Chapter

1

Introduction

Organic chemistry is the branch of chemistry that deals with the structure, properties, composition, reactions and preparation of all chemical compounds containing the element carbon. Organic compounds are having large number of groups like alcohols, ketones, acids, ethers, etc. They are the main constituents of drugs, petrochemicals, paints, food, plastics, explosive materials, etc. Some of the primary industries that utilize organic chemistry for their research and development purposes include the pharmaceutical, petrochemical, food, biotechnology, and cosmetic industries.

The objects of study in organic chemistry include hydrocarbon, compounds containing carbon and hydrogen and the compositions based on carbon but containing other elements. Organic compounds form the basis of earthly life and their range of application is enormous. Organic analysis is performed for their identification which includes determination of several physical and chemical properties of the compound. The compound used for analysis must be pure because an impure compound will not give a sharp and correct melting point or boiling point. An impure compound may be purified by crystallization and impure liquids are purified by distillation process. After physical constant determination, a systematic qualitative analysis for identification of the compounds is to be performed. The basic laboratory techniques utilized by organic chemists can be separated into four major categories, which include:

1. General laboratory techniques
2. Crystallization and recrystallization
3. Extraction
4. Chromatography

1. GENERAL LABORATORY TECHNIQUES

There are number of laboratory techniques. Some common laboratory procedures are given below.

Glassware Handling

Dirty glassware may be cleaned with soap and water using a brush. However, glassware which has persistent stains from organic substances requires soaking in chromic acid cleaning solution. This mixture has to be used carefully as it is very corrosive. Glass tubing with unpolished ends is a hazard since it can cause serious cuts when trying to insert it into a cork. Therefore, only glass tubing with polished ends must be used. When forcing glass tubing into a cork, grasp it as close as possible to the cork and be careful not to break it. Quickfit glass joints should always be lubricated with a suitable lubricant

(grease). A thin film of grease is applied to the joints to provide an air-tight seal and to prevent the joints from being stuck together. There should be no excess grease extending inside the apparatus as it might contaminate the reaction mixture. It is also recommended that old grease be wiped off with a piece of tissue paper before applying a new film.

Heating Devices

There are various heating devices in the laboratory. The Bunsen burner and water bath are the most commonly used. A limitation of the Bunsen burner is that it should not be used directly for heating flammable solvents. Flammable and volatile liquids are heated in a water bath when temperatures under 100 are required. If an electrical steam bath is not available, a large beaker filled with water may be used instead. It is heated to boiling with a Bunsen burner and the flame extinguished before heating the flammable liquid in the bath. Bumping may be prevented by continuous stirring to ensure homogenous and steady heating of the liquid or by the use of boiling stones which achieve a similar effect through formation of bubbles.

Refluxing

The technique of refluxing is commonly used when it is necessary to heat a reaction in order to bring it to completion in a reasonable time span. A reflux condenser is used to minimize loss through evaporation of volatile reactants, products or solvent by allowing the vapors to recondense and return to the reaction vessel.

2. CRYSTALLIZATION AND RECRYSTALLIZATION

Crystallization is a simple, effective, and very important technique to separate and purify solids. Crystallization is used to purify a solid. It is based on the fact that all organic compounds are more soluble in hot than in cold solvents, so that solid gets dissolved on heating and is obtained back on cooling. The process requires a suitable solvent. A suitable solvent is one which readily dissolves the solid (solute) when the solvent is hot but not when it is cold. The best solvents exhibit a large difference in solubility over a reasonable range of temperatures (e.g. water can be crystallization solvent between 0 and 100°C; hydrocarbon solvents such as hexanes or petroleum ether have a different T range since they can be cooled below 0 degrees but boil below 100 degrees). Crystallization can be performed using either water, a single solvent, or multiple solvents, depending upon the specific requirements of a given compound.

Steps Involved in Crystallization

The following steps are involved in the purification by crystallization:

- Selection of a solvent
- Dissolution of the sample
- Decolourisation of the solution
- Hot filtration
- Cooling for crystallization
- Cold filtration
- Washing the crystals
- Drying the crystals

- Checking the purity
- Melting point determination
- Boiling point determination and distillation

Common Solvents for Crystallization

Common solvents for crystallization are acetone, chloroform, carbon tetrachloride, water, petroleum ether, diethyl ether, ethanol, benzene, cyclohexane, acetic acid, etc.

Characteristics of Solvents

a. Chosen for solubilizing power— solubility usually increases with increasing time.
b. Polarity is important—like dissolves and polar compounds are more soluble in polar solvents; nonpolar compounds in nonpolar solvents.
c. Should be inert but a few, e.g. acetic acid is sometimes used as a solvent although it will certainly react with basic compounds.
d. Almost all solvents are **combustible**—avoid flames.
e. Mixed solvents (e.g; 1:1 water/methanol) provide a huge range of possible solvents but they must be soluble in one another.

In certain cases, recrystallization may be used for the separation of a solid mixture. When the impure solid is dissolved in a minimum volume of a suitable hot solvent and the resulting solution is gradually cooled, saturation and eventual crystallization of the pure compound occurs. Impurities in a solid are of two kinds—soluble and insoluble, and recrystallization involves the removal of both to purify a solid. Insoluble impurities are first removed by gravity filtration of the hot solution while the soluble impurities remain dissolved in the cold saturated solution (*mother liquor*) after precipitation of the desired compound. The pure crystals are separated from the supernatant liquid by suction filtration. After drying, the purity is checked by a melting point determination.

Filtration

Filtration is used whenever an insoluble solid is to be separated from a liquid. Simple gravity filtration (usually hot filtration) is employed to remove insoluble solid impurities from a liquid, while suction filtration (usually cold filtration) is used to collect a desired solid or crystalline product.

Preparation of a Fluted Filter Paper for Filtration

The filter paper is first divided into eight equal sectors by making fourfold in the paper. The folding is continued, the edge 2, 1 is then folded on to 2, 6 and 2, 3 to 2, 5 to produce new folds 2, 7 and 2, 8, respectively. Further 2, 3 to 2, 6 and 2, 1 to 2, 5 give new folds 2, 9 and 2, 10 respectively. Finally, a fold is made on each of the eight segments, e.g. between 2,3 and 2,9/2,9 and 2,6 and so on in a direction opposite to the first series of folds to give a fan arrangement which on opening gives a fluted filter paper. The above sequence is shown in Fig. 1.1.

Decolorization

Most organic compounds are colorless. Highly conjugated compounds (e.g. polar polymers) will absorb light in the visible region of the spectrum and thus, be “colored”.

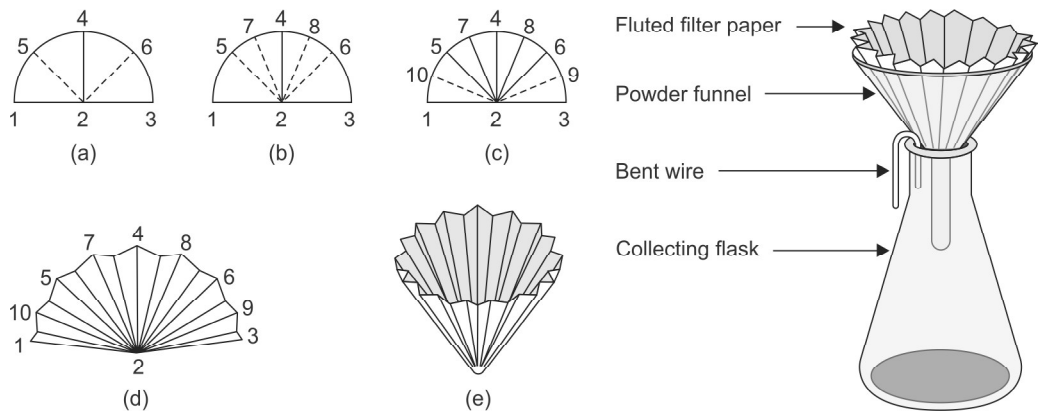


Fig. 1.1: Fluted filter paper and apparatus for gravity filtration

If these highly polar, large molecules are impurities, they can be removed by use of finely granulated activated charcoal. Polar compounds (e.g. polar impurities) adsorb to the charcoal which is insoluble in the solvent and can be filtered away from solution. Decolorization is used for the removal of colored impurities from a solution. This is achieved by the addition of activated charcoal to the solution and mixing thoroughly. If charcoal is added to a cold solution, the solution is first brought to a boil before hot filtration. When however, it is added to a hot solution, the flask should be removed from the heat source before the addition, otherwise bumping will occur. Charcoal is finally removed by filtration leaving an almost colorless solution.

Drying

The process of drying, if applied to a solid substance is aimed to remove residual solvent (organic or water) adhering to the solid particles/crystals. This is usually done by air drying (spreading over a sheet of paper/filter paper) and/or heating in an oven to enhance evaporation of the solvent. Drying of an organic liquid, however, involves the removal of traces of water (moisture) using chemical drying agents. Such cases are encountered in extraction where the organic phase is in direct contact with the aqueous phase. After separating the layers, traces of water in the organic phase are removed by the addition of a suitable drying agent. Some common examples are: Calcium chloride, magnesium sulfate, sodium sulfate, sodium hydroxide and potassium hydroxide.

Melting Point Determination

The melting point of a solid is the temperature at which transition from solid to liquid occurs at atmospheric pressure; or the temperature at which solid and liquid phases are in equilibrium at a pressure of one atmosphere. A simple device for determining melting points is used and it consists of a thermometer fitted through a cork and suspended into a long-necked flask which is three quarters filled with a high boiling and stable liquid like paraffin oil, dibutyl phthalate or silicon oil. The thermometer bulb should be about 1 cm above the bottom of the flask. The sample in the capillary tube is fastened to the thermometer with a rubber band placed above the level of the oil. The capillary tube should be close to and on a level with the thermometer bulb. To determine the melting point of a solid, a small amount of the powdered substance is introduced into a capillary

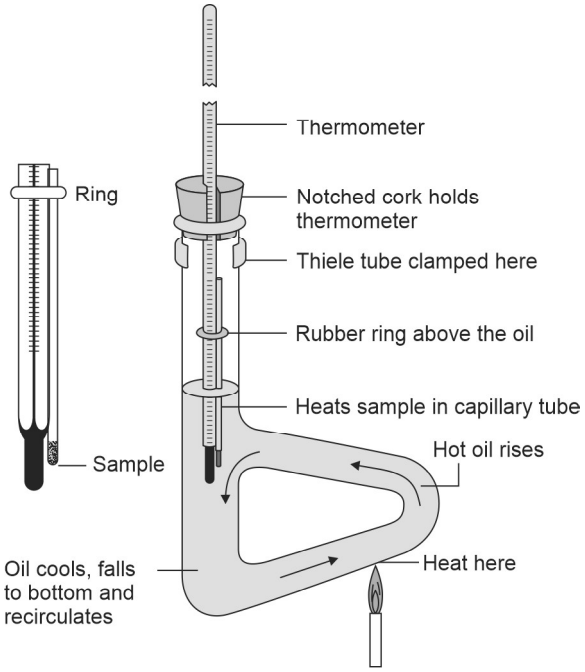


Fig. 1.2: Determine melting point

tube which is then attached to a thermometer and placed in the oil bath. The bath is heated rapidly to within 20 °C of the expected melting point then slowly, and at a constant rate of 2–3 degrees per minute, close to the melting point. The temperature at which the solid begins to melt, and that at which it is completely liquid, is recorded as the melting point range of that substance.

Boiling Point Determination and Distillation

The boiling point of a liquid is defined as the temperature at which the vapor pressure of the liquid equals the external pressure (usually 1 atmosphere). It is also defined as the temperature at which vapor and liquid are in equilibrium at a given pressure. The boiling point, like the melting point, is a physical constant and may be used to identify unknown organic liquids. Distillation is the process of heating a liquid to its boiling point, condensing the vapor by cooling, and collecting the liquid distillate. It is a technique for the purification of liquids and for the separation of liquid mixtures. As the distillation progresses, the mixture will gradually have less of the more volatile component and its boiling point will gradually rise. Consequently the distillate will contain a continually decreasing proportion of the more volatile component until finally all has been collected and the less volatile component is left as a residue.

In practice, separation of a liquid mixture into its components by a single distillation (simple distillation) is possible only when the boiling points of the components are 80 degrees or more apart. For mixtures of liquids having boiling points much less than 80 degrees apart, separation can be achieved only by fractional distillation. Such a distillation is equivalent to several repeated simple distillations. It uses a fractionating column which provides a large surface area for continuous heat exchange between the hot ascending vapor and the cooler descending liquid, thus resulting in a series of

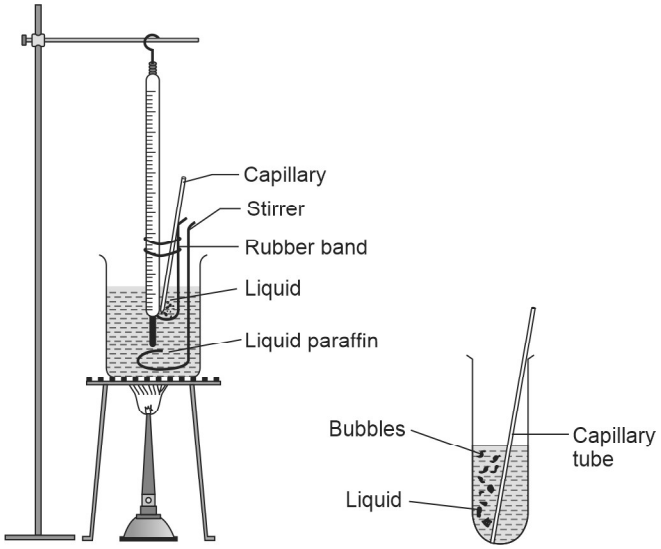
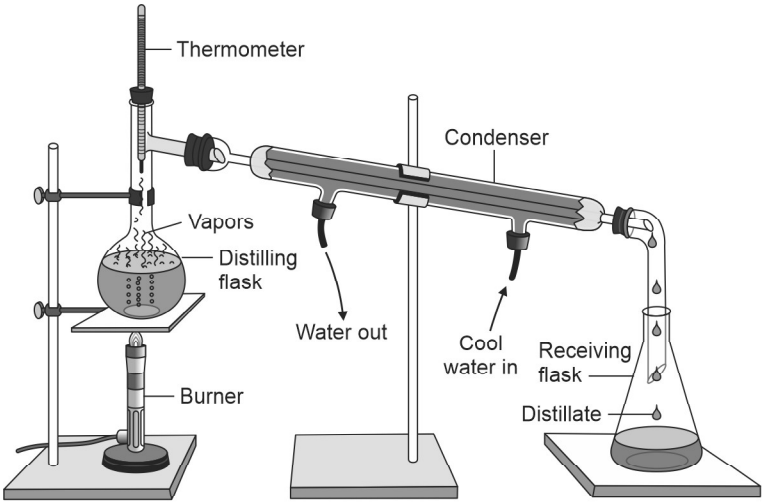
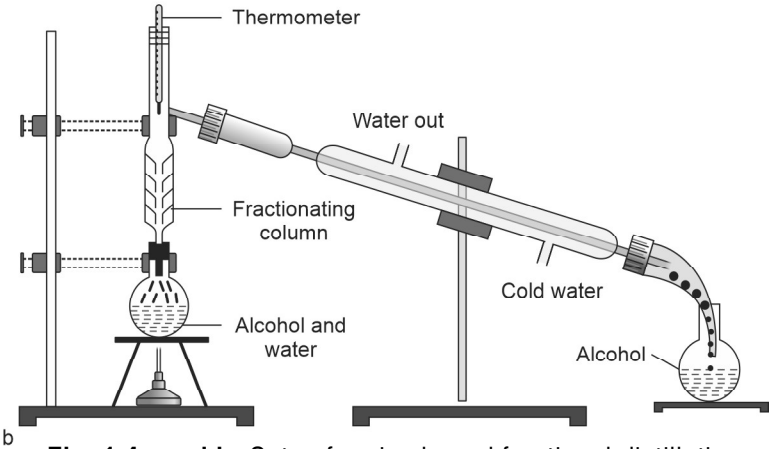


Fig. 1.3: Determine the boiling point



a



b

Fig. 1.4a and b: Setup for simple and fractional distillation

evaporations and condensations leading to separation of the two components. Vacuum distillation is a technique for the distillation of high boiling liquids, and for compounds that decompose at atmospheric pressure. At the low pressures employed, those compounds distil at much lower temperatures.

3. EXTRACTION

Extraction techniques in used to separate and transfer specific compounds from a mixture into a different solvent or phase. If the substance is extracted from a solid phase, the process is called solid-liquid extraction, as in the isolation of caffeine from tea leaves by means of hot water. The most commonly used extraction technique is liquid–liquid extraction, which involves the use of a separatory funnel. A compound of interest is placed directly into the funnel that contains a mixture of two liquid layers that are typically a mixture of an aqueous solution and an organic solvent. Since the organic solvent is immiscible, the specific components of the original compound will move from either the aqueous or organic layer, depending on their hydrophilicity or hydrophobicity, respectively.

4. CHROMATOGRAPHY

Chromatography is an important organic chemistry technique that allows researchers to separate, identify and purify the components present within a given mixture for analysis purposes. The basic principle behind any chromatography technique is that the molecules of a mixture are placed onto the surface of a solid material, which is otherwise referred to as the stationary phase. The mobile phase of this technique is a liquid or gaseous component that assists in the separation of the molecules within the mixture along the stationary phase.

Some of the most common chromatography methods that will be utilized in an organic chemistry lab include column, ion-exchange, affinity, paper, thin-layer, gas and high-pressure liquid chromatography (HPLC). Two principles are basically involved in chromatography: Adsorption (as in thin layer chromatography) and partition (as in paper chromatography), and certain terms are common to both types of chromatography. In adsorption chromatography, separation depends on the selective desorption of the components of a mixture by the eluent (mobile phase) from the surface of a solid adsorbent (stationary phase). The adsorbent may be packed in a column (column chromatography) or spread as a thin layer on a glass plate as in thin-layer chromatography. In partition chromatography, separation depends on partition of the components of a mixture between the stationary and mobile phases. The mobile phase may be a liquid (liquid–liquid partition chromatography) or a gas (gas-liquid partition chromatography).

Each of these laboratory techniques requires a variety of different supplies and equipment to be performed. For example, thin-layer chromatography (TLC) utilizes an absorbent material like alumina, silica gel or cellulose as its stationary phase that is placed within a glass container or plate for the separation procedure. Comparatively, HPLC requires an HPLC device that is equipped with a solvent depot, high-pressure pump, and commercially prepared column that is suitable for the researcher's specific project, detector, recorder and a computerized system that is used to record all obtained measurements.