T. D. C. Part I ; Chem. (Hons.)

Paper II (Gr. B) org. chem

org. compds. ~~are~~ contains C, H, O, N, S and halogens. The presence of C and H is usually assumed while the presence of oxygen is deduced from the results of the preliminary tests. In order to identify the N, S and halogens "Lassaigne's test is done.

Lassaigne's Test :->

This test is used for the detection of N, S and halogens. In this test the compound to be examined is ~~[illegible]~~ fused with sodium. After fusion the elements — N, S and halogens form ionisable inorg. compds sodium cyanide, sodium sulphide and sodium halide respectively.

$$Na + C + N \longrightarrow NaCN \rightleftharpoons Na^+ + CN^-$$

$$2Na + S \longrightarrow Na_2S \rightleftharpoons 2Na^+ + S^{--}$$

$$2Na + X_2 \Rightarrow 2NaX \rightleftharpoons 2Na^+ + 2X^-$$

$(X = Cl, Br, I)$,

Lassaigne's test is based on the preparation of sodium extract (Lassaigne's Solution). Sodium extract is used for the detection of different elements.

Detection of 'N' :->

Na-extract (1-2 c.c. of ext. A) + 1 drops of NaOH sol^n + Freshly prepared $FeSO_4$ sol^n 2-3 drops

+ Boil + acidified the sol^n with

Formation of prussian blue or greenish blue colour or ppt. confirms the presence of nitrogen.

$$Na + C + N \longrightarrow NaCN$$

$$FeSO_4 + 2NaOH \longrightarrow Fe(OH)_2 + Na_2SO_4$$

$$Fe(OH)_2 + 6NaCN \longrightarrow Na_4[Fe(CN)_6] + 2NaOH$$

Sod. ferrocyanide

$$3\,Na_4[Fe(CN)_6] + 4FeCl_3 \longrightarrow$$

$$Fe_4[Fe(CN)_6]_3 + 12NaCl$$

Prussian blue colour

(Ferric ferro cyanide)

or,

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

$$Fe_4[Fe(CN)_6]_3 + 6Na_2SO_4$$

In the presence of sulphur and nitrogen both it gives blood red colour with the drops $FeCl_3$:

$$Na + C + N + S \longrightarrow NaCNS$$

$$FeCl_3 + 3NaCNS \longrightarrow Fe(CNS)_3 + 3NaCl$$

Ferric thiocyanate

(Blood red colour)

Detection of S :-

(i) Na-extract + A drop freshly prepared sodium nitroprusside

violet or purple colouration con
the presence of S.

$2Na + S \rightarrow Na_2S$

$Na_2S + Na_2[Fe(CN)_5NO] \longrightarrow$

Sod. nitroprusside

$Na_4[Fe(CN)_5NOS]$.

purple colour.

Sod. thionitroprusside

(ii) Na-extract (1.c.c. ind. b.t) + Lead acetate $\longrightarrow$ Blac
confirms
presence of S

$Na_2S + (CH_3COO)_2Pb \rightarrow PbS\downarrow + 2CH_3$

Black ppt.

(iii) Na-extract + sod. plumbite $\longrightarrow$ Blac
pp
confirms.

$Na_2S + Na_2PbO_2 + 2H_2O \longrightarrow$

Sod. plumbite

$PbS\downarrow + 4NaOH$

Black ppt.

Detection of halogens —

(a) Silver nitrate Test :—

Boil 2 c.c of HO-extract with 1 c.c conc. HNO_3 and then add silver nitrate solution. Note that

(a) white ~~ppt~~ curdy ppt. Soluble in NH_4OH — Cl present.

$NaCl + AgNO_3 \rightarrow AgCl\downarrow + NaNO_3$
white ppt.

$AgCl + 2NH_4OH \rightarrow Ag(NH_3)_2Cl + 2H_2$
soluble

(a) pale yellow ppt. ~~Soluble in~~ partial Soluble in NH_4OH — Br^- present

$NaBr + AgNO_3 \rightarrow AgBr\downarrow + NaNO$
pale yellow

$AgBr + 2NH_4OH \rightarrow Ag(NH_3)_2Br + 2$
partially soluble.

(c) yellow ppt insoluble in NH_4OH — I^- present

B. $NaI + AgNO_3 \rightarrow AgI\downarrow + Na$
yellow.

$AgI + 2NH_4OH \longrightarrow$ insoluble

(When N and S is present then before done the Silver nitrate test boil the Na extract with dil. HNO_3 for 10 minutes to decompose the cyanide or Sulphide formed as a result of Sodium fusion of cyanide or Sulphide formed as a result of Sodium fusion is not decomposed before adding $AgNO_3$ sol? a white or black ppt respectively will be formed and so they will interfere)

$$NaCN + AgNO_3 \rightarrow \underset{\text{white ppt}}{AgCN} + NaNO_3$$

$$Na_2S + 2AgNO_3 \rightarrow \underset{\text{Black ppt}}{Ag_2S} + 2NaNO_3$$

(ii) Beilstein's Test :—

It is a general test for halogens. In this test a clean copper wire is heated in the non-luminous flame of the burner untill it is free from green colour. Place a pinch of org. compd. on the hot wire and again heat it strongly. A green colour indicates the presence of halogen in the org. compound. (This test is not be employed in the presence of urea or thiourea as they also give green colouration on heating with flame).