

PURIFICATION AND SEPARATION OF ORGANIC COMPOUNDS

Organic compounds, whether solids , liquids or gaseous, when are separated from organic reactions are seldom pure. They may be contaminated with other compounds which are formed as a byproduct, owing to a side reaction.

These organic compounds have to be purified before using them in other chemical reaction. Several methods of purification have to be :-

- 1- Crystallization.
- 2- Sublimation.
- 3- Extraction.
- 4- Distillation.
- 5- Chromatographic adsorption.

The method employed depends upon the nature of the material to be separated and purified.

1- Purification of organic compound by crystallization:-

Crystallization is one phenomena which is involved in the production of pure crystals form solution , after dissolving the impure substance in a suitable solvent or mixture of solvents.

The choice of the solvent is very important in this process, water or any other organic solvent (ethyl alcohol, methyl alcohol, acetone, glacial acetic acid, ethyl acetate, benzene, petroleum ether, ether, chloroform.....etc.) can be used.

Ether could be avoided whenever possible for its high inflammability.

A distinct relation has to be existed between the constitution of the organic compound and the solvent, so they may undergo into solution. As the old rule said "like dissolves like ", therefore, polar organic compound dissolve in non polar solvents and so on.

It is also assumed that:-

- 1) The solvent should not react chemically with the substance to be purified.
- 2) It should dissolve the impurities readily.
- 3) It should well-formed crystals of the purified compound.
- 4) It must be capable of easy removal from the crystals of the purified compound.

In some cases mixture of two of the solvents might be used, especially when a substance is highly soluble in one solvent and sparingly soluble in other solvent, the mixture of the two solvents can be used for crystallization.

Purification by crystallization may be improved by means of some adsorbing material such as animal charcoal or boneblack.

These materials have the property of adsorbing, on their surface areas, colored impurities present in many organic substances.

The following discussion illustrates the techniques used in purification by crystallization. The impure substance is placed in a flask, add the chosen solvent gradually with constant stirring, heat the mixture on a water bath, nearly to boiling, away from direct flame (since most of the solvents mentioned above are inflammable) until a clear solution is formed. Filter the hot solution through a fluted- filter paper, and collect the hot filtrate in a dry clean flask.

(Fluted filter paper – is a folded filter paper several times , back and forth in pleats like .)

The funnel has to be kept hot , to avoid crystallization on its stem . set your filtration apparatus as is shown on the board . leave the filtrate to cool down gradually . after the crystallization is complete, the crystals are filtered form the remaining “mother liquor” by means of suction filtration with a Buchner funnel .

The crystals are well pressed on the filter with the aid of the flat top of a glass stopper, and washed a few times with small portions of the cold solvent . the suction is continued few minutes longer, and the hose on the suction flask is removed before the water is turned off. (set your apparatus as is shown on the board).

The crystalline mass is spread upon a porcelain plate covered with a filter paper, and a allowed to stand until perfectly dry .

Some organic substances do not crystallize readily, even from supersaturated solutions. A small crystal of the pure material may be added to induce the crystallization process- a technique known as “ seeding” . crystallization can be induced also by scratching the sides or bottom of the container with a glass rod.

The microscopic scratches in the glass surface provide sharp edges upon which crystal growth may start.

EXPERIMENTAL PROCEDURE:-

Proceed as it is explained above and crystallize acetanilide from water .

- 1- Place about 10 gm of acetanilide in a 600 ml flask, add water gradually with constant stirring and heat, until a clear solution is formed.
- 2- Filter, set aside to cool while crystallization is complete.
- 3- Filter through suction filtration, collect the crystals after drying
- 4- Weight them and calculate the percentage yield of purified crystals.

2- purification of solid organic compound by sublimation:-

Sublimation :- is the transformation of certain solid organic compound directly to the vapour state at high temperature, then condensing on a cold surface to the solid state without passing through the intermediate liquid state.

Such a process is a convenient means of separation and purification of certain compounds, that are characterized by sublimation, such as – camphor, benzoic acid, naphthalene, salicylic acid and the quinines.

EXPERIMENTAL PROCEDURE :-

- 1- Place a mixture of 1 gm. of one of the sublimed substances and 5 gm. of any other organic compound (e. g. benzoic acid and sugar) in a 400 ml. beaker, covered with a round bottomed flask.
- 2- Filled with cold water, the beaker is placed on a sand bath or a low flame.
- 3- The sublimed substance (i, e. the benzoic acid) will collect on the bottom of the cold flask and on the side walls of the beaker in pure, crystalline form .
- 4- Scrap the sample of sublimed material from the flask and beaker.
- 5- Collect in a small flask , weigh, and determine the M.P. of the pure substance . Compare to the original sample .

3- Separation and Purification of Organic Compounds by Extraction with Solvents:-

The process of extraction with solvents is generally employed either for the isolation of dissolved substances from solution or from solid mixtures or for the removal of undesired soluble impurities from mixtures.

In this case, solvents also have to be chosen . generally diethyl ether , di-isopropyl ether, benzene, chloroform, carbon tetrachloride and petroleum ether are employed.

The solvent selected will depend upon the solubility of the substance to be extracted in that solvent and upon the ease with which the solvent can be

separated from the solute . thus ether is widely used owing to its powerful solvent property and its low – B.P. ,(fire should be away from ether).

The following discussion illustrates the techniques used in purification by extraction :

- 1- Mix gently the mixture of the impure organic compound with the chosen solvent (such as ether) , in an Erlenmeyer flask . introduce the mixture into the separatory funnel , which is mounted in a ring on a stand with a firm base , the barrel and plug of the of the stopcock are well dried and treated lightly with a lubricant. The funnel is then shaken gently , inverted , and the lower stopcock opened in order to relieve the excess pressure, which is formed from the vaporized ether (or any other solvent).
- 2- Repeat this step three or four times , until most of the organic substance is transferred to the solvent layer, and then returned to the stand in order to allow the mixture to settle.

When two sharply defined layers have formed , separate the two layer into two different flasks. Choose the layer that has taken the organic substance.

- 3- If ether is the solvent, usually in the upper layer since its density so light, if other solvents have been used, students have to check the difference in the density of the solvent and the mother liquor, the heavier the lower layer is , and vice versa.
- 4- Collect the mixture that contains the organic substance and expel the solvent either on a water bath in a hood, or by distillation, followed by recrystallization to get the purified organic substance.

It is not always to use organic solvents in extraction of organic compounds, sometimes certain chemically active solvents, such as acids or basis are used. This is used in the separation of acidic organic compounds or basic organic compounds from their solutions.

Experimentally this will be done in the future experiments.

4-Separation and Purification of Organic Compound by Distillation:-

Liquid organic compounds, can be purified and isolated from certain impurities which have been contaminated during the preparation, by distillation.

Distillation is the conversion of the liquid organic compound to the vapour state with the aid of heat, and condensation of the vapours to the liquid state.

The temperature at which the liquid distills, is a definite value (at a given pressure) for every pure organic compound and is known as the boiling point.

Some organic compounds do decompose at high temperature or nearly their boiling points under normal pressure. Therefore, certain modification in distillation process has to be carried on to overcome the decomposition, such as decreasing the pressure which leads to lower the B.P. and avoid decomposition. There are four types of distillation commonly employed by the organic chemistry, are :

- 1- Simple distillation.**
- 2- Fractional distillation.**
- 3- Vacuum distillation.**
- 4- Steam distillation.**

1-simple distillation:-

Is the mostly used for the liquid organic compounds, which boil at ordinary high temperature, do not decompose at this point and are not mixed with several other low boiling point substances. It consists of a distilling flask attached by a cork to a water cooled Liebig condenser, upon the end of which an adapter is

fitted and immersed in a flask to receive the distillate – the receiver. The thermometer is fitted into the neck of the distilling flask by means of a well – bored cork, the bulb of the thermometer should be in the center of the neck of the flask and slightly below the level of the side tube.

The distilling flask may be heated on a wire gauge with asbestos center, or in a water bath if the organic substance is of a low B . P . or on a sand bath. Few pieces of broken porcelain chips (or boiling stones) are placed in the distilling flask with the substance to be distilled. They prevent bumping , by producing a constant stream of bubbles which keeps the liquid in motion . if the organic substance is of B .P . higher than 120°C , air condenser has to be used . I . e . water should not run through the condenser during the distillation process. The high temperature vapour , when passes through the cold surface of the condenser , the glass walls will crack down, therefore the condenser should not be water – cooled , air – cooled is enough.

2-Fractional distillation :-

When the organic substance is contaminated with the impurities or mixed with other volatile organic substances of different B . P . , purification or isolation of the organic substance will take place gradually by fractions, I . e . when the whole mixture is heated , the lower B.P. constituent will evaporate, condense and distil first , followed by the second higher B. P. constituent And so on .

Every constituent will be evaporated and distilled at its own B.P. When the B.P. of the constituents are close to each other , a modified condensing tube which is made of a series of bulbs or pieces of broken glass tubes . these increase the condensing surface and lessen the resistance to the passage of vapours the receiver and the separation or purification will take place by fraction . such distillation is known as fractional distillation .

There are many types of condenser that can be used in such a process, there is no need to explain these in details , since they are beyond the scope of this subject.

3-Vacuum Distillation :-

Is mostly used when the organic compounds do decompose at their boiling point , or nearly to the B.P. "the B.P. may be defined as that temperature at which the vapour pressure equals the pressure of the atmosphere above the liquid " . by reducing the external pressure to 1 – 30 mm. of mercury , the B.P. is considerably reduced , and the distillation may usually be conduced without danger of decomposition . the pressure is reduced by means of a high capacity water pump , preferably constructed of metal, to 7 – 20 mm.

4-Steam Distillation

Is widely used in the purification of very high B.P. organic compounds , by passing steam to the distilling flas;, the importance of the steam in this case is to distil the organic substance in a lower B.P. the vapour pressure of the steam will be added to the vapour pressure of the organic substance, producing a mixture of vapour that can be pushed to the condenser at a lower temperature than what it should have for the single component .

The distillate, therefore, containing both the organic substance and water , can be isolated by a separatory funnel.

Experimentally these will be done in the future experiments and several subjects.

5 – Separation and Purification of organic compounds by chromatographic adsorption

Chromatographic adsorption is used both in separation between two or more different colored components mixed together and in a crystallization of the organic substance, that could not be crystallized by any of the previous methods.

The process is based upon the selective adsorption from solution on the active surface of certain finely divided solids, (such as Alumina, Talc, Silica gel, Sugar, Calcium oxide) in different powers of adsorption.

In case of impure substances the solution of the mixture (usually an organic solvent is employed) being drawn through along glass tube (14 * 150 mm), which is well packed with the adsorbent . the impurities will be adsorbed on the surface of the adsorbent, and the pure substance will drain down, using the organic solvent substance to be drained gradually , collected crystallized the pure organic substance.

To separate between the components of a mixture, such as used in the separation of complex plant and animal pigments, using not only the power – column method, but paper – chromatography is widely used . A high grade of filter paper in strips, acts the adsorbent, and the paper chromatography is developed by a suitable solvent or solvent mixture.

The end of the paper strip, which is treated with a drop of the mixture to be separated, dips into the solvent. The various substances have different rated flow and may be identified at different areas on the paper by proper reagents.

PHYSICAL DETERMINATION OF ORGANIC COMPOUNDS

The physical determination of the organic compound gives a valuable clues about its nature and structure, and determines the criteria of its purity , such as **Melting point , Boiling point ,Density, Refractive Index, Optical Rotation, Surface tensions and conductivity**. The most important ones are M . P. , B.P. and refractive index.

Organic compounds, solids, liquids or gases , all possess a very different physical character than that of inorganic compounds.

The inorganic compounds are ionic, and the force that holds the ions together is powerful. Thus a very energy is needed to overcome this powerful inter ionic force, to change its physical character from one state to another. While the organic compounds are non ionic, in which the atoms are held to each other entirely by covalent bonds , forming crystals in which the structural units are molecules . these molecules are held together by an intermolecular force, which is very weak , compared to the ionic force.

Thus they need much less energy to overcome this force, and changes its state from one to another.

1- Melting point :-

The particles in solid organic compounds are arranged orderly in a very regular and symmetrical way, due to the intermolecular forces that holds these particles together. Melting is the change from the highly ordered arrangement of these particles to the more random arrangement that characterizes a liquid state . it occurs when a temperature is reached at which thermal energy of the particles is great enough to overcome the intermolecular forces that holds these particles in position . such a temperature is known as **Melting point** .or is the temperature at

which the solid begins to change into liquid under a pressure of equilibrium between liquid and solid states

Pure organic compound melts at a definite and sharp temperature, within a small range, while impure organic compound melts at a lower temp. and within a higher range. i. e. does not melt at a sharp temperature.

(range :- is the time needed to change substance from solid to liquid state).

The M.P. may be determined by several methods either using an electrical apparatus, or using the capillary tube method which is the most common method for the beginner.

EXPERIMENTAL PROCEDURE

The capillary – tube method :-

thin walled capillaries, about 1 mm. in diameter, are made by heating and drawing out tubing that has previously been washed with distilled water and dried . the capillaries are sealed at one end and loaded by pressing the open end into the finely powdered material, followed by tapping to force the sample to the bottom. The length of solid in the tube need not exceed 1 mm.

the tube is next inserted in a suitable bath ((bath is a small beaker (50 ml.) or Thiele – M.P. tube- half filled with either concentrated sulfuric acid or paraffin oil)), with the sample adjacent to the thermometer bulb, and the whole heated until melting occurs. The rate of heating should be regulated so that the rise in temperature does not exceed 1 °C per minute in the vicinity of the melting point .

reading are usually observed on a thermometer ranging from 0 – 360 °C. the melting point is taken as the point where the first appearance of liquefaction occurs . if the sample is pure, the rang from the temperature of initial to complete melting should not exceed 0.5 – 1 °C , and may well be less. If the compound does not melt sharply, record the temperature range over which it melts, and

take the average of them . repeat this determination second and third time , and be sure that the temperature is more or less the same.

Determine the M.P. of the following :- benzoic acid, urea, and salicylic acid in a pure state. Than prepare a mixture of urea and benzoic acid and study the difference in the M.P. determination.

2- The boiling point :-

liquid organic compounds consists of particles that are less regularly arranged than in solid compounds . each particle is attracted by a number of other particles , by an intermolecular force. Boiling is the change from the liquid state to the vapour state, where the particles are freer in motion. Thus an amount of energy is needed to break off the intermolecular forces, and to bring the vapour state and the liquid state into equilibrium under the atmospheric pressure.

such an amount of energy is known as the **Boiling point.** Apure liquid will have similarly a sharp boiling – point which will remain constant until the whole of the liquid has boiled off, leaving no residue. Impure liquid boil at different rang of temperature, depends largely on the physical nature of the impurities.

It's define as the temperature at which it's vapour pressure equals the atmospheric pressure over the liquid, or temperature at which the vapour and liquid phases are in equilibrium at a given pressure.

EXPERIMENTAL PROCEDURE:-

Unless only minute quantities of the liquid are available, the boiling point usually determined by simple distillation. The apparatus used is the same as

that explained under the simple distillation experiment. Place about 100 ml. of the liquid , that its boiling point has to be determined, in a 250 ml. clean and dry Pyrex distilling flask. Set the apparatus as it is shown in the figure.

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Heat the flask gently and slowly, until the liquid starts to boil. The vapour will raise up and pass through the side arm to the condenser. Thus the thermometer will be so arranged, that the top of the bulb is just leveled with the center of the side arm of the distilling flask to measure the temperature of the vapour at that point. When the thermometer reading is constant, and the condenser vapour will distil off regularly drop by drop , record the boiling point of the substance. If the liquid substance is known, check its B.P. to the values found in the hand – book .

Apparatus for determining boiling points of minute quantities of the liquids is differed than that explained above. It only consists of a dry –clean Pyrex test tube, and a thermometer.

- 1- Place 2 ml. of the liquid substance in the test –tube, suspend the thermometer in the tube, so that the bulb is about 1 inch above the surface of the liquid .
- 2- Heat the tube until the liquid boils gently
- 3- When the liquid boils , the cool sides of the tube cause the vapours to condense and a ring appears where the condensation stops.
- 4- By controlling the rat of boiling ,the height of this ring may be regulated. Apply the heat to the tube carefully and keep the condensation ring below the clamp.
- 5- But the ring should be at least 0.5 inch above the thermometer bulb.
- 6- When the thermometer reading is constant, record the boiling point of substance, and check that of the know substance from that found in the hand – book.

Or by other way :-

- 1- In a capillary tube closed from one end is inverted upside down and is attached to thermometer by a rubber ring.
- 2- Place them in a clean and dry test tube containing a small quantity of a liquid whose boiling point is to be measured (the rubber ring should be above the surface of the liquid).
- 3- The whole assembly is to be placed in an oil bath.
- 4- Start heating with continuous stirring until a rapid stream of bubbles comes out of the capillary tube (inside the liquid).
- 5- Remove the flame and allow the oil bath to cool so that the bubble stream will become slower and slower as the temperature drops until a point is reached at which bubbling ceases and the liquid starts to raise inside the capillary tube.

6- Record this temperature as the boiling point.

Isolation and Purification of Ethyl Alcohol From Water / Alcohol Mixture

This experiment is used to purify and isolate the ethyl alcohol from water/ alcohol mixture . at the same time the B.P. of ethyl alcohol is determined.

- 1- Take 150 ml . of the mixture into a distilling flask .
- 2- Set the apparatus as is shown in the figure above. Heat the solution gradually , until the first component starts to distil, and the temperature stabilize at a certain point . continue distillation until the temperature raise up .
- 3- Measure the quantity of the alcohol that distilled and read the temperature which is the boiling of the ethyl alcohol (around $80^{\circ}\text{C} \pm 2^{\circ}\text{C}$). Then continue distillation at higher temperature and collect the distillate which is a mixture of alcohol / water and boils at about $(92^{\circ}\text{C} \pm 2^{\circ}\text{C})$, measure the quantity then measure the undistilled mixture , and watch the difference from the original solution.

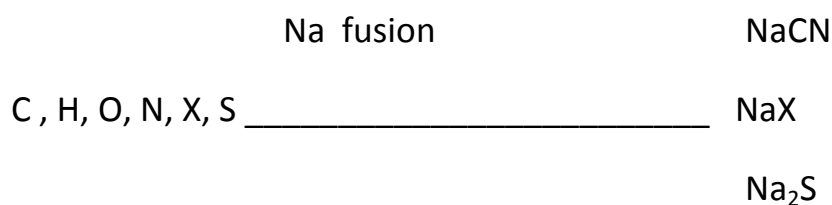
THE MAIN ELEMENTAL FOR THE ELEMENTS IN ORGANIC COMPOUNDS

The main elemental constituents of the organic compounds are carbon, hydrogen and oxygen. The next elements, in the order of their importance are nitrogen, halogen , sulfur and phosphorous.

Before the usual qualitative tests can be applied, however, the elements must be converted from the covalent form in which they usually occur in organic into water soluble ionic compounds, for which routine tests are applied.

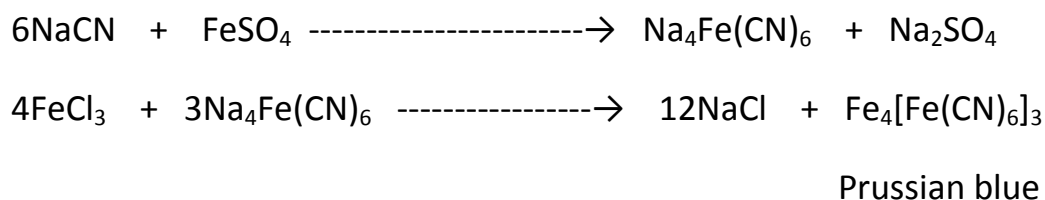
Carbon and hydrogen can be detected by the oxidation decomposition of the organic compound with copper oxide powder . carbon will be converted to carbon dioxide, which can be detected by precipitation of carbonate with a solution of barium hydroxide, and hydrogen to water.

The detection of nitrogen, halogen and sulfur, depends mostly of converting these elements of the organic compounds into their ionic form by with metallic sodium.



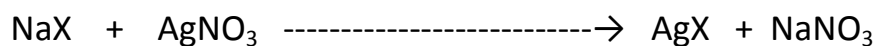
NITROGEN:-

Appears in the fusion product as cyanide ion, upon addition first of ferrous sulfate and then of ferric chloride, both under controlled PH, the characteristic bright color of Prussian blue appears:



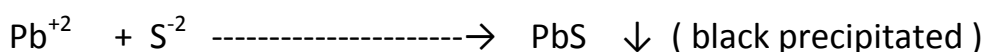
HALOGENS:-

Are converted into halide, which can be precipitated as silver halide (AgX) on the addition of silver nitrate in the presence of nitric acid.



SULFUR:-

Is converted into sulfide, forms a black precipitate of lead sulfide with lead acetate in a solution acidified with acetic acid.



No test is ordinarily made for oxygen. A test phosphorous is not included in this experiment.

The beilstein test:-

A preliminary test for the possible presence of halogen, called the beilstein test , can be made directly on the original unknown. In this test , a small sample of the unknown is burned on a previously ignited copper spiral in the oxidizing portion of a hot flame. Any halogen present is converted to the corresponding copper 2 halide, which imparts a bluish green color to the mantle of the flame as it volatilizes.

Soda lime test for nitrogen:-

Ammonia can be liberated for most compounds containing amino nitrogen by heating the compound with soda lime (soda lime is a mixture of fused NaOH and CaO). The ammonia is tested with moist red litmus.

EXPERIMENTAL PROCEDURE

1- Carbon and hydrogen – cupric oxide test :-

- 1- Place about 1 gm. Of a mixture of cupric oxide and the organic compound in a Pyrex test tube, (the cupric oxide has to be heated in a porcelain dish for 5 minutes with a small flame, cool, and mix with an equal amount of the organic compound).
- 2- Fill about half of the remaining space with the dry cupric oxide, attach to the open end a short piece of rubber tubing and insert a glass tube 12 – 15 cm. long. The ends of the glass tubes should always be fire – polished before inserting them in rubber tubes or stoppers.
- 3- Fasten the test tube containing the mixture in a horizontal position on a ring stand and allow the delivery tube to extend downward into a test tube containing a little clear limewater.
- 4- Heat first the layer of pure cupric oxide and then the mixture containing cupric oxide and the organic compound. when the reaction is complete, remove the tube from the limewater.
- 5- Explain your results for the detection of carbon and hydrogen.
- 6-

2- Nitrogen , sulfur and the halogens – the sodium fusion:-

- 1- Dry a piece of freshly cut sodium about 4 mm. in diameter with a piece of filter paper and place it in a 12 cm. Pyrex test tube, that is supported vertically by a clamp lined with a piece of asbestos cloth.
- 2- Heat the tube with a hot flame until the vapours of the sodium rise about 2 inch in the tube. Then drop a small amount of the organic compound to be analyzed directly into the sodium vapour.
- 3- Take particular care that the material does not touch the inside of the tube, there may be a slight explosion when the organic material in contact with the sodium vapour, consequently the eyes should be well protected.
- 4- After the sample has been added , heat the tube to redness for approximately one minute. Allow the tube to cool , add 3ml. of methyl alcohol to decompose any unreacted sodium , fill the tube to half its volume with distilled water and boil gently for a few minutes .

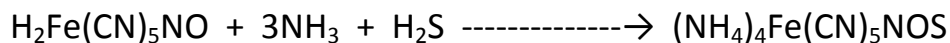
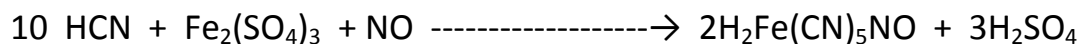
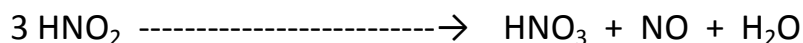
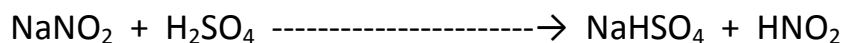
5- Filter the aqueous solution and use the clear, colorless filtrate in the following tests. Save the Pyrex test tube for regular use in sodium fusions.

A- **Test for the presence of nitrogen:-**

- To 3ml. of the filtrate, add 5 drops of a freshly prepared 5% solution of ferrous sulfate , and 5 drops of a 10% solution of potassium fluoride.
- Boil the resulting mixture gently for a few seconds, filter while hot, cool, and treat with 2 drops of 5% ferric chloride solution sufficient dilute sulfuric acid (20 – 50 %) dissolve the insoluble iron hydroxides.
- If nitrogen is present , a brilliant blue precipitate of Prussian blue appears at this point.

dissolve some crystals of NaNO_2 in 3ml. of the filtrate

- Add 2 drop of FeCl_3 solution and acidify the resulting solution with diluted H_2SO_4 .
- Heat the mixture until boiling and make it alkaline by ammonia solution.
- Filter , add to the filtrate 1 drop of H_2S solution (or a solution of alkali sulfide), appearance of a purple blue color confirm the presence of nitrogen.

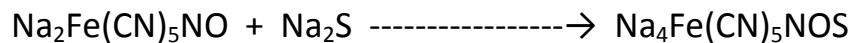


It difficult to test for nitrogen in a nitro compound. But the nitro group mostly gives a deep red coloration with the alkali NaOH .

B – **test for the presence of sulfur :-**

- Make 1 ml of the filtrate acid with acetic and then add few drops of a solution of lead acetate. A black precipitate of lead sulfide is indicative of sulfur.

- To 2 ml. of the fusion solution , add 2 – 3 drops of a freshly prepared dilute solution of sodium nitroprusside (0.1 %)
 $\text{Na}_2\text{Fe}(\text{CN})_5\text{NO}$ the latter may be prepared by adding a minute crystal of the solid to about 2ml. of water a purple coloration indicates the presence of sulfur. A purple coloration indicates the presence of sulfur, the coloration slowly fades on standing.



C-The halogen test :-

Acidify 2ml. portion of the filtrate from the sodium fusion with dilute nitric acid , boil to expel all of the H_2S or HCN , if there is any sulfur or nitrogen cool, add few drops of a silver nitrate solution . a white or pale yellow precipitate that rapidly darkens on exposure to light shows the presence of halogen.

D- Test for bromine and iodine in the presence chlorine :-

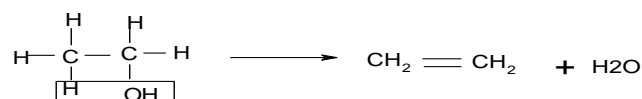
Acidify 4ml. of the solution from the sodium fusion with dilute sulfuric acid and boil to expel any hydrogen sulfide that may be present. Cool, and add with shaking 0.5 ml. of carbon tetrachloride followed by a drop of freshly prepared chlorine water. If iodine is present the carbon tetrachloride layer becomes purple in color. as the addition of chlorine water drop by drop is continued the purple color disappears from the carbon tetrachloride and, if bromine is present, is replaced by a brown color.

ELIMINATION REACTION AND ADDITION REACTION

Preparation of ethylene and ethylene bromide

Discussion :-

Ethylene is the first member of series of the unsaturated hydrocarbons known as the olefins (alkenes C_nH_{2n}). Ethylene is derived from ethyl alcohol ($CH_3.CH_2OH$) by the removal of an – OH group and an H- atom from two adjacent carbon – atoms to form a molecule of water.



Several reagents may be used for this purpose, but most of the processes may be classified as acid – catalyzed dehydration . sulfuric acid is the reagent most frequently employed in the laboratories.

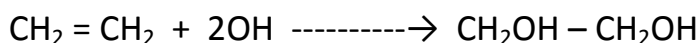
The reaction is conducted a temperature of about 180°C .the mechanism of the reaction probably involves the loss of water from the conjugate acid of ethyl alcohol (ethyl hydronium ion), forming an ethylcarbonium ion from which ethylene is obtained by loss of a proton. معادلة ص 21

In addition to this reaction definite sidereaction products are obtained . for example, the sulfuric acid acts as an oxidizing agent at this temperature and oxidizes ethyl alcohol to acetaldehyde. The sulfuric acid is reduced to sulfurous acid , which liberates sulfur dioxide. The sulfur dioxide is removed by bubbling the gaseous mixture through a dilute solution of sodium

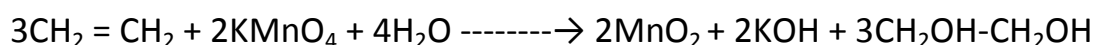
hydroxide (a method is used to purify and extract a gaseous organic matter from acidic impurity).

A small amount of diethyl ether is also formed as a side - reaction product.

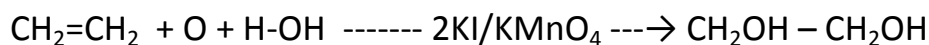
Ethylene is much more reactive chemically than methane and gives definite addition reactions with halogens, halogen acids, and sulfuric acid . strong oxidizing agents are capable of oxidizing ethylene to carbon dioxide and water. Milder oxidizing agents, such as alkaline potassium permanganate, oxidize ethylene to ethylene glycol. This may be indicated as the addition of OH groups to the double bond :



This reaction is known as Baeyer's test for a double bond. The complete equation for this reaction is somewhat complex:



The essential observations to be made from above equation are the oxidation of the organic molecule and the organic product formed. For this reason, it is more convenient to indicate a balanced equation between the organic molecule and the number of nascent oxygen [O] atoms required in the oxidation. The above reaction may be written:



In writing an equation in this manner, it is necessary always to indicate the oxidizing agent employed. The student must recognize the fact that every chemical reaction is capable of being expressed by a completely balanced equation. The shorthand method indicated above gives a balanced equation so far as the organic molecules are concerned but not the completely balanced equation from the standpoint of all substances taking part in the reaction.

See the diagram on the last page

Ethylene is a colorless gas, has a sweet odor, and is slightly soluble in water . it forms an explosive mixture with air . in this preparation small quantities of the ethylene are used for chemical tests , but the bulk of the ethylene is bubbled through bromine for the preparation of ethylene bromide. Ethylene adds bromine readily to form ethylene bromide, a colorless oil with a sweet odor and a boiling point of 131.5°C . sodium bromide is added to the water in the bottle with the bromine in order to increase the solubility of bromine in water. Ethylene bromide yields ethylene quite readily when heated with metallic zinc using amyl alcohol as a solvent.

Equation page 23

Experimental procedure:-

Prepare an apparatus as shown in the fig. all stoppers must be rubber, and all connections must be tight. The reaction flask is a 1 – liter round bottom flask connected a 500 ml distilling flask (which serves as a safety trap) by an 8 – diameter glass tube. (use a plain wire gauze , not asbestos). The 250 ml wash bottles are connected with 6 – mm –diameter glass tubing , care being taken to see that the tube lengths correspond to the diagram that rubber connections are used between wash bottles . the second wash – bottle should be placed in the water bath or metal pan , and ice should be available to cool the solution.

Place in a beaker 25 ml . of special denatured alcohol (pkg.), and add, carefully with stirring , 75 ml. of concentrated H_2SO_4 ,and cool. Pour this mixture into the 1 – liter round – bottom flask . in the same manner, add 100 ml. of concentrated H_2SO_4 to 100 ml. of special denatured alcohol, mix, cool , and place in the separatory funnel of the apparatus. Fill the wash bottles un the absorption train as follows :-

In the first one place 50 ml. of 10 percent solution of NaOH (desk) (for the purpose of removing SO_2 formed by the reduction of H_2SO_4).

In the second bottle , place 32 gm .(10.2 ml.) of bromine (pkg.). (this bottle should be packed in ice).

The third bottle in the train is a trap; the fourth contains 10 percent NaOH (30 ml.) to prevent the escape of bromine vapors.

(caution:- make certain that the length of tubes in each bottle agrees with the fig.).

The thermometer in the generator flask should dip into the reaction mixture. At this point, obtain the instructor's approval of the apparatus .

Heat the mixture in the generator to 170°C . now add slowly the mixture from the dropping funnel , and adjust the flame so that the temperature remains between 165°C and 175°C . as soon as a rapid flow of a gas is passing through the train and all the air is expelled, disconnect the train and collect four small bottles of the gas by displacement of water. Stopper them, and save for later tests.

Reconnect the train , and continue passage of ethylene through the apparatus until the color of the bromine disappears. Occasionally shake the bottle which contains the bromine.

If the reaction mixture begins to foam, regulate the heating very carefully so that the foam does not run over into the trap.

If the foam enters the trap, the reaction must be stopped. If the bromine water is not completely decolorized, ask the instructor for a suggestion concerning its treatment. Save the bottle containing the ethylene bromide.

Perform the following tests on ethylene:-

- (a) Reaction with bromine . to the first bottle , add 1 ml of bromine water and shake.

Observation.....

(b) Reaction with alcoholic iodine. To the second bottle, add 2 drops of alcoholic iodine solution.

Observation.....

(c) Reaction with alkaline permanganate. To the third bottle , add 2 drops of KMnO_4 solution and then 1 ml of Na_2CO_3 solution (5 percent).

Observation

(d) Combustion test. Burn the last bottle of the gas, noting the character of the flame.

Observation

Save the first three tests, and have them approved by the instruction.

Allow the acid residue in the generator to cool, and pour the liquid portion down the drain with plenty of water. Any solid matter in the flask should be rinsed with water , the water decanted, and the solid placed in the waste jar.

SUBSTITUTION REACTION

Preparation of butyl bromide

The butyl bromide may be prepared by heating the alcohol with potassium bromide and concentrated sulfuric acid. The yield is very good for primary alcohols only, secondary and tertiary are readily dehydrated to olefins under these conditions.

The hydroxyl group of alcohol will be substituted by the bromide ion, as follows: the primary alcohol and the hydrogen bromide unite to form an addition compound:

Equation page 26

The oxygen atom of the alcohol acts as a base, accepting the proton of the acid upon one of its unshared pairs of electrons, which leads into the weakening of the bond between the oxygen and carbon for oxygen normally has two pairs of unshared electrons. The carbon – oxygen bond is further weakened by the attraction of the ethyl group for the negative bromide ion, as shown in the following equation:

And substitution of the - OH group by the bromide ion will take place. Watch the temperature of the reaction.

Experimental procedure :-

- 1- To 250 gm of 48% hydrobromic acid contained in 500 ml. round bottom flask add 75 gm . (41 ml.) concentrated H₂SO₄, in portions with shaking, some HBr may be evolved.
- 2- Add 88 gm (110 ml.) of n – butyl alcohol followed by 60 gm . (32.5 ml) of concentrated H₂SO₄ in portions with shaking , and finally a few chips of broken glass. Attach a reflux condenser to the flask and reflux the mixture gently on a wire gauze for 2 – 3 hours.
- 3- During this period the formation of n – butyl bromide is almost complete and a layer separates above the acid.
- 4- Allow the contents of the flask to cool , remove the condenser and set it for downward distillation , connect the condenser to the flask by means of a wide (7 – 8) bent glass tube . distill the mixture until no more oily drops of n – butyl bromide pass over (30 – 40 min.)
- 5- Transfer the distillate to a separatory funnel and remove the halide which forms the lower layer. Wash it successively with water, an equal volume of concentrated HCl , water, 5% NaHCO₃ OR Na₂CO₃ solution and water.
- 6- Separate the water as completely as possible and dry with 2-3 gm. Of anhydrous calcium chloride or anhydrous magnesium sulphate . the desiccant should be left in con tact with the bromide for at least 30 minutes and shaken occasionally .
- 7- Filter the dried product through a small funnel supporting a fluted filter paper or small cotton wool plug into a 200 ml. distilling flask.
- 8- Add a few drops of porous porcelain and distl either from a bath or an asbestose centred wire gauze , collect the portion boiling at 100 – 103 OC , the yield is 155 gm.

Reactions and characterization of alkyl halides:-

1- Beilshtein's test .

2- Alcoholic silver nitrate solution :

Shake 0.1 gm of the substance with 2 ml of alcoholic silver nitrate solution .
alkyl iodides usually yield silver iodide instantly , alkyl bromides react rapidly , but may require warming ; alkyl chlorides give very little precipitate in the cold, but a copious precipitate is obtained by warming on a water bath. The order of reactivity is :-

1 > Br > Cl and tertiary > secondary > primary

CHEMISTRY OF AICOHOL

Discussion :-

A general rule concerning the solubility of organic compounds states that compounds are soluble in solvents of like structure. Hence , we may expect compounds with a large number of hydroxyl groups (OH) in the molecule , as compared with the number of carbon atoms in the molecule, to be quite solution in water and not very soluble in hydrocarbon solvents. An increase in the number of carbon atoms in a compound, and a proportional decrease in the number of hydroxyl groups present, will result in the reduction of solubility in water and an increase in the solubility in hydrocarbon solvents.

The monohydric alcohols form an homologous series. The number of isomers for any given number of carbon atoms is greater than for the corresponding paraffin . it will be interesting to observe how the alcohol series compares with the paraffin series in physical properties.

Alcohols are the hydroxides of the hydrocarbon radicals, or, an alcohol may be defined as an hydroxyl (OH) substitution product of the corresponding hydrocarbon .

An alcohol may also be regarded as a derivative of water in which one of the hydrogen atoms of water molecule $H-O-H$ has been replaced by an alkyl group $R-O-H$.

The properties of the alcohols will, therefore , resemble those of the hydrocarbon, on the one hand , and those of water on the other . since paraffin have a low degree of chemical reactivity, most of the properties studied will be those characteristic of the hydroxyl group.

The addition of ionizing salts , such as sodium chloride or potassium carbonate, to a water solution of an organic compound may diminish the solubility of the organic compound in water to such an extent that the organic substance is forced out of solution. This is known generally as a “ salting out “ process.

The properties of monohydric alcohols:

(1) Solubility in water :-

place 1 ml . of water in each of the five separate test tubes and test each of the following alcohols:-

Methyl, ethyl, isopropyl, n – butyl and isoamyl as follows : add the alcohol drop by drop with gentle shaking until an equal volume of the alcohol has been added . observe and record the solubility of each one in water.

now saturate those solutions showing partial or complete solubility with solid potassium carbonate. Observe , and record the results.

(2) Reaction with sulfuric acid :-

place 1 ml of concentrated H_2SO_4 in each of 5 dry test tubes. Add each of the five alcohols, tested in (1) above, to a separate tube of the acid , drop by drop , with cooling and shaking . Observe the results.

(3) Reaction with metallic sodium:-

Place 1 ml. of each of the above alcohols in a separate test tube. The test tubes must be perfectly clean and dry. Now add a small piece of freshly cut sodium to each. Observe and record any difference in the relative rates of reactivity.

After the sodium in the tube containing ethyl alcohol has dissolved completely, evaporate it carefully to dryness. Use ethyl alcohol to dissolve any unreacted sodium before discarding the contents of the above tubes.

(4) Esterification with acetyl chloride:-

Place 1 ml of each of the above alcohols in a clean, dry test tube. Add drop by drop, with gentle shaking, an equal volume of acetyl chloride (hood – care). After the reaction is complete, dilute the mixture with an equal volume of water, and neutralize carefully with dilute NaOH. Note and describe the odor in each case. Also, observe the solubility of each ester by the fact of miscibility or immiscibility.

(5) Rate of reaction for primary, secondary, and tertiary alcohols:-

Place 1 ml of each the four butyl alcohols in a separate test tube, add 6 ml. of HCl /ZnCl (Lucas reagent) to each, and warm in a water bath to (26 – 27 0C). Stopper the tubes, shake the mixture, and allow to stand.

Observe the tubes at each of the following periods:-

- 1- Immediately upon mixing;
 - 2- after staining 5 minutes;
 - 3- after standing for an hour.
- Observe the relative rates of reaction, and record your observation.

(6) Oxidation of alcohols:-

Place 1 ml. of each of the four butyl alcohols in a separate test tube, and several drops of potassium dichromate solution and a little dilute H₂SO₄. Provide the test tube with a rubber stopper bearing a delivery tube with an exterior arm 5 in long. Warm the reaction mixture gently until 3- 4 drops of distillate have distillate, and add 2ml of fuchsine – aldehydes reagent (Schiff's reagent).observe , and record results.

Rinse the delivery tube thoroughly, and proceed with successive tubes of alcohol in a similar manner until all have been tested.

(7) Iodoform reaction:-

Place 3 drops of each of the butyl alcohols in a separate test tube, and 10 drops of a solution of iodine in KI solution, until the solution just becomes decolorized. Warm gently, shake and set aside for 1 hour. Observe and compare the results with these obtained in the Iodoform test.

(8) Tests for water in alcohols:-

1- With anhydrous copper sulphate:-

Add 0.5 gm of anhydrous copper sulphate alcohol in a dry test tube and shake vigorously. Repeat with 5 ml of absolute alcohol.

2- With paraffin oil :-

Add 1 drop of paraffin to 5 ml sample of absolute alcohol and 95 % alcohol, respectively . note the difference. Test similarly the relative solubility of ammonium chloride, anhydrous sodium sulphate , acetanilide, naphthalene and sucrose in absolute and in 95 % alcohol.

(9) Distinguishing tests for ethyl and methyl alcohols:-

1- Acetate test:-

Add 1ml of conc. H₂SO₄ to a mixture of 1 ml of absolute ethyl alcohol and 1 ml glacial acetic acid in a test tube, and warm gently (do not boil).note the characteristic odor of the ester ethyl acetate.

2- Salicylate test:-

Add 1 ml of conc. H₂SO₄ to a mixture of 1 ml of pure methyl alcohol and about 0.25 gm of salicylic acid .warm gently for a few minutes, then cool, and pour into 10 ml of cold water contained in a small beaker.

Note the odor of methyl salicylate.

(10)Specific test of alcohols:-

(an important test for alcohols is with ceric nitrate reagent).

1- dilute 0.5 ml. of ceric nitrate reagent with 3 ml of distilled water and mix it well. Add 5 drops of the compound under test . shake the mixture well and notice the change of color , perform the test on ethyl

alcohol, glycine , glucose, tartaric acid , phenol. Alcohol give red color .
phenols give brown color in dioxane solution only.

2- For insoluble compounds in water:-

To 0.5 ml of the reagent add 3 ml. of dioxane , if a ppt. appears , add 4 drops of water and shake the test tube to get a clear solution .

Add now 5 drops of the test compound . notice the change in color .
perform the test on neptyl alcohol, benzyl alcohol, salicylic acid.

N.B :- If the compound is solid , dissolve it in the dioxane . add 5 drops dioxane solution to the reagent.

Chemistry of aldehydes and ketones

Aldehydes and ketones both have the general formula $C_nH_{2n}O$ and containing a carbonyl group. The aldehydes group is $-CO-H$, which can only occur at the end of a chain. The ketonic group $R_2-C=O$, which cannot occur at the end of a chain since in each of which is joined to a carbon atom.

The reactivity of carbonyl group depends on the nature of the alkyl groups attached to it, the smaller the alkyl group, the more reactive is the carbonyl group. They mostly undergo an addition reaction, and possess a reducing character.

(a) Aldehydes:- such as formaldehyde, acetaldehyde, chloral hydrate, benzaldehyde, salicylaldehyde etc., all are colorless.

Formaldehyde HCHO , is a gas, and only its 40% aqueous solution, which has a characteristic pungent odor , is considered, and know as formalin. Acetaldehyde, is a liquid ,b.p. 21 °C , generally used in aqueous solution , which has also a characteristic odor . chloral hydrate is a solid substance, with a characteristic odor and is readily soluble in water

General chemical reactions:-

1- Schiff's reagent:-

Add about 1 ml of Schiff's reagent to an equal volume of formaldehyde or acetaldehyde. a red color rapidly develops in the cold .

2- Oxidation of aldehydes:-

- With permanganate solution:-

Acidify a faintly pink solution of KMnO_4 with a few drops of dil. H_2SO_4 And add small amount of acetaldehyde or formalin. Note the result.

- With ammoniacal silver nitrate:- (Tollen's reagent)

Place about 5 ml of silver nitrate solution in a thoroughly clean test tube , and add 2-3 drops of dil. NaOH solution .

Add dil . ammonia solution , drop by drop , until the precipitated silver oxide is almost redissolved, then add 2-3 drops of formaldehyde or acetaldehyde. A silver mirror is formed.

- With Fehling solution:-

To 1 ml of the aldehydes, add about 1 ml of 10 % Na_2CO_3 solution and the a few drops of Fehling's solution , and boil the mixture gently for 1 minute . the solution usually turns green and on standing a fine yellow or red precipitate of cuprous oxide slowly separates.

A liphatic aldehydes reduce Fehling's solution rapidly , benzaldehyde very slowly and indecisively, salicylaldehyde does not reduce it .

3- Addition reaction:-

- Addition of sodium bisulphate:-

Shake 1 ml of one of the aldehydes with about 5 ml of saturated sodium bisulphate solution . the mixture becomes warm. With

formaldehyde and acetaldehyde the addition products are so soluble that they rarely crystallize, while with benzaldehyde white addition product separates rapidly.

The addition products may be hydrolyzed very easily in diluted solution of Na_2CO_3 into pure aldehydes compound.

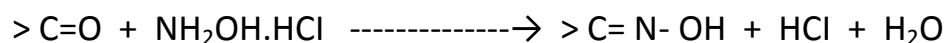
- Phenyl hydrazine:-

Aldehydes may add phenyl hydrazine with elimination of one molecule of water, and phenyl hydrazones derivatives may be formed. To 3 drops of the solution of acetaldehyde, add 3 ml of phenylhydrazine reagent. Heat the mixture carefully, and cool. Let stand a few minutes.

- 2,4 – dinitrophenylhydrazine:-

To a few drops of formalin, add a few drops of 2,4 – dinitrophenylhydrazine reagent, a yellow precipitate is produced in the cool. Acetaldehyde gives an orange colored precipitate.

- Hydroxylamine HCl test:-



To 1 ml of the reagent add drop by drop (or few crystals of the compound) and see the change in color. If there is no change in color, heat to boiling. The change in color from orange to red is a positive test, perform the test on 1) n-butylaldehyde, 2) acetone, 3) benzophenone, 4) glucose.

4 – action of sodium hydroxide:- (polymerization of acetaldehyde)

Place 2 ml of acetaldehyde in a test tube which is immersed in a mixture of 1 ml and salt. Insert a thermometer in the tube, and observe the temperature. Remove the thermometer and wipe it with clean cloth add a drop of concentrated H_2SO_4 on the end of the thermometer to the acetaldehyde. Remove the test tube from the freezing mixture. Stir with a thermometer for about a minute and note the rise in temperature. Add 3-4 ml of water and observe the formation of liquid polymer (paraldehyde) which is insoluble in water.

5-nitroprusside reaction:-

Add 1 ml of a freshly prepared solution of sodium nitroprusside to the aldehydes or its solution. Add dil NaOH solution in excess, a red coloration is produced.

6-iodoform reaction:-

To 1 ml of the aldehydes solution, add 5 ml of 10 % I₂ solution and 10 ml of freshly prepared sodium hypochlorite solution. Yellow crystals of Iodoform, CHI₃ soon separate.

7-naphthol reaction :-

Dissolve 0.2 gm of B-naphthol in 2 ml of cold glacial acetic acid containing 2 drops of conc. HCl. Add drop of acetaldehyde. Shake the mixture, then warm for 5 minutes at 60 °C. And finally to boiling. Cool the mixture, shake vigorously to induce crystallization, add 1 drop of 50% ethyl alcohol and shake again.

Recrystallize the white crystalline compound (ethylidene di-B-naphthol) from alcohol. It should have m.p. of 172 – 173 °C

EQUATION 34

KETONENS

Such as acetones, acetophenone, benzophenone.....etc.

All are colorless, acetone, CH₃COCH₃ b.p. 56 °C, soluble in water, characteristic odor. Acetophenone CH₃-CO-C₆H₅, M.P. 20 °C, sparingly soluble in water.

Benzophenone C₆H₅-CO-C₆H₅, M.P. 48 °C insoluble in water.

General reactions:-

1- Schiff's reagent:-

Add about 1 ml of schiff's reagent to about 1 ml of acetone and note the very slow formation of amagenta color. Higher ketones such as acetophenone or benzophenone do not react in this way .

2- Ketones do not reduce ammoniacal silver nitrate or fehling's solution.

3- Addition reaction:-

- **Addition of sodium bisulphite:-**

Shake 1 ml of acetone in 0.5 ml of a saturated solution of sodium bisulphite. A white precipitate is formed, the mixture becoming warm and then, on cooling, almost solid.

- **Phenylhydrazines:-**

The phenylhydrazine of acetone has a low m.p. and is difficult to isolate. The phenylhydrazone of acetophenone and benzophenone are readily obtained. To 0.5 ml of water add about 1 ml of glacial acetic acid and 1 ml of phenylhydrazine. Then add 3 drops of the aldehydes solution, and shake the mixture. A precipitate of the phenylhydrazone is produced on warming and scratching.

- **2,4- dinitrophenylhydrazines:-**

To a few drops of acetone, add a few drops of dinitrophenylhydrazine reagent , an orange colored precipitate is produced in the cold.

- **Semicarbazide reaction:-**

- a- **Soluble ketones in water:-**

In a test tube dissolve 0.5 gm of the aldehydes or ketone, 0.5 gm of Semicarbazide HCl and 0.8 gm of sodium acetate ,1.5 ml of water . shake the mixture vigorously and place the test tube in boiling water. Let it cool. Put the test tube in an ice bath. Filter the crystals.

- b- **Insoluble ketones in water :-**

Dissolve 0.5 ml of the aldehydes or ketones in 5 ml of ethyl alcohol. Add sufficient amount of water to get turbidity. Remove the turbidity with few drops of ethyl alcohol. Add now 0.5 gm of Semicarbazide HCl and 0.8 gm sodium acetate complete as in (a) . the reaction is accelerated by the addition of acetic acid.

4- Iodoform reaction :-

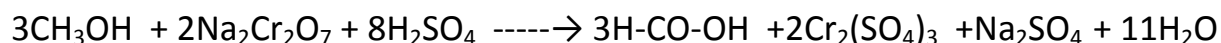
To 0.5 ml of acetone, add 5 ml of 10% KI solution and 10 ml of freshly prepared sodium hypo chloride solution (or I₂ / NaOH solution), and mix well. A pale yellow precipitate of Iodoform is rapidly formed without heating.

5- Sodium nitroprusside reaction:-

Add 1 ml of a freshly prepared solution of sodium nitroprusside to 0.5 ml of acetone or acetophenone . add diluted NaOH solution in excess; ared coloration is produced. This is not given by benzophenone.

CHEMISTRY OF CARBOXYLIC ACIDS

Preparation of formic acid from methanol:-



Procedure:-

Place a solution containing 16 gm of sodium dichromate , 50 ml of water , and 10 ml of concentrated sulphuric acid in a 125 ml distilling flask and immerse the flask in a pan of cold water . add 10 ml of methanol dropwise, with continous shaking of the flask . after the initial spontaneous reaction has subsided , attach a glass tube 50 cm. in length to the distilling flask to serve as a reflux condenser (see the figure) and set the flask in a beaker of hot water for 5 minutes . attach the flask to a condenser and distill 25 – 30 ml of the liquid. The distillate consists of an aqueous solution of formic acid and may be used for the tests described below.

Figure

Special reaction for formic acid HCOOH

1- Carbon monoxide test:-

Warm together carefully 1 ml of formic acid (or 0.5 gm of a formate) and 1 ml of conc. H_2SO_4 . identify the carbon monoxide by igniting the gas evolved and observing the pale blue flame travel down the test – tube . note that dilute solution of formic acid will not give this test. $\text{HCOOH} - \text{H}_2\text{O} = \text{CO}$.

2- Mercuric chloride test:-

Add mercuric chloride solution to formic acid or a solution of formate and warm . a white precipitate of mercurous chloride is produced . sometimes

the reduction proceeds as far as metallic mercury, which appears as a grey precipitate.

3- reduction reactions:-

(a)reduction of acid permanganate:-

Add a few mls. Of dil. H₂SO₄ to a solution of formic acid of a formate , add a dilute solution of potassium permanganate drop and note the decolorization , which is hastened by warming .

(b)reduction of alkaline permanganate :-

Dissolve about 0.1 gm of a formate (or 2 -3 drops of a formic acid solution) in 5 ml of a 10 % Na₂CO₃ solution , add 1 % aqueous potassium permanganate drop by drop , immediate decolorization takes place in the cold with the simultaneous precipitation of manganese dioxide.

4- Reduction of ammoniacal silver nitrate:-

Add a few drops of neutral solution of a formate to ammoniacal silver nitrate. A silver mirror more usually a grey precipitate of metallic silver is produced on boiling.

Characters of carboxylic acids

Discussion:-

Acetic acid is prepared readily in the laboratory by the action of sulfuric acid on sodium acetate , the salt of acetic acid. This method of preparation presents an example of the general principle of general chemistry . I.e, that a strong acid will displace a weaker one from one of its salts . a number of important organic acids occur in nature as salts (oxalic , tartaric) , and the free acids are produced by the action of a dilute mineral acid on the salts . although acetic acid is not prepared in the present exercise, the student will distil a sample of glacial acetic acid and study certain physical and chemical properties.

1- General reaction of carboxylic acids:-

a) Solubility in sodium hydroxide solution.

b) Solubility in sodium carbonate solution .

Note:- that phenols will dissolve in sodium carbonate with out the evaluation of CO_2 .

c) Ester formation :

Heat gently 1 ml of ethyl alcohol with 0.5 of the acid or one of its salts and a few drops of concentrated H_2SO_4 for about 1 minute . cool and pour into a few mls. Of water in a test tube and note the odor.

2- Reactions of acetic acid

Acetic acid does not reduce potassium permanganate , mercuric chloride or ammoniacal silver nitrate.

EXPERIMENTAL PROCEDURE

a) Ferric chloride reaction:-

For the success of this reaction it is important that the solution should be neutral. Test for acetic acid and the hydrolysis of ferric acetate. To 1 ml of 10 % NaOH add dilute acetic acid drop wise (medicine dropper) until the solution is slightly acid to litmus (15 -25 drops). Now add a few drops of 5 % ferric chloride, a deep red coloration will be formed which is due to ferric acetate . if a precipitate forms, repeat the test.

Divide the solution into three equal parts . heat one part to boiling in a test tube . a reddish – brown precipitate of the basic ferric salt will be formed.

To second portion of the solution of ferric acetate ,add a few drops of dilute HCl until the color changes . observe, and compare with the third and original potion of the solution.

b) Esterification of acetic acid:-

To 1 ml of ethyl alcohol in a test tube , add 10 drops of acetic acid (glacial) and 5 drops of dilute H_2SO_4 , and warm. Neutralize the mixture with dilute NaOH solution . observe the odor .

3- **Reaction of oxalic acid HOOC- COOH**

a) **Calcium chloride test:-**

Add calcium chloride solution to a neutral solution of an oxalate , a white precipitate of calcium oxalate is formed, insoluble in acetic acid, but soluble in diluted HCl.

b) **Reduction of acid permanganate:-**

Add few mls. Of diluted H_2SO_4 to 1 ml of solution of oxalic acid or of an oxalate. Warm gently and add dilute solution of potassium permanganate drop by drop and note the decolorization.

4- **Reaction of tartaric acid [CH (OH) COOH]₂**

a) **Sulphuric acid test :-**

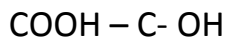
Warm 0.5 gm of tartaric acid or a tartrate with 1 ml of concentrated H_2SO_4 . heavy charring takes place , CO and SO_2 being evolved.

b) **Reduction of ammoniacal silver nitrate:-**

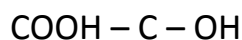
Add 1 drop of diluted NaOH solution to about 5 mls of silver nitrate solution , and add diluted ammonia solution drop by drop until the silver oxide is almost redissolved. Add silver nitrate solution until a faint but permanganate precipitate is obtained. Then add 0.5 ml of a neutral tartrate solution . place the tube in warm water; a silver mirror is formed in a few minutes.

c) **Fenton's reagent:-**

To a solution of tartaric acid or a tartrate add 1 drop of freshly prepared *ferrous sulphate* solution, 2 drops of *hydrogen peroxide* solution and then excess of *NaOH solution* an intense *violet coloration is produced*, due to the ferric salt of dihydroxy = fumaric acid



II



d) **Calcium chloride test:-**

Add calcium chloride solution to a neutral concentrated solution of a tartrate ; a white precipitate of calcium tartrat is produced in the cold

5- **Reaction of citric acid $\text{HOOC} \cdot \text{CH}_2 \cdot \text{C}(\text{OH})(\text{COOH}) \cdot \text{CH}_2\text{COOH} :-$**

a) **Sulpharic acid test:-**

Heat 0.5 gm of citric acid or a citrate with 1 ml of H_2SO_4 carbon monoxide and carbon dioxide are evolved and the mixture turns yellow , but does not char. Acetone dicarboxylic acid , $\text{OC}(\text{CH}_2\text{COOH})_2$, is also one of the products and is tested for , after heating the mixture for 1 minute ; cool, add a few mls. Of water and make alkaline with NaOH solution . add a few mls. Of a freshly prepared solution of sodium nitroprosside and note the intense red coloration.

b) Dose not reduce **ammoniacal silver** nitrate solution (cf. tartaric acid)

c) No coloration with **Fenton's reagent** (cf. tartaric acid).

d) **Calcium chloride test:-**

Add calcium chloride solution to a neutral concentrated solution of a citrate . no precipitate is formed in the cold, but on boiling a white precipitate of calcium citrate is produced, in solution in acetic acid.

Place 77 gm of ammonium acetate and 80 gm (or 80 mls.) glacial acetic acid in a 250 ml round bottomed flask and add few chips of porcelain . equip the flask with a functioning column. Carry a thermometer and leading to a condenser, set for downward distillation. heat the flask preferably in an air bath , so that the mixture boils very gently and the vapours do not rise appreciably in the functioning column.

After one hour increase the heat slightly so that the water formed in the reaction and a part of the acetic acid distils off very slowly at a uniform rate. The temperature rises to about 110°C , and remains at $110 - 112^{\circ}\text{C}$ during 2.5 hours 85 ml (90 gm) of liquids are collected . the temperature may rise to about 115°C towards the end of distillation , but soon drops below 100°C , indicating that all the acetic acid has been removed the residue in the flask crystallizes completely upon cooling. It consists of almost pure acetamide and melts at 78°C . redistill the crude amide from a 100 ml distilling (or claisen) flask equipped with an air condenser, there is a small low boiling point fraction (b.p. up to 195°C) consisting of the 'hold-up ' of fractionating column and the acetamide passes over at $195 - 230^{\circ}\text{C}$ largely at 215°C . the yield of pure colorless acetamide m.p. 81°C is 57 gm.

Alkaline hydrolysis:-

Treat a small portion of acetamide with 10 % NaOH solution in a test tube , and warm . note the odor of the gas evolved.

Action of nitrous acid on acetamide :-

To a small quantity (0.5 gm) of acetamide in a test tube , add 3 or 4 ml of sodium nitrite (NaNO_2) solution and a few drops of dilute HCl.

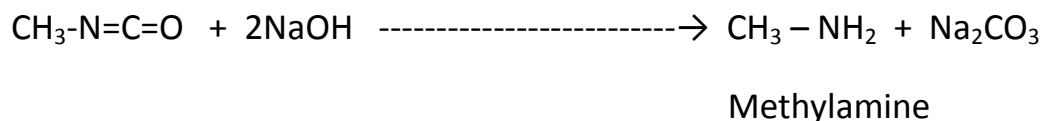
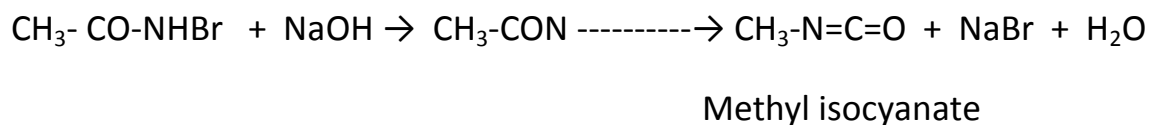
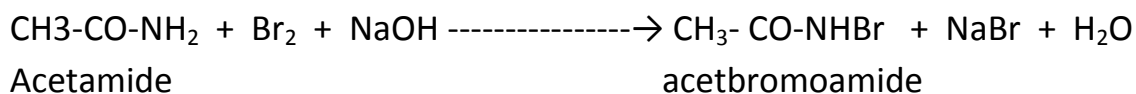
2- Hofmann Bromoamide Reaction :-

preparation of methylamine

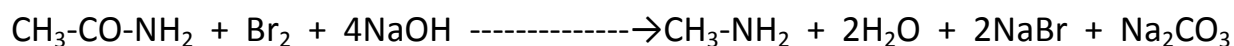
Discussion :-

The Hofmann bromoamide reaction for the preparation of pure primary amines is a very good example of molecular rearrangement. In this reaction a nitrogen migrates from the acyl carbon to the adjacent alkyl carbon. The reaction also serves as a convenient means of 'stepping down' the homologous series, with a loss of one carbon atom.

The Hofmann bromoamide reaction products are more easily isolated where the hydrocarbon structure is aromatic or of high molecular weight. The yields, however, for the higher amines are lower as a result of the formation of the corresponding RCN compounds.



Effective reaction:-



EXPERIMENTAL PROCEDURE

Preparation of methylamine :- (start this exercise at the beginning of a laboratory period). Prepare an approximately 20 % NaOH as follows:-

Place 275 ml of water in a 600 –ml . beaker , and add 60 gm of solid NaOH (pellets or flake)

(Caution :- sodium hydroxide is very corrosive . do not make up this solution of NaOH unless it is to be used the same day) . stir the solution until the NaOH has dissolved entirely , and cool in ice. Place 20 gm of acetamide and 17 ml . of bromine **(caution:-** handle with care) , in a 500 ml round – bottom flask . add gradually , with frequent shaking , 100 ml. of the above solution of NaOH . do not cool the mixture unless the reaction mixture becomes very hot and beings to effervescence (keep a pan of ice handy). If a yellow solid separates , add a little water to dissolve it. Add the NaOH solution over a period of minutes for best results.

Place the remainder of the caustic soda solution in a 1 – liter round – bottom flask, and attach a dropping funnel and condenser (fig , 34) . place about 30 ml of water in the receiver (cool in ice) , and have the tip of the adapter below the surface of the water. Have your instructor approve the apparatus .

Place the caustic soda solution of bromine and acetamide in the dropping funnel , and heat the solution in the 1 – liter flask to 65 - 70 °C. at this temperature, add the solution from the dropping funnel in a slow continuous stream. If the temperature rises above 75 OC , interrupt the operation and cool the flask and the contents by immersion in cold water. **(caution :-** loosen the adapter leading to the receiver before cooling) . When the reaction mixture has been kept at this temperature until it is practically colorless (20 -30 minutes), bring the mixture

gradually to boiling . continue the distillation for a period of 1 full hour. A water solution of methylamine distils over. Note the odor of the solution.

Test for methylamine water solution:-

Add 1 ml of acetone and few drops of sodium nitroprusside solution to a 1 ml. methylamine solution .a violet red coloration will be formed (**Rimini test**).

Formation of methylamine hydrochloride:-

Make the remainder of the solution from above slightly acid with dilute HCl. (the preparation should be carried to this point in one laboratory period). Add a few pieces of porous chips , and evaporate the solution carefully to a volume of 75 ml . at this point , transfer the remaining solution to an evaporating dish , and evaporate it to dryness on the water bath.

Place the dry residue in a 200 ml. round – bottom flask with 50 ml . of absolute ethyl alcohol, and heat to boiling for a few minutes under a reflux condenser , a residue of ammonium chloride remains, which is insoluble in absolute alcohol. Filter the mixture.

Place the filtrate in an evaporating dish, and evaporate it to dryness on a water bath or steam plate . regenerate the methylamine by warming a small portion of the methylamine hydrochloride with diluted NaOH solution in a test tube , and note the odor of the gas evolved.

Repeat the tests above by heating a small amount of the insoluble residue from above with dilute NaOH . observe its odor , and determine if it will burn. Compare results with those above.

Action of nitrous acid on methylamine:-

Dissolve a small portion (about 0.5 gm) of the methylamine hydrochloride in 5 ml . of water ; add a little dilute HCl and then a few drops of a solution of sodium nitrite (NaNO_2) . Note the gas evolved. Will the gas burn?

3) reaction and characterization of aliphatic amines

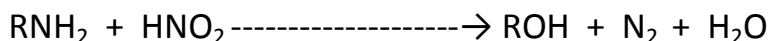
The more important reactions of aliphatic amines, which will assist in their detection, are given below.

Salts of amines are generally soluble in water. Upon treatment with 10 % NaOH solution , the amine will separate if it is insoluble or sparingly soluble in water ; if the amine is water- soluble , it can be partially volatilised by gently warming and its presence will be suggested by a characteristic odor.

1- Primary amines:-

a) Reaction with nitrous acid:-

Dissolve 0.2 gm of the substance in 5 ml of 2N HCl ; cool in ice and add 2 ml of ice – cold 10 % aqueous NaNO₂ solution . warm gently upon water bath, when nitrogen will be freely evolved:



If desired , the alcohol may be identified as the 3:5 –di- nitrobenzoate it is then best to repeat the experiment on a larger scale and to replace the dilute HCl by dilute H₂SO₄ . it must ,however, be pointed out that the reaction is not always so simple as indicated in the above equation .

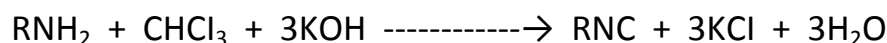
olefin formation and rearrangement of the alcohol, sometime occur :
thus n- propylamine yields n- propyl alcohol, isopropyl alcohol and propylene.

b) Rimini's test:-

To a suspension or solution of 1 drop of the compound or to an equivalent quantity of the solution , add 1 ml of pure acetone and 1 drop of freshly prepared 1 % aqueous solution of sodium nitroprusside [$\text{Na}_2\text{Fe}(\text{CN})_5\text{NO}\cdot 2\text{H}_2\text{O}$]. A violet – red color will develop within 1 minute.

c) Carbylamines test:-

To 1 ml of 0.5 N alcoholic KOH solution (or to a solution prepared by dissolving a fragment of KOH half the size of a pea in 1 ml . of alcohol), add 0.05 – 0.1 gm of the amine and 3 drops of chloroform , and heat to boiling . a carbylamines (isocyanides) is formed and will be readily identified by its extremely nauseating odor ;-



When the reaction is over, add concentrated HCl to decompose the isocyanide and pour it away after the odor is no longer discernible . the test is extremely delicate and will often detect traces of primary amines in secondary and tertiary amines ; it must therefore, be used with due regard to this and other factors.

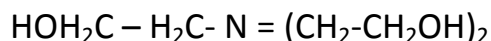
d) 5- nitrosalicylaldehyde reagent test:-

This test is based upon the fact that 5 – nitrosalicylaldehyde and nickel ions when added to a primary amine produce an immediate precipitate of the nickel derivative of the 'iminie' or Schiff's base.

to 5 ml . of water add 1 -2 drops of the amine ; if the amine does not dissolve, add a drop or two concentrated HCl . add 0.5 – 1 ml. of this amine solution to 2 -3 ml. of the reagent ; and almost immediate precipitate indication the presence of a primary amine . a sligh turbidity indicates the presence of a primary amine as an impurity (primary aromatic amines generally erquire 2-3 minutes for the test . urea and other amides , as well as amino acid, do not react).

The 5- nitrosalicylaldehyde reagent is prepared as follows:-

Add 0.5 gm of nitrosalicylaldehyde (m.p.124 – 125 °C) to 15 ml of pure triethanolamine.

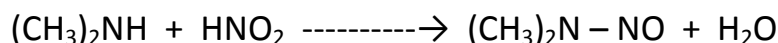


And 25 ml. of water ; shake until dissolved. Then introduce 0.5 gm of crystallized nickel chloride dissolved in a few mls. Of water , and dilute to 100 ml. with water. If the triethanol amine contains some athanolamine (thus causing a precipitate), it may be necessary to add afurther 5.5 gm of the aldehydes and to filter off the resulting precipitate. The reagent is stable for long periods.

2- Secondary amines:-

a) Reaction with nitrous acid:-

Secondary amines upon treatment with nitrous acid yield nitrosamines, which are stable , neutral yellow liquids:- e.g.



N – Nitrosodimethylamine

They are readily hydrolysed by dil. HCl and the original amine can be converted by neutralization with alkali and steam distillation . primary aliphatic amines are unaffected .

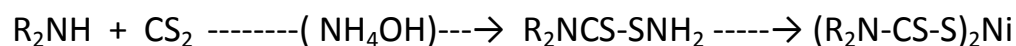
In a 100 ml. Erlenmeyer flask , dissolve 1 gm of the secondary amines hydrochloride in 1 ml. of water and add dil. H2SO4 until acid to congo red paper , then add 1 gm of pure NaNO2 in 1 ml. of hot water , boil then watch the separation of the oily layer of the N-nitrosamine product.

b) Simon's test:-

To a solution or suspension of 1 drop of the compound (or an equivalent quantity of solution) in 3 mls. Of water, add 1 ml of freshly prepared acetaldehyde solution, followed by 1 drop of a 1% aqueous solution of sodium nitroprosside. A blue coloration is produced within 5 minutes , after which the color gradually changes through greenish – blue to pale yellow.

c) Carbon disulphide reagent test:-

This test is based upon the formation from a secondary amine and carbon disulphide of a dialkyl dithiocarbamate; the later readily forms a nickel derivative with a solution of a nickel salt:-



To 5 ml of water add 1-2 drops of the secondary amine; if it does not dissolve , add a drop or two of concentrated HCl . place 1 ml of the reagent in a test – tube, add 0.5 ml of concentrated NH₄OH solution , followed by 0.5 – 1 ml of the above amine solution . a precipitate indicates a secondary amine. A slight turbidity points to the presence of a secondary amine as an impurity.

The carbon disulphide reagent is prepared by adding to a solution of 0.5 of crystallized nickel chloride in 100 ml of water enough carbon disulphide so that after shaking a globule of carbon disulphide is left at the bottom of the bottle . the reagent is stable for long periods in a well- stoppered bottle. If all the carbon disulphide evaporates, more must be added.

3- Tertiary amines:-

- 1- Do not give the isocyanide reaction .
- 2- Do not give acetyl or benzoyl derivatives.
- 3- Do not give any oily or do not show any specific reaction with nitrous acid

Benzene sulphonyl chloride test (Hansberry's test)

(to distinguish between primary, secondary and tertiary amines)

To 0.3 ml of aniline in a test tube add 5 ml of 10 % NaOH solution and 0.4 ml of benzene sulphonyl chloride. Close the test tube with a clean cork and shake it vigorously for 25 minutes (the mixture must be alkaline to this point).

Cool the solution and filter, acidify the filterate and cool it. Repeat with another amine like methylamiline, dimethylamiline.

Reactions and characterization of urea and acid amides

Discussion:-

Urea commands a significant place in organic chemistry not only for the reason that it was the first organic compound produced in the laboratory form "inorganic materials (wohler's discovery) , but also for its physiological importance and for the use of it and its derivatives in the preparation of durgs , plastics , fertilizers , dyes ,and rubber accelerators. Form a chemical standpoint, urea (carbonide)is the diamide of carbonic acid , $\text{CO}(\text{NH}_2)_2$.

The student will note that the chief methods for the preparation of urea (textbook) allow closely the general methods employed for amides. Urea displays slightly basic properties as a result of the presence of two- NH₂ groups.

1- Reactions of urea:-

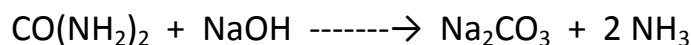
The student should carry out the following reactions of urea:-

a) Solubility:-

Confirm that urea is very solution in water and dissolves in hot methyl , ethyl and amyl alcohol, but is almost insoluble in ether.

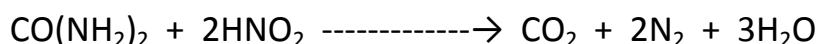
b) Sodium hydroxide solution:-

Dissolve 0.2 gm of urea in 5 ml of dilute NaOH solution and warm. Observe that ammonia is evolved.



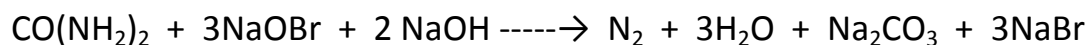
c) Nitrius acid:-

Dissolve 0.2 gm of urea in 2-3 ml of dilute HCl and add 3 ml of dilute (about 5 % NaNO₂ solution . effervescence occurs, and nitrogen and carbon dioxide are evolved:-



d) Sodium hypobromite (or hypochlorite) solution:-

Dissolve 0.5 gm of urea in 3 ml of water and add 5 – 10 ml of dilute sodium hypochlorite or hypobromite solution . nitrogen is evolved.



e) Urea nitrate:-

Dissolve 0.5 gm of urea in 3 ml of water and add 1 ml of concentrated HNO₃ .white crystals of urea nitrate [CO(NH₂)₂ , HNO₃] separate immediately.

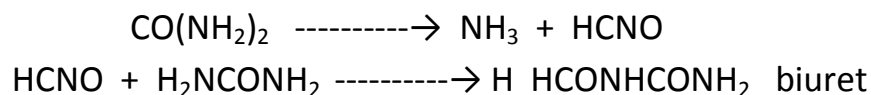
f) Urea oxalate:-

Dissolve 0.5 gm of urea in 3 ml of water and add a solution of 0.6 gm of oxalic acid in 7 ml of water upon stirring urea oxalate crystallizes out $[2\text{CO}(\text{NH}_2)_2, \text{H}_2\text{C}_2\text{O}_4]$.

Urea oxalate is also sparingly soluble in amyl alcohol and since urea is soluble in this alcohol, the property may be utilized in separating urea from mixtures. An aqueous extract of the mixture is rendered slightly alkaline with NaOH solution and extracted with ether; this removes all the basic components, but not urea. The residual aqueous solution is extracted with amyl alcohol (to remove the urea): upon adding this extract to a solution of oxalic acid in amyl alcohol crystalline urea oxalate is precipitated.

g) Biuret reaction :-

Place 0.5 gm of urea in a dry test tube and heat gently just above the m.p. for 1 – 2 minutes. Ammonia is first evolved and the residue solidifies with the formation of biuret:-



The latter may be identified by dissolving the residue in 5 ml of water and adding 1 drop of very dilute copper sulphate solution and 2 drops of 10 % NaOH solution, a violet color is produced.

h) Xanthohydrol reaction:-

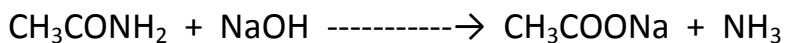
Add a solution of 0.1 gm of urea in 2 ml of acetic acid to 1 -2 ml of a 5 % solution of xanthohydrol in acetic acid or methyl alcohol and warm. Filter off the dioxanthhydryl urea and recrystallize it from aqueous dioxin; wash with a little alcohol and ether, and dry at 80 °C. Determine the m.p.

2-reactions and characterization of aliphatic amides

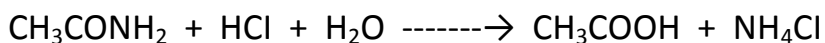
Reactions and characterization of acetamide:-

- a) Boil 0.5 gm of acetamide with 3 ml of 10 % NaOH solution . note that ammonia is evolved.

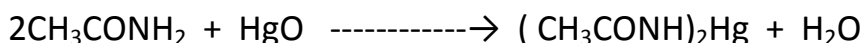
Acidify and test for acetic acid in the solution .



- b) Boil 0.5 gm of acetamide with 3 ml. of dilute HCl (1 :1) or , better , with 10 % sulphuric acid. Observe that acetic acid is evolved.

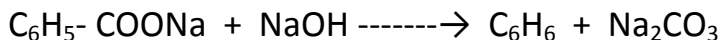


- c) Dissolve 1 gm of acetamide in 2 ml. of water, add about 0.1 gm of yellow mercuric oxide , and warm gently . the mercuric oxide passes into solution, and a water – soluble , non- ionic mercury derivative is produced.



CHMISTRY OF AROMATIC COMPOUNDS

a) **Preparation of benzene by the decarboxylation of sodium benzoate**



In a 6 – inch evaporating dish place 10 gm. (0.25 mole) of NaOH and 20 ml

Of water. Warm the dish gently over the Bunsen burner until the NaOH has dissolved and then add 12 gm. (0.1 mole0 of benzoic acid . while stirring the solution continuously , evaporate it to dryness by gently application of heat form the burner.

Caution:- wear your goggles

Transfer the dry mixture of sodium benzoate and NaOH to 225 * 200 mm . test tube which is connected to a delivery tube and condenser as shown in the fig. heat the tube with the Bunsen burner until no more liquid is collected in the receiver. Separate the upper layer of benzene from the layer of water, dry it over a little calcium chloride, and determine the yield of benzene by measuring its volume in a graduated cylinder. The density of benzene at 20 is 0.879. note the boiling point of benzene by the method described in experiment 1 upon the calibration of thermometer.

b) **Properties of benzene:-**

• **Solubility** :-

test the solubility of 2 ml potions of benzene , obtained from the side shelf, in water , ethanol , gasoline and ether.

• **Benzene as a solvent:-**

Determine the solubility of a small amount of iodine , paraffin wax , and of cotton seed oil in a few mls. Of benzene.

• **Flammability:-**

Ignite a few drops of benzene in a small evaporating dish. Note the character of the flame and the appearance of the dish when the flame dies.

- **Halogenations of benzene:-**

Pour about 5 ml of benzene into a test tube, take the tube to the hood and after adding 2 – 3 drops of bromine, pour one half of the solution into another test tube. In one of the tubes introduce 2 or 3 small iron tacks and observe the difference in the rates of reaction in the two tubes. If the reaction does not begin at once, set the tubes in a beaker of warm water. The comparative rates of reaction may be judged by blowing your breath across the mouth of each tube. What is the gas evolved? Write the equation for the reaction of benzene with bromine.

- **Permanganate test:-**

Shake a few drops of benzene with dilute potassium permanganate solution. Compare the behavior of benzene in this test with that of an alkene.

- **Oxidation of a side chain by alkaline permanganate:-**

Aromatic hydrocarbons containing side chains may be oxidized to the corresponding acids: the results are generally satisfactory for compounds with one side chain (e.g.)

toluene or ethylbenzene → benzoic acid; nitrotoluene → nitrobenzoic acid), or with two side chains (e.g. o-xylene → phthalic acid).

Suspend in a round-bottomed flask 1 gm of the substance in 75 – 80 ml. of boiling water to which about 0.5 gm of Na_2CO_3 crystals have been added, and introduce slowly 4 gm. of finely powdered potassium permanganate. Heat under reflux until the purple color of the permanganate has disappeared (1 – 4 hours). Allow the mixture to cool and carefully acidify with dilute sulfuric acid. Heat the mixture under reflux for a further 30 minutes and then cool. Remove any excess of manganese dioxide by the addition of a little sodium bisulfate. Filter the precipitated acid and recrystallize it from a suitable solvent (e.g., benzene, alcohol, dilute alcohol or water). If

the acid does not separate from the solution , extract it with ether, benzene or carbon tetrachloride.

- **Sulfonation of benzene:-**

Add 1 ml of benzene to 5 ml. of concentrated sulfuric acid contained in a test tube . does the benzene dissolve in the cold? Heat the tube in a beaker of water at 70 0 C and shake it frequently for 10 minutes or until a clear solution is obtained. During this heating period go on to the nitration of benzene .

Cool the tube and pour its contents carefully into 25 – 30 ml of cold water. Write the equation for the form been produced.

- **Nitration of benzene:-**

In a large test tube cautiously add 2 ml of concentrated sulfuric acid to 3ml of concentrated nitric acid. Then introduce 1 ml. of benzene dropwise . note the exothermic character of the reaction . shake the tube 2-3 minutes and pour the contents into about 25 ml. of cold water. What is the heavy oil that separates? Write the equation for the reaction.

Note:-

Benzene , nitrobenzene , aniline and various other aromatic compounds have certain degrees of toxicity . harmful amounts may be absorbed through the skin as well as by inhalation of the vapor . use reasonable precautions in working with such materials.

Tests for aromatic structure:-

a) The chloroform - aluminum chloride test :-

Compounds that have an aromatic structure usually react with chloroform in the presence of aluminum chloride to produce colored products.

Place 100 mg of aluminum chloride in a dry 4 – inch test tube and heat it in a strong flame to sublime aluminum chloride up onto the sides of the tube . allow the tube to cool. Prepare a solution of 10 -20 mg of the compound in 5 to 8 drops of chloroform and run this solution

down the side of the test tube containing the sublimed aluminum chloride. Note any color produced by contact of the solution with the salt.

Note:-

Stock samples of aluminum chloride generally have absorbed and reacted with water vapor. Freshly sublimed salt is a much more efficient catalyst for this reaction . if this test is carefully performed it is useful but not completely reliable for detecting aromatic type structures . it is most useful for distinguishing aromatic hydrocarbons or their chlorine compounds from non aromatic hydrocarbons and their chlorine compounds. Many non aromatic compounds that contain bromine produce yellow colors , and many non aromatic compounds that contain iodine produce violet colorations. As a rule, non aromatic compounds fail to produce a color on the aluminum chloride, whereas monocyclic aromatic compounds give rise to a yellow – orange or red color; bicyclic aromatics give blue or purple , and more complex aromatics produce green colorations on the salt.

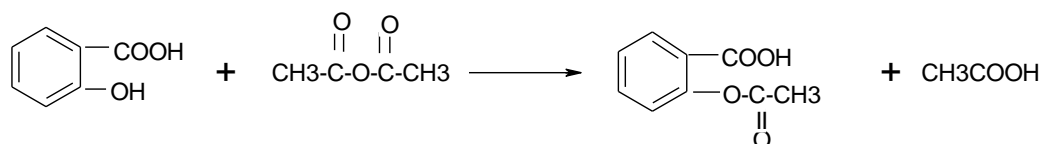
b) **Familiarity with other hydrocarbons:-**

On the supply shelf the storekeeper will have placed specimens of ether aromatic hydrocarbons, such as toluene, ethyl benzene, xylene, cumene, mesitylene, naphthalene, anthracene, phenanthrene and perhaps others. Each bottle will be labeled with the name and boiling point , or melting point, or the material that it contains. Make note of these physical properties as well as the appearance and odor of each specimen. write the formula for each of the compounds presented. Mostly have the same chemical character as for benzene.

ACETYLATION REACTION

PREPARATION OF ASPIRIN (Acetylsalicylic acid)

Mix 2 gm of salicylic acid with 5 ml of acetic acid anhydride in 125 ml flask add 5 drops of concentrated sulfuric acid to the mixture and stir . when the reaction starts , heat will be liberated. If the flask does not become warm, add another drop of sulfuric acid to the mixture. When the heat effect has been observed, heat the reaction mixture in a water bath at 50 for 5 minutes in order to complete the reaction. Cool the flask and add 27 ml. of water. Stir the mixture until a solid is formed and is well dispersed through the liquid. Filter the product by suction on a small Hirsch funnel, and wash with cold water. Recrystallize from hot water. Use decolorizing carbon if the product is colored. Cool the solution , filter off the crystalline product , dry, and determine its weight , and melting point.



NITRATION OF PHENOL

Preparations of picric acid (2: 4 : 6 – trinitrophenol)

Required:-

Phenol ,8 gm ; sulphuric acid , 10 ml ; nitric acid, 30 ml .

Weight out 8 gm of phenol into a dry 750 ml flat – bottomed flask , add 10 ml (18.5 gm) of concentrated sulphuric acid , and shake the mixture , which becomes warm . now heat the flask on a briskly boiling water – bath for 30 minutes to complete the formation of the phenol – sulphuric acid, and then chill the flask thoroughly in an ice – water mixture. Place the flask on a wooden block (or on some similar non- conducting surface) in an efficient fume – cupboard, and without delay , i.e., whilst the phenol – sulphonic acid is still a cold viscous syrup, add 30 ml of concentrated nitric acid and at once thoroughly mix the liquids by shaking for a few seconds . then allow the mixture to stand undisturbed. Usually within one minute a vigorous (but harmless) reaction occurs, and red fumes pour out of the flask . when the action subsides, heat the flask on a boiling water – bath for 90 minutes ,with occasional shaking.

During this period the heavy oil , which is present at the beginning , ultimately forms a mass of crystals. When the heating is complete , add 100 ml of cold water, mix well and then chill thoroughly in ice – water.

Filter the yellow crystals at the pump, wash thoroughly with water to eliminate all inorganic acid and drain . recrystallise from a mixture of 1 volume of alcohol and 2 volumes of water, about 90 ml of mixed solvent being required . picric acid is obtained in beautiful yellow leaflets, m.p. 122°C . dry by pressing between sheets of drying – paper , or in a desiccators. Yield of recrystallised material, 13 gm.

Picric acid if stored in bulk should , for safety, first be damped. Smaller quantities may be safely kept whilst dry, but should be stored in bottles having cork or rubber stoppers : glass stoppers should never be used for potentially explosive substances, because on replacing the stopper some of the material may be ground between the neck of the flask and the stopper, and so caused to explode.

Reaction of picric acid :-

- 1- The presence of the three nitro groups in picric acid considerable increases the acidic properties of the phenolic group and therefore picric acid , unlike most phenols, will evolve carbon dioxide from sodium carbonate solution. Show this by boiling picric acid with sodium carbonate solution , using the method described **in section 5 . p 248** . the reaction is not readily shown by a cold saturated aqueous solution of picric acid , because the latter is so dilute that the sodium carbonate is largely converted into sodium bicarbonate without loss of carbon dioxide.
- 2- To a cold aqueous solution of picric acid , add about an equal volume of dilute potassium cyanide solution . an orange coloration develops and rapidly darkens to a deep red.

Uses of picric acid :- the following further reactions of picric acid are used for analytical purposes in the laboratory.

- 3- **Identification of aromatic hydrocarbons**:- picric acid combines with many aromatic hydrocarbons, giving addition products of definite m.p. thus with naphthalene it gives yellow naphthalene picrate, $\text{C}_{10}\text{H}_8(\text{NO}_2)_3\text{C}_6\text{H}_2\text{OH}$ m.p. 152°C , and with anthracene it gives red anthracene picrate, $\text{C}_{14}\text{H}_{10}(\text{NO}_2)_3\text{C}_6\text{H}_2\text{OH}$, m.p. 138°C .

4- **Identification of aromatic amines:-** picric acid combines with many amines to give crystalline picrates, of general formula B, $(\text{NO}_2)_3\text{C}_6\text{H}_2\text{OH}$, where B is a molecule of a monacidic base. These picrates have usually sharp melting – or decomposition – points, and serve to characterize the amines concerned. They may be formed either by :-

- a) Direct union of the acid and the base in suitable solvent, or
- b) By the interaction of sodium picrate and a salt of the amine in aqueous solution.
 - Dissolve 3 -4 drops of pyridine in about 3 ml of alcohol, and add a cold picrate, $\text{C}_5\text{H}_5\text{N}, (\text{NO}_2)_3\text{C}_6\text{H}_2\text{OH}$, at once separates. It may be filtered gives quinoline picrate, $\text{C}_9\text{H}_7\text{N}, (\text{NO}_2)_3\text{C}_6\text{H}_2\text{OH}$, m.p. 203°C .
 - If an alcoholic solution of picric acid is similarly added to one of aniline , no precipitation occurs, owing to the high solubility of aniline picrate in alcohol. If, however, a cold aqueous solution of aniline hydrochloride is added to a similar solution of sodium picrate and the mixture shaken, yellow crystals of aniline picrate, m.p. 165°C , soon separate.

5- **Detection of potassium in the presence of sodium:-** add a cold saturated aqueous solution of sodium picrate to a solution of potassium chloride. A rapid precipitation of the less soluble potassium picrate occurs, even from a 1% solution of potassium chloride.

Picric acid is used on a large scale as a high explosive, but for this purpose requires a detonator. If a few small crystals of the pure acid are heated on a crucible lid , they first melt, and ultimately burn harmlessly with a smoky flame. Metallic salts of picric acid are much less stable than the free acid , and should always be stored damp. Aqueous solution of picric acid are sometimes used in medicine for the treatment of burns.

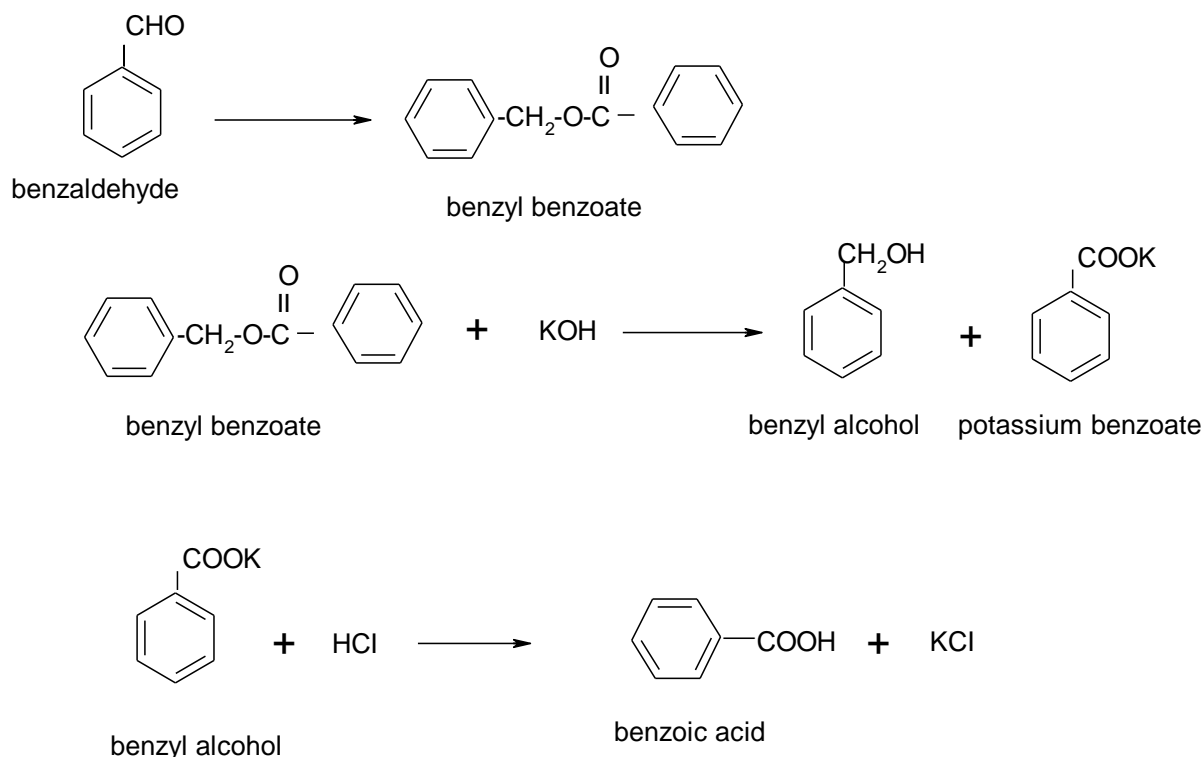
Diazotization of aromatic amines:-

Dissolve 1 ml .(1gm) of aniline or any other aromatic amine in 3 ml of concentrated HCl acid and 5 ml of water , cool the solution to $0 - 5^\circ\text{C}$, add a cold

solution of 1 gm. Sodium nitrite in 5 ml of water slowly (preferably by means of dropper) and with stirring until after standing for 3 – 4 minutes an immediate positive test for nitrous acid is obtained. Add 0.4 gm of binaphthol 1.4 ml of 5% NaOH solution .orange – red dye is formed.

CANNIZZARO REACTION

Benzyl alcohol and benzoic acid



Discussion:-

This experiment involves an auto – oxidation – reduction process, in which one molecule of benzaldehyde acts as an oxidizing agent on another molecule of benzaldehyde and is itself reduced in the reaction . since an aldehydes is the intermediate oxidation product between an alcohol and an acid , it is to be expected that in the presence of a suitable reagent there might be set up an equilibrium which could be forced to completion by removal of one of the reacting substances . the formation of benzyl benzoate from the alcohol and acid in this reaction and the saponification of this compound to yield the potassium salt of benzoic acid effectively remove the benzoic acid from the reaction mixture.

Experimental procedure :-

Preparation of benzyl alcohol and benzoic acid . in a 250 ml . glass – stoppered bottle, with the glass stopper replaced by a solid rubber stopper:-

- 1- Place 20 ml of fresh benzaldehyde and 15 gm of solid KOH ,dissolve in 10 ml of water . stopper the bottle tightly , hold a towel over the stoppered end , shake vigorously, and let stand overnight.
- 2- Add sufficient water to dissolve the solid substance (potassium benzoate), but avoid an excess. Place the solution in a separatory funnel, wash out the bottle with a few milliliters of ether, and extract the solution with three separate 30 ml. portions of ether.(save both layers).
- 3- Combine the ether extracts and evaporate to a volume of 30 to 35 ml . on the steam bath. Place the ether solution in a small separatory funnel and shake with two 5 ml portions of 40 % sodium bisulphate(NaHSO_3) solution.
- 4- Then shake once with 5 ml of Na_2CO_3 solution. Separate the ether layer, and place in a small bottle over a small quantity of anhydrous sodium sulphate (Na_2SO_4)
- 5- Remove the ether by evaporation on the steam bath, and distil from a small flask , using an air condenser. collect the distillate boiling above 200°C as the sample of benzyl alcohol to be handed in. determine the weight of alcohol.
- 6- The alkaline layer (aqueous layer from the ether extraction above) is acidified with concentrated HCl (care) which precipitates the benzoic acid as a white mass.
- 7- Cool the mixture, filter by suction , and wash with water. transfer the benzoic acid to a beaker, and recrystallize from hot water (being with 400 ml of hot water in an 800 ml beaker, and add hot water in small portions until the crystals dissolve), using a pinch of charcoal .
- 8- Filter while hot ,cool, filter the product by suction again, and dry between filter papers. Turn in the total quantity of benzoic acid as a sample.

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