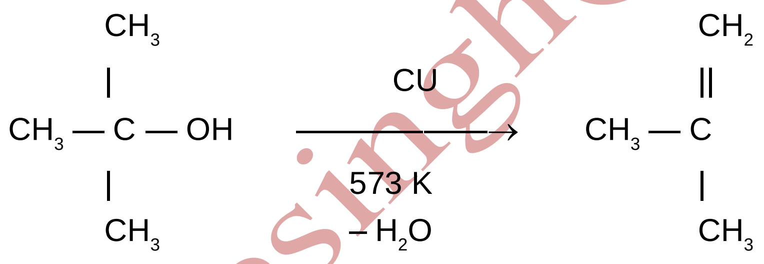
UNIT—10

HALOALKANES AND HALOARENES

1 MARK QUESTIONS

Q. 1. What happens when tert-butyl alcohol is treated with Cu / at 573 K.

Ans. Dehydration reaction will take place. Isobutene will be formed.



$$CH_3-\overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{C}}-OH \xrightarrow[573\text{ K},\ -H_2O]{CU} CH_3-\overset{\overset{CH_2}{||}}{\underset{\underset{CH_3}{|}}{C}}$$

Q. 2. Arrange the following halides in order of increasing SN^2 reactivity :

CH_3 — Cl, CH_3 — Br, CH_3CH_2Cl, $(CH_3)_2$ CHCl

Ans. $(CH_3)_2$ CHCl < CH_3CH_2Cl < CH_3Cl < CH_3Br.

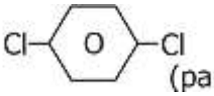
(**Hint :** As the size of the alkyl group increases SN^2 reactivity decreases.)

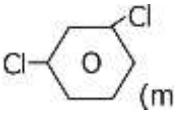
Q. 3. Alkyl halides, though polar, are immiscible with water. Why ?

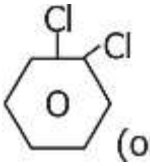
Ans. Alkyl halides cannot form H-bonds with water molecules and hence are insoluble in water.

Q. 4. p-Dichlorbenzene has higher melting point and lower solubility than those of o- and m- isomers. Discuss.

Ans.


(para)


(meta)


(ortho)

The p-isomer being more symmetrical fits closely in the crystal lattice and thus has stronger intermolecular forces of attraction than those of o- and m- isomers. Since during melting or dissolution, the crystal lattice breaks, therefore a larger amount of energy is needed to melt or dissolve the p- isomer than the corresponding o- and meta isomers.

Q. 5. The treatment of alkyl chlorides with aq KOH leads to the formation of alcohols but in presence of alcoholic KOH, alkenes are the major products. Explain.

Ans. In aq. solution, KOH is almost completely ionised to give OH^- ions which being a strong nucleophile brings about a substitution reaction to form alcohols. Further in aq. solution, OH^- ions are highly solvated (hydrated).

This solution reduces the basic character of OH^- ions which fail to abstract a hydrogen from the β-carbon of the alkyl halide to form an alkene.

However an alcoholic solution of KOH contains alkoxide (RO^-) ions which being a much stronger base than OH^- ions preferentially abstracts a hydrogen from the β-carbon of the alkyl halide to form alkene.

Q. 6. Grignard reagents should be prepared under anhydrous conditions. Why ?

Ans. Because Grignard reagents have a very strong affinity for H^+ ions. In presence of water, they abstract H^+ ions from water and form alkanes. To prevent this, they should be prepared under anhydrous conditions.

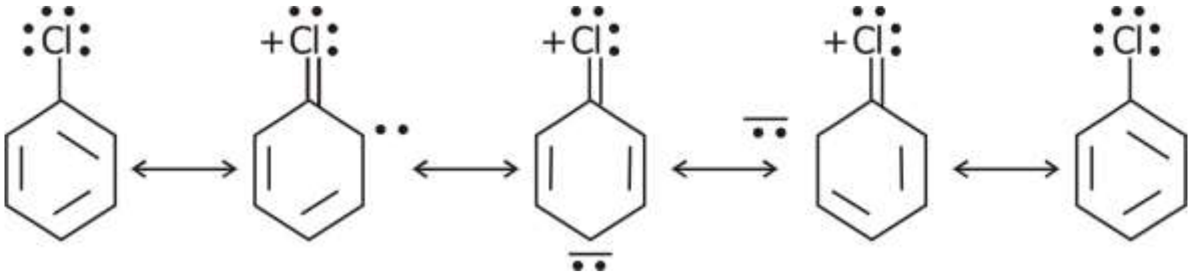
Q. 7. Haloalkanes react with KCN to form alkyl cyanides as major product while AgCN form isocyanide as the chief product. Explain.

Ans. KCN is a ionic compound and provides cyanide ions in solution. Although both carbon and nitrogen atoms are in a position to donate electron pairs, the attack takes place mainly through Carbon atom and not through nitrogen atom since C — C bond is more stable than C — N bond. However AgCN is mainly covalent in nature and nitrogen is free to donate electron pair forming isocyanide as the main product.

Q. 8. Explain why is Chlorobenzene difficult to hydrolyse than ethyl chloride ?

Ans. The lone pair of electrons of Chlorine is Chlorbenzene participates into resonance with the benzene ring.

As a result C — Cl bond acquires a partial double bond character. Therefore, this C — Cl bond is stronger than C — Cl bond in ethyl chloride which is a pure single bond. As such the Chlorobenzene is difficult to hydrolyse than ethyl chloride.



Q. 9. Tert-butyl chloride reacts with aq. NaOH by SN¹ mechanism while n-butyl chloride reacts by SN² mechanism. Why ?

Ans. Tert-butyl chloride reacts via SN¹ mechanism because the heterolytic cleavage of C — Cl bond in tert-butyl chloride gives 3 carbocation which is highly stable and favourable for SN¹ mechanism. Moreover, tert-butyl chloride (3°) bring a bulky molecule has steric hindrance which will not allow SN² mechanism to take place. Hence only SN¹ mechanism can occur in tert-butyl chloride. However n-butyl chloride (1°) reacts via SN² because 'C' of C — Cl bond is less crowded and favourable for nucleophile to attack from back side results in the formation of transition state. It has less steric hindrance which is a favourable factor for SN² mechanism.

Q. 10. (a) Which of the following two compounds would react faster by SN² pathway : 1-bromobutane (OR) 2-bromobutane.

(b) Allyl Chloride is more reactive than n-propyl Chloride towards nucleophilic substitution reactions. Explain.

Ans. (a) The reactivity in SN² reaction depends upon the extent of steric hindrance. i-bromobutane is a 1° alkyl halide and 2-bromobutane is a 2° alkyl halide. Since there will be some steric hindrance in 2° alkyl halide than in 1° alkylhalide, therefore 1°-bromobutane will react faster than 2-bromobutane in SN² reaction.

(b) Allyl Chloride readily undergoes ionization to produce resonance stabilized allyl carbocation. Since carbocations are reactive species they readily combine with OH^- ions to form allyl alcohol.

$$CH_2=CH-CH_2-Cl \xrightarrow[\text{Slow}]{\text{Ionization}} CH_2=\overset{+}{CH}-CH_2$$

$$\updownarrow$$

$$CH_2=CH-CH_2OH \xleftarrow[\text{Fast}]{OH^-} {}^{+}CH_2-CH=CH_2$$

In contrast, n-propyl chloride does not undergo ionization to produce n-propyl carbocation and hence allyl chloride is hydrolysed more readily than n-propyl chloride.

Q. 11. R—Cl is hydrolysed to R—OH slowly but the reaction is rapid if a catalytic amount of KI is added to the reaction mixture.

Ans. Iodide ion is a powerful nucleophile and hence reacts rapidly with RCl to form RI.

$KI \longrightarrow K^+ + I^-;\quad R-Cl + I^- \longrightarrow R-I + Cl^-$

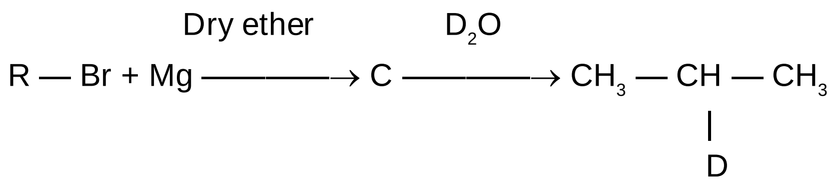
Further I^- is a better leaving group than Cl^- ion, therefore, RI is more rapidly hydrolysed than RCl to form ROH.

$HO^- + R-I \longrightarrow R-OH + I^-$

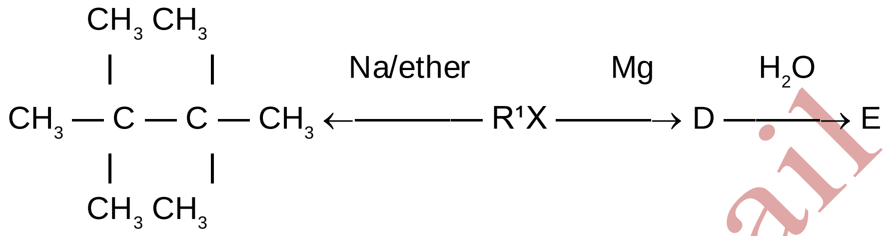
Q. 12. Identify A, B, C, D, E, R, R¹ in the following :

Dry ether H_2O

(i) $Br + Mg \longrightarrow A \longrightarrow B$

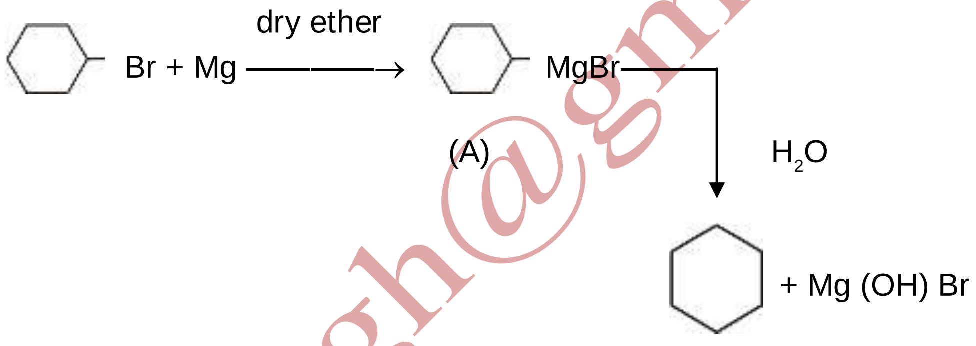


(ii) $$R-Br + Mg \xrightarrow{\text{Dry ether}} C \xrightarrow{D_2O} CH_3-\underset{\underset{D}{|}}{CH}-CH_3$$



(iii) $$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \xleftarrow{\text{Na/ether}} R^1X \xrightarrow{Mg} D \xrightarrow{H_2O} E$$

Ans. (i)



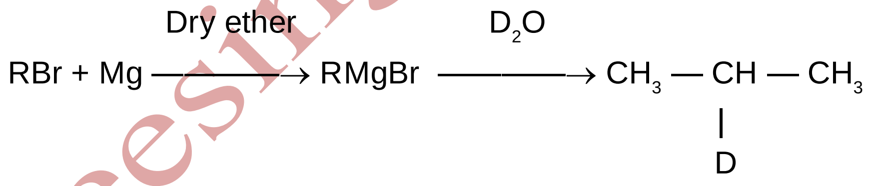
Br + Mg dry ether ⟶ MgBr

(A)

H_2O

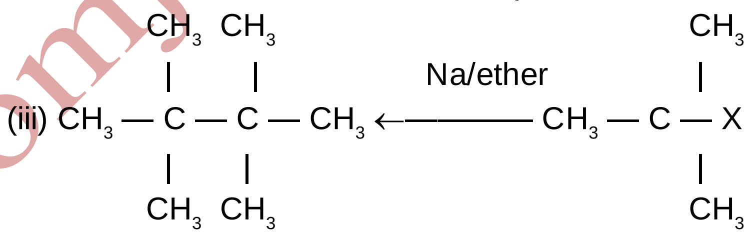
+ Mg (OH) Br

(B)

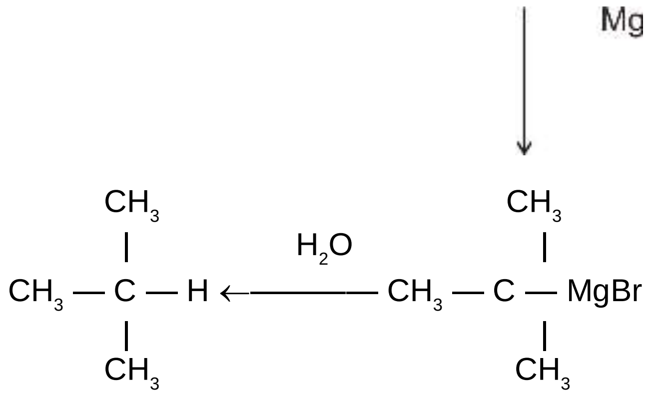


(ii) $$RBr + Mg \xrightarrow{\text{Dry ether}} RMgBr \xrightarrow{D_2O} CH_3-\underset{\underset{D}{|}}{CH}-CH_3$$

Here $R = \underset{|}{CH_3CHCH_3}$



(iii) $$CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-CH_3 \xleftarrow{\text{Na/ether}} CH_3-\underset{\underset{CH_3}{|}}{\overset{\overset{CH_3}{|}}{C}}-X$$



$$\mathrm{CH_3-\underset{CH_3}{\overset{CH_3}{C}}-H} \xleftarrow{\mathrm{H_2O}} \mathrm{CH_3-\underset{CH_3}{\overset{CH_3}{C}}-MgBr}$$

1 MARK QUESTIONS

Q. 1. Explain why :

Haloalkanes undego nucleophilic substitutions whereas Haloarenes undegoes electrophilic substitutions.

Ans. Haloalkanes are more polar than haloarenes.

∴ C-atom carrying the halogen in haloalkanes is mroe e^- deficient than that in haloarenes.

∴ Haloalkanes undergo nucleophilic substitution readily

In haloarenes, the love pair of electrons present on the halogen atom goes into resonance with the aryl ring. The aryl ring being rich in electron density, undergoes electrophilic substitutions.

Q. 2. Why alkyl halides are generally not prepared in laboratory by free radical halogenation of alkanes ?

Ans. It is because :

(i) It gives a mixture of isomeric monohalogenated products whose boiling points are so close that they cannot be separated easily.

(ii) Polyhalogenation may also take place, thereby making the mixture more complex and hence difficult to separate.

Q. 3. Why preparation of aryl iodide by electrophilic substitution requires presence of an oxidising agent ? Why can aryl flouride not be prepared by this method ?

Ans. Reactions with I_2 are reversible in nature and require presence of oxidising agent (HNO_3, etc.) to oxidise HI formed during iodination and promote forward reaction.

Fluoro compounds cannot be prepared due to high reactivity of flourine.

Q. 4. Why is Sulphuric acid not used during reaction of alcohol with KI ?

Ans. H_2SO_4 cannot be used along with KI in conversion of an alcohol to alkyl iodide as it converts KI to corresponding HI and then oxidises it to I_2.

Q. 5. Why aryl halides are extremely less reactive towards nucleophilic substitution ?

Ans. (i) Resonance effect :

Due to resonance C — Cl bond acquires partial double bond character.

(ii) Difference in hybridisation of Carbon in C —X bond :

in haloarene C-atom attached to halogen in sp^2 hybrid while sp^3 in haloalkane.

C — X bond length in sp^2 hybrid is shorter and hence stronger and difficult to break.

(iii) Instability of phenyl cation

(iv) Possible repulsion of nucleophile to approach e^- rich arenes.

Q. 6. Why thionyl chloride method is preferred for the preparing alkyl chloride from alcohols ?

Ans. Because by products of the reaction, i. e., SO_2 and HCl being gases escape into atmosphere leaving behind pure alkyl chloride.

Q. 7. (i) Arrange in order of property indicated :
$CH_3CH_2CH_2CH_2Br$, $(CH_3)_3$ Br, $(CH_3)_3$ $CHCH_2$ Br
(Increasing boiling point)

(ii) CH_3F, CH_3I, CH_3Cl, CH_3Br (nucleophilic substitution)

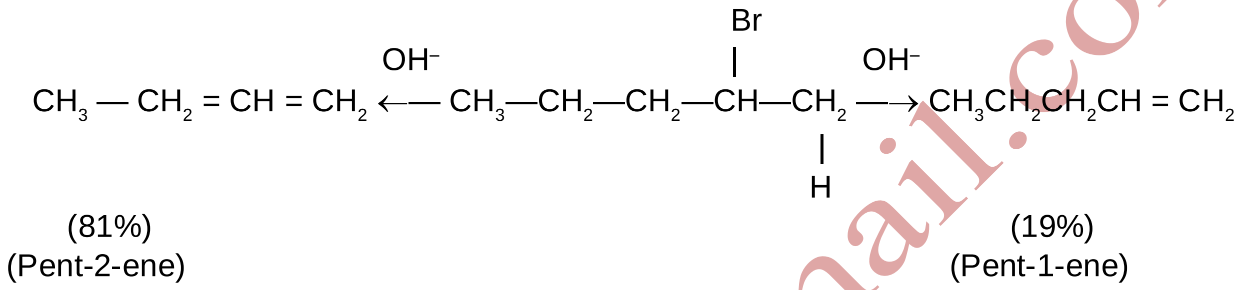
Ans. (i) B. P. decreases with increase in branching due to decrease in Van der Waals forces of attraction.

$(CH_3)_3 CBr < (CH_3)_2 CHCH_2 Br < CH_3CH_2CH_2CH_2Br$

(ii) Reactivity increases as C — X bond dissociation energy decreases.
$CH_3F < CH_3Cl < CH_3Br < CH_3I$

Q. 8. Why does 2 bromopentane gives pent-2-ene as major product in elimination reaction ?

Ans.



$$CH_3 — CH_2 = CH = CH_2 \xleftarrow{OH^-} CH_3—CH_2—CH_2—\overset{Br}{CH}—\underset{H}{CH_2} \xrightarrow{OH^-} CH_3CH_2CH_2CH = CH_2$$

(81%) (Pent-2-ene)

(19%) (Pent-1-ene)

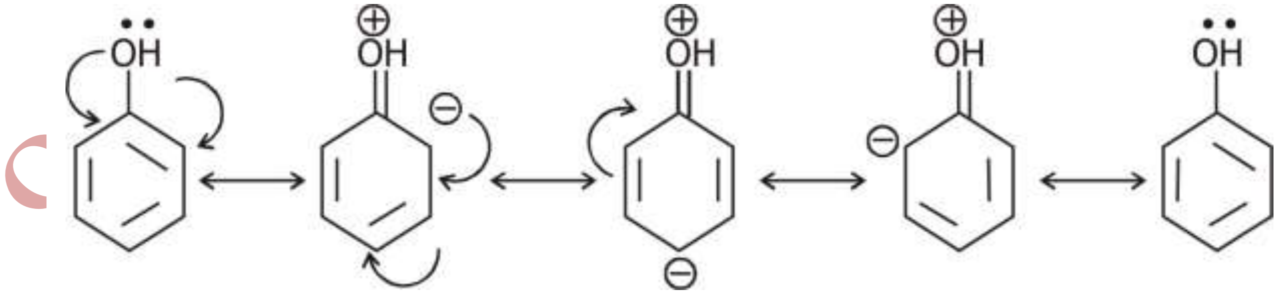
This is because of Saytzeff's rule — In dehydrohalogen reactions, the preferred product is that alkene which has the greater number of alkyl groups attached to the doubly bonded carbon atoms.

Q. 9. Why is bond angle in ethers slightly greater than tetrahedral angle ?

Ans. Because, the interaction beetween the two bulky groups is quiet repulsive. Hence angle is slightly larger.

Q. 10. Alcohols reacts with halogen acids to form haloalkenes but phenol does not form halobenzene. Explain.

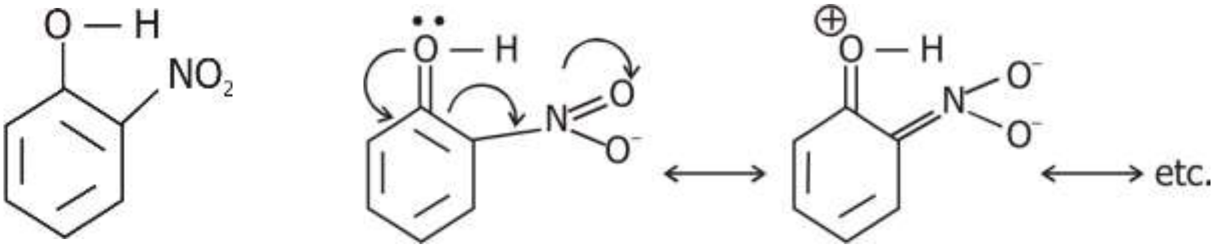
Ans. The C—O bond in phenol acquires partial double bond character due to resonance and hence be cleared by X^- ions to form halobenzenes.



But in alcohols a pure C — O bond is maintained and can be cleared by X^- ions.

Q. 11. Explain why o-nitrophenol is more acidic than o-methoxy phenol ?

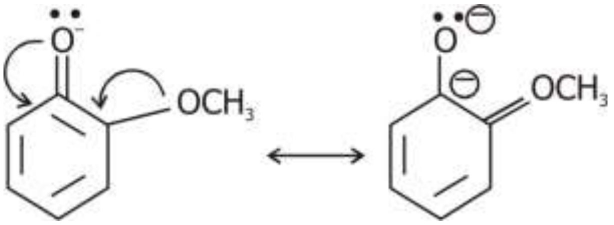
Ans. Due to — R and — I effect of — NO_2 group, e^- density on 'O' if O — H bond decreases and loss of H^+ is easy.



– I effect + ve charge on c-atom

⟶ release of H^+ easier.

In contrast in o-methoxy phenol due to + R effect, – OCH_3 increases. e^- density on 'O' of O — H group, and hence less of H^+ is difficult.



(both –ve charge repel each other)

Q. 12. Why is preparation of ethers by acid catalysed dehydration of 2° and 3° alcohols not a suitable method ?

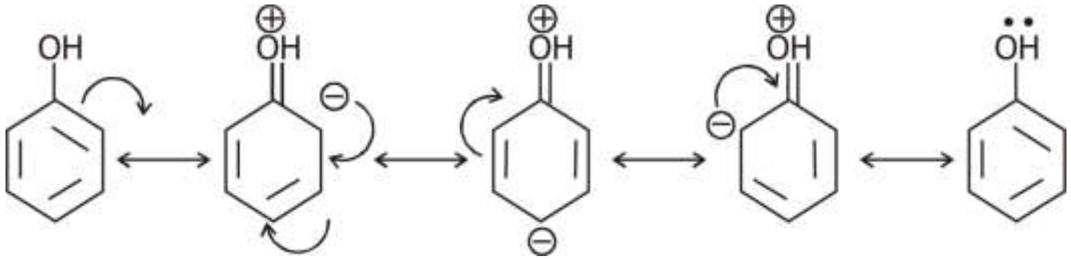
Ans. Acid catalysed dehydration of 1° alcohols to ethers occurs by SN² reaction involving attack of nucleophile by alcohol on protonated alcohol molecule.

Under these conditions, 2° and 3° alcohols give alkenes rather than others. Due to steric hindrance nucleophilic attack on protonated alcohol does not occur instead they lose one H_2O and produce alkenes.

Q. 13. Of benzene and phenol, which is more easily nitrated and why ?

Ans. Nitration is an electrophilic substitution reaction.

The — OH group in phenol increases the e^- density at o- and p- position as follows :

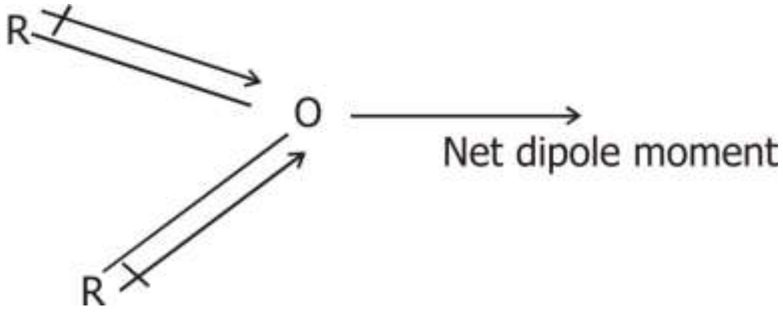


Since phenol has a higher electron density due to electron releasing nature of OH group, compared to benzene, therefore nitration is easy in phenol than benzene.

Q. 14. How will you account for the following :

Ethers possess a net dipole moment even if they are symmetrical in structure ?

Ans.



Because of greater electronegativity of o- atom than carbon C – O bonds are polar.

C – O bond are inclined to each other at an angle of 110° (or more), two dipoles do not cancel out each other.

Q. 15. How do 1°, 2° and 3° alcohols differ in terms of their oxidation reaction and dehydrogenation ?

Ans. (I) Oxidation reaction :

$$\text{1° alcohol} \xrightarrow{(O)} \text{aldehyde} \xrightarrow{(O)} \text{carboxylic acid}$$

$$\text{2° alcohol} \xrightarrow{(O)} \text{ketone} \xrightarrow{(O)} \text{carboxylic acid}$$

(acid with loss of 1 carbon atom)

$$\text{3° alcohol} \xrightarrow{(O)} \text{resistant to oxidation}$$

(II) Hydrogenation reaction :

$$\text{1° alcohol} \xrightarrow{\text{give}} \text{aldehyde}$$

$$\text{2° alcohol} \longrightarrow \text{ketone}$$

$$\text{3° alcohol} \longrightarrow \text{alkene}$$

3° alcohols prefer to undergo dehydration and form alkene.

Q. 16. (I) How is diethyl ether prepared from ethyl alcohol ?

Ans. Ethyl alcohol is first treated with sodium to form sodium ethoxide.

$$C_2H_5OH + Na \longrightarrow C_2H_5O^- Na^+ + H_2$$

Sodium ethoxide is then treated with ethyl halide to form di ethyl ether.

$$C_2H_5O\ Na + X - C_2H_5 \xrightarrow{SN^2} C_2H_5O\ C_2H_5 + NaX$$

(Williamson synthesis)

(II) Complete the rxn :

(a) $CH_3OCH_3 + PCl_5 \longrightarrow$

(b) $C_2H_5OCH_3 + HCl \longrightarrow$

(c) $(C_2H_5)_2\ O + HCl \longrightarrow$

Ans. (a) $2\ CH_3Cl$

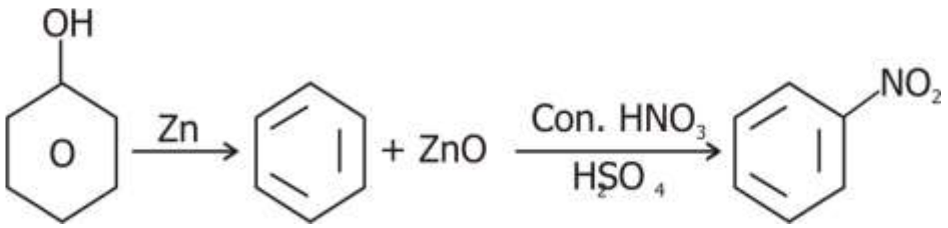
(b) $CH_3Cl + C_2H_5OH$

(c) $C_2H_5Cl + C_2H_5OH$

Q. 17. Why is reactions of alcohol/phenol and with acid chloride in the presence of pyridine ?

Ans. Because esterification rxn is reversible and presence of base (pyridine) neutralises HCl produced during reaction thus promoting forward reaction.

Q. 18. How can we produce nitro benzene from phenol ?



Ans. (I) First convert phenol to benzene by heating with Zn dust.

(II) Nitration of benzene with conc. nitric acid in presence of conc. sulphuric acid.

❑❑❑

UNIT—11

ALCOHOLS, PHENOLS AND ETHERS

1 MARK QUESTIONS

Q. 1. What is the main product obtained when vapours of t-butyl alcohol are passed over copper at 300° ?

Ans. Isobutylene (2-Methyl propene)

Q. 2. What is usually added to ethyl alcohol to make it unfit for drinking purposes ?

Ans. Methanol and Pyridine.

Q. 3. Phenol has smaller dipole moment than methanol.

(OR)

Why are dipole moments of phenols smaller than dipole moments of alcohols ?

Ans. Due to electron-withdrawing effect of the benzene ring, the C — O bond in phenol is less polar but in case of methanol due to electron-donating effect of — CH_3 group, C — O bond is more polar.

Q. 4. Name the products obtained when anisole is treated with HI.

Ans. Phenol and methyl iodide.

Q. 5. Why are Grignard reagents soluble in ether but not in benzene ?

Ans. Grignard reagents from co-ordination complexes with ether but not benzene since the former has lone pair of electrons but the later does not.

Q. 6. Alcohols are easily protonated than phenols. Justify.

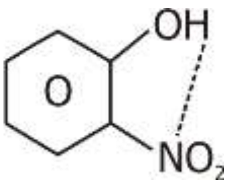
Ans. In phenols lone pair of electrons on the oxygen atom are delocalised over the benzene ring due to resonance and hence are not easily available for protonation. In contrast in alcohols, the lone pairs of electrons on the oxygen atom are localized due to absence of resonance and hence are easily available for protonation.

Q. 7. Di-tert butyl ether cannot be made by Williamson's synthesis. Explain why ?

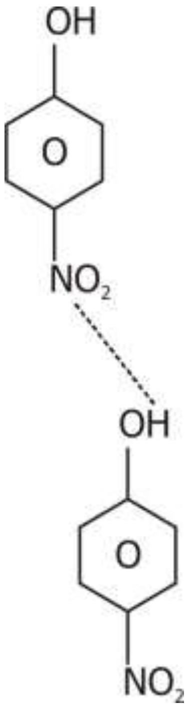
Ans. To prepare di tert-butyl ether by Williamson's synthesis, we need tert-butyl bromide and Sodium tertiary butoxide. Since tert-butyl bromide being 3°-alkyl halide prefers to undergo elimination rather than substitution, therefore the product obtained is isobutylene rather than ditertiary butyl ether.

Q. 8. While separating a mixture of ortho and para-nitro phenols by steam distillation, name the isomer which will be steam volatile. Give reasons.

Ans. In o-nitrophenol, there is intramolecular hydrogen bonding as follows :



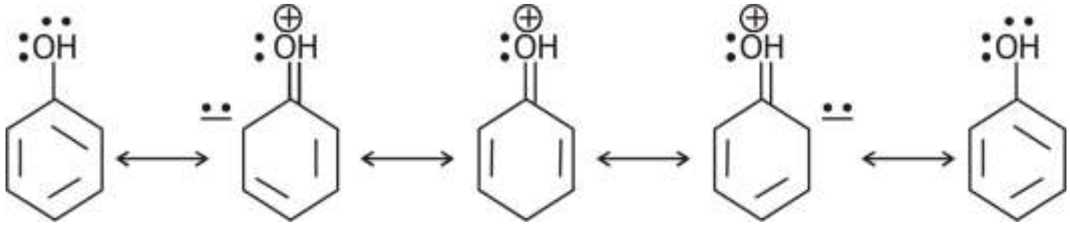
In p-nitrophenol, there is intramolecular hydrogen bonding as follows :



Due to intermolecular H bonding in p-nitrophenol, its b. p. is much higher than that of o-nitrophenol. Hence o-nitraphenol due to its lower b. p. is steam volatile while p-nitrophenol is not.

Q. 9. How an — OH group attached to carbon in the benzene ring activates benzene towards electrophilic substitution ?

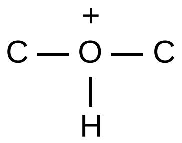
Ans.



The lone pair of electrons present on oxygen atom enter into resonance with the benzene ring. As a result, the electron density becomes higher at o- and p- position and due to higher electron density, the ring gets activated towards electrophilic substitution.

Q. 10. Ethers are cleaved by acids not by based. Why ?

Ans. The C — O — C bond in ethers like the C — OH bond in alcohols is quite strong. In order to weaken it, the oxygen atom must be protonated. A subsequent nucleophile attack by a strong nucleophile such as Br^- as I^- ion on the less hindered carbon atom of the protonated :



$$C - \overset{+}{\underset{\displaystyle H}{\underset{|}{O}}} - C$$

bond brings about the cleavage of ethers to form an alcohol and an alkyl halide. The acids only can provide the H^+ ion required for protonation of O atom of ether and therefore only acids can bring about the cleavage of ethers and not bases.

Q. 11. Phenols do not undergo substitution of the — OH group like alcohols. Explain.

Ans. The C — O bond in phenols has some double bond character due to resonance and hence cannot be easily cleaved by a nucleophile. In contrast, the C — O bond in alcohols is a pure single bond and hence can be easily cleaved by a nucleo phile.

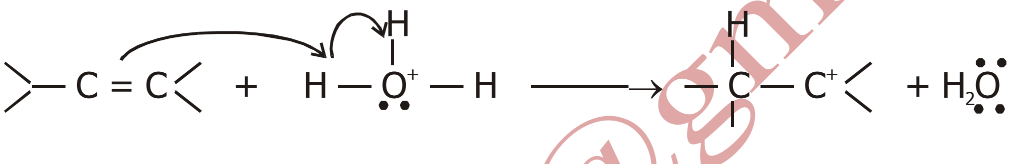
Q. 12. Alcohols acts as weak bases. Explain.

Ans. The oxygen atom of the hydroxyl group has two lone pairs of electrons. Therefore alcohols accept a proton from strong mineral acid to form oxonium ions. Hence act as weak bases.

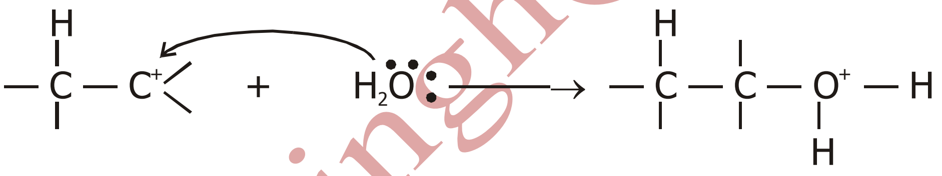
Q. 13. Write the mechanism of hydration of ethene to yield ethanol.

Ans. $H_2O + H^+ \longrightarrow H_3O^+$

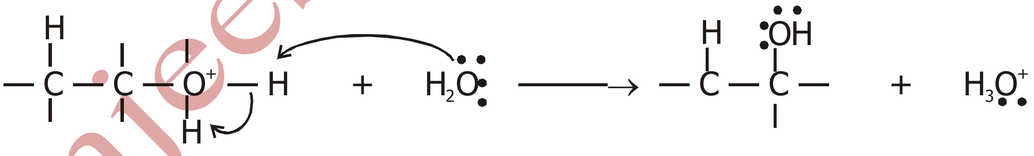
Step (i) : — Protonation of alkene to form carbocation by electrophilic attack :



Step (ii) : — Nucleophilic attack of water on carbocation :



Step (iii) : — Deprotonation to form an alcohol :



❑❑❑

UNIT—12

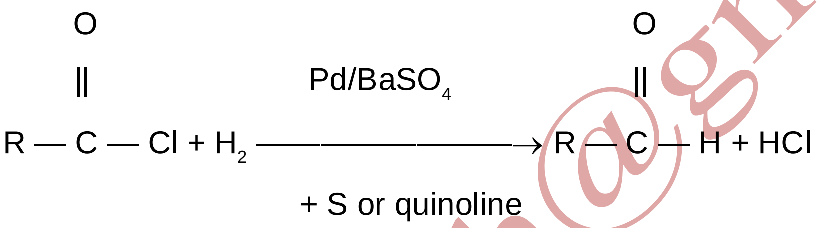
ALDEHYDES, KETONES AND CARBXYLIC ACID

1 MARK QUESTIONS

Q. 1. Name the reaction and the reagent used for the conversion of acid chlorides to the corresponding aldehydes.

Ans. Name : Rosenmund's reaction

Reagent : H_2 in the presence of Pd (supported over $BaSO_4$) and partially poisoned by addition of Sulphur or quinoline.



$$R-\overset{\overset{O}{||}}{C}-Cl + H_2 \xrightarrow[+\text{ S or quinoline}]{Pd/BaSO_4} R-\overset{\overset{O}{||}}{C}-H + HCl$$

Q. 2. Suggest a reason for the large difference in the boiling points of butanol and butanal, although they have same solubility in water.

Ans. The b. pt. of butanol is higher than that of butanal because butanol has strong intermolecular H-bonding while butanal has weak dipole-dipole interaction. However both of them form H-bonds with water and hence are soluble.

Q. 3. What type of aldehydes undergo Cannizaro reaction ?

Ans. Aromatic and aliphatic aldehydes which do not contain α hydrogens.

Q. 4. Out of acetophenone and benzophenone, which gives iodoform test ? Write the reaction involved.

(The compound should have CH_3CO-group to show the iodoform test.)

Ans. Acetophenone ($C_6H_5COCH_3$) contains the grouping (CH_3CO attached to carbon) and hence given iodoform test while benzophenone does not contain this group and hence does not give iodoform test.

$$C_6H_5COCH_3 + 3\,I_2 + 4\,NaOH \longrightarrow CHI_3 + C_6H_5COONa + 3\,NaI + 3\,H_2O$$

Acetophenane Iodoform

$$C_6H_5COC_6H_5 \xrightarrow{I_2/NaOH} \text{No reaction}$$

Q. 5. Give Fehling solution test for identification of aldehyde gp (only equations). Name the aldehyde which does not give Fehling's soln. test.

Ans. $R — CHO — 2\,Cu^{2+} + 50\,H^{-} \longrightarrow RCOO^{-} + Cu_2O \downarrow 3\,H_2O$

Benzaldehyde does not give Fehling soln. test.

(Aromatic aldehydes do not give this test.)

Q. 6. What makes acetic acid a stronger acid than phenol ?

Ans. Greater resonance stabilization of acetate ion over phenoxide ion.

Q. 7. Why HCOOH does not give HVZ (Hell Volhand Zelinsky) reaction but CH_3COOH does ?

Ans. CH_3COOH contains α hydrogens and hence give HVZ reaction but HCOOH does not contain α-hydrogen and hence does not give HVZ reaction.

Q. 8. During preparation of esters from a carboxylic acid and an alcohol in the presence of an acid catalyst, water or the ester formed should be removed as soon as it is formed.

Ans. The formation of esters from a carboxylic acid and an alcohol in the presence of acid catalyst in a reversible reaction.

$$RCOOH + R'OH \overset{H_2SO_4}{\rightleftharpoons} RCOOR' + H_2O$$

Carboxylic acid alcohol Ester

To shift the equilibrium in the forward direction, the water or ester formed should be removed as fast as it is formed.

Q. 9. Arrange the following compounds in increasing order of their acid strength.

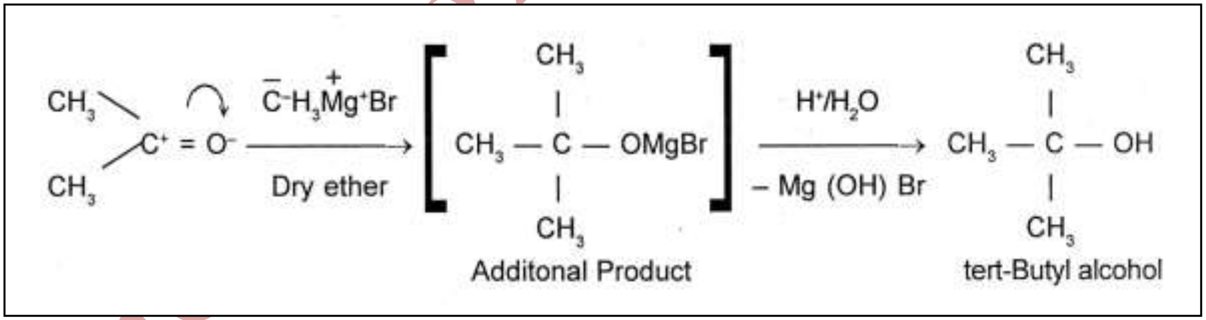
Benzoic acid, 4-Nitrobenzoic acid, 3, 4-dinitrobenzoic acid, 4-methoxy benzoic acid.

Ans. Since electron donating gps. decrease the acid strength therefore 4-methoxybenzoic acid is a weaker acid because methoxy sp. is E. D. G. than benzoic acid. Further since electron withdrawing gps. increase the acid strength, therefore both 4 nitrobenzoic acid and 3, 4-dinitrobenzoic acids are stronger acid than benzoic acid. Further due to the presence of additional NO_2 gp at m-position wrt COOH gt, 3, 4-dinitrobenzoic acid is a lattice stronger acid than 4-nitrobenzoic acid. Thus the increasing order of acid strength will be :

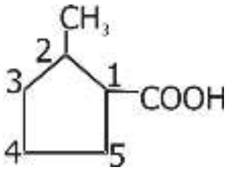
4-methoxybenzoic acid < benzoic acid < 4-nitrobenzoic acid < 3, 4, dinitrobenzoic acid.

Q. 10. How is tert-butyl alcohol obtained from acetone ?

Ans.



Q. 11. Give IUPAC name of the following compound :



Ans. 2-methylcyclopent-3-ene-1-oic acid

Q. 12. How will you distinguish between methanol and ethanol ?

Ans. By Iodoform test :

Ethanol having α-methyl gp will give yellow ppt. of iodoform whereas methanol does not have α-methyl gp will not give ppt. of iodoform.

Q. 13. Distinguish between :

(i) Acetaldehyde and acetone

(ii) Methanoic acid and Ethanoic acid.

Ans. (i) Acetaldehyde will give positive tests with Tollen's reagent and Fehling Solns. whereas acetone will not give these test.

(ii) Methanoic acid gives Tollen's reagent test whereas ethanoic acid does not due to difference in their boiling points.

Q. 14. Why are aldehydes more reactive than ketones ?

Ans. It is because of 2 reasons :

The carboxyl compounds (both aldehydes & ketones) undergo nucleophilic addition reaction.

(i) + I effect : The alkyl group in ketones due to their e^- releasing character decrease the electrophilicity / + ve charge on c-atom and thus reduce its reactivity.

(ii) Steric hindrance : Due to steric hindrance in ketones, they are less reactive.

Q. 15. Give the composition of Fehling A and Fehling B ?

Ans. Fehling A = aq. $CuSO_4$

Fehling B = alkaline sodium potassium tartarate

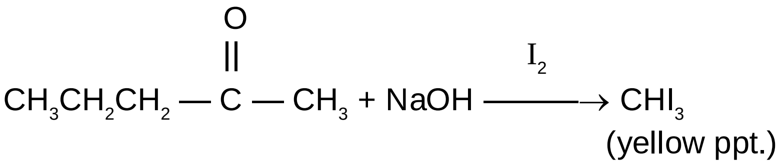
(Rochelle Salt)

Q. 16. Name one reagent which can distiguish between 2-pentanone and 3-pentanone ?

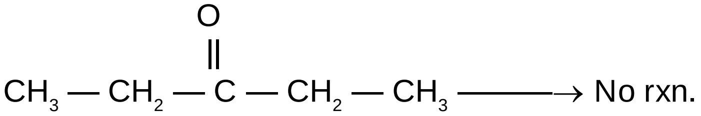
Ans. 2-pentanone has a CH_3CO-group, hence gives positive iodoform test.

3-pentanone does not have a CH_3CO-group, hence does not give positive iodoform test.

Iodoform test $\longrightarrow$ $I_2/NaOH$



$$CH_3CH_2CH_2-\overset{\overset{O}{||}}{C}-CH_3 + NaOH \xrightarrow{I_2} \underset{\text{(yellow ppt.)}}{CHI_3}$$



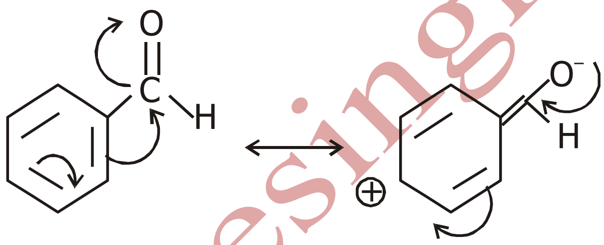
$$CH_3-CH_2-\overset{\overset{O}{||}}{C}-CH_2-CH_3 \longrightarrow \text{No rxn.}$$

Q. 17. Why pcc cannot oxidise methanol to methane and while $KMnO_4$ can ?

Ans. This is because pcc is a mild oxidising agent and can oxide methanol to methanal only. While $KMnO_4$ being strong oxidising agent oxidises it to methanoic acid.

Q. 18. Would you expect benzaldehyde to be more reactive or less reactive in nucleophlic addition reaction than propanal ? Explain.

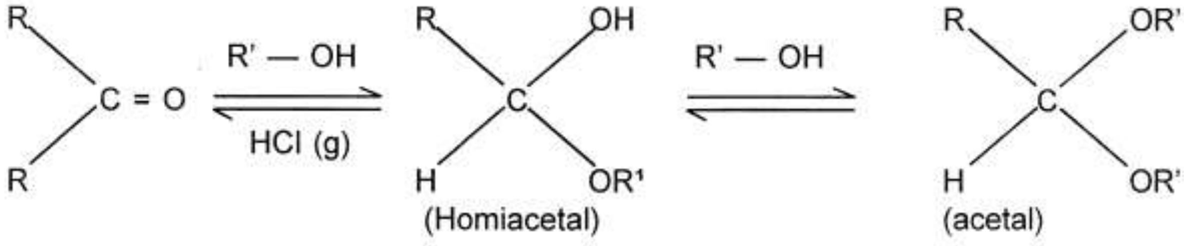
Ans. C-atom of carbonyl group of benzaldehyde is less electrophilic than C-atom of carbonyl group in propanal. Polarity of carbonyl group is in benzaldehyde reduced due to resonance making it less reactive in nucleophilic addition reactions.



There is no such resonance effect in propanal and so the polarity of carboxyl group in it is more than in benzaldehyde. This makes propanal more reactive than benzaldehyde.

Q. 19. What are Hemiacetal and acetal ?

Ans. Hemiacetal and acetals are formed by addition of alcohols on carboxyl compounds.



Q. 20. Why does methanal not give aldol condensation while ethanol gives ?

Ans. This is because only those compounds which have α hydrogen atoms can undergo aldol reaction. Ethanol possesses α-hydrogen and $\therefore$ undergoes aldol condensation. Methanal has no α hydrogen atoms, hence does not undergo aldol condensation.

Q. 21. Why does methanal undergoes Cannizaro's rxn ?

Ans. Because it does not possesses α hydrogen atom. Only those aldehydes can undergo Cannizaro reaction which do not possess α hydrogen atoms.

Q. 22. Arrange the following in order of increasing boiling points :

$CH_3CH_2CH_2OH$, $CH_3CH_2CH_2CH_3$, $CH_3CH_2 — OCH_2CH_3$, $CH_3CH_2CH_2CHO$

Ans. $CH_3CH_2CH_2CH_3 < C_2H_5OC_2H_5 < CH_3CH_2CH_2CHO < CH_3\ (CH_2)_2\ OH$

(hydrogen) (ether) (aldehyde) (alcohol)

$\xrightarrow{\hspace{8cm}}$

increase in bond polarity.

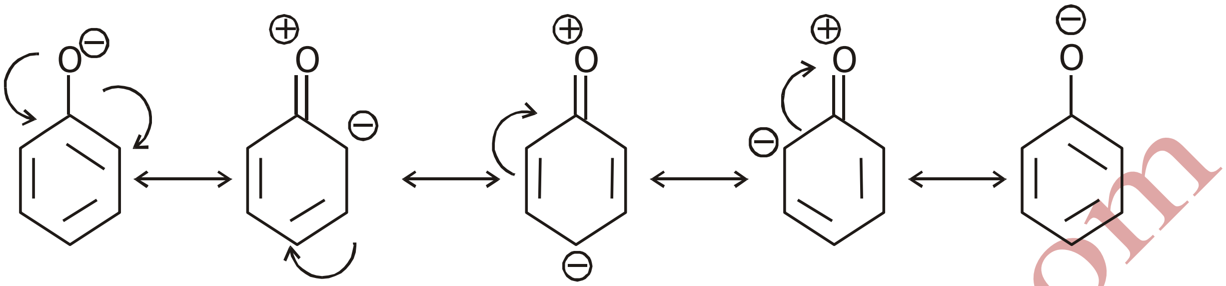
Q. 23. Why does solubility decreases with increasing molecular mass in carboxylic acid ?

Ans. Because of increase in alkyl chain length which is hydrophobic in nature.

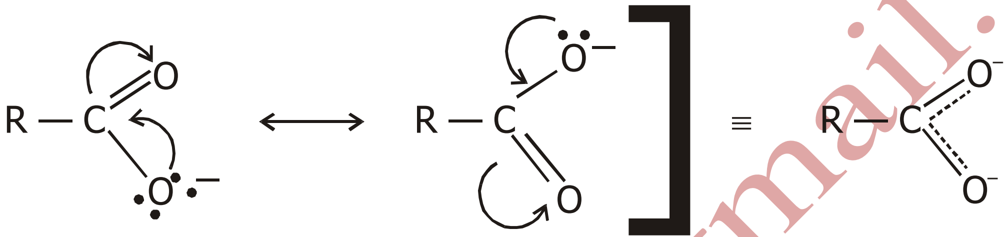
Q. 24. Although phenoxide ion has more no. of resonating structures than carboxylate ion, carboxylic acid is a stronger acid. Why ?

Ans. Conjugate base of phenol $\longrightarrow$ phenoxide ion has non equivalent resonance structures in which –ve charge is at less electronegative C-atom and +ve charge is at more electronegative O-atom.

$\therefore$ Resonance is not so effective.

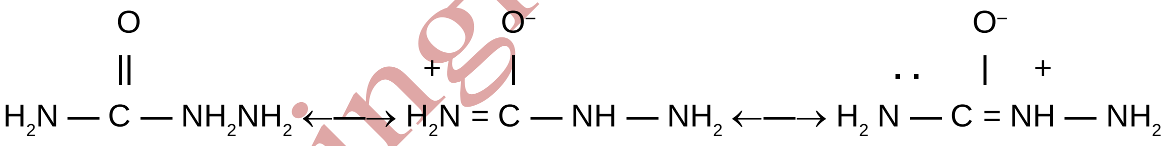


In carboxylate ion, – ve charge is delocalised on two electronegative O-atoms hence resonance is more effective.



Q. 25. There are two — NH_2 group in semicarbazide. However, only one is involved in formation of semicarbazones. Why ?

Ans. Although semicarbazide has two — NH_2 groups but one of them is involved in resonance.



$$H_2N - \overset{O}{\overset{\|}{C}} - NH_2NH_2 \longleftrightarrow H_2\overset{+}{N} = \overset{O^-}{\overset{|}{C}} - NH - NH_2 \longleftrightarrow H_2\,\ddot{N} - \overset{O^-}{\overset{|}{C}} = \overset{+}{N}H - NH_2$$

As a result, e^- density on one of the — NH_2 group is reduced and hence it does not act as nucleophile.

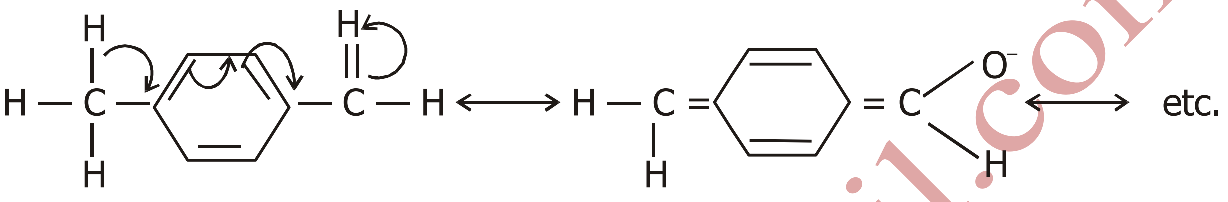
∴ Lone pair of other — NH_2 group is not involved in resonance and is available for nucleophilic attack.

2 MARKS QUESTIONS

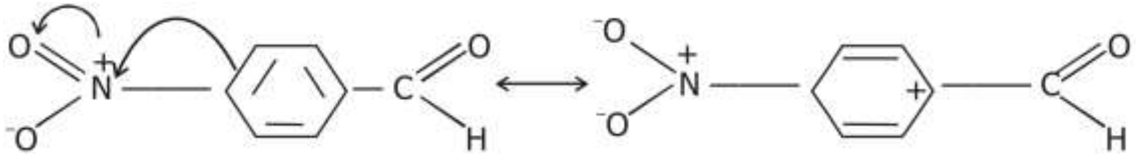
Q. 1. Arrange the following carboxyl compounds in increasing order of their reactivity in nucleophilic addition reactions. Explain with proper reasoning :

Benzaldehyde. p-tolualdeyde, p-nitrobenzaldehyde, Acetophenone.

Ans. Acetophenone is a ketone while all others are aldehydes, therefore it is least reactive. In p-tolualdehyde, there is methyl group (CH_3) at para position w.r.t. to the carboxyl gp, which increases electron density on the carbon of the carboxyl gp by hyperconjugation effect thereby making it less reactive than benzaldehyde.



On the other hand, in p-nitrobenzaldehyde, the NO_2 gp is a powerfuil electron-withdrawing gp. It withdraws electrons both by inductive and resonance effect thereby decreasing the electron density on the carbon atom of carboxyl gp. This facilitates the attack of the nucleophile and hence makes it more reactive than benzaldehyde.



Therefore, the overall order of increasing reactivity :

acetophenone < p-tolualdehyde < benzaldehyde < p-nitrobenzaldehyde.

Q. 2. Arrange the following compounds in increasing order of their boiling points. Explain by giving reasons.

CH_3CHO, CH_3CH_2OH, CH_3OCH_3, $CH_3CH_2CH_3$.

Ans. The molecular masses of all these compounds are comparable :

CH_3CHO (44), CH_3CH_2OH (46), CH_3COCH_3 (46), $CH_3CH_2CH_3$ (44).

CH_3CH_2OH exists as associated molecule due to extensive intermolecular hydrogen bonding and hence its boiling point is the highest (351 K). Since dipole-dipole interaction are stronger in CH_3CHO than in CH_3OCH_3, hence boiling point of CH_3CHO (293 K) is much higher than that of CH_3OCH_3 (249 K). Further, molecules of $CH_3CH_2CH_3$

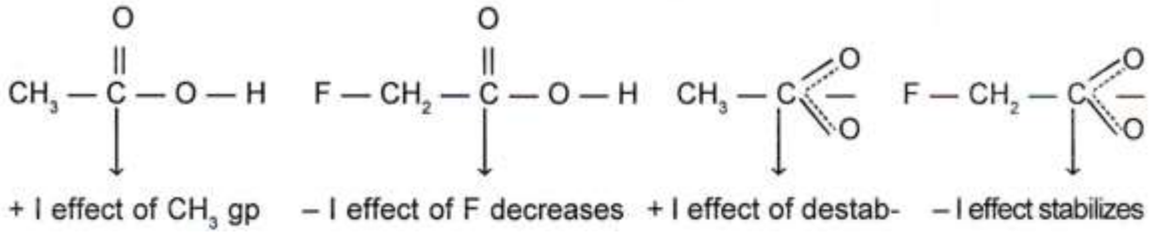
have only weak Vander Waals forces while the molecules of CH_3OCH_3 have little stronger dipole-dipole interactions and hence the boiling point of CH_3OCH_3 is higher (249 K) than that of $CH_3CH_2CH_3$ (231 K). Thus the over all increasing order of boiling points is :

$$CH_3CH_2CH_3 < CH_3OCH_3 < CH_3CHO < CH_3CH_2OH$$

Q. 3. Which acid of each pair shown here would you expect to be stronger ?

CH_3CO_2H or FCH_2CO_2H

Ans.



increases the electron density in the O — H bond thereby making the relase of a proton difficult.

the electron density in the O — H bond thereby making the release of a proton easier.

lizes the carboxylate ion by intensifying the – ve charge.

the carboxyate ion by dispersing the – ve charge.

Thus due to lesser electron density in the O — H bond and greater stability of FCH_2COO^- ion over CH_3COO^- ion FCH_2COOH is a stronger acid than CH_3COOH.

Q. 4. Which acid is stronger and why ?

F_3C —  **— COOH or $H_3C \rightarrow$**  **— COOH**

Ans. F_3C — — C $CH_3 \rightarrow$ — C

CF_3 has a strong – I effect. CH_3 has a weak + I effect.

It stabilises the carboxylate ion It stabilises the carboxylate ion

by dispersing the – ve charge. by intensifying the – ve charge.

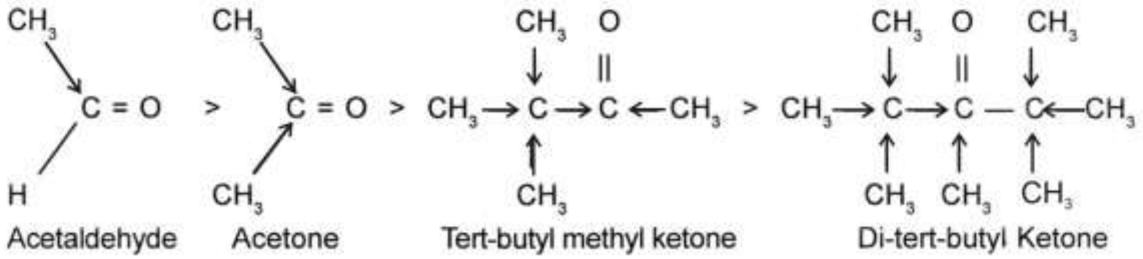
Therefore due to greater stability of $F_3C — C_6H_4 — COO^-$ (p) ion over $CH_3 — C_6H_4COO^-$ (p) ion, $F_3C — C_6H_4 — COOH$ is a much stronger acid than $CH_3 — C_6H_4 — COOH$.

Q. 5. Arrange the following compounds in increasing order of their reactivity towards HCN. Explain it with proper reasoning.

Acetaldehyde, Acetone, Di-tert-butyl ketone, Methyl tert-butyl ketone.

Ans. Addition of HCN to the carboxyl compounds is a nucleophilic addition reaction.

The reactivity towards HCN addition decreases as the + I effect of the alkyl gp/s increases and/or the steric hindrance to the nucleophilic attack by CN^- at the carboxyl carbon increases. Thus the reactivity decreases in the order.



——————— + I effect increases——————→

——————— Steric hindrance increases——————→

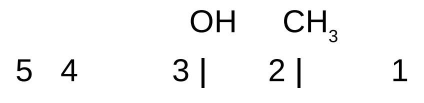
——————— Reactivity towards HCN addition decreases ——————→

In other words, reactivity increases in the reverse order, i. e.,

Ditert-butyl Ketone < tert-Butyl methyl Ketone < Acetone < Acetaldehyde

Q. 6. Write structural formulae and names of four possible aldol condensation products from propanal and butanal. In each case, indicate which aldehyde acts as nucleophile and which as electrophile.

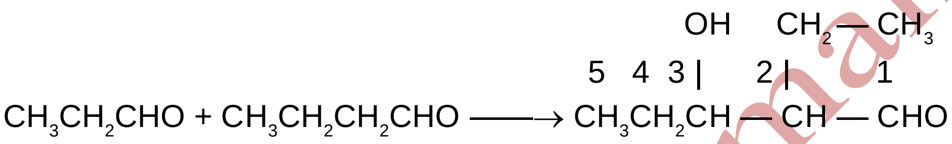
Ans. (i) Propanal as nucleophile as well as elecrophile.



$$CH_3CH_2CHO + CH_3CH_2CHO \longrightarrow \overset{5\quad 4}{CH_3CH_2} - \overset{\overset{OH}{3\,|}}{CH} - \overset{\overset{CH_3}{2\,|}}{CH} - \overset{1}{CHO}$$

Propanal Propanal 3-hydroxy-2-methyl pentanal

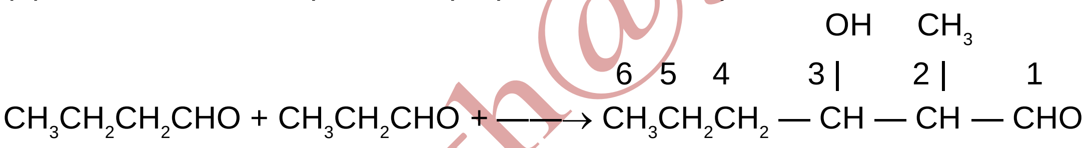
(ii) Propanal as electrophile and butanal as nucleophile.



$$CH_3CH_2CHO + CH_3CH_2CH_2CHO \longrightarrow \overset{5\quad 4}{CH_3CH_2}\overset{\overset{OH}{3\,|}}{CH} - \overset{\overset{CH_2-CH_3}{2\,|}}{CH} - \overset{1}{CHO}$$

Propanal (Electrophile) Butanal (Nucleophile) 2-ethyl-3-hydroxy pentanal

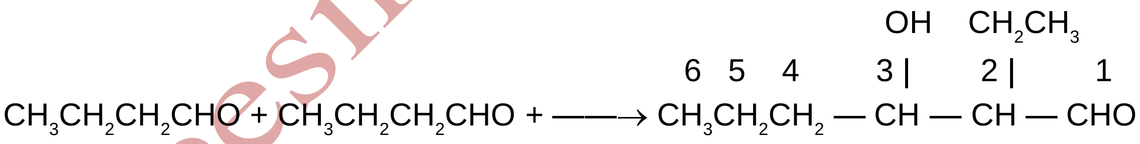
(iii) Butanal as electrophile and propanal as nucleophile.



$$CH_3CH_2CH_2CHO + CH_3CH_2CHO + \longrightarrow \overset{6\quad 5\quad 4}{CH_3CH_2CH_2} - \overset{\overset{OH}{3\,|}}{CH} - \overset{\overset{CH_3}{2\,|}}{CH} - \overset{1}{CHO}$$

Butanal (Electrophile) Propanal (Nucleophile) 3-hydroxy-2-methyl pentanal

(iv) Butanal both as nucleophile as well as an elecrophile.



$$CH_3CH_2CH_2CHO + CH_3CH_2CH_2CHO + \longrightarrow \overset{6\quad 5\quad 4}{CH_3CH_2CH_2} - \overset{\overset{OH}{3\,|}}{CH} - \overset{\overset{CH_2CH_3}{2\,|}}{CH} - \overset{1}{CHO}$$

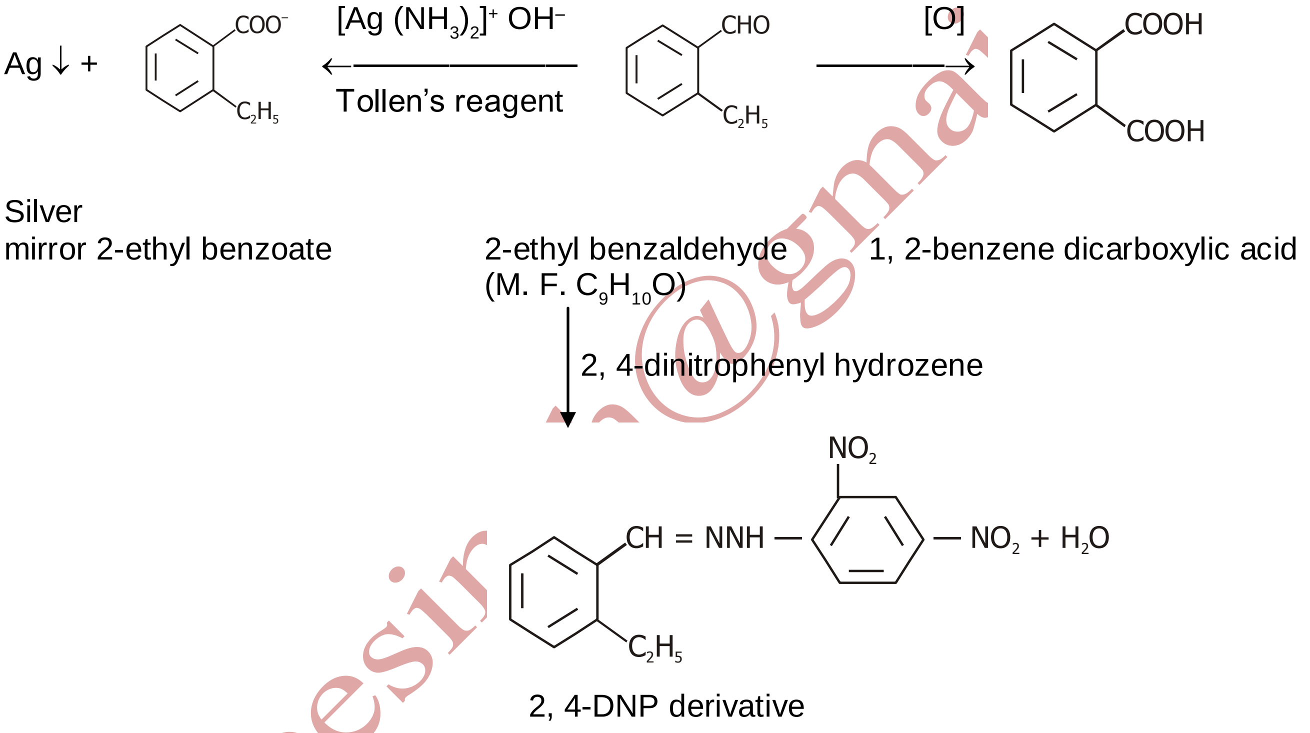
Butanal (Electrophile) Butanal (Nucleophile) 2-ethyl-3-hydroxy hexanal

Q. 7. An organic compound with the molecular formula $C_9H_{10}O$ forms 2, 4-DNP derivative, reduces Tollen's reagent and undergoes Cannizaro reaction. On vigorous oxidation, it gives 1, 2-benzenedicarboxylic acid. Identify the compound.

Ans. (i) Since the given compound with M. F. $C_9H_{10}O$ forms a 2, 4-DNP derivative and reduces Tollen's reagent, it must be an aldehyde.

(ii) Since it undergoes Cannizaro reaction, therefore CHO gp. is directly attached to the benzene ring.

(iii) Since on vigorous oxidation, it gives 1, 2-benzene dicarboxylic acid, therefore it must be an ortho substituted benzaldehyde. The only o-substituted aromatic aldehyde having M. F. $C_9H_{10}O$ is 2-ethyl benzaldehyde. All the reactions can now be explained on the basis of this structure.

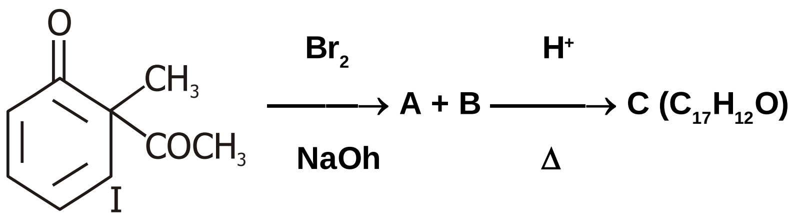


Q. 8. Explain why o-hydroxybenzaldehyde is a liquid at room temperature while p-hydroxybenzaldehyde is a high melting solid.

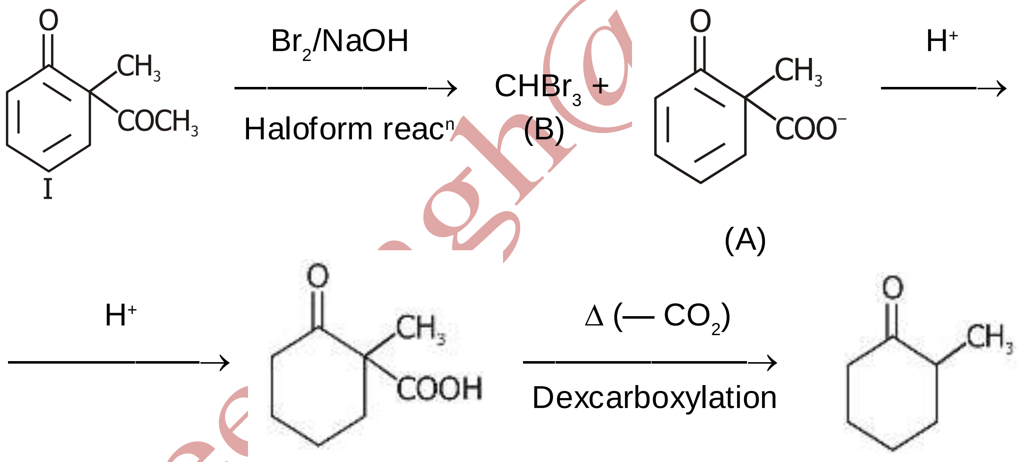
Ans. Due to interamolecular H-bonding ortho-hydroxy benzaldehyde exists as discrete molecule whereas due to intermolecular H-bonding, p-hydroxybenzaldehyde exists as associated molecules. To break these intermolecular H-bonds, a large amount of energy is needed. Consequently, p-hydroxybenzaldehyde has a much higher m. pt. and

b. pt. than that of o-hydroxy benzaldehyde. As a result, o-hydroxy benzaldehyde is a liquid at room temperature while p-hydroxy benzaldehyde is a high melting solid.

Q. 9. Identify A, B and C and give their structures :



Ans. The given compound (I) contains CH_3CO gp and hence in the presence of Br_2/NaOH undergoes haloform reaction to give sodium salt of carboxylic acid (A) and bromoform $CHBR_3$ (B). (A) on protonation gives the corresponding acid (II). (II) being a β-ketoacid readily undergoes decarboxylation to give 2-methylcylohexanane (C).



(A β-keto acid)

2-methyl cyclo hexanone
(C) M. F. = $C_7H_{12}O$

❑❑❑

UNIT—13

ORGANIC COMPOUNDS CONTAINING NITROGEN

1 MARK QUESTIONS

Q. 1. Why the presence of a base is essential in the ammonolysis of alkyl halides ?

Ans. During ammonolysis of alkyl halides, the acid liberated during the reaction combines with the amine formed to form amine salt. To liberate free amine from the amine salt, a base is needed.

Q. 2. Although — NH_2 gp is an ortho and para directing gp, nitration of aniline gives along with ortho and para, meta derivatives also.

Ans. Nitration is carried out with a mixture of Conc. NO_3 + Conc. H_2SO_4 (nitrating mix). In the presence of these acids, most of aniline gets protonated to form anilinium ion. Therefore, in the presence of acids, the reaction mixture consists of aniline and anilinium ion. Now $-NH_2$ gp in aniline is O, p-directing and activating while $-N^+H_3$ gp in anilinium ion is m-directing and deactivating hence a mixture of all three–ortho, para and meta derivatives is formed.

Q. 3. Pk_b of aniline is more than that of methyl amine.

Ans. In aniline, the lone pair of electrons on the N-atom are delocalized over the benzene ring. As a result electron density on the nitrogen decreases. In contrast in CH_2NH_2, + I effect of CH_3 increase the electron density on the N-atom. Therefore, aniline is a weaker base than methylamine and hence its Pk_b value is higher than that of methylamine.

Q. 4. Aniline gets coloured on standing in air for a long time. Why ?

Ans. Due to strong electron-donating effect (+ R effect) of NH_2 gp, the electron density on the benzene ring increases. As a result, aniline is easily oxidised on standing in air for a long time to form coloured products.

Q. 5. CH_3CONH_2 is a weaker base than $CH_3CH_2NH_2$.

Ans. Due to resonance, the lone pair of electrons on the nitrogen atom in CH_3CONH_2 is delocalised over the keto gp. There is no such effect in $CH_3CH_2NH_2$. Due to reduction in electron density on N of CH_3CONH_2, it is a weaker base than $CH_3CH_2NH_2$.

Q. 6. Aromatic primary aminies can't be prepared by Gabriel phthalimide synthesis.

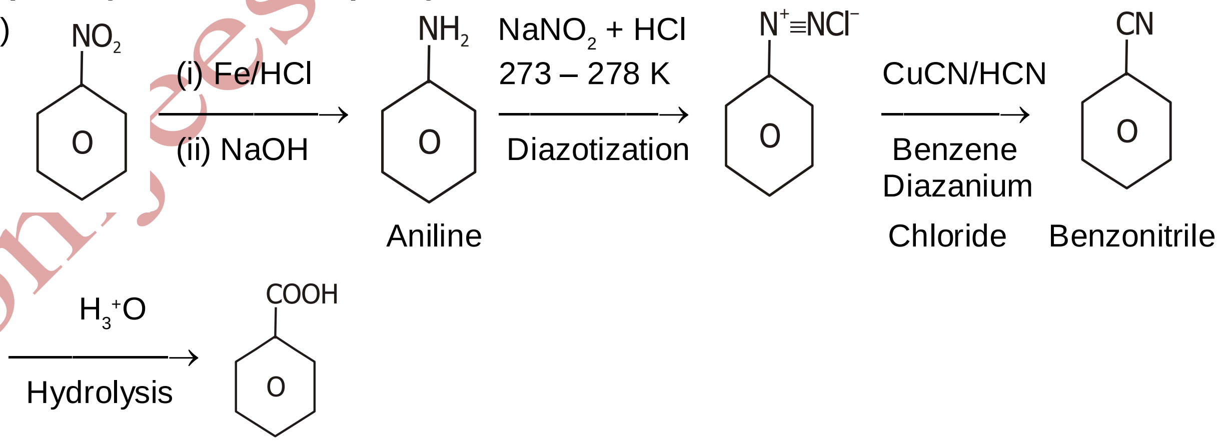
Ans. The preparation of aromatic primary amines (Aniline) by Gabriel phthalimide reaction requires the treatment of pot. phthalimide with C_6H_5Cl or C_6H_5Br, which is a nucleophilic substitution Rx^n. Since aryl halides do not undergo nucleophilic substitution under ordinary laboratory conditions, therefore C_6H_5Cl or C_6H_5Br does not react with pot. phthalimide to give N-phenyl. Phthalimide and hence aromatic primary amines can't be prepared by this method.

Q. 7. Accomplish the following conversions :

(i) Nitrobenzene to benzoic acid

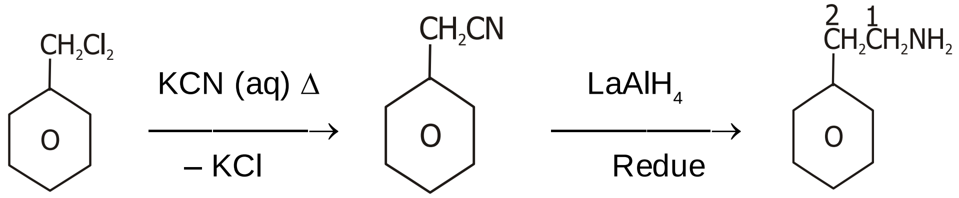
(ii) Benzyl Chloride to 2-phenylethanamine

Ans. (i)



Benzoic acid

(ii)



Benzyl Chloride Phenyl ethanenitrite 2-phenylethanamine

Q. 8. Give the structures of A, B and C in the following compounds :

(i) $\mathbf{CH_3CH_2I \xrightarrow{NaCN} A \xrightarrow[\text{Partial Hydrolysis}]{OH^-} B \xrightarrow{NaOH + Br_2} C}$

(ii) $\mathbf{CH_3COOH \xrightarrow[D]{NH_3} A \xrightarrow{NaOBr} B \xrightarrow{NaNO_2/HCl} C}$

Ans.

(i) $CH_3CH_2I \xrightarrow{NaCN} \underset{\text{Propanenitrile (A)}}{CH_3CH_2CN} \xrightarrow[\text{(Partial Hydrolysis)}]{OH^-} \underset{\text{Ethanamide (B)}}{CH_3 — \overset{\overset{O}{\|}}{C} — NH_2}$

$\xrightarrow[\text{Hofmann bromamide reac}^n]{NaOH + Br_2} \underset{\text{Methanamine (C)}}{CH_3 — NH_2}$

(ii) $\underset{\text{Ethanoic acid}}{CH_3COOH} \xrightarrow[D]{NH_3} \underset{\text{Ethanoimide (A)}}{CH_3CONH_2} \xrightarrow[\text{(Hofmann bromamide reac.)}]{NaOBr} \underset{\text{Methanamine (B)}}{CH_3NH_2} \xrightarrow{NaNO_2/HCl} CH_3OH$ ↓ Methanol (C)

Q. 9. Why is it difficult to prepare pure amines by ammonolysis of alkyl halides ?

Ans. By ammonolysis of alkyl halides, a mixture of primary, secondary and tertiary amines is formed. So it is difficult to separate it.

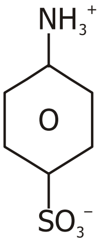
$NH_3 \xrightarrow{Rx} \underset{\text{1° amine}}{R — NH_2} \xrightarrow{Rx} \underset{\text{2° amine}}{R_2 — NH} \xrightarrow{Rx} \underset{\text{3° amine}}{R_3 — N} \xrightarrow{Rx} \underset{\text{Quaternary Salt}}{R_4\, N^+\, X^-}$

Q. 10. Can tertiary amines undergo acetylation reactions ? Explain.

Ans. For an amine to undergo acetylation, it should have a replaceable hydrogen atom**.** Tertiary amines cannot undergo acetylation reactions because these do not have replaceable hydrogen atom.

Q. 11. Sulphanilic acid has acidic as well as basic group; but it is soluble in alkali but insoluble in mineral acids. Explain.

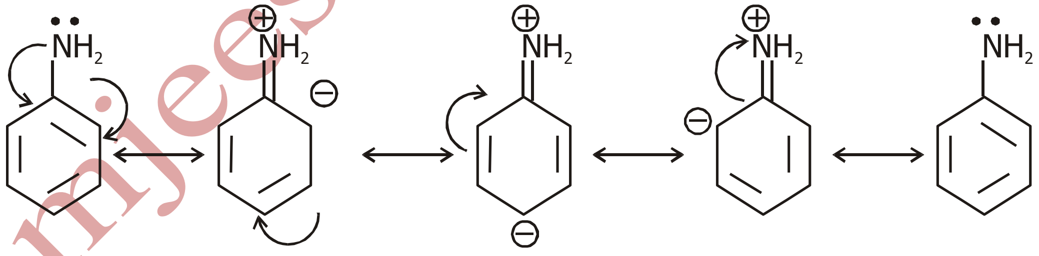
Ans. Sulphanilic acid exists as Zwitter ion as :



In the presence of dil. NaOH the weakly acidic — NH_3^+ group transfers its H^+ to OH^- to form soluble salt P — $NH_2C_6H_4SO_3^-Na^+$. On the other hand, — SO_3^+ group is a very weak base and does not accept H^+ from dil HCl to form $NH_3C_6H_4SO_3H$ and therefore, it does not dissolve in dil HCl.

Q. 12. Why are aliphatic amines more basic than aromatic amines ?

Ans. In Aromatic amines, due to resonance, N-atom acquries +ve charge and ∴ lone pair of N-atom is less available.



In aliphatic amines, due to e^- releasing nature of alkyl groups lone pair of e^- on N-atom is more available.

∴ More basic.

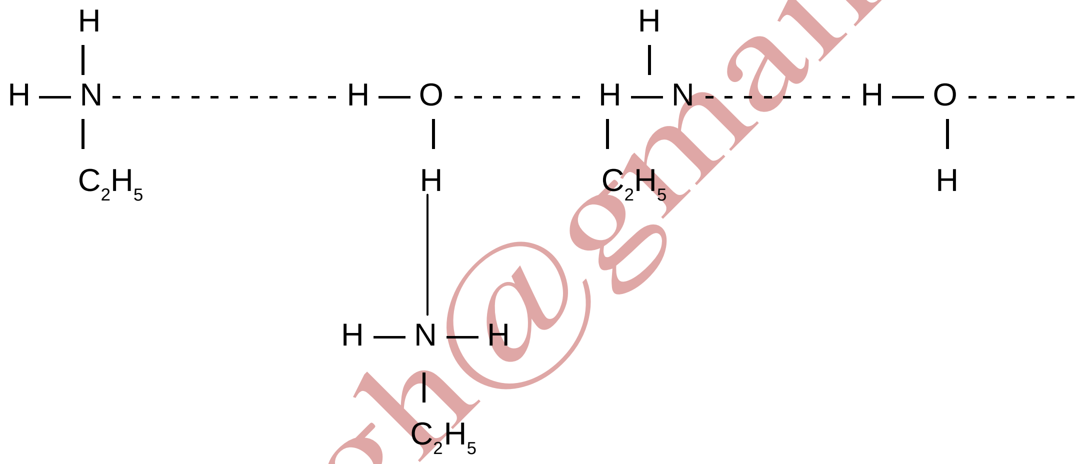
Q. 13. Explain why :

(i) Ethylamine is soluble in water but aniline is not.

(ii) Aniline does not undergo Friedel Crafts reaction.

(iii) Diazonium salts of aromatic amines are more stable than that of aliphatic amines.

Ans. (i) Ethyl amine dissolves in water due to formation of H-bonding with water molecules.



However in Aniline, due to larger hydrophobic alkyl part extent of H-bonding decreases considerably

∴ insoluble in water.

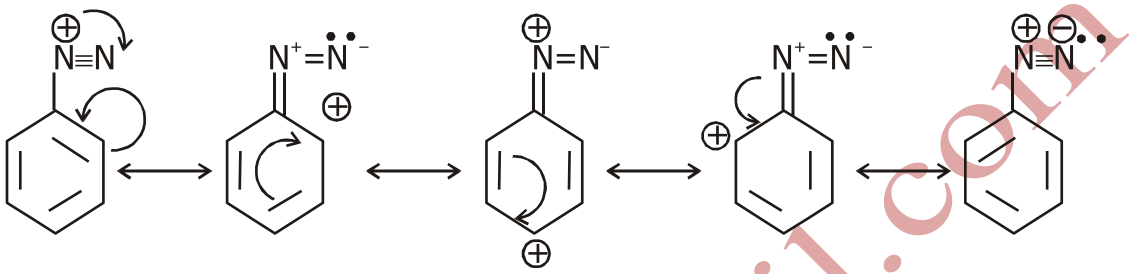
(ii) Aniline being a Lewis base reacts with Lewis acid $AlCl_3$ or $FeCl_3$ to form a salt.

$$C_6H_5NH_2 \quad + \quad AlCl_3 \longrightarrow C_6H_5NH_2^+AlCl_3^-$$

Lewis base Lewis acid

As a result, N-atom acquires + ve charge and hence acts as a strong deactivating group for electrophilic reaction.

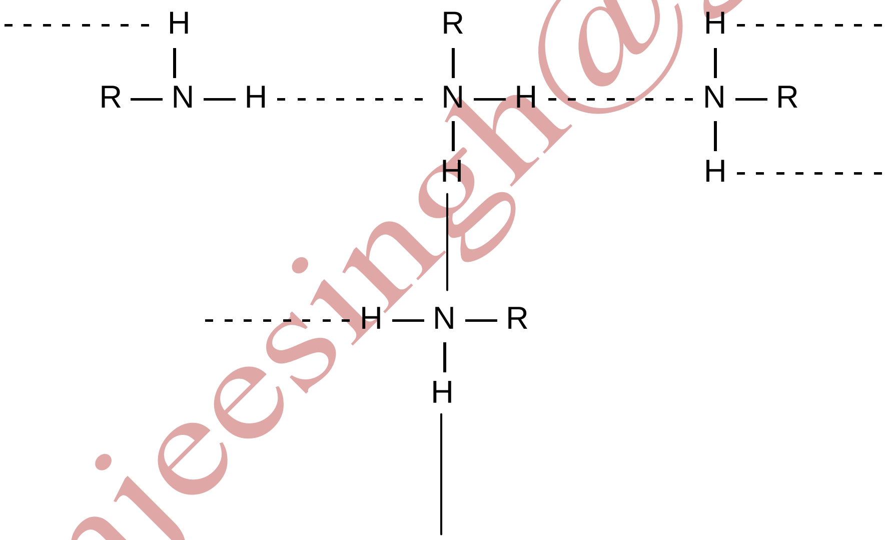
(iii) Diazonium salts of aromatic amines are more stable due to dispersal of +ve charge on benzene ring due to resonance.



In aliphatic amines, there is no such dispersal of + ve charge due to absence of resonance.

Q. 14. Why 1° amines have got higher boiling point than 3° amines ?

Ans. Due to presence of two H-atoms, in 1° amines they undergo extensive hydrogen bonding while due to absence of H-atom in 3° amines do not undergo H-bonding.



Due to extensive hydrogen bonding in 1° amines, they have higher boiling point – 7 than 3° amines.

Q. 15. How can you distinguish between 1° and 2° amine ?

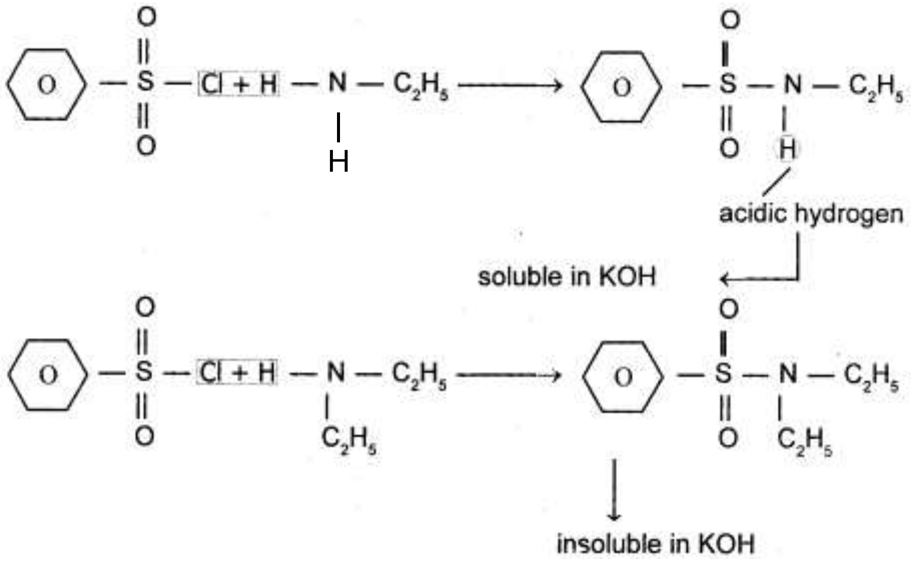
Ans. (i) Carbylamine test :

$$R - NH_2 + CHCl_3 + 3\,KOH \longrightarrow R - NC + 3\,KCl + H_2O$$

(pungent smelling)

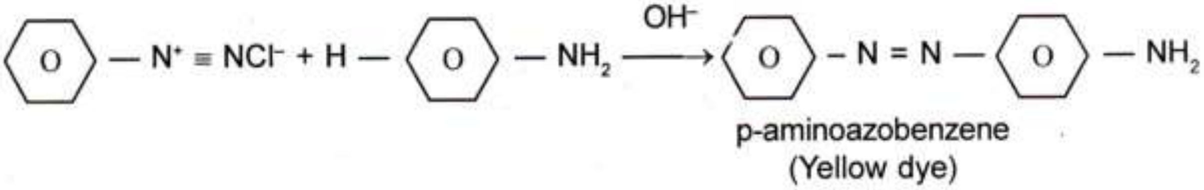
2° amines do not give this test.

(ii) Aryl sulphonyl chloride test :



Q. 16. How can you distinguish between aromatic and aliphatic amines ?

Ans. The diaronium salts of Aromatic amines undergo coupling reactions with phneol or andine to form coloured compounds used as dyes.



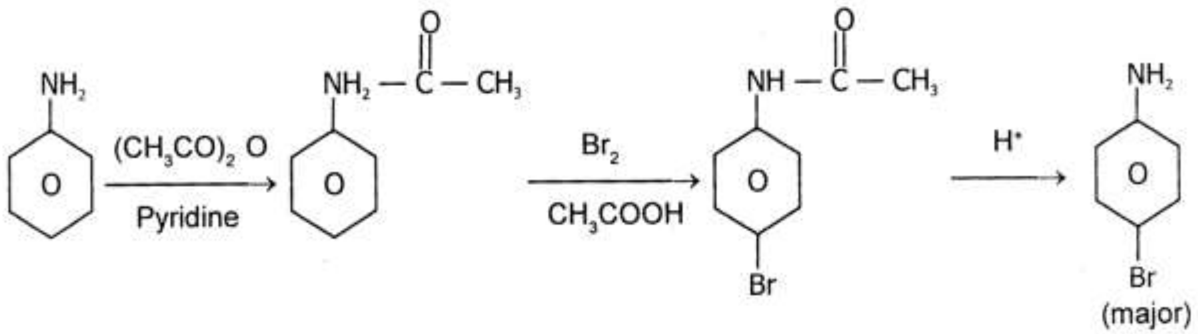
No such reactions are given by aliphatic amines.

Q. 17. How can tri substitution of Bromine be prevented in aniline ?

OR

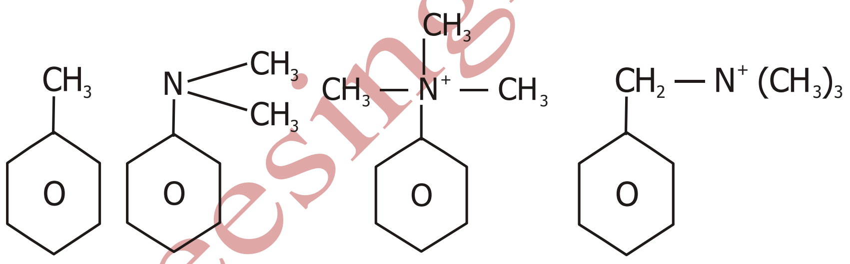
How can we prepare mono bromo aniline ?

Ans. Because of high reactivity of aromatic amines substitution tends to occur at o- and p-positions. Monosubstituted aniline can be prepared by protecting — NH_2 group by acetylation with acetic anhydride, then carrying out substitution followed by hydrolysis of substituted amide.

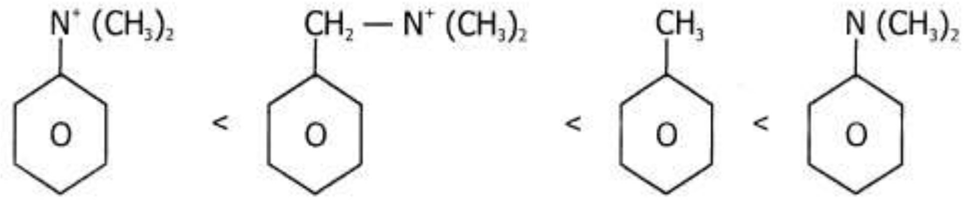


2 MARKS QUESTIONS

Q. 1. Give increasing order of reactivity towards electrophilic substitution reaction of the following compounds :

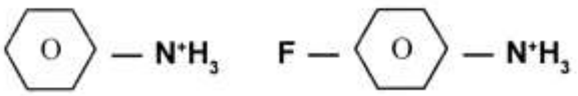


Ans. Higher the electron density in the benzene ring, more reactive is the aromatic compound towards electrophilic substitution reaction. Now due to the presence of a lone pair of electrons on the N-atom which it can directly donate to the benzene ring. N $(CH_3)_2$ (due to two alkyl groups on N) is a much stronger electron donating gp than CH_3 gp. (only one alkyl group on N). The remaining two gps contain a positive charge on the N-atom and hence act as electron withdrawing gps. But in $(CH_3)_3$ N^+ — gp, the +vely charged N is directly attached to the benzene ring, therefore, its electron withdrawing ability is much stronger than — $CH_2N^+ (CH_3)_2$. From the above, it follows that the electron density in the benzene ring increases in the order :

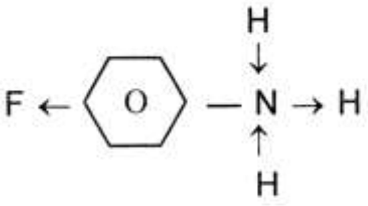


Therefore, their reactivity towards elecrophilic substitution reactions also increases in the same order.

Q. 2. Which one is more acidic ? Explain :



Ans. Due to powerful – I effect to the F-atom, it withdraws electrons from N^+H_2 gp. As a result, electron density in the N — H bond of p-fluoroanilinium ion decreases and hence release of a proton from p-fluoroanilinium ion is much more easier than from anilinium ion. Therefore, p-fluoroanilinium ion is more acidic than anilinium ion.



Q. 3. Explain the order of basicity of the following compounds in (i) Gaseous phase and (ii) inaqueous soln. :

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

Ans. Due to + I effect of alkyl gps, the electron density on the N-atom of 1°, 2° and 3° amines is higher than that on the N-atom in NH_3. Therefore, all amines are more basic than NH_3.

(i) In gaseous phase, solvation effects are absent and hence the relative basicity of amines depends only on + I effect of the alkyl gps. Now since + I effect increases in going from 1° to 2° to 3° amine, so the basicity of amines decreases in the order :

3° amine > 2° amine > 1° amine

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

(ii) In aq. soln, the basicity depends upon two factors :

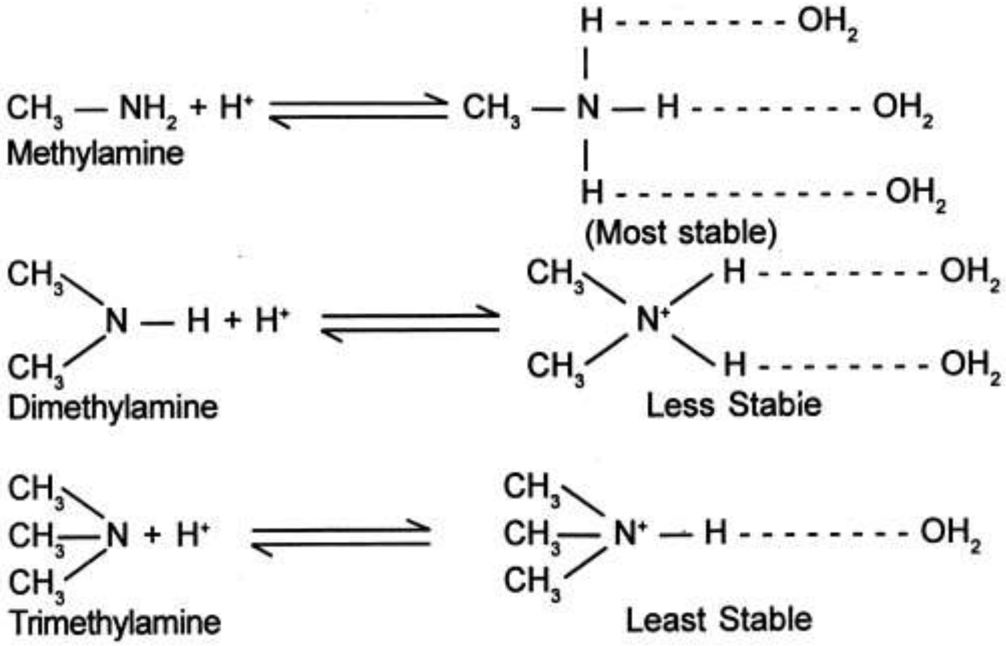
(a) + I effect of CH_3 gp and

(b) Solvation effect.

Stabilization of the conjugate acid (formed addition of a proton to amine) by H-bonding explained above on the basis of + I effect, the order will be :

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

On the basis of Stabilisation of conjugate acids by H-bonding alone as explained below :



The order will be :

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

The combined effect of these two opposing factors is that $(CH_3)_2$ NH is the strongest base. In case of CH_3NH_2 and $(CH_3)_3$ NH, the stability due to H-bonding predeminates over stability due to + I effect of CH_3 gp, thereby making CH_3NH_2 stronger than $(CH_3)_3$ NH. So the overall order in aq. soln will be :

$(CH_3)_2 NH > CH_3NH_2 > (CH_3)_3N > NH_3$

❑❑❑

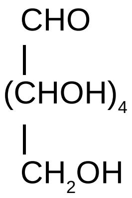
UNIT—14

BIOMOLECULES

1 MARK QUESTIONS

Q. 1. Which carbohydrate is called grape-sugar ? Give its condensed structural formula.

Ans. Glucose is called grape-sugar ? Its condensed structural formula is :



$$\begin{array}{l} CHO \\ | \\ (CHOH)_4 \\ | \\ CH_2OH \end{array}$$

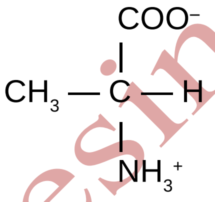
Q. 2. Which of the following is not an α-amino acid ?

Histidine, trypsin, cysteine, proline

Ans. Trypsin, it is a protein made from amino acids.

Q. 3. Write the structure of Zwitter ion formed from Alanine.

Ans.

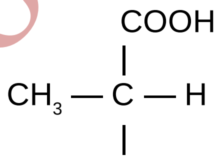


$$\begin{array}{ccccc} & & COO^- & & \\ & & | & & \\ CH_3 & - & C & - & H \\ & & | & & \\ & & NH_3^+ & & \end{array}$$

Q. 4. Wreite the name and structure of the simplest amino acid which can show optical activity.

Ans. Alanine,

Structure :



$$\begin{array}{ccccc} & & COOH & & \\ & & | & & \\ CH_3 & - & C & - & H \\ & & | & & \end{array}$$

NH_2

Q. 5. How many hydrogen bonds are present between (i) A and T (ii) C and G in a double helix structure ?

Ans. (i) between A and T there exist two hydrogen bonds :

A - - - - - - - - - - T
- - - - - - - - - -

(ii) between C and G there exist three hydrogen bonds :

- - - - - - - - - -
C - - - - - - - - - - G
- - - - - - - - - -

Q. 6. When RNA in hydrolysed there is no relationship among the quantities of four bases obtained like DNA. What does this fact indicate about structure of RNA ?

Ans. This indicate that RNA has a single strand structure.

Q. 7. Where does the water present in the egg go after boiling the egg ?

Ans. After boiling, the water soluble globular protein of egg while get denatured and it cogulates into hard and rubbery insoluble mass.

Q. 8. Which vitamin is helpful in healing wound and cuts ? What is the chemical name of this vitamin ?

Ans. Vitamin-C is helpful in healing wounds and cuts, its chemical name is Ascorbic acid.

2 MARKS QUESTIONS

Q. 1. What type of bonding helps in stabilising the α-helix structure of proteins ?

Ans. In a α-helix structure, polypeptide chain of amino acids coils as a right handed screw because of the formation of all possible Hydrogen bonds between — NH group at each amino residue and > C = 0 group of adjacent turn of helix.

Q. 2. Name the water insoluble fraction of Starch. Name the monomer of this.

Ans. Amylopectin is water insoluble fraction of starch. It is a polymer of α-glucose.

Q. 3. What are the products of hydrolysis of (i) lactose (ii) sucrose. Also name the enzyme used for reaction.

Ans. (i) $$\underset{\text{Lactose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Lactase}} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{glactose}}{C_6H_{12}O_6}$$

(ii) $$\underset{\text{Sucrose}}{C_{12}H_{22}O_{11}} + H_2O \xrightarrow{\text{Invertase}} \underset{\text{glucose}}{C_6H_{12}O_6} + \underset{\text{fructose}}{C_6H_{12}O_6}$$

Q. 4. How will you prove that all the carbon atoms of glucose are in straight chain ?

Ans. The reaction of glucose with HI gives n-hexane and it proves that all sin-carbon-atom are in straight chain.

$$\text{Ho } CH_2 — (CHOH)_4 — CHO \xrightarrow[\text{Heat}]{\text{HI}} \underset{\text{n-hexane}}{CH_3 — (CH_2)_4 — CH_3}$$

Q. 5. Enumerate two reactions of glucose which cannot be explained by its open chain structure.

Ans. (i) Glucose does not give Schiff's Test although it contains aldehyde group.

(ii) Glucose does not form crystaline product with $NaHSO_3$.

Q. 6. B-complex is an often prescribed Vitamin. What is complex about it ? What is its usefulness ?

Ans. It is a type of Vitamin which contains B_1, B_2, B_6 and B_{12}. It required to release energy from food and to promote healthy skin and muscles. Its deficiency causes beri-beri (Vitamin B_1) and Anaemia (Vitamin B_{12}).

Q. 7. What are anomers ? Give two points of difference between two anomer of glucose.

Ans. The pair of optical Isomers which differ in the orientation of H and OH gp only at C_1 Carbon atom are called anomers.

Difference between two anomers of glucose :

α-D (+) glucose	β-D (+) glucose
(1) The specific rotation is + 111°.	(1) The specific rotation is + 19.2°.
(2) The – OH gp at C_1 is below the plane.	(2) The – OH gp at C_{-1} is above the plane.

* * *

UNIT—15

POLYMERS

1 MARK QUESTIONS

Q. 1. Write an equation for the Chemistry involved when a drop of hydrochloric acid make a hole in nylon stockings.

Ans. The (— CO — NH —) amide bond in nylon gets hydrolysed.

Q. 2. Fibres are of crystalline structure. Why ?

Ans. Fibres have strong intermolecular forces of attraction which leads to close packing of their chains and impart crystalline structure.

Q. 3. Which artificial polymer is present in bubble gum or chewing gum ?

Ans. Bubble gum or chewing gum contains synthetic Styrene-butadiene rubber.

Q. 4. Name the polymer used for making medicinal Capsule.

Ans. PHBVUC Polyhydroxy butyrate-CO-β-hydroxy valerated.

Q. 5. Which polymer is used in making electrical goods and why ?

Ans. Bakelite because of its electrical insulator property.

Q. 6. Is $(CH_2 — CH — C_6H_5)_n$ a homo polymer or a copolymer.

Ans. It is a homo polymer and the monomer from which it is obtained in styrene C_6H_5 CH = CH_2.

Q. 7. Which colligative property is used to determine the molecular masses of the polymers ?

Ans. Osmotic pressure is the colligative property used to determine the molecular masses of polymer.

2 MARKS QUESTIONS

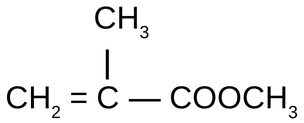
Q. 8. Write the names of monomers and structure used for getting the following polymers ?

PmmA, PVC, Teflon

Ans. (i) PVC — monomer — Vinylchloride, $CH_2 = CH — Cl$

(ii) Teflen — monomer — Tetrafluoro ethylene, $F_2C = CF_2$

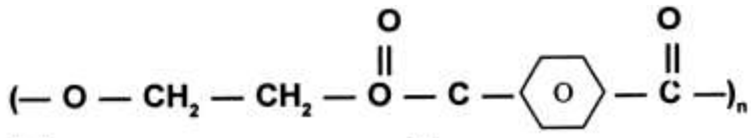
(iii) PMMA — monomer — Methyl methacrylate,



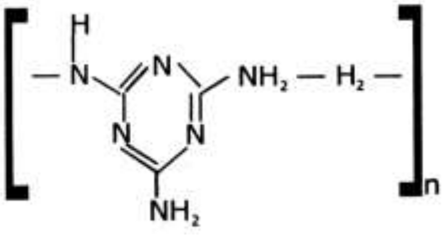
$$CH_2 = \overset{\overset{CH_3}{|}}{C} — COOCH_3$$

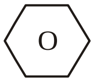
Q. 9. Identify the monomer in the following polymer structures :

(i)



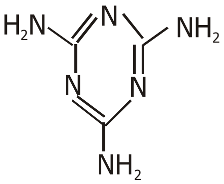
(ii)



Ans. (i) $HOCH_2 — CH_2OH$ and HOOC —  — COOH

ethane-1, 2-dial | Benzene-1, 4-dicarboxylic acid

(ii) Melamine | Formaldehyde



and HCHO

Q. 10. How do double bonds in the rubber molecule influence their structure and reactivity ?

Ans. Due to presence of double bond the rubber molecule show cis-configuration because which the polymer chains can not come close to each other and get boiled but as they have their hindrance problem. This causes them to have weak Vander Waals intraction between the molecules consequently they get elastic property, solubility in organic solvents etc.

Q. 11. Why are the No. of 6, 6 and 6 put in the names of nylon-6, 6 and nylon-6 ?

Ans. The no. of 6, 6 in nylon-6, 6 implies that both the monomers of nylon-6, 6 namely hexamethylene diamine and adipic acid contain six carbon atom each. The no. of 6 in nylon-6 contains six carbon atom each. The no. of 6 in nylon-6 indicates that its monomer Caprolectum has six carbon atom in its molecule.

Q. 12. Could a copolymer be formed in both addition and condensation polymerisation or not ? Explain.

Ans. Yes, though copolymers are mostly addition polymers like styrcue butadiene rubber and butyl rubber, the term can be used for condensation polymers also eg. for example.

(i) Addition polymerisation of styrene and butadiene form copolymer styrene butadiene rubber.

$$n\ CH_2 = CH — CH = CH_2 + n\ C_6H_5CH = CH_2 \longrightarrow$$

C_6H_5
|

$$(\text{— CH}_2\text{ — CH = CH — CH}_2)_n\text{ — CH}_2\text{ — CH —})_n$$

(ii) Condensation polymer became thylene diamine and adipic acid form nylon-6, 6.

$$\underset{\text{adipic acid}}{\text{n HOOC — (CH}_2)_4\text{ — COOH}} + \underset{\text{hexamethylene diamien}}{\text{n H}_2\text{N — (CH}_6)\text{ — NH}_2} \xrightarrow[\text{— n H}_2\text{O}]{} (\text{— NH (CH}_2)_6\text{ — NH — CO — (CH}_2)_4\text{ — CO —})_n$$

Q. 13. Arrange the following polymer in increasing order of their molecular forces :

(a) nylon-6, 6, Buna-S, polythene.

(b) nylon-6, Neoprene, polyvinyl chloride.

Ans. (a) Buna S < Polythene < Nylon-6, 6.

(b) Neoprene < Polyvinyl Chloride < Nylon-6.

Q. 14. Explain the difference between Buna— S and Buna — N.

Ans. Buna — N is a copolymer of 1, 3-butadiene and acrylo nitrile, Buna — S is a copolymer of 1, 3-butadiene and styrene.

Q. 15. Why should we always use purest monomer in free radical mechanism ?

Ans. Monomer has to be as pure as possible because the presence of any other molecule during free radical polymerisation can act chain initiator or inhibitor which will interfere with the normal polymerisation reaction.

❑❑❑

UNIT—16

CHEMISTRY IN EVERYDAY LIFE

1 MARK QUESTIONS

Q. 1. Give an example of a chemical substance which can act both as an antiseptic and disinfectant.

Ans. Phenol.

Q. 2. What is the chemical name of antiseptic chloroxylenol ?

Ans. 4-Chloro-3, 5-dimethyl phenol.

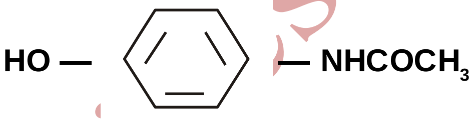
Q. 3. Which alkaloid is used to control hypertension ?

Ans. Reserpine.

Q. 4. Which alkaloid is used to treat malaria ?

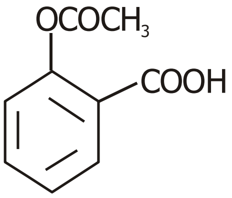
Ans. Quinine.

Q. 5. Identify the following :



Ans. Paracetamol.

Q. 6. What is the use of the following compound :



Ans. Analgesic.

Q. 7. Which artificial sweetner has the lowest sweetness value ?

Ans. Aspartame.

Q. 8. Which artificial sweetner has the highest sweetness value ?

Ans. Alitame.

Q. 9. What kind of a drug is Chlorpheniramine maleate ?

Ans. Anti histamine drug.

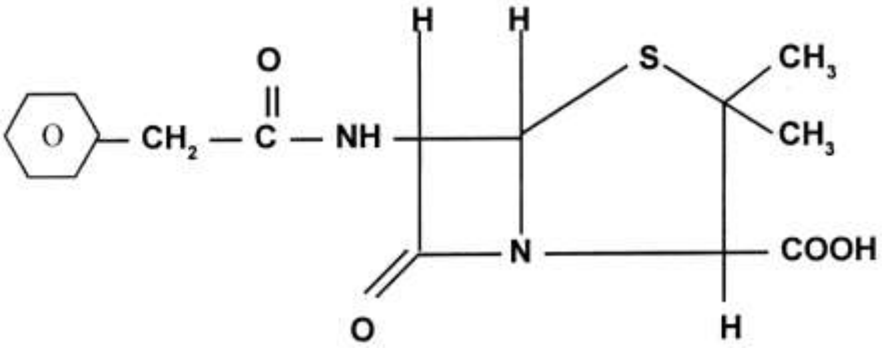
Q. 10. What is the chemical name of aspirin ?

Ans. 2-Acetoxy benzoic acid.

Q. 11. Name the antibacterial present in toothpaste.

Ans. Triclosan.

Q. 12. Identify the drug :



Ans. Penicillin G.

Q. 13. Which antibiotic contains NO_2 group attached to aromatic nucleus in its structure ?

Ans. Chloramphenicol.

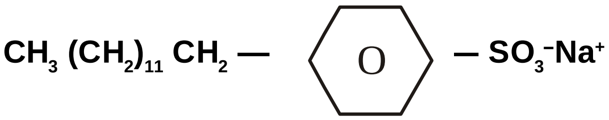
Q. 14. What is the use of barbituric acid ?

Ans. Tranquilizer.

Q. 15. Name one analgesic drug which is also used to prevent heart attacks.

Ans. Aspirin.

Q. 16. What is the application of the following molecule in everyday life ?



Ans. It is a detergent.

Q. 17. Give an example of a drug that is antipyretic as well as analgesic.

Ans. Paracetamol.

Q. 18. Out of morphine, N-Acetyl-para-aminophenol, Diazepam and tetrahydrocatenol, which can be used as analgesic without causing addiction ?

Ans. N-Acetyl-para-aminophenol.

Q. 19. Name a sugar substitute which is 160 times as sweet as surcrose.

Ans. Aspartame.

2 MARKS QUESTIONS

Q. 1. When a mixture of salicylic acid, acetic anhydride and acetic acid is refluxed, what is the product obtained and what is its use in everyday life ?

Ans. Aspirin used as analgesic.

Q. 2. Distinguish between a narrow spectrum and broad spectrum antibiotic.

Ans. A narrow spectrum antibiotic works against a limited range of microbes whereas a broad spectrum antibiotic works against a large variety of microbes.

Q. 3. What is Salvarson ? To which class of drugs does it belong ? For what distance is it used ?

Ans. Antimicrobial agent.

Used for the treatment of STD called Syphilis.

Q. 4. How does apirin act as an analgesic ?

Ans. It inhibits the synthesis of prostaglandins which stimulates inflammation of the tissue and cause pain.

Q. 5. What are barbiturates ? To which class of drugs do they belong ?

Ans. 5, 5-derivatives of barbituric acid are called barbiturates. They belong to the class of tranquilizers. They also act as sleep producing agents.

Eg. Luminal, Veronal.

Q. 6. What is tincture iodine ? What is its use ?

Ans. Alcoholic Solution of I_2.

Used as an antiseptic.

Q. 7. To what class of medicines does chloramphericol belong ? For what disease can it be used ?

Ans. Broad spectrum antibiotic

Used to cure typhoid, dysentry, acute fever.

Q. 8. Pick the odd one amongst the following on the basis of their medicinal properties mentioning the reason.

(i) Luminal, seconal, phenacetin, equanil

(ii) Chloroxylenol, phenol, chlorampherical, bithional

Ans. (i) Phenacetin is an antipyretic while all the rest are tranquilisers.

(ii) Chlorampherical is an antibiotic while all the remaining are antiseptics.

Q. 9. Why is bithional added to soap ?

Ans. Acts as an antiseptic and reduces the odours produced by bacterial decomposition of organic matter on the skin.

Q. 10. Why are cimetidine or ranitidine better antacids than sodium bicarbonate or magnesium or aluminium hydroxide ?

Ans. If excess of $NaHCO_3$ or $Mg(OH)_2$ or $Al(OH)_3$ is used, it makes the stomach alkaline and thus triggers the release of even more HCl. In contrast, cimetidine or ranitidine prevent the interaction of histamine with the receptor cells in the stomach wall and thus release lesser amount of HCl.

Q. 11. Why is the use of aspartame limited to cold foods and drinks ?

Ans. It decomposes at baking or cooking temperatures and hence can be used only in cold foods and drinks.

Q. 12. What problem arises in using alitane as artificial sweetener ?

Ans. It is a high potency artificial sweetener. Therefore it is difficult to control the sweetness of the food to which it is added.

Q. 13. What is the purpose of adding antioxidants to food ? Give two examples of antioxidants.

Ans. They are added to prevent oxidation of fats and oils present in food thus preventing food from becoming rancid.

Eg. BHA (Butylated hydroxy anisole)
BHT (Butylated hydroxy toluene)

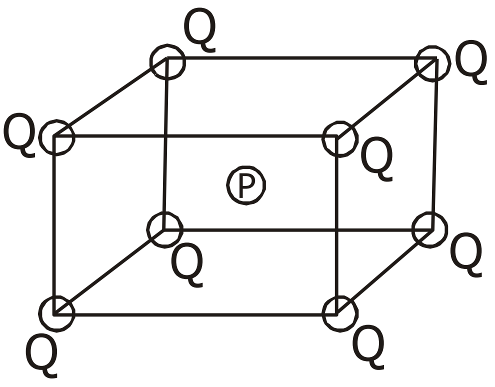
❑❑❑

General Instructions :

- *(1) All questions are compulsory.*
- *(2) Marks against each question are indicated.*
- *(3) Questions from one to eight are very short answer type questions carrying one mark each.*
- *(4) Questions from nine to eighteen are short answer type questions carrying two marks each.*
- *(5) Questions from nineteen to twenty seven are short answer type questions carrying three marks each.*
- *(6) Questions from twenty eight to thirty are long answer type questions carrying five marks each.*
- *(7) Use log tables, if necessary. Calculators are not permitted.*

Q. 1. A cubic solid is made of 2 elements P & Q are at the corners of the cube & P at the body centre. What is the formulae of the compound ? What are the coordination no. of P & Q ?

Ans.



$\because$ At the corners each atom is equal to $\frac{1}{8}$

$\therefore$ total Q = $\frac{1}{8} \times 8 = 1$ atom

$\therefore$ formula is PQ

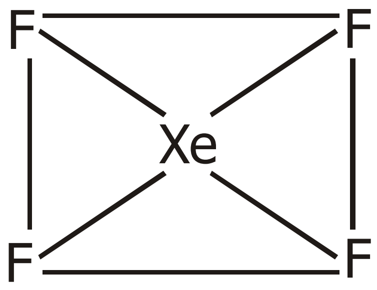
Cordination No. is 8 : 8.

Q. 2. Name one important catalyst used in petroleum industry. For what purpose it is used for ?

Ans. It is ZSM–5. It converts alcohol directly into gasoline.

Q. 3. Give the hybridisation and shape of XeF_4.

Ans.



$Sp^3 d^2$ hybridisation

“Square planar shape”.

Q. 4. Zn, Cd, Hg are not regarded as transition elements. Why ?

Ans. Zn, Cd, Hg have completely filled d-orbitals in them. Hence, they are not regarded as transition elements.

Zn (30) = $3d^{10} 4s^2$

Cd (40) = $4d^{10} 5s^2$

Hg (80) = $5d^{10} 6s^2$

Q. 5. Write IUPAC name of the following compounds :

(i) $CH_3 — C — CH — CH_3$

|| |
O   Br

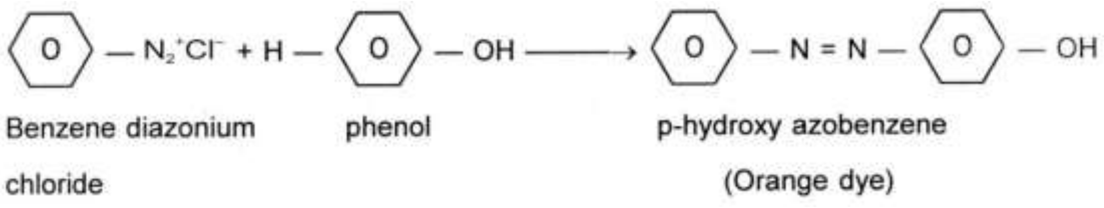
(ii) COOH
|
COOH

Ans. (i) 3-Bromo-2-butanone

(ii) Ethane-1, 2-dioic acid

Q. 6. What do you understand by the term coupling reaction ?

Ans.



Q. 7. What are anomers ?

Ans. The isomers which differ in their configuration at C_1 Carbon are known as anomers.

Q. 8. What is a broad spectrum antibiotic ? Give examples.

Ans. An antibiotic which can be used for curing from several types of microorganisms i. e. several diseases is called as a broad spectrum antibiotic.

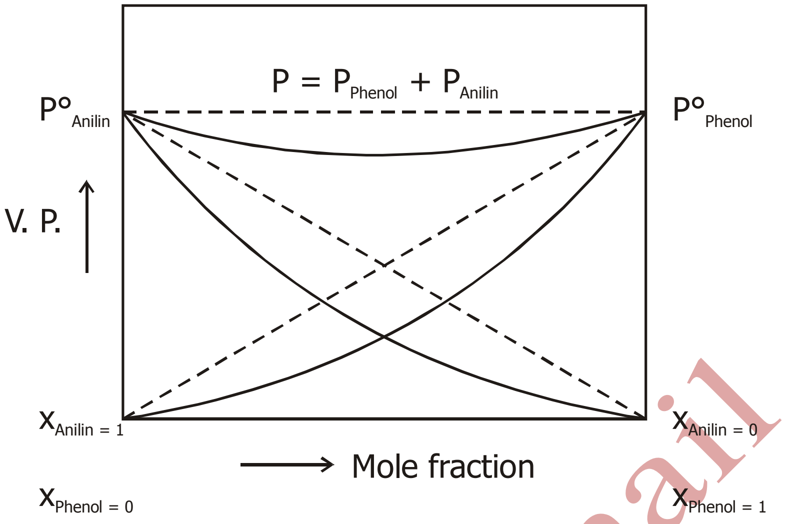
eg. Chloramphenicol.

Q. 9. Show the graph of the deviation shown by anilin and phenol, give reason.

Ans. Negative deviation, ∴ A — B interactions are stronger than A — A and B — B interactions.

OR

H-Bonding between phenolic H^+ and lone pair on nitrogen atom of anilin is stronger than individual molecules.



Q. 10. (a) Write the unit of molar conductivity.

(b) Why does the conductivity of a solution decrease with dilution ?

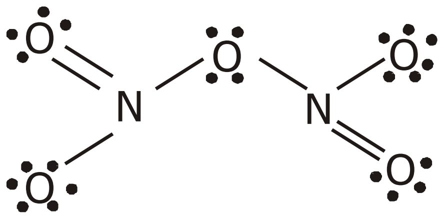
Ans. (a) Ohm^{-1} cm^2 mol^{-1}

(b) Conductivity of a solution depends upon number of ions present in per unit volume. On dilution, the number of ions per unit volume decreases, ∴ conductivity also decreases.

Q. 11. (i) What is the covalence of Nitrogen in N_2O_5 ?

(ii) Cl_2 is a bleaching reagent. Justify.

Ans. (i)



It is evident that its covalence is 4.

(ii) It is due to oxidation.

$Cl_2 + H_2O \longrightarrow HCl + HOCl$

Due to the presence of the nescent oxygen in HOCl it possess bleaching property.

Coloured Substance + O ———→ Colourless Substance

Q. 12. Give reason for the following :

(i) Zr & Hf exhibit similar properties.

(ii) Transition elements forms alloys.

Ans. (i) Due to lanthanoid contraction, Hf & Zr have almost similar size & therefore, their properties are similar.

(ii) Transition elements have nearly the same atomic size. Hence, they can substitute one another in crystal lattice to form substitutional alloys.

Q. 13. Describe the steps involved in the preparation of potassium permanganate from manganese dioxide.

Ans. Step 1 : $2\,MnO_2 + 4\,KOH + O_2 \longrightarrow 2\,K_2MnO_4 + 2\,H_2O$

Step 2 : $MnO_4^{2-} \longrightarrow MnO_4^- + e^-$ (Anode)

green purple

$2\,H^+ + 2\,e^- \longrightarrow H_2$ (Cathode)

Electrolytic Oxidation

OH^- ions remain in the soluⁿ.

OR

Write the steps involved in the preparation of $K_2Cr_2O_7$ from Chromite ore.

Ans. (i) $4\,FeCrO_4 + 16\,NaOH + 7\,O_2 \longrightarrow 8\,Na_2CrO_4 + 2\,Fe_2O_3 + 8\,H_2O$

(ii) $2\,Na_2CrO_4 + H_2SO_4 \longrightarrow Na_2Cr_2O_7 + Na_2SO_4 + H_2O$

(iii) $Na_2Cr_2O_7 + 2\,KCl \longrightarrow K_2Cr_2O_7 + 2\,NaCl$

Q. 14. Write a brief notes on :

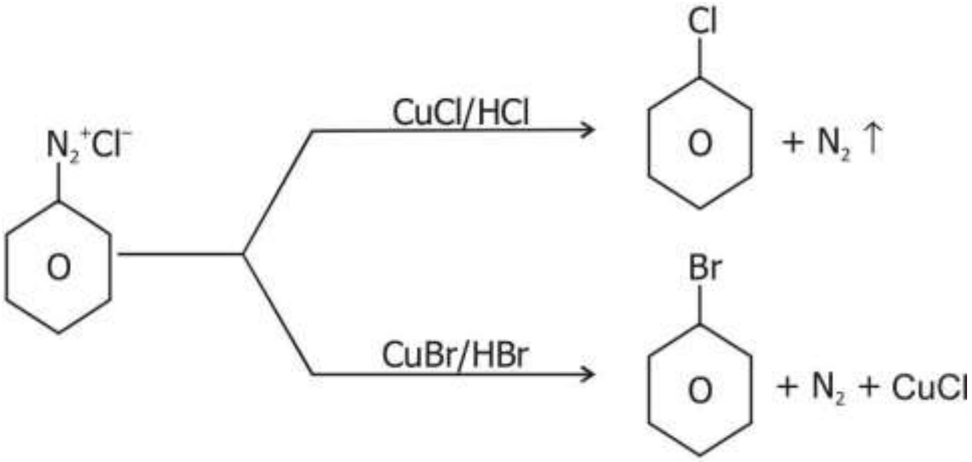
(a) Williamson's ether synthesis

(b) Sandmeyer's reaction.

Ans. (a) Alkylhalides react with sodium alkoxides to give symmetrical/unsymmetrical ethers :

$$R - \boxed{X + Na} - O - R' \longrightarrow R - O - R' + NaX$$

(b) The conversion of benzene diazonium chloride into chlorobenzene/bromobenzene using CuCl — HCl/CuBr — HBr is known as Sandmeyer's reaction.



Q. 15. Explain why :

(a) Alkylhalides, though polar, are immiscible with water.

(b) Grignard reagents should be prepared under anhydrous conditions.

Ans. (a) Alkylhalides can not form H-Bonds with water and hence Alkylhalides are insoluble in water.

(b) Grignard reagent react with water and get decomposed :

$$R\,Mg\,X + H_2O \longrightarrow R - H + Mg\,(OH)\,X$$

Hence they have to be prepared under anhydous conditions.

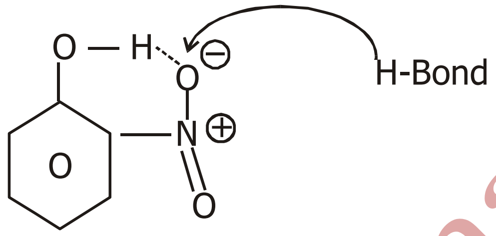
Q. 16. Give reasons :

O-nitrophenol has lower boiling point than p-nitrophenol.

Ans. O-nitrophenol shows intra molecular hydrogen bonding and exists as discrete molecules.

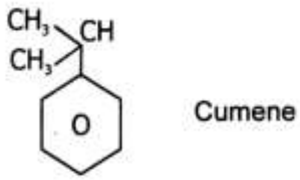
Low intermolecular forces, low boiling point.

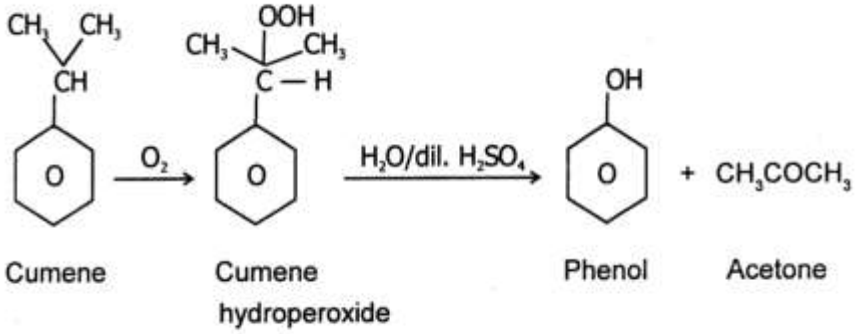
Intermolecular H-bonding takes place in p and m nitro phenol, form associated molecule, high intermolecular forces, high boiling point.



Q. 17. What is cumene ? How is phenol prepared from cumene ? Isopropyl or 2 phenyl propane is cumene.

Ans.





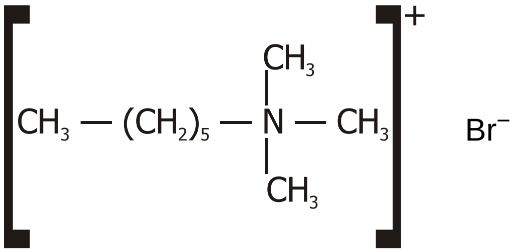
Q. 18. Explain with examples :

(a) Cationic detergent

(b) Anionic detergent

Ans. (a) Cationic Detergent :

Acetates, chlorides or bromides of quarternary ammonium salts with long hydrocarbon chain forming cationic part.



$$\left[CH_3 - (CH_2)_5 - \overset{\overset{CH_3}{|}}{\underset{\underset{CH_3}{|}}{N}} - CH_3 \right]^+ \quad Br^-$$

(b) Anionic Detergent :

Alkyl hydrogen sulphonates with long carbon chain forming Alkyl part.

$CH_3\,(CH_2)_{10} - CH_2 - OSO_3 - Na^+$

Sodium louryl sulphonate

Q. 19. (a) Gold (atomic radius = 0.144 nm) crystallises in a face centered unit cell. What is the length of a side of the cell ?

(b) If NaCl is doped with 20% $CdCl_2$. What is the concentration of cation vacancies.

Ans. (a) For fcc $a = 2 \times r$

$= 2 \times 1.414 \times 0.144$

$= 0.407$

(b) 20% vacancies

Na^+	Cl^-	Na^+	Cl^-
Cl^-	$\boxed{Cd^{2+}}$	Cl^-	Na^+
Na^+	Cl^-	$\boxed{}$	Cl^-

Q. 20. 45 g of ethylene glycol ($C_2H_6O_2$) is mixed with 600 g water. Calculate :

(a) freezing point depression

(b) freezing point of solution

Given that K_f for water = 1.86 K kg mol^{-1}

Ans. $\Delta T_f = \dfrac{K_1 \times W_b \times 1000}{M_B \times W_A}$

$\Delta T_f = \dfrac{1.86 \times 45 \times 1000}{62 \times 600} = 2.25\,K = 2.25\,K$

then $\Delta T_f = T_0 - T_1 = 273 - T_1$

$T_1 = 273 - 2.25 = 270.75\,K$

Q. 21. Following data were obtained during the first order thermal decomposition of N_2O_5 (g) at constant volume :

$$2\,N_2O_5\,(g) \longrightarrow 2\,N_2O_4\,(g) + O_2\,(g)$$

Calculate the rate constant if :

S. No.	Time/s	Total pressure/atm
1	0	0.5
2	100	0.512

Ans.

	$2\,N_2O_5\,(g) \longrightarrow$	$2\,M_2O_4\,(g)$	$+ \; O_2\,(g)$
Initially	0.5 atm	0 atm	0 atm
At tiem (t)	(0.5 – 2 x) atm	2 x atm	2 x atm

Pt = (0.5 – 2 x) + 2 x + x = 0.5 + x

x = Pt – 0.5

= 0.5 – 2 (pt – 0.5) = 1.5 – 2 Pt

At t = 100 sec.

Pt = 0.512 atm

PN_2O_5 = 1.5 – 2 × 0.512 = 0.476 atm

Using Ist order reaction

$$K = \frac{2.303}{t}\log\frac{P_{initial}}{P_A}$$

$$= \frac{2.303}{100\ sec}\log\frac{0.5\ atm}{0.476\ atm}$$

$$= \frac{2.303}{100\ sec}\times 0.0216 = 4.98\times 10^{-4}\ sec^{-1}$$

Q. 22. Explain the following observations :

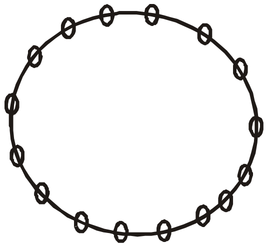
(a) Physical adsorption in multilayered, while chemisorption is unilayer.

(b) Adsorption is always exothermic process.

(c) Ferric hydroxide sol^n coagulates on addition of potassium sulphate.

Ans. (a) Physical adsorption is non-specific i. e. adsorbade can be held on adsorbadely weak Vander-waal forces. Therefore no bonds have to be set up, therefore it continues while chemisorption is highly specific, chemical bonds have to be set up.

(b)

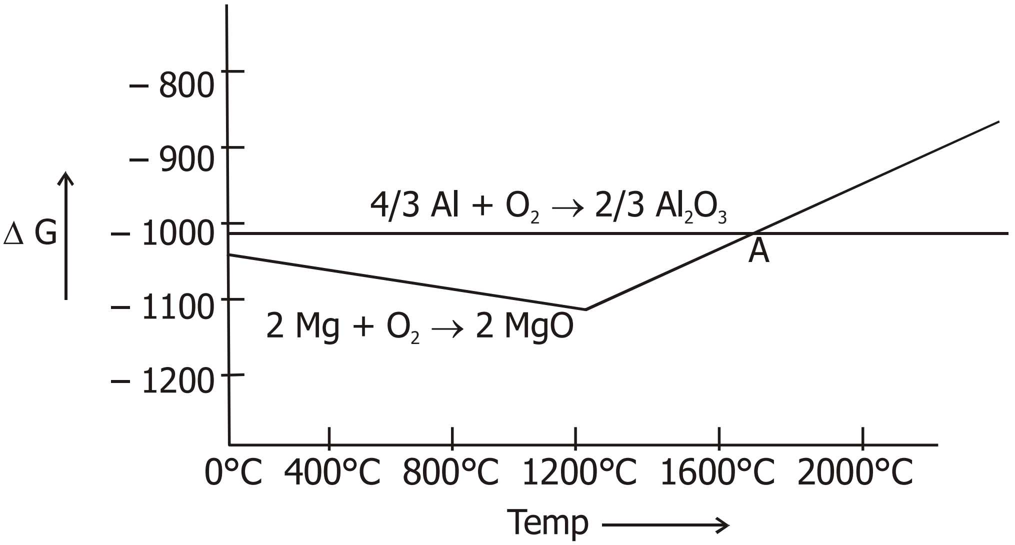


In Adsorption order increases. Therefore ΔS becomes (–) ve for a reaction to be spontaneous i. e. ΔG should always benegative that is possible only :

ΔH	ΔS	$\Delta G = \Delta H - T\Delta S$
– ve	– +	$-\Delta H > T\Delta S$

(c) Coagulation takes place, since adsorption of SO_4 ions on $Fe(OH)_3$ which is positively charged colloid.

Q. 23.



(a) What is the significance of point A in the above graph ?

(b) Suggest a condition under which magnesium can reduce aluminium.

(c) Give method for refining nickel.

Ans. (a) At point 'A' $\Delta G°$ becomes O for the reaction.

(b) Below this point magnesium can reduce alumina above this point. Aluminium can reduce magnesium oxide.

(c) Mond Process is used where nickel is heated in stream of CO.

$$Ni + CO \xrightarrow{330 \text{ to } 350\ K} Ni\ (CO)_4$$

Tetracarboxyl nickel
(volatile)

$$450\text{-}470\ K \Big\downarrow \text{High temperature Decomposed}$$

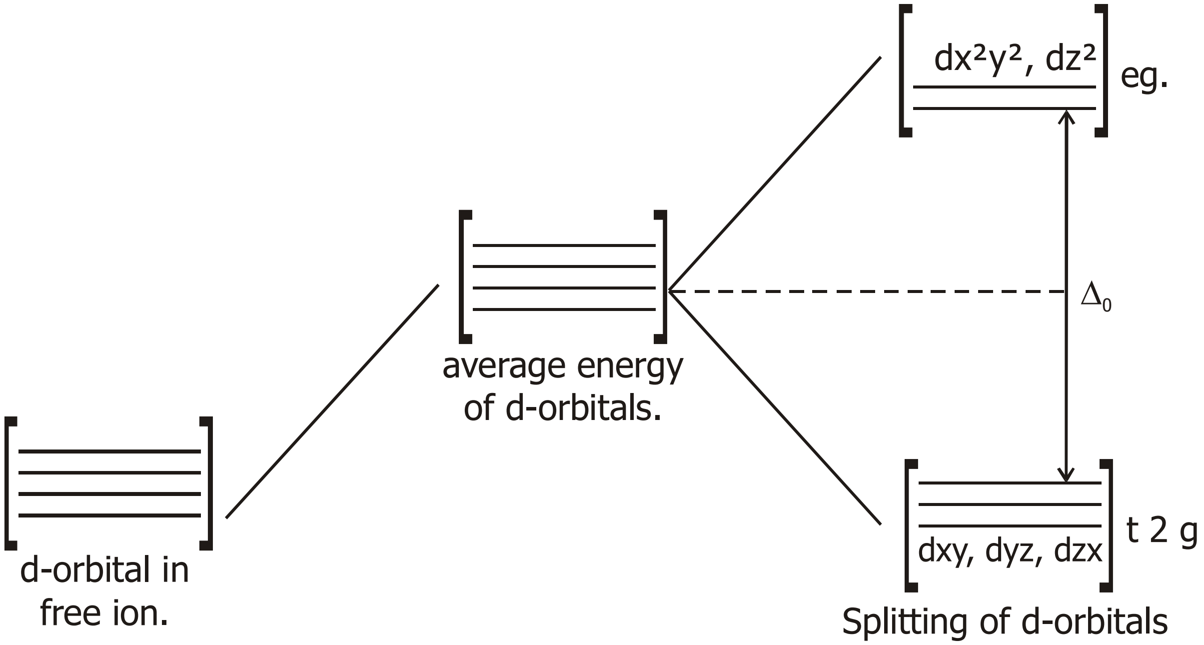
$Ni + 4\ CO$
(Pure metal)

Q. 24. Draw a figure to show splitting of degenerate d-orbitals in an octahedral. How is the magnitude of Δ_0 affected by :

(i) Nature of ligand.

(ii) Oxidation State of metal ion.

Ans.



Splitting of d-orbitals in an octahedral crystal field.

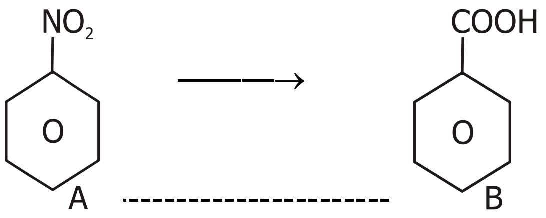
(a) Stronger the ligand, more is the splitting.

(b) Higher the oxidation state, greater is the magnitude of Δ_0.

Q. 25. Complete the following reactions :

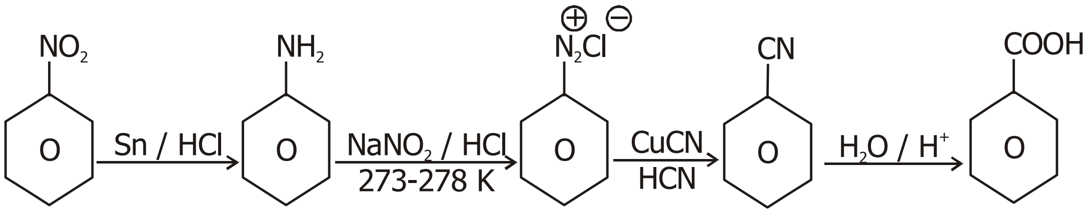
(1) $R - Cl \xrightarrow{A} B \xrightarrow{4\,[H]} RCH_2NH_2$

(2)



Ans. (1) $$\mathrm{RCl} \xrightarrow{\mathrm{KCN}} \mathrm{RCN} \xrightarrow{4\,[\mathrm{H}]} \mathrm{RCH_2NH_2}$$

(2)



Q. 26. (1) Write the monomers of BUNA-S & Teflon.

(2) Differentiate between Nylon-6 and Nylon-66.

(3) Give an example of each thermoplastic & thermosetting plastic.

Ans. (1) BUNA-S — 1-3 butadiene $CH_2 = CH — CH = CH_2$

styrene

Teflon — $(CF_2 = CF_2)$

(2) Nylon-6 — Condensation polymer of caproductum.

Nylon-66 — Condensation polymer of Adipic acid :

$(HOOC — CH_2 — CH_2 — CH_2 — CH_2 — COOH)$

& hexamethylene diamine :

$H_2N — (CH_2)_6 — NH_2$

(3) Thermoplatic — Polythene

Thermosetting plastic — Bakelite

Q. 27. Answer the following questions briefly :

(a) What are reducing sugars ?

(b) What are nucleotides ?

(c) Define enzymes.

Ans. (a) The sugar which contain free aldehydic group and reduce Tollen's reagent or Fehling's reagent.

(b) Nucleotide is a phosphate ester of nucleoside.

(c) Enzymes are the biological catalyst which increases the rate of metabolism and they are highly specific in nature.

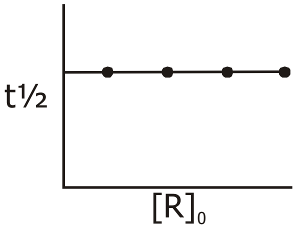
Q. 28. (a) Write the Nearnst equation and the emf of the following cells at 298 K :

Sn / Sn^{2+} (0.050 M) // H^+ (0.020 M) / H_2 (g) / Pt (s)

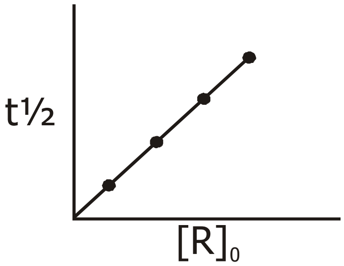
1 bar

(b) (i) Give the order of the reaction :

(a)



(b)



(ii) Write Arrhenius equation showing the effect of temperature on rate of reaction.

Ans. (a) Reaction :

At Anode $Sn \longrightarrow Sn^{2+} + 2\,e^-$

At Cathode $H^+ + e^- \longrightarrow H_2 \times 2$

$Sn + 2\,H^+ \longrightarrow H_2 + Sn^{2+}$

$\therefore$ n = 2

Neutral Equation

$$E_{cell} = E°_{cell} - \frac{0.059}{2} \log \frac{[Sn^{2+}]}{[H^{+}]^{2}}$$

$$= \{0 - (-0.14)\} - \frac{0.059}{2} \log \frac{0.05}{(0.02)^2}$$

$$= 0.14 - \frac{0.059}{2} \log 125$$

$$= 0.14 - \frac{0.059}{2} \times 2.0969$$

$$= 0.078 \text{ Volt.}$$

(b) (i) (a) Order as $t\frac{1}{2}$ is independent of $[R]_0$.

(b) Zero Order $\because$ $t\frac{1}{2} \; \alpha \; [R]_0$

(ii) $K = A\, e^{-Ea/Rt}$

$$\log K = \log A - \frac{Ea}{2.303\, RT}$$

OR

Q. 28. (a) Predict the products of electrolysis of dilute aqueous solution of H_2SO_4 with platinum electrodes.

(b) How will you calculate λ_0 of $Ba(OH)_2$ with the help of Kohlrausch's law.

Ans. (a) $H_2SO_4\,(aq) \longrightarrow 2\,H^+\,(aq) + SO_4^{2-}\,(aq)$

$$H_2O \rightleftharpoons H^+ + OH^-$$

At Cathode $H^+ + e^- \longrightarrow H$

$H + H \longrightarrow H_2\,(g)$

At Anode $OH^- \longrightarrow OH + e^-$

$4\ OH \longrightarrow 2\ H_2O + O_2 \uparrow$

Thus H_2 is liberated at cathode, and O_2 is liberated at anode.

(b) $\Lambda^\circ_m\ Ba(OH)_2 \longrightarrow \lambda^\circ\ Ba^{2+} + 2 \times \lambda^\circ\ OH^-$

Q. 29. Complete the following reactions :

(a) (i) $PCl_5 + H_2O \longrightarrow$

(ii) $XeF_2 + PF_5 \longrightarrow$

(iii) $NaCl + MnO_2 + H_2SO_4 \longrightarrow$

(b) H_3PO_4 is tribasic whereas H_3PO_3 is dibasic.

(c) PCl_5 is solid in ionic state.

Ans. (a) (i) $PCl_5 + H_2O \longrightarrow POCl_3 + 2\ HCl$

$POCl_3 + 3\ H_2O \longrightarrow H_3PO_4 + 3\ HCl$

(ii) $XeF_2 + PF_5 \longrightarrow [XeF]^+ [PF_6]^-$

(iii) $4\ NaCl + MnO_2 + 4\ H_2SO_4 \longrightarrow MnCl_2 + 4\ NaHSO_4 + 2\ H_2O + Cl_2$

(b) $H_3PO_4 + H_2O \longrightarrow H_3O^+ + H_2PO_4^-$

$H_2PO_4^- + H_2O \longrightarrow H_3O^+ + HPO_4^{2-}$

$HPO_4^{2-} + H_2O \longrightarrow H_3O^+ + PO_4^{3-}$

(c) $[PCl_4]^+ [PCl_6]^-$ because of formation of this ionic compound.

OR

(a) Give the hybridisation of ClF_5.

(b) Complete the following reactions :

(i) $F_2 + 2\ X^- \longrightarrow$

$X = ?$

(ii) $MnO_2 + 4\ HCl \longrightarrow$

(iii) $XeF_2 + 2\,H_2O \longrightarrow$

$PbS + O_3 \longrightarrow$

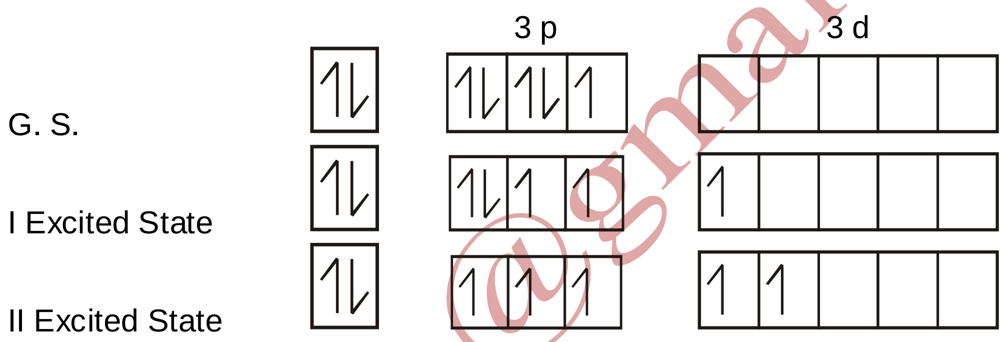
(c) Give reasons :

(i) NH_3 is more basic than PH_3.

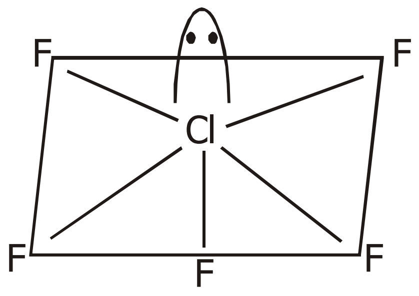
(ii) ICl is more reactive than I_2.

Ans. (a) Structure + hybridisation of ClF_5

$Cl = 3s^2\,3p^5$



∴ sp^3d^2



Square Pyramidal

(b) (i) $F_2 + 2\,X^- \longrightarrow X_2 + 2\,F^-$

$X = Cl^-, Br^-, I^-$

(ii) $MnO_2 + 4\,HCl \longrightarrow MnCl_2 + Cl_2 + 2\,H_2O$

(iii) $O_3 \longrightarrow O_2 + O \times 4$

$PbS + 4\,[O] \longrightarrow PbSO_4$

$$4\,O_3 + PbS \longrightarrow 4\,O_2 + PbSO_4$$

(c) (i) Because of high electronegativity & small size of nitrogen electron density is high because lone pair are diffused over a smaller area.

(ii) I — Cl bonds are weaker than I — I because of ineffective overlapping.

Q. 30. (a) By which test the following pairs of organic compounds can be distinguished :

(i) CH_3CHO and C_6H_5CHO

(ii) $H—COOH$ and CH_3COOH

(b) Complete the following :

(i) $CH_3COCl \xrightarrow{Pd — BaSO_4 / S}$

(ii) $C_6H_5CHO \xrightarrow{\text{Conc. NaOH}}$

(iii) $CH_3CH_2COOH \xrightarrow{Cl_2 / \text{Red } P_4}$

Ans. (a) (i) Iodoform test :

CH_3CHO give + ve test for Iodoform :

$$CH_3CHO \xrightarrow{NaOH + I_2} Cl_3CHO \xrightarrow{NaOH} \underset{\text{Iodoform}}{CHI_3} + HCOONa$$

$$C_6H_5CHO \xrightarrow{NaOH + I_2} \underset{\text{Iodoform}}{NO}$$

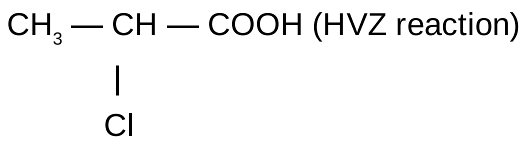
(ii) Tollens reagent test :

$$HCOOH + \underset{\text{Tollen reagent}}{2\,[Ag\,(NH_3)_2] + OH^-} \xrightarrow{\text{heat}} \underset{\text{mirror}}{2\,Ag} + 4\,NH_3 + CO_2 + 2\,H_2O$$

$CH_3COOH \longrightarrow$ Na
mirror

(b) (i) $CH_3 — CHO$ (Rosenmund reduction)

(ii) $C_6H_5CH_2OH$ and C_6H_5COONa (Cannizaro's reaction)

(iii) 

$$\underset{\displaystyle Cl}{\underset{|}{CH_3 — CH}} — COOH$$ (HVZ reaction)

OR

(a) How will you distinguish between aniline and N-Methylaniline (write the chemical reaction.) ?

(b) What happens when :

(i) Acetamide is treated with Br_2 / NaOH.

(ii) Acetaldehyde is treated with aq. NaOH.

(iii) Ethylamine is treated with HNO_2.

Ans. (a) By carbylamine test we can distinguish aniline and N-methylaniline.

$$C_6H_5NH_2 + CHCl_3 + 3\ KOH \longrightarrow C_6H_5NC + 3\ KCl + 3\ H_2O$$

$$C_6H_5 — NH — CH_3 + CHCl_3 + 3\ KOH \longrightarrow \text{No reaction}$$

(b) (i) CH_3NH_2 will be formed. (Hoffmann's reagent)

(ii) Hydroxybutanol will be formed. (Aldol Condensation reaction)

(iii) $C_2H_5 — OH$ will be formed.

* * *