QUALITATIVE ANALYSIS OF ORGANIC COMPOUNDS

Exploration of the constituents within any organic compound is a crucial phase in its study. Aside from carbon and hydrogen, organic compounds often include other elements such as nitrogen, sulfur, halogens, etc., which can be identified through specific detection methods:

(a) Detection of Carbon and Hydrogen

Carbon and hydrogen are discerned by subjecting the compound to heating in the presence of copper (II) oxide. In this process, carbon within the compound undergoes oxidation to produce carbon dioxide, while hydrogen is transformed into water vapors through the following reactions:

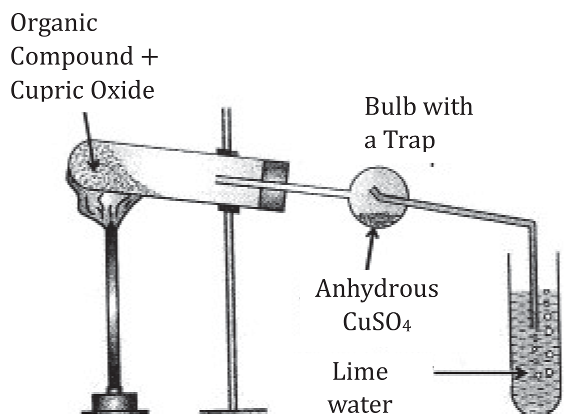
$$\underset{\text{(From Organic Compound)}}{C} + 2CuO \rightarrow 2Cu + CO_2$$

$$\underset{\text{(From Organic Compound)}}{H} + CuO \rightarrow Cu + H_2O$$

The evolved gaseous products are directed first over anhydrous copper sulfate powder (appearing white) housed in a bulb and then through lime water. The presence of water vapor turns copper sulfate blue, while the presence of only carbon dioxide has no effect on copper sulfate but causes lime water to turn milky.

$$\underset{\substack{\text{Colourless} \\ \text{(White)}}}{CuSO_4(s)} + 5H_2O \rightarrow \underset{\text{Blue}}{CuSO_4 \cdot 5H_2O}$$

$$\underset{\substack{\text{Lime} \\ \text{water}}}{Ca(OH)_2} + CO_2 \rightarrow CaCO_3 + H_2O$$



This process is commonly referred to as the copper oxide test.

Detection of Other Elements (Nitrogen, Sulfur, Halogens, Phosphorus): The identification of nitrogen, sulfur, halogens, and phosphorus in an organic compound is accomplished through Lassaigne's test. To conduct this test, a sodium extract or Lassaigne's extract must be prepared. This involves introducing a small piece of dry sodium metal into a fusion tube, gently heating until it forms a glossy globule. Subsequently, a small quantity of the organic compound is added, and the tube is vigorously heated until it reaches a red-hot state. The red-hot tube is then immersed in distilled water within a China dish, boiled for a period, cooled, and filtered. The resulting filtrate is termed the sodium extract.

During the fusion process, the elements existing in the organic compound combine with sodium to form ionic sodium compounds.

$$Na + C + N \rightleftharpoons NaCN$$
$$2Na + S \rightleftharpoons Na_2\,S$$
$$Na + X \rightarrow NaX[X = Cl, Br, I]$$

Carbon, nitrogen, sulfur, and X originate from the organic compound.

(b) Test for Nitrogen

In this procedure, approximately 2 ml of sodium extract is placed in a test tube and rendered alkaline by the addition of NaOH solution. To this alkaline mixture, a freshly prepared solution of $FeSO_4$ is introduced, and the resulting mixture is boiled for a duration of 3–4 minutes. The presence of nitrogen is indicated by the emergence of Prussian blue coloration or precipitate.

The associated reactions can be delineated as follows:

$$Na + C + N \rightarrow \underset{\substack{\text{Sodium cyanide} \\ \text{(sodium extract)}}}{NaCN}$$
$$FeSO, + 2NaOH \rightarrow Na_2SO_4 + Fe(OH)_2$$
$$6\,NaCN + Fe(OH)2 \rightarrow \underset{\substack{\text{Sodium ferrocyanide} \\ \text{(sodium hexacyanoferra II)}}}{Na_4[Fe(CN)_6]} + 2NaOH$$

Upon heating with concentrated H_2SO_4, some iron (II) ions undergo oxidation to form iron (III) ions in the reaction.

$$\underset{\text{Sod.ferrocyanide}}{Na_4[Fe(CN)_6]} + Fe^{+3} \rightarrow \underset{\substack{\text{Iron (III) hexacyanoferra (II) (ferric} \\ \text{ferrocyanide) Prussian blue in colour}}}{Fe_4[Fe(CN)_6]_3}$$

(c) Test for Sulphur

(i) Lead Acetate Test:

A portion of the sodium extract is subjected to the Lead Acetate Test. Acetic acid and lead acetate are introduced to the sodium extract, resulting in the formation of a black precipitate, confirming the presence of sulphur.

The chemical reactions involved are as follows:

$$\underset{\text{From sodium extract}}{Na_2\,S} + \underset{\text{Lead acetate}}{(CH_3COO)_2\,Pb} \rightarrow \underset{\text{Black ppt}}{PbS} + \underset{\text{Sodium acetate}}{2CH_3COONa}$$

(ii) Sodium Nitroprusside Test:

In another segment of the sodium extract, a few drops of sodium nitroprusside are added. The appearance of a violet coloration indicates the presence of sulphur.

The chemical reaction is expressed as:

$$\underset{\text{From sodium exiract.}}{Na_2\,S} + \underset{\text{Sodium Nitroprusside}}{Na_2[Fe(CN)_5NO]} \rightarrow \underset{\text{Violet colour}}{Na_4\,[Fe(CN)_5NOS]}$$

(iii) Lassaigne's Test:

When the organic compound under scrutiny contains both nitrogen and sulphur, the Lassaigne's Test is conducted, resulting in the formation of sodium thiocyanate.

The reactions can be represented as:

$$\underset{\substack{\text{From organic} \\ \text{compoune}}}{Na + C + N + S} \rightarrow NaSCN$$
$$3NaSCN + Fe^{+3} \rightarrow \underset{\substack{\text{Fernic silphocyanisa} \\ \text{(Biood res coiour)}}}{Fe(SCN)_3}$$

The appearance of a blood-red color in Lassaigne's test serves as an indicator of the presence of both nitrogen and sulphur in the organic compound.

(d) **Test for Halogens**

A segment of the sodium extract is subjected to a Halogen Detection Test. The procedure involves boiling with 2-3 milliliters of concentrated nitric acid (HNO_3), followed by cooling and subsequent addition of silver nitrate ($AgNO_3$) solution. The observations for each halogen are as follows:

(i) **Chlorine Test:**

If the appearance of a white precipitate is observed, which is soluble in ammonia solution (NH_4OH) but insoluble in diluted nitric acid (HNO_3), it indicates the presence of chlorine. The chemical reaction can be expressed as:

$$NaCl + AgNO_3 \rightarrow \underset{\text{White ppt}}{AgCl} + NaNO_3$$

$$\downarrow NH_4OH$$

Soluble

(ii) **Bromine Test:**

The identification of a pale-yellow precipitate, partially soluble in ammonia solution, suggests the presence of bromine:

$$NaBr + AgNO_3 \rightarrow \underset{\text{Paie yellow ppt}}{AgBr} + NaNO_3$$

(iii) **Iodine Test:**

The emergence of a yellow precipitate, insoluble in ammonia solution, signifies the presence of iodine:

$$NaI + AgNO_3 \rightarrow \underset{\text{Yellow ppt}}{AgI} + NaNO_3$$

Lassaigne's Extract with Nitric Acid Treatment: When nitrogen, sulphur, and halogens coexist in the organic compound, the Lassaigne's extract contains sodium sulphide (Na_2S) and sodium cyanide (NaCN) along with sodium halide. To overcome interference, nitric acid is added to decompose sodium cyanide and sodium sulphide:

$$NaCN + HNO_3 \rightarrow NaNO_3 + HCN$$

$$Na_2S + HNO_3 \rightarrow 2NaNO_3 + H_2S$$

If cyanide and sulphide ions are not decomposed, they may react with silver nitrate and cause interference:

$$NaCN + AgNO_3 \rightarrow \underset{\substack{\text{Silver cyanide} \\ \text{White ppt}}}{AgCN} + NaNO_3$$

$$Na_2S + 2AgNO_3 \rightarrow \underset{\substack{\text{Silver sulphide} \\ \text{(Black ppt)}}}{Ag_2S} + 2NaNO_3$$

(e) **Test for Phosphorus**

Phosphorus Detection Test: The presence of phosphorus is ascertained by fusing the organic compound with an oxidizing agent, specifically sodium peroxide (Na_2O_2). During this process, phosphorus undergoes oxidation to form sodium phosphate (Na_3PO_4).

The chemical reaction can be expressed as:

$$5Na_2O_2 + \underset{\text{from organic compound}}{2P} \rightleftharpoons 2Na_3PO_4 + 2Na_2O$$

Subsequently, the fused mass is extracted with water, and the resulting aqueous solution is boiled with concentrated nitric acid (HNO_3). Following this, ammonium molybdate solution is introduced. The presence of a yellow precipitate or coloration, attributed to the formation of ammonium phosphomolybdate, serves as an indicator for the presence of phosphorus. The relevant reactions are outlined as follows:

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

$$H_3PO_4 + \underset{\text{Ammonium Molybdate}}{12(NH_4)_2MoO_4} + 21HNO_3 \rightarrow \underset{\substack{\text{Ammonium Phosphomolybdate} \\ \text{(Yellow colour)}}}{(NH_4)_3PO_4\ 12MoO_3} + 21NH_4NO_3 + 12H_2O$$