THE CLASSIFICATION OF ORGANIC COMPOUNDS

Classification of an organic compound concerns the detection of its functional groups. Knowledge of the functional group may be deduced from the chemical properties that the compound shows.

Determination of the structural formula of a compound may involve the following stages:

Stage 1: Preliminary examination - melting or boiling point, the determination of solubilities, etc

Stage 2: Lassaigne's test, quantitative composition analysis of the elements present.

Stage 3: Classification i.e. functional group analysis - deduced from the chemical properties of the compound.

Stage 4: Assignment of possible structures, and confirmation of one of these structures.

Stage 3: Classification - is of vital importance in the process of identification of an unknown organic substance. It is necessary to perform reliable chemical reactions through which the functional groups may be detected in the unknown compound.

A few guidelines are given below which are intended to show the investigator how to follow up, in a logical and systematic manner, the first positive results obtained. The scheme aims to discourage the application of specific tests at random to the unknown substance.

STEP 1: Physical characteristics.

STEP 2: Note effect of heat on substance.

STEP 3: Check its solubility at 20 - 30 mg per mL solvent in water, aq. NaOH, HCl and dichloromethane.

STEP 4: If no clear indication as to the class of the unknown appears after Step 3, use the following sequence of tests, starting at (i) and proceeding towards (ix).

(i) For ketones and aldehydes - use Brady's reagent
(ii) For aldehydes only - check with Schiff's reagent
(iii) For phenols - use two test
(iv) For acids - check by esterification

(v) For alcohol - check by esterification
(vi) For esters or acid amides - by basic hydrolysis
(vii) For carbohydrates - by specific test
(viii) For amines, aromatic nuclei, unsaturated substances
(ix) For other classes - by specific test

In Step 4, the tests are arranged in an order giving the least interference amongst different groups of compounds. The test is made for carbonyl compounds first, because virtually none of the classes will give a positive test with the reagent used.

NOTE WELL

All these tests depend on the production of a precipitate or the formation of a colour; and they can be quite sensitive. A control experiment should always be performed, consisting of all the conditions of the experiment - reagents, concentrations, temperature, time, etc, - but with the substance under test being left out. If there is no difference in the result between the test on the unknown and in the control experiment then the result is negative.

A carelessly executed test is worse than none attempted, in that it may be misleading, **IF DOUBT ARISES, CARRY OUT THE TEST ON KNOWN COMPOUNDS AND COMPARE THE RESULTS WITH THOSE OF THE UNKNOWN.**

SOLUBILITY TESTS

Solubility tests are usually carried out using common solvents and reagents. The result of the solubility test may be used according to the rough scheme below in order to make a tentative classification of the unknown compound:

<u>Readily soluble in water and dichloromethane</u> - Almost every kind of monofunctional organic compound of five or fewer carbon atoms pre molecule.

<u>Soluble in water but insoluble in dichloromethane</u> - Salts, Polyhydroxy compounds, Amino acids.

<u>Insoluble in water but soluble in aq. NaOH</u> - Acids and Phenols

<u>Insoluble in water but soluble in aq. HCl</u> - Certain amines

<u>Insoluble in water, aq. NaOH, aq. HCl but soluble in dichloromethane</u> - Neutral compounds (e.g. carbonyls, halides, esters, amides, higher homologues of alcohols etc.)

<u>Insoluble in water, aq. NaOH, aq HCl, dichloromethane</u> - Water-insoluble salts, higher molecular weight compounds.

EXPERIMENT 13 SOLUBILITY TESTS

Procedure:

All solubility tests are performed as follows:

Place 20 - 30 mg of finely powdered solid (or 0.1-mL liquid) in a dry test tube and add the 'solvent' drop wise with shaking to a total of one mL. Only if the solution is complete is the test substance described as soluble.

A. Petroleum ether Test: (mixture of C_5H_{12} and C_6H_{14})
(in a 10 * 75 test tube)

1. Physical properties
2. Solubility in
    - (a) water, cold or hot: if soluble, reaction to litmus.
    - (b) dil HCl
    - (c) dil NaOH
    - (d) dil $NaHCO_3$ (note if CO_2 evolves)
    - (e) dichloromethane

B. Phenol Tests: 1 and 2 as for Petroleum Ether

C. Ethanol Tests: 1 and 2 as for Petroleum Ether

D. Ethanal (Acetaldehyde) Tests: 1 and 2 as for Petroleum Ether

E. Glucose Tests: 1 and 2 as for Petroleum Ether

F. Acetone Tests: 1 and 2 as for Petroleum Ether

G. Acetic Acid Tests: 1 and 2 as for Petroleum Ether

H. Ethyl Acetate Tests: 1 and 2 as for Petroleum Ether

I. Ethyl Amine Tests: 1 and 2 as for Petroleum Ether

J. Glycine Tests: 1 and 2 as for Petroleum Ether

Exercises:

1. Record observations in tabular form.
2. Write down the structural formula for each authentic compound tested above.

EXPERIMENT 14 FUNCTIONAL GROUP TESTS

Carry out functions group tests on the samples provided which include all of the examples investigated in Experiment 13. Use the relevant procedures given below. The actual test chosen from those below will surely be determined by the suggestions from the results of the 'solubility test' of the previous section.

(i) Test for carbonyl compounds:

To one mL of a solution of the unknown substance in ethanol, add 3 mL saturated solution in 2M HCl of 2,4- dinitrophenylhydrazine solution (Brady's reagent). A yellow - orange - red precipitate indicates an aldehyde or a ketone.

Aldehydes reduce freshly prepared solution of ammoniacal silver nitrate (Tollen's test). Ketones do not reduce this reagent. (Tollen's reagent is used fresh after adding ammonia hydroxide solution to first precipitate AG_2O and then to just re-dissolve the precipitate in a clean test tube containing 2 mL aq. $AgNO_3$).

PLACE ALL SILVER RESIDUES IN CONTAINER PROVIDED.

Aldehydes also produce a red - violet colour in the cold with Schiff's reagent (bisulphite salt or magenta dye), ketones do not.

(ii) Test for Phenols

Prepare a neutral $FeC1_3$ solution by slowly adding dilute NaOH to the bench reagent until the precipitate of ferric hydroxide starts to form. Filter off the precipitate, and use the clear filtrate for the test.

Phenols produce purplish colours with this solution.

(iii) Test for Acids

(a) The solution of the unknown in ethanol or water turns blue litmus red

(b) Acids also produce effervescing CO_2 from saturated $KHCO_3$ solution.

(iv) Test for Alcohols:

Heat the suspected alcohol (1mL) with 1 mL glacial ethanoic acid and 3 drops of conc. H_2SO_4 in a test tube standing in a beaker of boiling water. Cool and then pour the cold system into a few mL of cold water into a small beaker. Note the fruity smell of an ester, and its insolubility in water.
(To check this, use ethanol in place of the unknown. Salicylic acid may be used (0.5g) instead of CH_3COOH.).

Molisch's Test - Place 0.1g of carbohydrate suspect in a test tube containing 0.5mL water and mix it with drops of 1% solution of α-naphthol in ethanol or in chloroform (ignoring traces of any precipitate). Carefully pour two mL of conc. H_2SO_4 down the side of the test tube so that it forms a heavy layer at the bottom. A deep violet colour where the two liquids meet denotes a positive test.

(The colouration is due apparently to the formation of an unstable condensation product of 1 - naphthol with furfural).

Glucose and other reducing sugars react with Tollen's and Fehling's reagent, like the aldehydes.

(vi) Test for Esters:

Warm and shake one mL of the suspected ester with 5 mL dil. NaOH solution. The upper layer of ester disappears after warming and the fruity odour of the ester disappears.

(vii) Test for Amines:

Using nitrous acid prepare in situ as follows. Dissolve 0.2g substance in 5 mL 2M HCl. Cool in ice and add 2mL cold 10% aq. $NaNO_2$ solution.

Aliphatic primary amines yield nitrogen and alcohols

Aliphatic secondary amines yield yellow oily nitrosoamines

Aliphatic tertiary amines do not react

Aromatic primary amines yield diazonium salts. When the cold mixture is added slowly to the cold solution of 2-naphthol in a considerable excess of 10% NaOH, a brilliant red dye is produced.

Aromatic secondary amines yield yellow oily nitrosoamines.

Aromatic tertiary amines yield bright green *p*-nitroso derivatives.

EXERCISES:

1. Tabulate your results under three headings: Test, Observations, Inference.
2. Write the relevant chemical equations for each reaction under inference column.

EXPERIMENT 15 IDENTIFICATION OF FUNCTIONAL GROUPS IN UNKNOWN SAMPLES

Procedure:
Record the labels of the unknown samples given.

1. Carry out the preliminary tests outlined.

2. Use the solubility tests given in Table 3 to deduce what type of compound may be present.

   NOTE: At this stage it is advisable to consult a demonstrator to make sure you are on the right track.

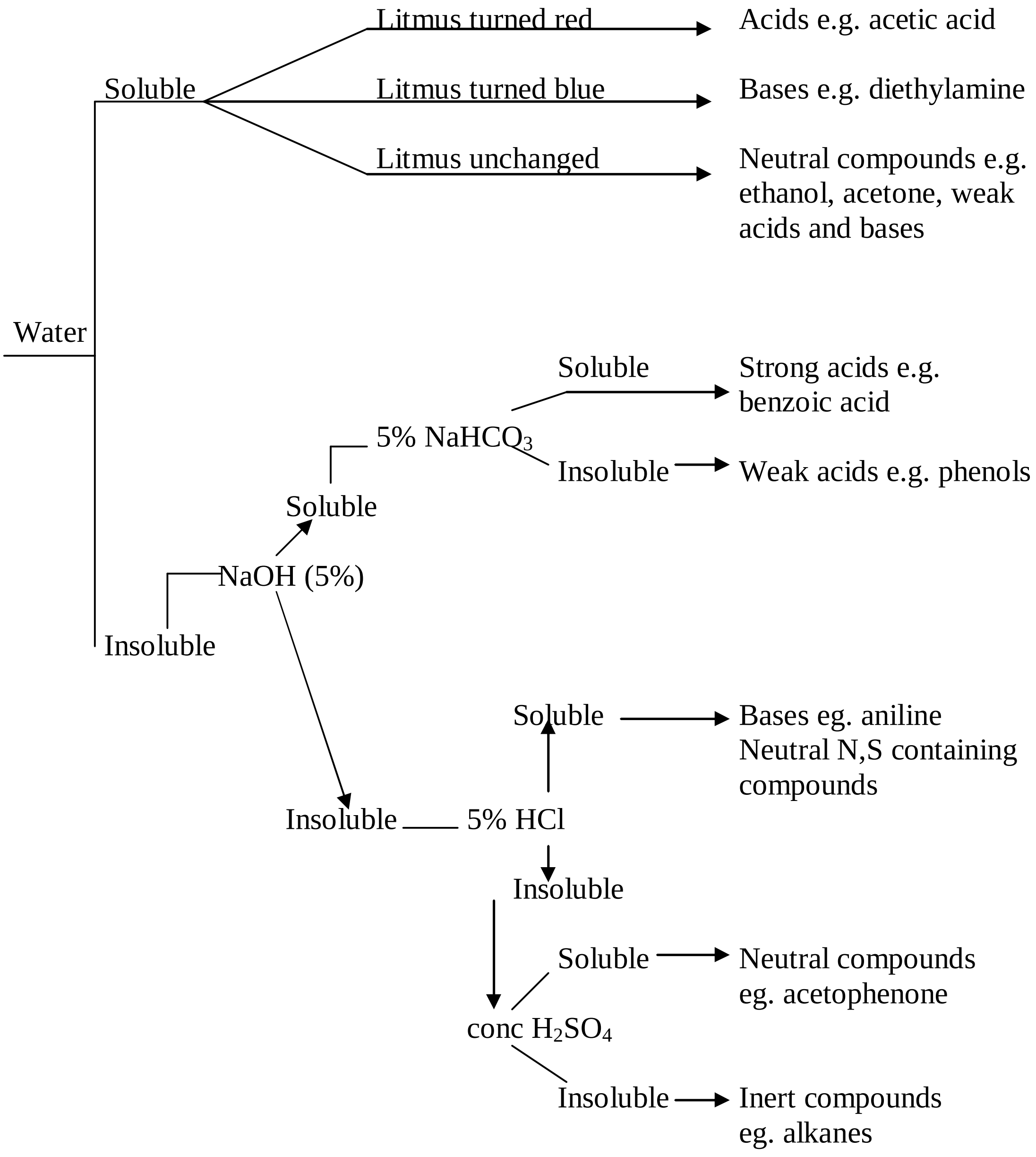
3. Use the functional group tests to confirm any inference drawn from steps 1 and 2. You may assume that only one functional group is present in each sample.

4. Tabulate your results under <u>three</u> headings: Test, Observations, Inference.

5. Show the relevant chemical equations in the case of each positive reaction carried out on your unknown compound.

6. State clearly the name of the functional group/s present in the unknown sample/s given.

TABLE 3 - SOLUBILITY TESTS FOR SIMPLE ORGANIC COMPOUNDS



EXPERIMENT 16 IDENTIFICATION OF ORGANIC COMPOUNDS BY MEANS OF THEIR MELTING POINTS

Objective:

At the end of this exercise you should be able to:

- i) Carry out a m.p. determination on a given solid accurately.
- ii) State whether the given solid is pure or impure based on the melting range obtained.
- iii) Determine whether the given solid is identical with any one of a set of given solids.
- iv) Consider how to purify an impure solid by recrystallisation.

Introduction

The m.p. of a solid could be defined as the temperature at which the solid is in equilibrium with the corresponding liquid state under a pressure of one atmosphere.

A **pure** compound exhibits a sharp melting point i.e. the change from all solid to all liquid occurs over a narrow temperature range (1 - 2°C). For an **impure** solid the melting point is usually lower and the melting range wider than that of the pure compound. **Thus the melting point of a compound can be used as an index of its purity.**

Melting points can also be used in compound identification as follows. If the melting point of a test compound when it is intimately mixed with a known compound (mixed melting point) is unchanged, then one can conclude that the two compounds are identical. If the so-called **mixed melting point** is well below that of either of the components and melting occurs over a wide temperature range, clearly then the components are not identical.

The technique of recrystallisation is used in the purification of an impure solid compound. A solvent is chosen in which the solid to be recrystallised is very soluble at temperatures near the boiling point of the solvent but only sparingly soluble in the solvent at room temperature.

Points to Note in Determining Melting Points:

Your laboratory supervisor will describe in detail the procedures for obtaining an accurate m.p. However, you should particularly note the following general points:

1. Your solid sample must be **dry.**

2. The solid should be pulverised.

3. As small a quantity of the powdered solid as can be properly observed should be used for the melting point determination.

4. The temperature of the heating medium (an oil bath or aluminum block) should be slowly raised (2°C per min.)

5. One should note the temperature at which the solid first begins to melt and the temperature at which melting is completed and report the melting range e.g. 67 - 69°C.

6. Thermometers sometimes read too high or too low by a few degrees. For most accurate work they are **calibrated** i.e. used to obtain the m.p.'s of standard compounds of known melting points and then appropriate correction made to subsequent readings of the thermometer. You can check your thermometer quickly by immersing it in an **ice-water** bath. It should read 0°C.

Procedure:

1. Place the given impure compound (mixture given) inside a conical flask. Add small amounts of boiling hot solvent - whilst warming the system - until all the soluble material just dissolves.
   (Note that when insoluble impurities are present you have to gravity filter the hot system through a warmed fluted filter paper (inside a hot conical funnel) to avoid premature crystallisation of the products.)

2. After filtration, set the flask - containing the clear filtrate aside, and allow it to cool without disturbance. Crystals should appear. Suction filter the crystals through a Buchner funnel. Collect the crystals on the filter paper and dry them.

3 Determine the melting point of the unknown compound provided. (It is useful to first determine the approximate melting point by heating rapidly. Then leave the heating medium to cool 10-15°C below the approximate melting point. Insert a second sample of your compound and heat the medium slowly until melting is achieved.)

4. Using the method of mixed melting points identify the compound as one of the compounds in the table of reference compounds available. Record your results in the report sheet provided.

Melting Points of some known compounds (°C)

Benzophenone	47 - 48	Urea	133
Benzhydrol	68	Cinnamic Acid	133
4 - Chloroaniline	69 - 71	Acetylsalicylic acid	135 - 138
Biphenyl	71	Anthranilic acid	146 - 148
Vanillin	80 - 81	4 - Nitroaniline	147
Naphthalene	81	Cholesterol	148
Acrylamide	84	Adipic acid	152 - 154
Acetanilide	114	Mannitol	166 - 169
Fluorene	115	4 - Aminobenzoic acid	187 - 189
Benzoic acid	122	Anthracene	216 - 218
2 - Naphthol	122	Inositol	225
Benzoin	132 - 133	Caffeine	236 - 238

Boiling Points (°C) of some commonly used solvents

Acetone	56	Methanol	65
Ethanol	77 – 79	Hexane	69
Benzene	79.5 – 80	Trichloromethane	61
Toluene	110 – 111	Carbon tetrachloride	77
Cyclohexanone	159 - 162		