CHAPTER - 10

ORGANIC CHEMISTRY - SOME BASIC PRINCIPLES AND TECHNIQUES - PART III

PURIFICATION AND CHARACTERISATION OF ORGANIC COMPOUNDS

SYNOPSIS

A. Purification of organic compounds

When an organic compound is synthesised or extracted from a natural source, it is essential to purify it, in order to study its properties. Methods of purification are based on the nature of the organic compound and the impurities associated with it

Purity of an organic compound is tested by a comparison of its melting point and / or boiling point with standard values. Impurity generally lowers the m.p. and elevates the bp of a pure substance. In the mixed meting point or mixed boiling point method, purified sample is mixed with a small quantity of the pure substance. If the mp / bp of this mixture is the same as that of pure substance, it indicates purity of the sample

Spectroscopic techniques and chromatography are newer methods for checking purity

The common methods of purification (separation of components of a mixture) are the following

1. Sublimation : Suitable to separate a sublimable solid from non-sublimable impurities, if the solid does not decompose on heating

2. Crystallisation : Based on the difference in solubilities of the compound and impurities in a given solvent

3. Distillation : Used to separate (i) volatile liquids from non-volatile impurities (ii) two liquids if their boiling points are largely different. Eg. a mixture of $CHCl_3$ (b.p. 334 K) and aniline (b.p. 457 K). The liquid mixture is heated to boiling. The vapours of the lower-boiling component are formed first, which are collected and condensed separately. This is simple distillation

4. Fractional distillation : used to separate components of a mixture of liquids if their boiling points do not differ much. Vapours of such a liquid mixture are passed through a fractionating column which provide many surfaces for heat exchange between ascending vapours and descending liquid. The vapours become richer in the low-boiling component ascending to the top of the fractionating column. This process gives lower boiling component as the vapour at the top of the fractionating column which is collected and condensed. The residual liquid in the distillation flask is richer in the higher boiling component

Eg. i) a mixture of acetone (bp 329 K) and methanol (bp 338 K)

ii) fractionation of crude oil

iii) Separation of heavy water from ordinary water

5. Steam distillation : used to separate liquids which are steam volatile and immiscible with water. On passing steam through the organic liquid to be distilled, the mixture will boil at a temperature when the total vapour pressure of the organic liquid and water equals atmospheric pressure. The vapours coming out are condensed and the liquid is separated from water using a separating funnel.

   Eg. Separation of aniline from aniline - water mixture

6. Distillation under reduced pressure and vacuum distillation

On reducing the applied pressure, a liquid boils at a lower temperature than its normal boiling point. When a high-boiling organic liquid decomposes at its normal boiling point, the applied pressure is reduced using a vacuum pump. It is then boiled, vapours collected and condensed.

Eg. Separation of glycerol from spent-lye.

7. Differential extraction

When an organic compound is present in aqueous medium, it is separated by shaking with an organic solvent (like ether) in which it is more soluble. The organic compound is said to be extracted to the organic solvent. The organic layer containing the organic compound is separated using a separating funnel and later distilled or evaporated to remove the organic solvent.

8. Chromatography : is a modern technique for separation and purification of components in a mixture. Purity of a substance can also be tested

Chromatography is based on the selective distribution of components of a mixture between two phases; a mobile phase and a stationary phase. This selective distribution can be done either by adsorption or by partition

a) Adsorption chromatography : makes use of the different affinity for adsorption of compounds on an adsorbent like silica gel or alumina Adsorbent forms the stationary phase

(i) In column chromatography, adsorbent is packed in a glass tube. On passing a suitable solvent (mobile phase) on the mixture of components through the column, separation takes place in the order of the relative affinity for adsorption of the various components. The most readily adsorbed is retained at the top

(ii) In thin layer chromatography (TLC), adsorbent is coated on a glass plate as a thin layer. The solution of the mixture is applied as a small spot at one end of the TLC plate. The components of the mixture move along with the eluant (mobile phase) to different distances depending on the relative degree of adsorption resulting in their separation

$$R_f = \frac{\text{Distance travelled by a compound from base line}}{\text{Distance travelled by the solvent from base line}}$$

b) Partition chromatography is based on the differential partitioning of components between stationary phase and mobile phase. Paper chromatography uses specially made chromatographic paper. Water trapped on this paper act as the stationary phase. The mixture is spotted at the base of a strip of this paper which is then suspended in suitable solvent. By capillary action the solvent rises (mobile phase) and selectively retains different components at various distances from the base line, according to the partitioning between the solvent and water. This results in the separation of the components of the mixture.

B. Qualitative analysis of organic compounds

1) Detection of C and H : A small amount of organic compound is oxidised by cupric oxide to CO_2 and H_2O

$C + 2CuO \rightarrow 2Cu + CO_2$ (turns lime water milky)

$2H + CuO \rightarrow Cu + H_2O$ (turns anhydrous $CuSO_4$ blue)

2) Lassaigne's test for N, S and halogens

A small amount of organic compound is fused with metallic sodium and boiled with distilled water. The filtrate, called sodium fusion extract, is used for the detection of N, S and halogens

Elements	Sodium salt of ion in Lassaigne's extract
N	NaCN
S	Na_2S
if both N & S	NaCNS
Halogen X	NaX

a) Detection of N

$$6C\bar{N} + Fe^{2+} \rightarrow \left[Fe(CN)_6\right]^{4-}$$

$$3\left[Fe(CN)_6\right]^{4-} + 4Fe^{3+} \xrightarrow{xH_2O} \underset{\text{Prussian blue}}{Fe_4\left[Fe(CN)_6\right]_3 xH_2O}$$

b) Detection of S

i. With sodium nitroprusside, violet colouration is produced.

$$\underset{\text{Sodium nitroprusside}}{Na_2S + Na_2\left[Fe(CN)_5 NO\right]} \rightarrow \underset{\text{(Violet colour)}}{Na_4\left[Fe(CN)_5 NOS\right]}$$

ii. $Na_2S + (CH_3COO)_2Pb \rightarrow 2CH_3COONa + \underset{\text{black ppt.}}{PbS}$

c) Detection of N and S is together present $Fe^{3+} + 3CNS^- \rightarrow \underset{\text{Blood red colour}}{Fe(CNS)_3}$

d) Detection of halogen - $AgNO_3$ test

$NaX + HNO_3 + AgNO_3$

- White ppt. soluble in NH_4OH - presence of Cl
- Yellowish ppt. sparingly soluble in NH_4OH - presence of Br
- Yellow ppt. insoluble in NH_4OH - presence of I

3) Detection of P

A little of organic compound is oxidised with sodium peroxide when P is oxidised to phosphate. The solution is boiled with con. HNO_3. A few drops of this solution is added to ammonium molybdate solution. A yellow colour or ppt. indicates presence of phosphorus

C. Quantitative analysis of organic compounds

1) Estimation of C and H - Liebig's method

$$\text{Oganic compound (known mass)} \xrightarrow[CuO]{O_2} CO_2 + H_2O$$

$$\% \text{ of C} = \frac{12}{44} \times \frac{\text{mass of } CO_2}{\text{mass of organic compound}} \times 100$$

$$\% \text{ of H} = \frac{2}{18} \times \frac{\text{mass of } H_2O}{\text{mass of organic compound}} \times 100$$

2) Estimation of N

a) Dumas method - Nitrogen is estimated as gaseous N_2

$$C_xH_yN_z + \left(2x + \frac{y}{2}\right)CuO \rightarrow xCO_2 + \frac{y}{2}H_2O + \frac{z}{2}N_2 + \left(2x + \frac{y}{2}\right)Cu$$

$$\% \text{ of N} = \frac{28}{22400} \times \frac{\text{vol. of } N_2 \text{ collected (STP) } cm^3}{\text{mass of organic compound}} \times 100 = \frac{V}{8m}$$

Where V = vol in ml; at STP m = mass in gm

b) Kjeldahl method

Nitrogen-containing organic compound is heated with con. H_2SO_4 to convert nitrogen to $(NH_4)_2SO_4$ which is decomposed to ammonia by excess alkali. The liberated ammonia is volumetrically estimated

$$\% \text{ of N} = 1.4 \times \frac{\text{molarity of acid} \times \text{basicity of acid} \times \text{volume of acid (ml) used}}{\text{mass of substance used}}$$

$$= 1.4 \times \frac{\text{normality of acid} \times \text{volume of acid used (ml)}}{\text{mass of substance used}}$$

$$\text{OR } \frac{1.4 \times \text{vol.of acid taken} \times \text{decrease in normality of acid}}{w}$$

3) Estimation of halogens - Carius method

A known mass of organic compound is heated with fuming HNO_3 and crystals of $AgNO_3$ in a Carius tube. Halogen is converted to insoluble AgX which is then separated and weighed

$$\% \text{ of X} = \frac{\text{atomic mass of X}}{(108 + \text{at.mass of X})} \cdot \frac{\text{mass of AgX}}{\text{mass of organic compound}} \times 100$$

4) Estimation of S - Carius method

S is oxidised to H_2SO_4 by heating the organic compound with fuming HNO_3. It is precipitated as $BaSO_4$ by adding excess $BaCl_2$ solution

$$\% \text{ of S} = \frac{32}{233} \times \frac{\text{mass of } BaSO_4}{\text{mass of organic compound}} \times 100$$

In the Messenger's method, S in the organic compound is oxidised to SO_4^{2-} using alkaline $KMnO_4$ instead of HNO_3

5) Estimation of P - Carius method

By heating a known mass of organic compound with fuming HNO_3, P in the organic compound is oxidised to H_3PO_4 which is then precipitated as $Mg(NH_4)PO_4$ by adding magnesia mixture ($MgCl_2$ + NH_4Cl + NH_4OH). The precipitated $Mg(NH_4)PO_4$ is ignited to magnesium pyrophosphate and weighed

$$\% \text{ of P} = \frac{62}{222} \times \frac{\text{mass of } Mg_2P_2O_7}{\text{mass of organic substance}} \times 100$$

6) Estimation of oxygen - Aluise method

$$\text{Organic compound} \xrightarrow[\text{stream of } N_2 \text{ gas}]{\Delta} O_2 + \text{gaseous products} \xrightarrow[\text{red hot coke}]{\Delta} CO \xrightarrow[I_2O_5]{\Delta} CO_2 + I_2$$

$$5O_2 + 10C + 2I_2O_5 \rightarrow 10CO_2 + 2I_2$$

$$\% \text{ of oxygen} = \frac{16}{44} \times \frac{\text{mass of } CO_2}{\text{mass of organic compound}} \times 100$$

% of oxygen is usually obtained by difference

% of O = 100 – (sum of % of all other elements)

D. Determination of molar mass

1) Victor Meyer's method - for volatile substances

$$\text{Molar mass} = \frac{22400}{\text{volume(at STP) cm}^3 \text{ of vapour produced}} \times \text{mass of substance used for vaporisation}$$

E. Empirical formula and molecular formula

Empirical formula = simplest whole number ratio of atoms of various elements present in one molecule of the compound; Molecular formula = $(\text{empirical formula})_n$

$$\text{Where n} = \frac{\text{molar mass of compound}}{\text{empirical formula mass of the compound}}$$

Section 1 - Straight objective type questions

1. A mixture of benzene (B.P. 353 K) and nitrobenzene (B.P. 484 K) can be separated by

   1) Simple distillation

   2) Vacuum distillation

   3) Fractional distillation

   4) Steam distillation

2. Steam distillation is used when the compound to be purified

   1) Is insoluble in water

   2) Has high boiling point

   3) Has considerable vapour pressure at 100°C

   4) All of these

3. A mixture of naphthalene and benzoic acid can be separated by which of the following methods?

   1) Sublimation

   2) Filtration followed by crystallisation

   3) Simple distillation

   4) Fractional crystallization

4. In steam distillation, the vapour pressure of volatile organic compound is

   1) Equal to atmospheric pressure

   2) Double to atmospheric pressure

   3) Less than atmospheric pressure

   4) More than atmospheric pressure

5. The most suitable method for the separation of a 1 : 1 mixture of ortho-nitrophenol and para-nitrophenol is

   1) Sublimation 2) Vacuum distillation

   3) Steam distillation 4) Solvent extraction

6. Petroleum products like LPG, gasoline, paraffin oil, diesel oil etc are separated from mineral oil by

   1) Steam distillation 2) Chromatography

   3) Vacuum distillation 4) Fractional distillation

7. **Assertion (A)** : A mixture of red and blue inks can be separated by distributing the components between stationary and mobile phases in paper chromatography

   Reason (R) : The coloured components of inks migrate at different rates because paper selectively retains different components according to their differing partition in the two phases.

   1) Both A and R are true and R is the correct explanation of Assertion

   2) Both A and R are true and R is not the correct explanation of Assertion

   3) A is true but R is false

   4) Both A and R are false

8. Which of the following is correct regarding paper chromatography?

1) Mobile phase is liquid and stationary phase is solid

2) Mobile phase is solid and stationary phase is liquid

3) Both mobile phase and stationary phase are solid

4) Both mobile phase and stationary phase are liquid

9. A mixture of acetone and methanol can be separated by :

1) Vacuum distillation 2) Steam distillation

3) Fractional distillation 4) Simple distillation

10. Which of the following statements is not correct regarding chromatography?

1) Paper chromatography is an example of partition chromatography

2) Retardation factor, $R_f = \frac{\text{Distance travelled by component from base line}}{\text{Distance travelled by solvent from base line}}$

3) In thin layer chromatography, adsorbent is a liquid

4) Thickness of adsorbent layer on TLC plate is approximately 0.2 mm

11. A nitrogen containing organic compound when fused with sodium metal forms

1) Sodium cyanate 2) Sodium cyanide 3) Sodium azide 4) Sodamide

12. The formula of the product formed when sodium fusion extract of a compound containing sulphur is treated with sodium nitroprusside is

1) NaCNS 2) Na_2S

3) $Na_4\left[Fe(CN)_5 NOS\right]$ 4) $Na_3\left[Fe(CNS)_2 NO\right]$

13. Match List-I with List-II

List-I (Compound)	**List-II (Colour)**
I) $Fe_4\left[Fe(CN)_6\right]_3.xH_2O$	P) White
II) $(NH_4)_3 PO_4.12MoO_3$	Q) Yellow
III) $\left[Fe(SCN)\right]^{2+}$	R) Red
IV) AgI	S) Blue
	T) Violet

1) $I \rightarrow T; II \rightarrow P; III \rightarrow S; IV \rightarrow Q$ 2) $I \rightarrow S; II \rightarrow Q; III \rightarrow R; IV \rightarrow Q$

3) $I \rightarrow S; II \rightarrow P; III \rightarrow T; IV \rightarrow P$ 4) $I \rightarrow T; II \rightarrow Q; III \rightarrow R; IV \rightarrow P$

14. In Dumas method, the nitrometer contains

1) Aq. $CuSO_4$ 2) KOH solution 3) CuO 4) Anh. $CaCl_2$

15. In Kjeldahl's method, nitrogen is estimated as

1) NH_3 2) N_2 3) Nitric acid 4) Sodium nitrite

16. The transformation occurring in Dumas method is given below

$$C_2H_7N+\left(2x+\frac{y}{2}\right)CuO \rightarrow xCO_2+\frac{y}{2}H_2O+\frac{z}{2}N_2+\left(2x+\frac{y}{2}\right)Cu$$

The value of $\left(2x+\frac{y}{2}\right)$ is _____

1) 7 2) 3.5 3) 9 4) 7.5

17. 0.8 g of an organic compound was analysed by Kjeldahl's method for the estimation of nitrogen. If percentage of nitrogen in the compound is 42%, then ____mL of 1 M H_2SO_4 would have been neutralized by ammonia evolved during the analysis.

1) 12 2) 24 3) 36 4) 20

18. Carius method can be used for the estimation of element(s)

1) Halogens 2) Sulphur 3) Phosphorous 4) All of these

19. 2.54 g of an organic compound gave 0.94 g of AgI in the Carius estimation. Percentage of iodine in the organic compound is

1) 15% 2) 20% 3) 25% 4) 40%

20. A compound contains carbon, hydrogen and nitrogen in the ratio of 9 : 1 : 3.5 by weight. If molar mass of the compound is 108, then its molecular formula will be

1) $C_2H_6N_2$ 2) C_3H_4N 3) $C_6H_8N_2$ 4) $C_9H_{12}N_3$

21. In Dumas method for the estimation of nitrogen, 0.35 g of an organic compound gave 55 mL of N_2 collected at 300 K and 715 mm pressure (aqueous tension of water at this temperature is 15 mm). Percentage of nitrogen in the organic compound is

1) 14.45% 2) 15.45% 3) 16.46% 4) 17.45%

22. 1 g of an organic compound containing 56% nitrogen was Kjeldahlised and the ammonia evolved was absorbed in 50 mL, $\frac{M}{2}H_2SO_4$. What volume of 0.5 N NaOH would be required to neutralise the residual acid?

1) 40 mL 2) 30 mL 3) 20 mL 4) 60 mL

23. 0.2 g of an organic compound gave 0.44 g of CO_2 during the estimation of oxygen. The percentage of oxygen in the organic compound is

1) 20% 2) 40% 3) 60% 4) 80%

24. Choose the incorrect statement from the following

1) Chemical formula of nitroprusside ion is $[Fe(CN)_5NOS]^{2-}$

2) Oxidation number of iron in the nitroprusside ion is +2

3) I_2O_5 is used as an oxidising agent in the Aluise's method for estimation of oxygen

4) The yellow precipitate of AgBr is partially soluble in NH_4OH

25. Match List-I with List-II

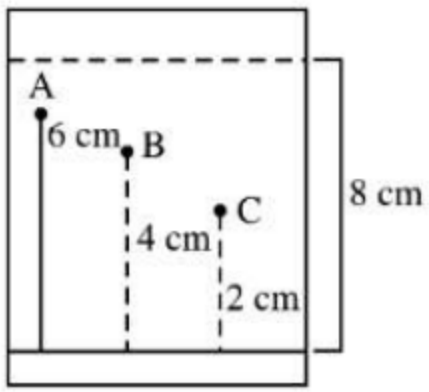
List-I (Element)	**List-II (Reagent used in estimation)**
I) N	P) $N_2 + C + I_2O_5$
II) S	Q) Conc. H_2SO_4 + $CuSO_4$
III) O	R) Na_2O_2 + $BaCl_2$
IV) P	S) Fuming HNO_3 + Magnesia mixture

1) $I \rightarrow Q; II \rightarrow S; III \rightarrow P; IV \rightarrow S$ 2) $I \rightarrow P; II \rightarrow R; III \rightarrow Q; IV \rightarrow S$

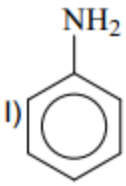
3) $I \rightarrow P; II \rightarrow S; III \rightarrow Q; IV \rightarrow R$ 4) $I \rightarrow Q; II \rightarrow R; III \rightarrow P; IV \rightarrow S$

Integer type questions

26. Three organic compounds A, B and C were allowed to run in thin layer chromatography using hexane and gave the following result (see figure). The R_f value of the most polar compound is _____ $\times 10^{-2}$



27. Among the following, the total number of compound(s) that do(es) not give Lassaigne's test for nitrogen is .....

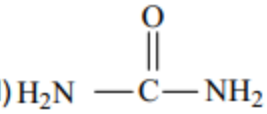
I) 

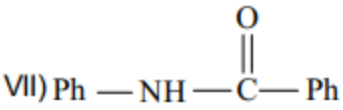
II) $H_2N - CH_2 - COOH$

III) NH_2NH_2

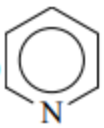
IV) $Ph - N = N - Ph$

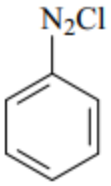
V) NH_2OH

VI) 

VII) 

VIII) $Ph - NO_2$

IX) 

X) 

28. How many of the following compounds may give blood red colour during Lassaigne's test for nitrogen?

Thiourea, Glycine, Methionine, sulphanilic acid, Benzenesulphonic acid

29. The total number of compound(s) among the following for which Kjeldahl's method is not applicable is .....

Nitrobenzene, Azobenzene, Pyridine, Benzenediazonium chloride, Aniline, Quinoline

30. If the percentage of nitrogen in an organic compound is 12.5, the volume of N_2 gas at STP (1 atm, 273 K) that may be obtained from 0.56 g of the compound in Dumas method will be ..... mL