Some more information on Organic Chemistry Practical

Qualitative analysis of Unknown organic compound

Detection of special elements

B.Sc. Hons (Chemistry)

Sem - III

by

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2. Detection of Elements :

The presence of carbon and hydrogen in an O.S. (i.e., organic sample) is usually assumed while the presence of oxygen is established by the method of difference from results of percentage composition. Special elements generally encountered in an O.S. are—

N, S, F, Cl, Br, I, P and metals.

Among the elements mentioned above, metals, phosphorous and fluorine compounds are normally not given for routine work.

A. Beilstein's Test :

A piece of stout copper wire, fitted with a cork to an end, is heated strongly in a non-luminous Bunsen flame till the copper wire fails to impart any coloured flame. The hot wire is then dipped into the O.S. to be tested and heated again in the non-luminous flame (the carbon present in O.S. burns away with luminous flame) and then the appearance of green or bluish-green flame indicates the presence of halogens (except fluorine). Other compounds such as urea, quinoline or pyridine derivatives, etc., impart green colour to the flame. Hence, the negative result indicates absence of halogens and the converse may not be true.

B. Lassaigne's Test :

A pea-sized sodium is taken in a fusion tube and it is just melted by warming. A small amount of O.S. is added to the sodium, so that no substance is adhered to the side of the fusion tube. The mixture is heated gently and then strongly to red hot. Then the fusion tube is quickly plunged into 20 ml of distilled water taken in a mortar. One or two more fusions may be performed and the fusion tubes are plunged into the same mortar. Then the mixture is ground thoroughly by a pestle and filtered. With the sodium-extract, the following tests are performed :

[**N.B.** : A dark-coloured filtrate may be obtained due to incomplete fusion of O.S. when it is taken in excess.]

Experiment	Observation	Inference
(i) **Prussian Blue Test :** A few drops of freshly prepared solution of $FeSO_4$ is added to 2 ml of the sodium-extract. The mixture is boiled, cooled under a tap, 2–3 drops of $FeCl_3$ solution is added and acidified with conc. HCl (should be checked with blue litmus paper). [**N.B.** : Dil. H_2SO_4 may be used instead of $FeCl_3$ and conc. HCl.]	(i) Light green ppt. of $Fe(OH)_2$ (Black ppt. indicates the presence of sulphur.)* Prussian blue or green ppt. or colour.	(i) N-present.
(ii) **Benzidine Copper Sulphate Test :** 2 ml of sodium-extract is acidified with 0·5 ml of acetic acid and added 2–3 drops of 1% solution of benzidine in 50% acetic acid. The mixture is shaken well and 1–2 drops of 1% $CuSO_4$ solution is added to it.	(ii) Blue colour or ppt. [**N.B.** : Greenish ppt. may be obtained in the presence of iodine.]	(ii) N-present.
(iii) **Lead Acetate Test :** 2 ml of sodium-extract is acidified with 2 ml of acetic acid and then 0·5 ml of lead acetate solution is added to it.	(iii) Black ppt.	(iii) S-present.

* The presence of sulphur may tend to obscure the test due to reduction of Fe^{+3} ion to Fe^{+2} ion. This test can be performed successfully by adding excess $FeSO_4$ to precipitate black FeS. The mixture is then boiled, filtered and treated with $FeCl_3$ solution and HCl.

Experiment	Observation	Inference
(iv) **Nitroprusside Test :** To 1 ml of sodium-extract 1 ml of dil. NaOH solution is added followed by 2–3 drops of sodium nitroprusside solution.	(iv) Violet or purple colour.	(iv) S-present.
(v) **Lauth's Violet Test :** 2 ml of sodium extract is acidified with 2 ml of conc. HCl, warmed, 2–3 drops of hydrochloric acid solution of phenylene diamine solution added, followed by 1 drop of $FeCl_3$ soln.	(v) Violet colour.	(v) S-present.
(vi) **Cobalt Nitrate Test :** 2 ml of sodium-extract is acidified with dil. HCl, 2 ml of alcohol is added to it, followed by 0·5 ml of cobalt nitrate soln.	(vi) Blue colour.	(vi) N and S-present together.
(vii) **Liebig Test :** 2 ml of sodium extract is acidified with dil. HCl followed by 2–3 drops of $FeCl_3$ solution.	(vii) Red colour.	(vii) Both N and S-present.
[**N.B.** : Test No. (vi) and (vii) are advised only when the presence of N and S have been confirmed individually from the earlier experiments.]		
(viii) **Silver Nitrate Test :** Another 2 ml portion of sodium extract is boiled with 1 ml of conc. HNO_3, cooled and $AgNO_3$ solution is added. The yellow ppt. is treated with dil. NH_4OH and is then filtered. The filtrate is treated with dil. HNO_3.	(viii) (a) White ppt. soluble in dil. NH_4OH but re-appears when acidified with HNO_3. (b) Yellow ppt. (c) (i) White ppt. (ii) No ppt.	(viii) (a) Cl-present. (b) Br or I or both (a white ppt. of AgCl may be admixed with yellow ppt.). (c) (i) Cl-present with Br or I or both. (ii) Cl-absent.
(ix) **Chlorine Water Test :** If yellow ppt. is obtained in expt. (viii), 1 ml of sodium extract is acidified with 1 ml of dil. H_2SO_4 or dil. HCl and 2 ml of CCl_4 or CS_2 is added. Then strong Cl_2-water is added drop by drop with shaking the mixture after each addition.	(ix) The organic layer turns : (a) Violet (b) Brown or reddish-brown.	(ix) (a) I-present. (b) Br-present.

Experiment	Observation	Inference
If organic layer turns violet, addition of Cl_2-water is continued with shaking.	(a) Organic layer turns reddish-brown with the disappearance of violet colour.	(a) Both I and Br present.
	(b) Organic layer turns colourless after disappearance of violet colour.	(b) I present, Br absent.
(x) **Zirconium-Alizarin Test** : 1 ml of sodium extract is acidified with dil. HCl, boiled and cooled. One drop of the solution is added to zirconium-alizarin solution taken on a spot plate or placed on zirconium-alizarin reagent paper.	(x) The violet colour of the reagent turns yellow.	(x) F- present.
(xi) **Ammonium Molybdate Test** : 1 ml of sodium extract is added to 2 ml of conc. HNO_3, boiled, 3 ml of ammonium molybdate solution added and finally the mixture is boiled and allowed to stand.	(xi) Canary yellow ppt.	(xi) PO_4^{3-} present.

C. Middleton's Test :

by a test, the subsequent tests for the same element may be omitted.]

Reactions Related to Detection of Special Elements Present in an O.S. :

Beilstein's Test :

$Cu + O_2$ (From air) $\longrightarrow 2CuO$

Halogen compound + $CuO \longrightarrow$ Copper halide (Volatile)

Lassaigne's Test :

$Na + C + N \longrightarrow NaCN$

$2Na + S \longrightarrow Na_2S$

$Na + C + N + S \longrightarrow NaSCN$ (Incomplete fusion)

$NaSCN + 2Na \longrightarrow NaCN + Na_2S$ (Complete fusion)

$Na + X \longrightarrow NaX$ (X = Cl or, Br or, I)

Tests for Nitrogen :

(i) Prussian Blue Test :

$6NaCN + FeSO_4 \longrightarrow \underset{\text{Sodium ferrocyanide}}{Na_4[Fe(CN)_6]} + Na_2SO_4$

$3Na_4[Fe(CN)_6] + 4FeCl_3 \longrightarrow \underset{\text{Ferrosoferricyanide (Prussian blue)}}{Fe_4[Fe(CN)_6]} + 12NaCl$

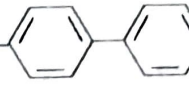
$3Na_4[Fe(CN)_6] + 2Fe_2(SO_4)_3 \longrightarrow Fe_4[Fe(CN)_6]_3 + 6Na_2SO_4$

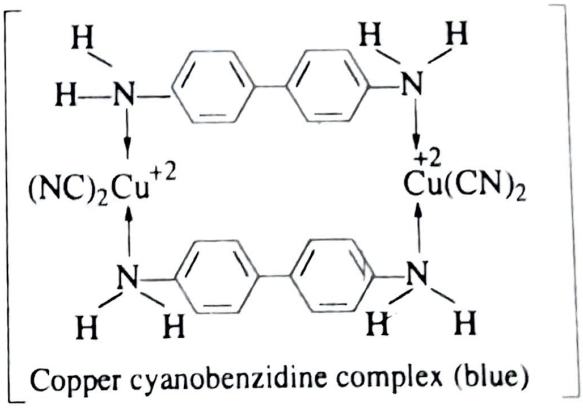
$Fe_2(SO_4)_3$ is produced from $FeSO_4$ by aerial oxidation.

$4FeSO_4 + 2H_2SO_4 + O_2 \longrightarrow 2Fe_2(SO_4)_3 + 2H_2O$

(ii) Benzidine-Copper Sulphate Test :

$CuSO_4 + 2NaCN \longrightarrow Na_2SO_4 + Cu(CN)_2$

$2Cu(CN)_2 + 2H_2N$–  –$NH_2 \rightarrow$



Copper cyanobenzidine complex (blue)

Tests for Sulphur :

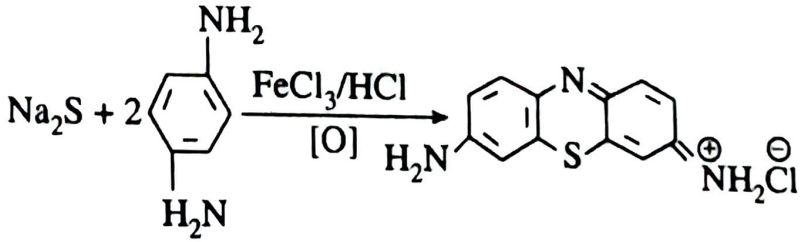
(i) Lead Acetate Test :

$Na_2S + (CH_3COO)_2Pb \longrightarrow \underset{\text{(Black)}}{PbS} + 2CH_3COONa$

(ii) Nitroprusside Test :

$Na_2S + Na_2[Fe(CN)_5NO] \longrightarrow \underset{\text{Sodium sulphonitroprusside}}{Na_4[Fe(CN)_5NOS]}$

(iii) Lauth's Test :



Tests for both nitrogen and sulphur when very small amount of O.S. and comparatively excess of sodium is used.

(i) Cobalt Nitrate Test :

$$NaSCN + HCl \longrightarrow HSCN + NaCl$$

$$4HSCN + Co(NO_3)_2 \longrightarrow \underset{\text{Cobaltithiocyanic acid (Blue colour)}}{H_2[Co(SCN)_4]} + 2HNO_3$$

(ii) Liebig Test :

$$3NaCNS + FeCl_3 \longrightarrow \underset{\text{Ferric thiocyanate (Blood-red colour)}}{Fe(SCN)_3} + 3NaCl$$

Tests for Halogens :

(i) Silver Nitrate Test :

$$NaCl + AgNO_3 \longrightarrow \underset{\text{(White)}}{AgCl\downarrow} \xrightarrow{NH_4OH} \underset{\text{(Soluble)}}{Ag(NH_3)_2^+ \bar{C}l}$$

$$Ag(NH_3)_2^+ \bar{C}l \xrightarrow{\text{dil. } HNO_3} AgCl\downarrow + NH_4NO_3$$

$$NaBr + AgNO_3 \longrightarrow \underset{\text{(Dirty yellow)}}{AgBr\downarrow} \xrightarrow[\text{Excess}]{NH_4OH} \underset{\text{(Soluble)}}{Ag(NH_3)_2^+ Br}$$

$$NaI + AgNO_3 \longrightarrow \underset{\text{(Yellow)}}{AgI\downarrow} \xrightarrow{NH_4OH} \text{Insoluble}$$

(ii) Cl_2-Water Test :

$$2NaI + Cl_2 \longrightarrow \underset{\text{(Violet organic layer)}}{I_2} + 2NaCl$$

$$2NaBr + Cl_2 \longrightarrow \underset{\text{(Brown organic layer)}}{Br_2} + 2NaCl$$

$$I_2 + 5Cl_2 + 6H_2O \longrightarrow \underset{\text{(Colourless)}}{2HIO_3} + 10HCl$$