Chm 116 made easy

Qualitative examination of unknown organic substances enables you to identify the functional groups and to place into its chemical class, any organic compound you will be given.

Qualitative analysis: Preliminary tests, Confirmatory test, Preparation of derivatives

I PRELIMINARY TESTS.

(A) IGNITION TEST: Place sample on a nickel spatula, heat gently, then strongly. Observe whether the substance SUBLIMES, MELTS, VOLATILIZES OR DECOMPOSE without melting. Also note if the substance burns. If it burns, NON-LUMINOUS FLAME may indicate AROMATIC COMPOUNDS. A white or coloured residue is probably a metal. A black residue indicates CARBON. To confirm, add a few drops of AMMONIUM NITRATE SOLUTION

(B) SODIUM FUSION TEST (CLASSAIGNE'S TEST): It is used to detect the presence of Nitrogen, Sulphur, or halogens (Cl, Br, I). When they occur in organic molecules, they are covalently bonded so they do not convert any N, S or X to ionisable inorganic substance

$$CHONSX + Na \xrightarrow{heat} NaCN + Na_2S + NaX + NaOH$$

Excess sodium is used, otherwise if S and N are both present, NaCNS may be produced, instead of NaCN and Na_2S as above. CNS does not give the blue ppt (prussian blue), but rather a red-colouration with ferric ion.

$$NaCNS + 2Na \longrightarrow NaCN + Na_2S$$

Sodium fusion mixture is then extracted with water to give an alkaline solution

$$FeSO_4 + 6NaCN \longrightarrow Na_4Fe(CN)_6 + Na_2SO_4$$

Upon boiling, ferric ions react with the $Fe(CN)_6$ present to form $Fe_4[Fe(CN)_6]_3$, which gives an insoluble blue ppt "prussian blue".

$$3Na_4Fe(CN)_6 + 2Fe_2(SO_4)_3 \longrightarrow Fe_4[Fe(CN)_6]_3 + 6Na_2SO_4$$

HCl could be used in place of H_2SO_4 but it is unsuitable because $FeCl_3$ that would be formed is yellow, making "Prussian Blue" appear greenish.

TEST FOR NITROGEN.

Add about 0.1g of ferrous sulphate to 2-3ml of the above filtrate, heat the mixture gently, with mixing till it boils. Add dil. H_2SO_4 to dissolve the iron hydroxide making the solution slightly acid.

A blue or greenish colouration or precipitate indicates the presence of N

TEST FOR SULPHUR

Acidify 2ml of the fusion filtrate with dilute acetic acid, and add a few drops of lead acetate solution. A black precipitate of PbS indicate the presence of S.

TEST FOR HALOGEN.

If N and CN or S are present place a few ml of the fusion extract in a beaker, add dilute H_2SO_4 and place a porous pot and boil till the liquid is reduced to half its original volume. Then add dilute HNO_3 and an excess of $AgNO_3$ solution. A precipitate indicates the presence of a halogen

NITRATE ION (BROWN RING TEST)

Add ml to conc. H_2SO_4 slowly to 2ml of the sodium carbonate extract. Now. Pour 2ml of freshly prepared saturated aqueous solution of $FeSO_4$ slowly The formation of a dark brown ring indicates NO_3. Red-brown ring indicates Br, Violet ring I.

SULPHATE ION.

Add dil. HCl to 2-3ml of sodium carbonate extract. Add few drops of $BaCl_2$. A heavy white ppt indicates the presence of SO_4^{2-}

HALIDE ION

Add dil. HNO_3 to 2-3ml of sodium carbonate extract. Add few drops of $AgNO_3$ reagent. A yellow ppt indicates Br (dissolves less readily in NH_3) A yellow ppt indicates I (insoluble in NH_3)

SOLUBILITY TESTS

A water-soluble substance might be ammonium salt, alkali salt of an acid, salt of an amine or mono and dissaccharides or lower aliphatic compounds.

A basic compound should be soluble in acid and be precipitated from the acidic solution upon addition of excess alkali

An acidic compound should dissolve in alkali and be precipitated from the alkaline solution upon the addition of excess acid

A neutral organic compound does not dissolve in either acid or alkali, but will dissolve in ethyl alcohol or other organic solvent

If the substance is basic, an amine is indicated

If the substance is acidic, a carboxylic acid or a phenol is indicated

Neutral substance include esters, aldehyde, ketones, amines, nitric compounds, carbohydrates, alkyl and aryl halides

II CONFIRMATORY TESTS.

(i) ISOCYANIDE REACTION: The product is poisonous & has an unpleasant odour.

(ii) NITROUS ACID: dissolve the substance in dilute HCl, cool in ice. Next add 2-napthol in NaOH(aq) PPt of brilliant red dye indicates that the substance is a primary aromatic amine.

(iii) TEST FOR CARBOXYLIC ACID: Add few drops of a saturated aqueous soln of $NaHCO_3$. An evolution of bubbles indicates carboxylic acid.

(iv) TEST FOR PHENOL: Dissolve in water or alcohol, add one drop of ferric chloride reagent. It will give an intense colour

(v) TEST FOR AMMONIUM SALTS AND AMIDE: Boil with aqeous NaOH, test the issuing vapour. The gas with characteristic smell of ammonia indicates the presence of simple amide.

(vi) TEST FOR NITRO COMPOUNDS

Reduction to hydroxylamine. Confirmatory test can be made with Tollen's reagent or Fehling's solution.

TEST FOR KETONES AND ALDEHYDES:

Dissolve the substance in a little alcohol and add a few ml of an alcohol solution of 2,4-dinitrophenylhydrazine reagent. Warm and cool. A ppt indicates an aldehyde or ketone.

(vii) TEST FOR REDUCING PROPERTIES ie aldehyde groups

(a) Fehling's solution: Mix equal vol. of Fehling's A & B. add a few drops of mixture to the organic compound in solution and warm. Disappearance of the blue colour & precipitation of red or yellow ppt of Cu_2O indicates red. agent

(b) Ammoniacal $AgNO_3$ ie Tollen's reagent: add dilute NH_4OH solution in drops to $AgNO_3$ containing a few drops of NaOH until the ppt Ag_2O almost completely dissolved. A silver mirror indicates a reducing agent

Some amines give positive result.

(viii) Iodoform test: for the presence of compounds containing $CO.CH_3$ or $CH_3CH(OH)$ groups (eg acetone CH_3COCH_3, ethyl alcohol CH_3CH_2OH - but not methyl alcohol CH_3OH). Dissolve in water & add 1ml of 6mol NaOH. Add iodine solution with shaking until the dark brown colour of iodine persists.

A fine yellow crystalline ppt of iodoform (characteristic smell) is positive. M.pt: 119-121°C.

(ix) Molisch's Test for sugar: A trace of 1ml of water is added to 2ml of Naphthol in alcohol or chloroform. 1ml of conc. H_2SO_4 is then cautiously added. A violet ring (or purple colour on gently mixing) indicates the presence of sugar

x) TEST for esters: Hydroxamic acid formation.

To a few drops of an ester, add hydroxylamine hydrochloride and NaOH solution and gently boil. Cool & acidify with dil. HCl and add few drops of ferric chloride solution. A violet or deep-red brown colour gives positive results.

xi) Test for unsaturation:

Add very dilute bromine water or neutral potassium permanganate solution. An immediate decolourization of the reagent indicates an unsaturated compound.

TECHNIQUES FOR SEPERATION AND IDENTIFICATION OF SOME ORGANIC COMPOUNDS.

Distillation is used to seperate substances with different boiling points.

Electrophoresis is used to seperate mixture according to differences in their particle size and their electrical charge.

Chromatography is a method of seperation of substances based on differences in their polarity and absorption on a stationary phase.

SEPERATION OF CATIONS INTO GROUPS.

GROUP I

Solid: AgCl, $PbCl_2$, Hg_2Cl_2 heat with water.

Black residue due to NH_2HgCl formed. Hg_2Cl_2 confirmed

Add dil NH_4OH. Solution may contain $Ag(NH_3)_2Cl$. Acidify with dil HNO_3. White ppt indicates Silver Ag.

White crystals of $PbCl_2$ may seperate. Test clear solution by adding dilute CH_3COOH and K_2CrO_4. Yellow ppt of $PbCrO_4$ indicates lead

GROUP II A

Solid $Bi(OH)_3$ & $Pb(OH)_2$; Boil gently with 1-3ml of HNO_3.
White ppt turns black on addition of Na_2SnO_2 solution. Indicates Bismuth
Solution Na_2PbO_2. Add dil. CH_3COOH & K_2CrO_4. Yellow ppt indicates lead
& blue, it contains copper.
Acidify with CH_3COOH & add $K_4Fe(CN)_6$. Brown ppt confirms copper
Add KCN until blue colour disappears. Pass H_2S, yellow ppt indicates Cadmium

GROUP II B

Solid: As_2S_3; boil with conc. HCl
Boil with Zn dust and add dil NaOH. Test gas with $AgNO_3$ paper. Brown
colour indicates Arsenic
Dilute and pass H_2S orange ppt indicates Antimony
Add iron wire warm. Pour clear liquid $HgCl_2$ solution. White ppt indicates
tin

GROUP III

Solid: $Fe(OH)_3$. warm with NaOH & H_2O_2. then boil.
Brown dissolved in HCl and KCN. A blood-red colour is obtained that indicate Iron
& yellow contains chromium. Acidify with CH_3COOH & add lead acetate. Yellow
Precipitate indicates chromium.
Add HCl until just acid. Then add ammonia gas. White ppt indicates Aluminium

GROUP IV.

Solid: treat with cold dilute HCl
Add amyl alcohol & solid NH_4SCN. Blue amyl alcohol layer indicates Cobalt
Make alkaline with ammonia & dimethylglyoxime scarlet red ppt indicate Nickel

* Aqua-regia: a mixture of nitric & HCl that dissolves gold or platinum.

Borate: $Na_2B_4O_7 \cdot 10H_2O$

Solid: Brown MnO_2. Dissolved in 1:1 HNO_3 & then add solid sodium bismuthate. Purple solution indicates Manganese

Solution: may contain Na_2ZnO_2. Acidify with dilute CH_3COOH and pass H_2S white ppt indicates Zinc

GROUP V

Solid: $BaCO_3$, $SrCO_3$, $CaCO_3$. Dissolves in hot dilute CH_3COOH & K_2CrO_4

Solid: Yellow $BaCrO_4$ add a drop of conc. HCl. Apply flame test: green flame indicates barium.

Add saturated $CaSO_4$ heat, white ppt indicate strontium. Add 1 drop conc. HCl. Apply flame test crimson flame indicates Strontium

Add dilute $(COONH_4)_2$ warm and allow to stand. White ppt indicates Calcium. Apply flame test. Brick red flame.

GROUP VI

Solid: $MgCl_2$, NaCl, KCl. Dissolve in water.

Add 2 drops of magneta reagent & dil NaOH. Blue ppt indicates Magnesium

Add magnesium uranyl acetate & allow to stand. Yellow ppt indicates Sodium

Add sodium cobaltinitrite. Yellow ppt indicates potassium

EXAMINATION FOR ANIONS.

Preparation of solution: Boil the solid with excess sodium carbonate for a few minutes

SULPHATE: Acidify with HCl & boil to remove CO_2 & $BaCl_2$. White ppt

Reducing agents: Acidify with H_2SO_4. add few drops of $KMnO_4$. Decolourizes.

Oxidizing agent: acidify with conc. HCl & add $MnCl_2$. Brown colour

Nitrates: mix solid with CaF_2 & 1 drop conc. H_2SO_4. Take up paste on platinum wire & hold at base of Bunsen flame. Green coloration indicates borate.