Chemistry Notes Class 11 Chapter 12 Organic Chemistry – Some Basic Principles and Techniques part 2

Organic compounds extracted from a natural source or synthesized in the laboratory requires purification. Various methods are used for the purification and are based on the nature of the compound and the impurity present in it. The purity of a compound is ascertained by determining its melting point or boiling point or by chromatographic and spectroscopic techniques.

Methods of Purification of Solids

1. **Cystallisation** In this process, a saturated solution of impure substance is prepared in hot solvent and heated with animal charcoal which adsorbs the impurities. The solution is filtered and filtrate on cooling deposits crystals of pure compound. Success of the process depends upon the selection of the solvent. The impurities must be least soluble. A process in which crystal formation is initiated by adding crystals of pure substance, is known as seeding.
2. **Fractional crystallisation** It is based on the different solubilities of different compounds in a solvent. The compound having less solubility crystallises out first on cooling leaving behind others in solution. Sometimes mixture of two solvents, e.g., alcohol and water. chloroform and petroleum ether, give better results.
3. **Sublimation** Some solids directly convert into vapours when heated without converting into liquid. These are known as sublimate and this process is called sublimation. The substances which sublime can be purified by this method provided the impurities present does not sublime. Camphor, naphthalene and anthracene are purified by sublimation.

Methods of Purification of Liquids

1. **Simple distillation** The vaporisation of a liquid by heating and subsequent condensation of vapours by cooling is known as distillation. The liquids boiling under ordinary conditions of temperature and pressure without decomposition and containing non-volatile impurities are purified by simple distillation.
2. **Fractional distillation** It is employed for separating mixture of two or more volatile liquids having boiling points close to each other e.g , acetone (boiling point 60°C) and methanol (boiling point 65°C). Components of petrolium are separated by this method. The vapours of the liquids are passed through the fractionating column which provides greater space for their cooling. The vapours of high boiling substance condense and fall back into distillation flask.
3. **Distillation under reduced pressure or vacuum distillation** Some liquids decompose when heated to their boiling points e.g., glycerol. Such liquids can be purified by distillation under reduced pressure much below than their boiling points.

4. **Steam distillation** The liquids insoluble in water, steam volatile in nature, having high molecular weight and high vapour pressure are purified by steam distillation provided the impurities present are not steam volatile. e.g., o-hydroxy acetophenone and jrhydroxy acetophenone are separated by this method.
5. **Separating funnel** By this, a mixture of two immiscible liquids can be separated.

Chromatographic Method

It was discovered by Tswett (1906).

It is based upon the principle of selective adsorption of various components of a mixture between the two phases: stationary or fixed phase and mobile phase.The various chromatographic
techniques are:

1. Adsorption Chromatography

Stationary phase- Solid or ion exchange resin. Mobile phase-Liquid or gas.

It includes liquid-solid chromatography, gas-solid chromatography or ion exchange chromatography.

2. Partition Chromatography

Fixed phase-liquid supported on inert solid. Mobile phase-liquid or gas.

This process is known as liquid-liquid partition chromatography or liquid-gaspartition chromatography on the basis ofits different phases.

3. Paper Chromatography

The principle of paper chromatography is based on the fact that solutes have the capacity to migrate through filter paper at different rates as a solution is drawn into strip of paper by capillary action.

In paper chromatography, the dissolved substance is applied as a small spot about 2-3 cm from the edge of a strip or square of filter paper and is allowed to dry. This strip is then suspended in a large close container where atmosphere is saturated with the solvent system. The end containing the sample is dipped into the mobile pbase which has already been saturated with the stationary phase. When the solvent front has reached at the other end of the paper, the strip is removed and the zones are located by analytical methods.

(The ratio of the distance travelled by a component to the distance travelled by the solvent front is characteristic of each component and is known as the R_f value.

R_f = (distance in em from starting line to the centre of zone/distance in cm from starting line to the solvent front)

4. Column Chromatography

It is an example of adsorption chromatography. Adsorbents used are alumina, silica gel, cellulose powder, animal charcoal, keiselguhr etc.

Liquid solvents used are benzene. petroleum ether, alcohol etc.

When the solvent is poured over the mixture present at the top of a column packed with adsorbent, the components are separated into, number of layers called zones, bands or chromatograms due to preferential adsorption.

Elution The continuous pouring of solvent from the top of the column is known as elution or running of column. Solvent is known as eluant. The most weakly adsorbed component is eluted first by least polar solvent while more strongly adsorbed component is eluted later by highly polar solvents.

Chemical Methods of Purification

The substance to be purified is treated with a suitable chemical reagent to form a stable derivative. It is then separated by suitable method and decomposed to get the pure compounds.

Examples

1. Mixture of amines (1°, 2° and 3°) is separated by Hinsberg's method.
2. Acetic acid from pyroligneous acid is separated by forming calcium salt.
3. Acids are separated by froming sodium derivatives with $NaHCO_3$·
4. Absolute alcohol is obtained from rectified spirit by quick lime process and azeotropic distillation.

1. Azeotropic Distillation

Azeotropes are constant boiling mixtures which distil off without any change in composition at a fixed temperature. Therefore, components of an azeotropic mixture cannot be separated by fractional distillation. A very common example of azeotropic mixture is rectified spirit which contains 95.87% ethyl alcohol and 4.23% water by weight which boils at 351.1 K.

(Such mixtures are separated by adding another component which generate a new lower boiling azeotrope that is heterogeneous (i.e., producing two immiscible liquid phases). e.g., C_6H_6 is added to H_2O and ethyl alcohol azeotrope to separate them.

2. Differential Extraction

This method is used to separate an organic compound present in aqueous solution which is more soluble in other solvent than in water.

Qualitative Analysis of Organic Compounds

1. Detection of Carbon and Hydrogen

This is done by heating the given organic compound with dry cupric oxide in a hard glass test tube when carbon present is oxidised to carbon dioxide and hydrogen is oxidised to water.

$$C + 2CuO \xrightarrow{\Delta} CO_2 + 2Cu$$
$$2H + CuO \xrightarrow{\Delta} H_2O + Cu$$

Carbon dioxide turns lime water milky.

$$Ca(OH)_2 + \underset{\text{from C}}{CO_2} \longrightarrow \underset{\text{milky}}{CaCO_3} + H_2O$$

Water condenses on the cooler parts of the test tube and turns anbydrous copper sulpbate blue.

$$\underset{\text{white}}{CuSO_4} + 5H_2O \longrightarrow \underset{\text{blue}}{CuSO_4 \cdot 5H_2O}$$

Lassaigne's Test

The organic compound is fused with a small piece of Na metal. When element (N, 8, X) of the organic compound combine to give NaCN,Na_2S or NaX; the red hot tube is plunged in distilled water, boiled and filtered. The filtrate is called Lassaigne's extract or sodium extract. The Lassaigne's extract is usually alkaline. If not, it is made alkaline by adding a few drops of a dilute solution of sodium hydroxide.

The purpose of fusing the organic compounds with sodium metal is to convert halogens, N, S, P etc., present in the organic compound to their corresponding soluble sodium salts (ionic compounds).

$Na + C + N \rightarrow NaCN$
$2Na + S \rightarrow N_2S$ (where, X = Cl, Br, I)
$Na + X \rightarrow NaX$

1. Detecton of Nitrogen

To a part of this alkaline solution is added a few drops of a freshly prepared solution of ferrous sulphate, because a dilute solution of $FeSO_4$ after a long time oxidise to basic ferric sulphate which is useless for analysis. The contents are warmed a little, cooled and then acidified with dil. H_2SO_4. Appearance of a green or Prussian blue colouration indicates the presence of nitrogen.

$$6CN^- + Fe^{2+} \longrightarrow [Fe(CN)_6]^{4-}$$

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

If S is also present alongwith N, a red colour in place of Prussian blue in the test of nitrogen appears, due to the formation of $Fe(CNS)_3$.

Hydrazine does not give Lassaigne's test for nitrogen since it does not contain carbon. In order to test the presence of N in such compounds, during fusion with Na, some charcoal or preferably strch (which contains C but not N, S, halogens etc.) is added. Under these conditions. C of starch or charcoal combines with N of the compound to form NaCN which will now give a positive test for nitrogen.

Lassaigne's test is not shown by diazonium salts because diazonium salts usually lose N_2 on heating much before they have a chance to I react with fused sodium metal.

2. Detection of Sulphur

(i) Sodium fusion extract is acidified with acetic acid and acetate is added to presence of sulphur.

(ii) On treating sodium fusion extract with sodium nitroprusside, apperance of a violet colour further indicates the presence of sulphur.

$$S^{2-} + [Fe(CN)_5NO]^{2-} \longrightarrow \underset{\text{violet}}{[Fe(CN)_5NOS]^{4-}}$$

3. Detection of Halogens

The sodium fusion extract is acidified with nitric acid and then treated with silver nitrate.

$X^- + Ag^+ \rightarrow AgX$

X represents a halogen -Cl Br, or I.

AgCl white ppt, AgBr-dull yellow ppt, AgI-bright yellow ppt.

Note Beilstein test is also a test for halogen but it is not a confirmatory test.

Detection of Phosphorus

The compound is heated with an oxidising agent (sodium peroxide). By this the phosphorus present in the compound is oxidised to phosphate.

The solution is boiled with nitric acid and then treated with ammonium molybdate. A yellow colouration or precipitate indicates the presence of phosphorus.

$$Na_3PO_4 + 3HNO_3 \longrightarrow H_3PO_4 + 3NaNO_3$$

$$H_3PO_4 + 12(NH_4)_2MoO_4 + 21HNO_3 \longrightarrow \underset{\substack{\text{ammonium}\\ \text{phosphomolybdate}\\ \text{(yellow ppt)}}}{(NH_4)_3PO_4 \cdot 12MoO_3} + 21NH_4NO_3 + 12H_2O$$

Detection of Oxygen

There is no direct method to detect oxygen in compounds. It is present in the form of functional groups such as -OH, -COOH. $-NO_2$ etc.

Qauantitative Estimation of Elements

1. Estimation of Carbon and Hydrogen (Liebig's Method) When a known mass of organic compound is strongly heated with dry euO, C and H present are quantitatively oxidised to CO_2 and H_2O respectively,

$$C_xH_y + \left(x + \frac{y}{4}\right)O_2 \longrightarrow xCO_2 + \frac{y}{2}H_2O$$

By knowing the amount of CO_2 and H_2O from known weight of organic compound, the percentage of carbon and hydrogen can be computed,

The water is absorbed in anhydrous $CaCl_2$.

The carbon dioxide is absorbed in concentrated solution of KOH.

$$\text{Percentage of carbon} = \frac{12}{44} \times \frac{\text{wt. of } CO_2 \times 100}{\text{wt. of organic substance}}$$

$$\text{Percentage of hydrogen} = \frac{2}{18} \times \frac{\text{wt. of } H_2O \times 100}{\text{wt. of organic substance}}$$

On heating with CuO, elements other than C and H are also modified as follows:

When organic compound contains nitrogen. the oxides of nitrogen

(NO,N_2O etc.) are absorbed by caustic potash. These are removed by the use of bright copper gauge.

$4Cu + 2NO_2 \rightarrow 4CuO + N_2$

$Cu + N_2O \rightarrow CuO + N_2$

Nitrogen is not absorbed by KOH solution.

When organic compound contains halogens, they are removed by using silver gauge by forming non-volatile silver halide.

When sulphur is present, it is removed by forming lead sulphate by using fused lead chromate and halogens form lead halides.

Estimation of Nitrogen

(i) Duma's method This method is used for nitrogenous compounds. Though tedious but it is better than Kjeldahl's method.

In this method, the nitrogenous compound is heated strongly with ceo in the atmosphere of CO_2 and the mixture obtained is passed over a roll of heated bright Cu gauze. The oxides of nitrogen again reduce to N_2. The resultant mixture is passed in KOH. All gases except N_2 are fairly absorbed. Nitrogen is collected over KOH and its volume at NTP is measured.

Organic compound + conc. H_2SO_4 + (small amount of K_2SO_4 and its volume at NTP is measured.

$$\text{Percentage of nitrogen} = \frac{28 \times \text{volume of } N_2 \text{ at NTP} \times 100}{22400 \times \text{wt. of organic compound}}$$

$$= \frac{\text{wt. of nitrogen} \times 100}{\text{wt. of organic substance}}$$

(ii) Kjeldahl's method Organic compound + conc. H_2SO_4 + (small amount of K_2SO_4 and

$$CuSO_4 \rightarrow (NH_4)_2SO_4 \xrightarrow{2NaOH} Na_2SO_4 + 2NH_3 + 2H_2O$$

Ammonia is passed through H_2SO_4 or HCl of known volume and normality. The volume of acid neutralised by NH_3 is calculated by neutralising the acid left by NaOH solution.

Percentage of nitrogen = (1.4 x N x V/wt. of organic compound)

N = normality of acid
V = volume of acid in mL neutralised by ammonia.

(In practice, K_2SO_4 is added to raise the boiling point of H_2SO_4 and $CuSO_4$ is added to catalyse the reaction).

Kjeldahl's method is not reliable as results obtained are generally low. It cannot be applied to compounds containing nitrogen directly linked to oxygen or nitrogen such as nitro, nitroso, azo and nitrogen present in ring as in pyridine.

Estimation of Halogen (Carius Method)

Organic compound + fuming HNO_3 + AgNOa → AgX

It is estimated gravimetrically.

Percentage of halogen = (wt. of halogen atom x wt. of AgX x 100/mol. wt. of AgX x wt. of organic compound)

Estimation of Sulphur

$$\text{Organic compound} + \text{Oxidising agent} \rightarrow H_2SO_4 \xrightarrow{BaCl_2} BaSO_4$$

It is estimated gravimetrically,

$$\text{Percentage of sulphur} = \frac{32 \times \text{wt. of } BaSO_4 \times 100}{233 \times \text{wt. of organic compound}}$$

Estimation of Phosphorus

Organic compound + Fuming nitric acid → H_3PO_4

$$\xrightarrow[\substack{\text{mixture} \\ (MgSO_4 + NH_4OH + NH_4Cl)}]{\text{Magnesia}} MgNH_4PO_4 \xrightarrow{\text{Ignition}} \underset{\substack{\text{(magnesium} \\ \text{pyrophosphate)}}}{Mg_2P_2O_7}$$

$$\text{Percentage of phosphorus} = \frac{62 \times \text{wt. of } Mg_2P_2O_7 \times 100}{222 \times \text{wt. of organic compound}}$$

Now a day CHN elemental analyser is used to estimate the C, H and N in the organic compound.

Determination of Empirical Formula

Empirical formula expresses the relative number of atoms present in the molecule. It is calculated from percentage composition of the compound.

Determination of Molecular Formula

Molecular formula = (Empirical formula)$_n$

n = (molecular weight/empirical formula weight)