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HAZARDOUS WASTE REDUCTION FOR CHEMISTRY INSTRUCTIONAL LABORATORIES

by

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ADVANCED

CHEMISTRY

LABORATORY

EXPERIMENTS

by

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PREFACE

In 1966, with the help of local industry, the Chemical Technology Program at St. Paul Technical Institute was developed to train qualified technicians to work in industrial chemistry laboratories. The emphasis of the training became chemistry principle applications in a laboratory situtation to reinforce chemistry theory.

With a special emphasis on the analytical aspects in the laboratory, the students are required to perform a wide variety of experiments and are trained to safely handle many chemicals. These experiences prepare them for the job related activities they will encounter.

The OSHA requirements in the industrial setting made it imperative that we begin training the students in chemical awareness and their right to know of the hazards related to materials they encounter on the job and in their training. Also, the cost of disposal of waste chemicals and storage requirements make it necessary for each training facility to evaluate their situation with regard of maintenance cost their program. This manual was developed to reduce the amount of hazardous materials and unnecessary exposure of the students and staff while still allowing for the maximum learning experience. This was done by microscaling quantities of chemicals used and by substituting other reagents where possible.

Although it was intended that all of the experiments be tested and evaluated during the year of writing, this, unfortunately, was not the case. There are a number of experiments that did not get a complete appraisal. Also, some of the tested laboratory experiments did not get a sufficient number of trials to verify their reliabilty at this time. We will continue to edit and revise over the next year and will be grateful for any suggestions that will aid in the producing of a highly useful manual.

PROJECT SUMMARY

Hazardous Waste Reduction for Chemistry Instructional Laboratories

W. Bergstrom and M. Howells

A total of 106 chemistry instructional laboratory experiments were written or modified to minimize hazardous waste generated by microscaling amounts of chemicals used or by making substitutions with less hazardous or non-hazardous chemicals. Each of the experiments was tested at least once by students as part of the curriculum and evaluated for clarity and performance. Each experiment was modified based on the evaluation and compiled into 2 manuals (first year and second year). These experiments should be useful to high school or college level instructors for incorporating into their curricula to reduce the generation of small quantities of hazardous waste from chemistry labs.

Introduction

Scope of Study

A number of chemistry laboratory experiments have been modified and evaluated for the purpose of reducing hazardous chemical usage and waste generation from instructional labs. The purpose of this project was two-fold: 1) to reduce exposure of the student to hazardous chemicals in the laboratory and in the work place and 2) to reduce the generation of hazardous wastes, thus reducing disposal costs. Several techniques were employed to minimize waste from these experiments, including microscaling experiments to use less chemicals in the experiments and substituting less-hazardous or non-hazardous chemicals in place of hazardous ones. This project will enable small generators of chemistry instructional laboratory waste to reduce hazardous material usage and hazardous waste generation by incorporating selected experiments into their upper-level high school or lower level college chemistry curriculum.

Background

Over the past 10 - 15 years, a significant amount of data concerning the effects of certain hazardous and toxic materials on the environment and the health of individuals exposed to these materials has been compiled. As a result, the Chemical Technology Program of the St. Paul Technical Institute became concerned about the students' knowledge and awareness of the many chemicals they would be working with once accepting positions in industry. A review of the Chemical Technology Program was conducted with regard to chemical usage, waste generation, and disposal cost. It was apparent that a concerted effort to reduce and/or eliminate the use of certain hazardous chemicals in the laboratory experiments would be beneficial in terms of reducing costs for new chemicals and waste disposal, as well as increasing health and safety for the students. Therefore, a one year project was undertaken in which two years' worth of chemistry

laboratory experiments (six quarters) were written or modified, eliminating or reducing the hazardous chemicals used through either microscaling or substitution techniques and thus reducing hazardous waste generation.

Results and Discussion

A total of 106 chemistry laboratory experiments were written or modified, tested in the instructional lab as part of the Chemical Technology Program, modified based on student/instructor review, and compiled into 2 laboratory manuals. The experiments were a combination of organic and inorganic tests taught to students to prepare them for industrial laboratory testing. The Chemical Technology Program is a two-year program in which the first and second year are taught concurrently by separate instructors. Thus, it was easy to complete the writing and testing of each experiment in one year. Experiments were rewritten from other sources or written as original experiments, taking care to microscale to small amounts of chemical used or to substitute less hazardous or non-hazardous waste. Each experiment was used and tested by at least one student during the school year as part of the curriculum and evaluated for clarity and performance. Based on the evaluation, the experiments were modified and finalized in 2 laboratory manuals.

Compared to previous years of operating the Chemical Technology Program, no solvent waste that could not be reclaimed and reused was generated during this past year of running the project using microscaled experiments. Only a very small amount of solid hazardous waste was generated and will have to eventually be shipped for incineration.

Conclusions and Recommendations

Through a combination of chemical microscaling and substitution techniques, a set of laboratory manuals was developed containing experiments useful in minimizing waste generation from chemistry instructional laboratories. These manuals should be beneficial to upper-level high school or lower-level college chemistry classes for both organic and inorganic experiments. The benefits of having the manuals is that instructors can select experiments that have been tested in the lab and feel confident that exposure of chemicals to students is minimized and that solvent use and waste is reduced.

Although the experiments have been written and tested at least once in the lab, it would be beneficial to obtain more data on the performance of each experiment as to reproducibility and reliability with respect to waste and solvent reduction. Also, it would enhance the utility of the manual if an accompanying instructors' guide and techiques sections could be added.

244CM/jk

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We would like to thank M. Renee Hanson for her help in editing and formatting of the manual this past year.

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LABORATORY SAFETY PRACTICES

The laboratory is a safe working place when precautions and proper techniques are employed. Your safety practices are as important to your employer or your school as they are to you they are to you since your personal safety, the safety of your fellow workers/students, and the protection of property and equipment are important to them. Most precautions are just common-sense practices. These include the following:

1. Wear safety glasses at all times while in the laboratory. It is the law in this state.

2. Wear shoes at all times.

3. Eating, drinking and smoking are strictly prohibited in the laboratory at all times.

4. Know where to find and how to use safety and first aid equipment.

5. Consider all chemicals to be hazardous unless you are instructed otherwise.

6. If chemicals come in contact with your skin or eyes, wash immediately with large amounts of water and then report it to your laboratory instructor.

7. Never taste anything. Never directly smell the source of any vapor or gas; instead, by means of your cupped hand, bring a small sample to your nose.

8. Any reactions involving skin irritating or hazardous chemicals, or unpleasant odors, are to be performed in the fume hood.

9. Never point a test tube that you are heating at yourself or your neighbor since it may splatter out of the opening.

10. No unauthorized experiments are to be performed in the laboratory.

11. Clean up all broken glassware immediately.

12. Always pour acid into water, **NOT** water into acid, because the heat of solution will cause the water to boil and the acid to splatter. For the same reason, always pour concentrated reagent solutions into diluted reagent solutions.

13. Avoid rubbing your eyes unless you are sure your hands are clean.

14. When inserting glass tubing or thermometers into rubber stoppers, lubricate the tubing and the hole in the stopper with glycerin. Wrap the tubing in a towel and grasp the tubing as close to the end being inserted as possible. Slide the tubing into the rubber stopper with a twisting motion. **DO NOT PUSH**. Keep your hands as close together as possible to reduce the leverage. Finally, remove excess lubricant by wiping with the towel.

15. Notify your instructor immediately in case of an accident.

16. Many common organic reagents such as alcohols, acetone and ether are highly flammable. Do not use them any where near an open flame.

17. Comply with all special precautions mentioned in your experiments and with all special directions emphasized by your instructor.

18. Never use any chemical found in an unlabelled container.

19. Read the reagent bottle label twice to be certain that it is the chemical you want. The label of the reagent will list content's purity and safety hazards. If there is no indication of safety hazards of the chemical, treat it as though it is **flammable**, **volatile**, and **poisonous** until you have check the Material Safety Data Sheet, MSDS, for the chemical.

20. **NEVER WORK ALONE IN THE LABORATORY**.

GOOD LABORATORY WORK HABITS

1. Read the assignment before coming to the laboratory.

2. Unless instructed to do otherwise, work independently.

3. Record your results directly into your notebook. DO NOT recopy from another piece of paper.

4. Do not clutter your working area with excess chemicals and/or equipment to avoid accidents.

5. Excess liquid reagents and solutions should be disposed of by pouring them in the sink and washing them away with large amounts of tap water, unless the experiment and instructor outlines a special disposal method.

6. Place excess solids in designated waste container. **Never return excess reagents to the original bottle.**

7. Do not place reagent-bottle stoppers and/or caps on the benchtop; hold them in your hand. Your instructor will demonstrate this technique. Replace the stopper on the same bottle, never a different one.

8. Leave the reagent bottles on the shelf where you found them.

9. Use only the amount of reagent recommended in the experiment.

10. Always use distilled water in these experiments.

11. Do not borrow apparatus for other lockers. If you need extra equipment, obtain it from your instructor.

12. When weighing, do not place chemicals directly on the balance pan.

13. Do not weigh hot or warm objects. Objects should be at room temperture.

14. **DO NOT** place hot objects on the benchtop. Place them on a wire gauze.

15. When finished with your experiment, return all equipment to its proper storage place and clean all glassware with detergent and tap water. The glassware should be rinsed several times with small quantites of distilled water and returned to your locker or appropriate storage place.

ISOLATION OF CAFFEINE FROM TEA

The purpose of this experiment is to extract or isolate caffeine from tea leaves. Although tea leaves are mainly cellulose which is insoluble in water there are other interferring materials. The main impurity is a material called tannin.

Tannins are a mixture of complicated structures that when hydrolyzed breakdown to glucose and gallic acid or other catechin molecules. Also, these molecules are acidic by nature and therefore are subject to precipitation by a base such as calcium carbonate.

The other water soluble products are eliminated when the caffeine is extracted with an organic solvent such as dichloromethane.

Procedure

In a 50ml Erlenmeyer flask place 5.0g of tea leaves, 10.0ml of water and 1.1g of anhydrous sodium carbonate being sure that the carbonate is in solution. With a gentle boil heat the mixture for 30min.

Remove the flask from the hot plate and allow to cool to around 40°C. Using a qualitative filter paper, filter the solution by gravity into a 12ml centifuge tube. Rinse the residue in the flask with two 1.0ml washings of hot water and add to the filtered material. Discard the tea leaves after extracting the remaining liquid by carefully pressing the leaves and filter paper.

Cool to room temperature and extract with 2.0ml of dichloromethane. Be careful to avoid an emulsion by too vigorously agitating the solution. Allow the layers to separate and withdraw the bottom layer with a Pasteur pipet and transfer to a small filtering flask by means of a funnel with a small layer of anhydrous sodium sulfate.(about 2.0g) Repeat the extraction procedure with four additional 2.0ml portions of dichloromethane and add these to the filtering flask.

The organic solvent is now evaporated to dryness using a steam bath or sand bath in the **HOOD**.

The product is now ready for purification and characterization which requires sublimation of the crude caffeine. Using an aspirator, a filtering flask and a cold finger the sublimation can be accomplished. First clamp the flask on a ring stand and connect to the aspirator. Next seal the cold finger in the flask about 1/2cm above the crude caffeine. Then with a microburner begin the heating process. Be sure not cause the crude caffeine to begin melting because it will then decompose. Continue this process until the sublimation is complete, no more caffeine forms on the cold finger. Remove the heat and allow the system to cool to room temperature under reduced pressure.

When the cooling is completed **carefully** remove the vacuum and the cold water connections. Then remove the cold finger from the flask and scrape the crystals of caffeine onto a weighing paper or other **preweighed** collecting container. A melting point and an IR spectrum should be included with this experiment.

Requirements for report

Follow the guidelines for report writing.

[Reference: **Introduction to Laboratory Techniques** by Pavia, et.al. published by Saunders College Publishing]

ISOLATION OF CAFFEINE FROM COFFEE

The purpose of this experiment is to extract or isolate caffeine from coffee. Although coffee beans are mainly matter which is insoluble in water there are interfering materials. Coffee contains caffeine, tannins, glucose, fats, proteins and cellulose.

The main impurity is a material called tannin. Tannins are a mixture of complicated structure that when hydrolyzed break down to glucose and gallic acid or other catechin molecules. Also, the molecules are acidic by nature and therefore are subject to precipitation by a base such as calcium carbonate.

The other water soluble products are eliminated when caffeine is extracted with the organic solvent such as dichloromethane.

Procedure

In a 50ml Erlenmeyer flask place 5.0g of coffee 10.0ml of water, after the coffee and water are up to temperature add 2.0g of calcium carbonate. With a gentle boil heat the mixture for 30min. Remove the flask from the hot plate and allow to cool to around 40°C. Using a qualitative filter paper, filter the solution by gravity into a 12ml centrifuge tube. Rinse the residue in the flask with two 1.0ml washings of hot water and add to the filtered material. Discard the coffee grounds after extracting the remaining liquid by carefully pressing the gropunds and filter paper.

Cool to room temperature and extract with 2.0ml of dichloromethane. Be careful to avoid an emulsion by to vigorous agitation of the solution. Allow the layers to separate and withdraw the bottom layer with a Pasteur pipet and transfer to a small filtering flask by means of a funnel with a small layer of anhydrous sodium sulfate.(about 2.0g) Repeat the extraction procedure with four additional 2.0ml portions of dichloromethane and add these to the filtering flask.

The organic solvent is now evaporated to dryness using a steam bath or sand bath in the **HOOD**.

The product is now ready for purification and characterization which requires sublimation of the crude caffeine. Using an aspirator, a filtering flask and a cold finger the sublimation can be accomplished. First clamp the flask on a ring stand and connect to the aspirator. Next seal the cold finger in the flask about 1/2cm above the crude caffeine. Then with a microburner begin the heating process. Be sure not to cause the crude caffeine to begin melting for it will then decompose. Continue this process until the sublimation is complete, no more caffeine forms on the cold finger. Remove the heat and allow the system to cool to room temperature under reduced pressure.

When the cooling is completed **carefully** remove the vacuum and the cold water connections. Then remove the cold finger from the flask and scrape the crystals of caffeine onto a weighing paper or other preweighed collecting container. A melting point and an IR spectrum should be included with this experiment.

Requirements for report

Follow the guidelines for report writing and include melting point data.

Questions

1. What should be used for the purification of the crude crystals?
2. What is an alkaloid?

[Reference: **Introductuion to Organic Laboratory Techniques** by Pavia, et.al. published by Saunders College Publishing}

ISOLATION OF CAFFEINE FROM A SOFT DRINK

The purpose of this experiment is to extract or isolate caffeine from Pop. Although pop is mainly a solution of flavored sugar in water there are other interferring materials. Some soft drinks contain ingrediants such as caffeine to enhance the flavor of the drink. Some of the impurities are the flavoring agents which may include some complicated organic structures and preservatives such as potassium benzoate.

The other water soluble products are eliminated when the caffeine is extracted with the organic solvent such as dichloromethane.

Procedure

In a 250ml Erlenmeyer flask place 100.0ml of pop then attach a hose to an aspirator and evacuate until the solution ceases to evolve carbon dioxide bubbles. At this time add 2.0g of çalcium carbonate and warm gently then filter. Using a qualitative filter paper, filter the solutionby gravity into a 125ml Erlenmeyer flask. Rinse the residue in the flask with two 10 ml washings of hot water and add to the filtered material. Discard the residue after extracting the remaining liquid by carefully pressing the residue and filter paper.

Cool to room temperature and extract with 4.0 ml of dichloromethane.

Be careful to avoid an emulsion by to vigorous agitation of the solution.

Allow the layers to separate and withdraw the bottom layer with a Pasteur pipet and transfer to a small filtering flask by means of a funnel with a small layer of anhydrous sodium sulfate.(about 2.0g) Repeat the extraction procedure with four additional 2.0ml portions of dichloromethane and add these to the filtering flask.

The organic solvent is now evaporated to dryness using a steam bath or sand bath in the **HOOD**.

The product is now ready for purification and characterization which requires sublimation of the crude caffeine.

Using an aspirator, a filtering flask and a cold finger the sublimation canbe accomplished. First clamp the flask on a ring stand and connect to the aspirator. Next seal the cold finger in the flask about 1/2cm above the crude caffeine. Then with a micro-burner begin the heating process. Be sure not cause the crude caffeine to begin melting for it will then decompose. Continue this process until the sublimation is complete, no more caffeine forms on the cold finger. Remove the heat and allow the system to cool to room temperature under reduced pressure.

When the cooling is completed **carefully** remove the vacuum and the cold water connections. Then remove the cold finger from the flask and scrape the crystals of caffeine onto a weighing paper or other preweighed collecting container. A melting point and an IR spectrum should be included with this experiment.

Requirements for report

Follow the established guidelines for report writing and include the IR spectrum and melting point data.

Questions

1. What procedure would help to purify the crystals?
2. What is an alkaloid?

CHOLESTEROL FROM GALLSTONES

Cholesterol is a natural constituent of animal chemistry. In the present day and age much discussion about the amount of cholesterol in our diet appears in various written forms. It is a basic molecular structure which is found in the hormonal chemicals that govern the functions of our body.

In this experiment we will procede to isolate cholesterol from its analogs and other impurities such as Bilirubin, a heme structure, also found in gallstones. One of the homologs of cholesterol is cholestanol which has the same structure but is minus the double bond at carbons 5-6. Because of this we can isolate the desired product by bonding bromine to the double bond and recrystallizing the product.[Review the techniques of filtration, recrystallization, handling flammable-volatile solvents and reflux].

Procedure

Weigh about 2.0g of crushed gallstones and place them in a 25-50ml Erlenmeyer flask with 10ml of diethyl ether. **Flammable** Using a steam bath, heat the mixture until a solution is obtained. There may be some dark solid particles that do not dissolve, but the quantity of solid should be small. Beware of the amount of ether in the flask for you may have to add extra to maintain the level of the solvent.

Filter the colored solution while hot through a fluted filter paper and rinse the paper with 2-3ml of ether. Add 10ml of methanol to the filtrate and a small amount of **Norite**. Return the filtrate to the steam bath and reheat. Pre-heat a funnel and filter the solution hot through a fluted filter paper. Reheat the filtrate and add distilled water slowly by eye dropper until just cloudy. Cool and collect the crystals by vacuum filtration. Wash with cold methanol and air dry. Weigh the crude product and determine the melting point.

Purification: Place about 1.0g of crude crystal in 10ml ether in a 25-50ml Erlenmeyer flask. The ether should be dried over anhydrous sodium sulfate. Warm on a steam bath until dissolved.

With an eye dropper, slowly transfer 5ml of a bromine-sodium acetate-acetic acid solution to the cholesterol containing solution. If a yellow color is not apparent add a slight additional amount of the bromine containing solution. The dibromide adduct will begin to crystallize in a few minutes. Cool the flask in an ice bath and stir the solution to affect complete precipitation. In another flask cool a mixture of 3ml of ether and 7ml of acetic acid.

Filter the crystals with vacuum on a small Buchner funnel and wash twice with the cooled wash solution above. Allow to dry in air.

Transfer the dried dibromide to a clean 50ml Erlenmeyer flask containing 20ml of ether- 5ml of glacial acetic acid- 0.2g of zinc powder. Heat gently until the crystals dissolve. A white paste should begin to appear in about 5-10minutes. Stir for an additional 5min. and add water dropwise until the paste just dissolves.

Decant the supernatant liquid to a small separatory funnel and extract to ether solution with two 10ml portions of distilled water. Then wash with a 10% sodium hydroxide solution until the ether no longer tests acidic(use litmus paper). Then wash with a saturated salt solution of equal volume of ether and separate the ether layer and filter through anhydrous sodium sulfate.

Add 10ml of methanol and evaporate to 1/3 volume. This should be about the quantity of ether that remained from above. Allow to cool to room temperature and stand, then cool on an ice bath. Collect the crystals by vacuum filtration. Wash with cold methanol and dry and weigh quickly. Determine the melting point with a minimum exposure to air and run an Infrared Spectra.

Requirements for report

Follow the established guidelines for report writing and include the IR spectrum and melting point data.

[Reference: **Techniques and Experiments for Organic Chemistry** by Mayo et.al. John Wiley & Sons publisher]

ISOLATION OF ESSENTIAL OILS

The odors we associate with various plants and trees in nature belong to a category generally called essential oils. They produce the fragrances and flavors we associate with pleasant tastes and smells along with some health benefits. These oils include a long list of members some of which are: allspice, cloves, cumin, cinnamon, caraway, spearmint, camphor, eucalyptus and turpentine.

Most of these are steam-volatile and can be separated from the plant tissue by steam distillation.

The family groups that these molecules belong to are esters, alcohols and phenols, carbonyl compounds, terpenes and phenylpropanoids. Most of the extracts in this experiment are of the phenolic or terpene families.

[Review the techniques for steam distillation and use of the separatory funnel]

Procedure

Prepare a sufficient amount of spice either ground or powdered for the experiment. ie.(15g allspice, cumin, cinnamon or 5g of cloves) Place the spice into a 500ml round bottom flask and add 150ml of water and assemble for steam distillation. Begin the distillation process and continue until approximately 100ml of distillate have been collected.

Transfer the distillate to a separatory funnel and extract with two 10ml portions of dichloromethane. Separate the layers carefully and dry over a small amount of anhydrous sodium sulfate. Then decant the solution into a pre-weighed test tube.

Evaporate the solvent using a steam bath in a **HOOD** until only an oily residue remains. **Caution** you must beware not to volatilize all of the sample. Weigh the test tube and residue and determine the percent recovery. Also, run an Infrared spectrum and a refractive index.

Requirements for report

Follow the established guidelines for report writing and include the spectrum and RI data.

[Reference: **CHEMICAL TECHNICIANS READY REFERENCE HANDBOOK** by Shugar et.al. p357-361. p303-307 **Introduction to Organic Laboratory Techniques** by Pavia et.al Saunders College Publishing]

LACTOSE EXTRACTED FROM MILK

Lactose, the sugar (disarccharide) synthesized by mammals, appears in milk. It is a water soluble molecule that when hydrolyzed produces D-glucose and D-galactose. These sugars are iimportant to the deveolpment of the young and almost all young can digest them. Some adults lose the ability to digest milk and have reactions to its presence in foods.

Milk has a number of other ingredients that make this isolation of lactose a little more difficult, such as the protein casein, fats and minerals. The fats can be eliminated as a problem by choosing skim or nonfat products of milk to be starting material. The elimination of the protein material is done by acid denaturization with a mild acid such as acetic acid.

[Review techniques for vacuum filtration, decantation, and recrystallization]

Procedure

Dry milk powder or skim milk may be used as a starting material. In this experiment we decribe the procedure for nonfat dry milk powder with the appropriate skim milk quantities in parentheses.

Starting with about 25 grams(200ml) of nonfat dry milk powder added to 90ml of water in a 250ml beaker(600ml). Warm gently until dissolved and adjust the temperature to about 45°C.

Using a 10% acetic acid solution, add 10ml with stirring until all the milk protein (casein) has been precipitated (when the solution becomes clear). Filter off the precipitate by gravity filtration using a very fast filter paper and decantation.

To the filtrate add about 2.0 grams of calcium carbonate while stirring. Bring the solution gradually to a boil and continue for about 10 minutes. Be careful of foaming. After the heating is complete add a small portion of **Norite**, stir and filter using a moist filter aid, such as **Celite** with a Buchner funnel.

Transfer the filtrate to a beaker and reduce the volume to about one third on a hotplate. Cool some and add 125ml of denatured alcohol with a little **Norite**. Stir and filter as before.

Transfer the filtrate to a stopper Erlenmeyer flask and allow to stand for one day. The crystals will form gradually and may be collected by vacuum filtration. Air dry and weigh.

If milk has a density of 1.03g/ml what is the per cent yield?

Requirements for report

Follow the established guidelines for report writing.

[Reference: **Organic Experiments** by Lindstromberg and Baumgarten, D.C. Heath publisher]

PIPERINE FROM PEPPER

Piperine, a complicated member of the piperidine family, is found in the spice pepper. It does not cause the aroma of pepper, but does impart a portion of the taste, a sharp tang that is noticable when using pepper on food.

Piperine contains two double bonds which allow several configurations. These stereoisomers make up a significant percentage of the weight of black pepper.

[Review the techniques for reflux, simple distillation, vacuum filtration and recrystallization]

Procedure

To 15 grams of black pepper in a 250ml round bottom flask add 1 gram of powdered calcium carbonate and about 100ml of isopropanol. Assemble for refluxing using a steam bath and reflux for one hour.

Filter the solution by gravity and transfer to a clean 250ml distilling flask. Arrange the apparatus for simple distillation and distill off all but about 10ml of the isopropanol.

. Transfer the residual solution to a small Erlenmeyer flask and set aside for one day to crystallize.

Collect the crystals by vacuum flitration, washing the flask and crystals with small portions of cold methanol. Air dry and prepare an Infrared spectrum.

Requirements for report

Follow the established guidelines for report writing and include your spectrum.

[Reference: **Techniques and Experiments for Organic Chemistry** by Addison and Ault published by Allyn abnd Bacon Inc.]

ISOLATION OF LIMONENE BY STEAM DISTILLATION

Limonene is an isoprene based molecule found in the peeling of the citrus fruits. Isoprene (2-methyl-1,3-butadiene) is a building block for a number of naturally occuring polymers. In smaller molecules they generate some typical fragrances such as pine, ginger and lemon.

It can be isolated easily by steam distillation from fruit peeling with a high degree of purity.

[Review the techniques for steam distillation, extraction, and simple distillation]

Procedure

Using the peel from either two medium oranges, lemon or one grapefruit, cut the peel into small pieces. Add the peel to a 500ml round bottom distillation flask with about 250ml of water. Arrange the apparatus simple distillation and rapidly distill over about 50ml.

Extract the distillate with three 7ml portions of pentane and dry the pentane over anhydrous magnesium sulfate. Filter the extract by gravity using decantation.

Transfer the filtrate to a 50ml distilling flask for simple distillation. Carefully distill over the pentane solvent using a steam bath as the heating source.

Draw out the limonene from the bottom of the distillation flask using a Pastuer pipet and determine the refractive index and run an Infrared spectrum.

Requirements for report

Follow the established guidelines for report writing and include the IR spectrum and the RI data.

[Reference: **Techniques and Experiments for Organic Chemistry** by Addison and Ault, Allyn and Bacon publisher]

CITRAL FROM LEMON GRASS OIL

Citral is a member of the terpene family by the combination of two isoprene units. It is a fragrant aldehyde found in lemon grass tea, a favorite beverage in Mexico.

Because of its volatile characteristics, it can be isolated as a fraction through steam distillation.
[Review the techniques of steam distillation, extraction and filtration]

Procedure

Add 10ml of lemon grass oil to a 250 ml round bottom distilling flask containing about 100ml of water. Arrange the apparatus to pass live steam through the flask while gently heating the flask with a heating mantle. Distill rapidly until about 250ml of distillate have been collected.

Cool the distillate and prepare a 125ml separatory funnel for extracting the citral by adding 50ml of diethyl ether to the funnel. Add a portion of the distillate to the funnel and shake. Allow to separate and drain off the lower layer and discard it. Add another portion of the distillate and repeat the above procedure until all the distillate has been extracted with the ether. Rinse the distilling flask with a few small portions of ether and add the rinse to the separatory funnel. **Ether is extremely flammable use caution.**

Transfer the ether solution to an Erlenmeyer flask and add 2.0g of anhydrous magnesium sulfate and allow to sit temporarily. Filter the extract solution by decantation into a 100ml round bottom flask and distill off the excess ether. Care must be taken to use a steam bath as the heating source.

Transfer the residue from the distilling flask to a tared vessel and evaporate the rest of the ether. Weigh the container and determine the percentage yield and determine its properties and run an Infrared spectrum.

Requirements for report

Follow the established guidelines for report writing and include the IR spectrum.

[Reference: **Introduction to Organic Laboratory Techniques** by Pavia et.al. Saunders College Publishing]

PLANT PIGMENT EXTRACTION

The predominant colores of some plant material can be traced to some isolatable carotanoid pigments. One of these is B-carotene, a yellow-orange colored organic compound which is converted by the liver to Vitamin A.

Another compound, lycopene, found in tomatoes can isolated with B-carotene and its isomers as a possible contaminant.

B-carotene is associated with the sensory ability of vision. The retina of the eye has two photosensitive cells called rods and cones which interact with a molecule derived from Vitamin A. The process is explained by Hubbard and Kropf in "Molecular Isomers in Vision". [Review the techniques for separatory funnel use, uv-vis spectrophotometer and Beer's Law]

Procedure

To a tared test tube add 0.2g of carrot paste. To the paste add 2.0ml of ethanol(denatured) and heat on a steam bath for 5 to 10min.

Transfer this slurry to a small Buchner funnel attached to a vaquum flask and filter. Save the ethanol solution and return the filter paper and paste to the original test tube and re-extract with 2.0ml of CH_2Cl_2. Repeat this step twice more. Combine all the extracts with the ethanol solution and transfer to a separatory funnel.

Add 10ml of water and wash the extract draining the lower layer through a few grams of anhydrous sodium sulfate. Collect the filtrate and evaporate to dryness by vacuum aspiration using a steam bath for heating.

Redissolve the residue in ethanol and transfer to a 50ml volumetric flask. Rinse the drying vessel with ethanol and add the rinsings to the volumetric flask. Make the flask up to volume with ethanol.

Determine the concentration of the B-carotene using a visible spectrophotometer setting the wavelenth at 453nm. The molar absorptivity a= 1.55×10^5. Using Beer's Law you can easily determine the conctration of sample.

Requirements for report

Follow the established guidelines for report writing along with the calcualtions for your extraction.

Questions

1. What effects do the isomers have on the value of c?
2. Suggest a method of separating these isomers from B-carotene.

DEHYDRATION OF AN ALCOHOL

Alcohols can be dehydrated fairly easily by heating the alcohol with an acid catalyst. The hydroxyl group of the alcohol is protonated by the acid and the careful heating helps to break the weakened bond from the carbon to the oxygen.

Some acids have the ability to proceed stepwise through the whole alcohol chain, concentrated sulfuric acid is one of these acids. It will completely dehydrate the molecule leaving only a carbon residue. This can be avoided by selecting either a more diluted acid solution or a less strenuous method.

The bond site of the hydroxyl group also must be considered when deciding on what method to use. For example, the primary alcohol requires a 60-75% solution of sulfuric acid and a temperature above 60°C, while a secondary alcohol needs only a 40-50% solution and a temperature around 60°C. Cyclic alcohols are generally considered to secondary alcohols but because of the stability of the cyclic olefin they form much more readily. Thus the use of a mild acid such as phosphoric acid is very acceptable. The product is easily separated by steam distillation and repurified.

[Review techniques for fractional distillation, extraction and simple distillation.]

$$R\text{-}CHOH\text{-}CH_3 \xrightarrow{H^+} R\text{-}CH{=}CH_2 + H_2O$$

Procedure

A. Procedure for cyclic alcohols. Place 10ml of the alcohol (cyclohexanol or the substituted alcohol) in a 50ml round bottom flask and add 3ml of 85% phosphoric acid and 3ml of 2-ethoxyethanol and a boiling chip.

Arrange the apparatus for fractional distillation and begin gentle heating. Make sure the temperature of the distilling fraction does not go over 96°C. Collect 8-10 ml of the distillate in a chilled receiving flask.

Transfer the distillate to a separatory funnel cantaining 2ml of a 10% sodium carbonate solution, shake and discard the water layer.

Transfer the organic layer to a clean dry flask containing a small amount of anhydrous calcium chloride. Allow to dry and determine the yield. Save the product for unsaturation tests and possible gas chromatographic analysis.

B. Procedure for an alkyl secondary alcohol. Using a 250ml round bottom flask coolde in an ice bath, add 30ml of water and carefully add 15ml of concentrated sulfuric acid. Cool the resulting solution and then add about 25ml of the designated secondary alcohol or tertiary alcohol. Mix the solution carefully and attach to the distilling apparatus.

Distill the hydrocarbon into a receiving flask immersed in an ice bath. Continue the distillation with careful heating to maintain a continuous flow of the distillate until no more hydrocarbon is evident.

Transfer the distillate to a separatory funnel and add 10ml of a 10% sodium hydroxide solution to remove any co-distilled acid. Drain the lower layer and discard. Dry your product with anhydrous sodium sulfate and using clean dry glassware and simple distillation redistill the hydrocarbon.

Collect the fraction designated by your instructor. Save your product for unsaturation tests and for possible gas chromatographic analysis.

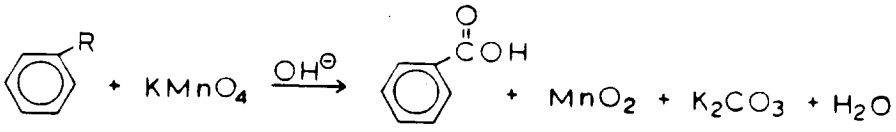
Requirements for report

Follow the established guidelines for report writing and prepare for the use of the gas chromatograph.

[Reference: **Practical Organic Chemistry** by Kemp, McGraw-Hill publisher]

OXIDATION OF AN ALKYL GROUP ON AN AROMATIC RING

The stability of the benzene ring against the attack of most oxidizing agents actually promotes the oxidation of a carbon side chain attached to the aromatic ring. The ring stabilizes the attached carbon while the oxidation occurs but the whole mechanism is not thoroughly explained, as of yet. The point of attack of the oxidizer is the bonds beyond the one attached to the ring. At any rate the outcome of the reaction is the production of an aromatic carboxylic acid.



Procedure

Place 2.5g of sodium carbonate(anhydrous) and 75ml of water in a 250ml round bottom flask. Add 5g of potassium permanganate and 1ml of toluene or ethyl benzene. Attach a reflux column and keep the reaction in progress for about one and a half hours, or until no evidence of the volatile aromatic is seen.

There will be a large quantity of manganese dioxide generated and this must be continuously watched to prevent bumping. It will also be necessary to reduce the MnO_2 before isolation of the aromatic acid can be accomplished.

When the reaction time (about 1.5 hrs)is complete the solution is acidified (test it) and the MnO_2 is reduced with sodium sulfite. The dark brown precipitate will turn colorless with about 3g of the sulfite and heating.

At this point check for acidity and then cool the solution to affect precipitation of the aromatic acid.

Collect the crystals by vacuum filtration, air dry and determine the melting point and run an Infrared spectrum.

Requirements for report

Follow the established guidelines for report writing and include your IR spectrum.

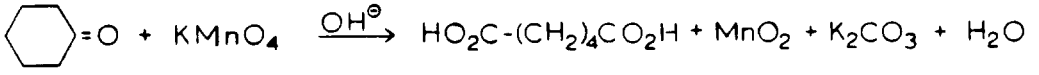
[Reference: **Practical Organic Chemistry** by Kemp, McGraw-Hill pub.]

OXIDATION OF CYCLOHEXANONE TO ADIPIC ACID

Strong oxidizers react vigorously with organic molecules and are very difficult to control. To get a desired product, the selection of the oxidizing agent is very important. In this reaction conversion of the ketone, cyclohexanone, to the dicarboxylic adipic acid is accomplished by an alkaline solution of $KMnO_4$. The moderately concentrated solution is monitored for heat generation or is diluted to the point where heat from the reaction does not effect the final reaction results.

The mechanism for the reaction appears to be the generation of an enol intermediate and then the cleavage of the double by the oxidant. Once the ring is opened the oxidation of the two terminal carbons is completed.

[Techniques to review vacuum filtration- recrystallization.]



Procedure

This reaction is easily completed by simply mixing the reactants and allowing the mixture to stand overnight. The yield is quite good.

Start with about 10ml of the ketone, cyclohexanone, and 30g of $KMnO_4$ added to 500ml of water in a 1000ml Erlenmeyer flask. Mix these ingrediants until dissolved and then adjust the temperature of the mixture to 30°C. Now add 10ml of a 10% NaOH solution and swirl to mix and set aside to react overnight.

The next day test the solution for any unreacted $KMnO_4$ by placing a small drop on a filter paper and looking for a telltale purple ring at the outside of the spot. If $KMnO_4$ is present, add small amounts of saturated sodium bisulfite until the test is negative. Filter the solution with suction and wash with water.

Reduce the volume of the filtrate to about 70ml and decolorize with **Norite** if needed. Refilter and again reduce to 70ml.

Acidify with concentrated HCl until the solution is pH 1-2 and add 10ml of concentrated HCl in excess. Cool and allow to precipitate. Filter and wash wsith small amounts of iced water. Air dry and determine the % yield, melting point and run an Infrared spectrum.

Requirements for report

Follow the established guidelines for report writing and include all the pertinent information collected.

Questions

1. Why isn't dichromate used in this experiment?
2. What is the balanced equation for this reaction?

[Reference: **Practical Organic Chemistry** by Kemp, McGraw-Hill pub.]

CYCLOHEXANOL TO CYCLOHEXANONE

Although cyclohexanol is a secondary alcohol and will undergo oxidation readily, care must be taken to prevent oxidation of all or part of the ring.

Usually the sulfuric acid solution of dichromate is utilized in this experiment with rigid control of the temperature of the reaction along with the addition of the oxidant. Since chromium salts are considered quite dangerous to the environment and disposal is difficult we will use a different oxidizing agent.
[Techniques to review: steam distillation, simple distillation, controlled addition and use of the separatory funnel]

Procedure

In a 2-necked 250ml round bottom flask, place 5g(5.2ml) of cyclohexanol, 12ml of glacial acetic acid and a stirring bar. Attach the flask to a Claisen head with a separatory funnel and a reflux condenser. Place a stirring motor under the flask and insulate the flask from the motor(a piece of cardboard will do).

. In the separatory funnel directly over the flask, place 80ml of household bleach. In the second neck of the flask, position a thermometer close to the bottom of the flask but clear of the spinning magnetic stirring bar.

Begin gradual addition of the bleach making sure the temperature does not rise above 35°C. When the addition is complete, test the solution to see if there is an excess of the bleach.(Use starch-iodide paper- a purple color is a positive test). If it's not a positive test, add 2ml of bleach and stir for another 15 minutes. A green-yellow color indicates an excess of bleach. This must now be reduced by small additions of concentrated sodium bisulfite solution until the color is gone and a negative starch-iodide test is achieved.

Arrange the apparatus for steam distillation and distill 25-35ml of liquid to a 125ml Erlenmeyer flask. Add about 3g of anhydrous sodium carbonate to neutralize any acid . Transfer liquid to a separatory funnel and drain off the lower aqueous layer (make sure that the lower layr is the water layer).

Dry the organic layer with a little anhydrous calcium chloride in a beaker and with a simple distilling set up redistill collecting the fraction between 150-155°C. Determine the yield and run an Infrared spectrum.

Requirements for report

Follow the established guidelines for report writing includ your yield and other data.

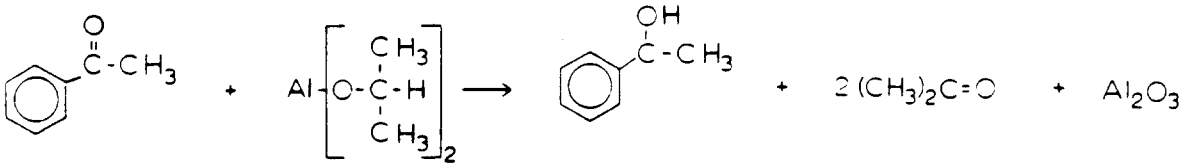
[Reference: **Microscale Organic Laboratory** by Mayo et.al. John Wiley & Sons publisher]

REDUCTION OF ACETOPHENONE

The Clemmensen or Wolff-Kishner reductions reduce the carbonyl cites to the methylene group, but there is a technique by which an alcohol may be generated at the carbonyl carbon.

The principle of the reduction is based on the establishment of an equilibrium between the ketone or aldehyde and an alcohol in the presence of an aluminum alkoxide.

Since the alcohol used in the reaction is converted to the corresponding aldehyde or ketone and generally has a lower boiling point than the selected ketone to be reduced, the reaction is pushed to completion by simply distilling off the by-product.
[Review techniques for fractional distillation-simple distillation-use of the separatory funnel]



Procedure

Using a 100ml round bottom flask, add 5ml fo the ketone selected (acetophenone), 50ml fo isopropyl alcohol and 5 grams of powdered aluminum isopropoxide. Attach a fractionating column to the flask and assemble for fractional distillation.

Place the distilling flask in an oil bath on a hotplate and slowly increase the temperature until the liquid begins refluxing and a slow distillation starts. The rate of the distilling material should be maintained at a rate of one drop per second and the temperature should not rise above 75°C. Continue the distillation for about one hour, adding isopropyl alcohol as needed to keep the volume of the reaction about the same.

At this point it is necessary to test for the absence of acetone, the by-product, by use of a small amount of either semicarbazide or 2,4-dinitrophenylhydrazine. If a positve test occurs, continue the distillation for another 15min. and retest the distillate for the presence of acetone. Repeat if necessary.

Transfer the residue from the distilling flask to a separatory funnel and wash with 20ml of dilute HCl and 20ml of water. Drain off the aqueous layer and transfer the product to a test tube with a small portion of anhydrous Na_2SO_4 and allow to dry overnight. Transfer to a tared container and determine yield, boiling point and run an Infrared spectrum.

Requirements for report

Follow the established guidelines for report writing and include the IR spectrum and data, plus a sample of your product.

Questions

1. Where does the acetone come from?
2. How could you beeter control the temperature?

[Reference: **Practical Organic Chemistry** by Kemp, McGraw-Hill pub.]

DETERMINATION OF AN EQUILIBRIUM CONSTANT

The Fischer esterification using an acid catalyst is well documented and the mechanism is known. Therefore, this reaction is a good reaction to use for the study of the equilibrium of an organic species.

The acid and the alcohol are combined and refluxed until an equilibrium mixture is obtained as determined by titration of the acid concentration. Since the starting material concentration is known and the reaction proceeds by an exact pathway, the equilibrium concentrations can be easily determined.

If K = [ester][water]/[acid][alcohol] then by kowing the moles or starting conc. of the acid and the alcohol(make them equal) we can monitor the reaction by testing a small aliquot periodically until there is no apparent change in concentration. Then if we letx equal aou starting concentration of the acid andj equal the final concentration then $K = [x-j]^2/[j]^2$. The values forx andj are determined by titration with a standard base and phenolphthalein. [Techniques to review-fractional distillation-refluxing-titration]

Procedure

Using a 100ml round bottom flask, place 0.30 mole of acetic acid and 0.30 mole of the assigned alcohol in the flask. Mix the solution thoroughly and draw out a 1.00ml aliquot and transfer it to an Erlenmeyer flask containing 25ml of water and a few drops of phenolphthalein. This is now titrated with base to the desired end point.

Now add the catalyst consisting of 4 drops of concentrated H_2SO_4 (about 100mg) and a boiling chip to the 100ml flask. Reflux the mixture for about 40 minutes.

Cool the solution and withdraw another 1.00ml for titration. Repeat the reflux for another 20 minutes and again cool; extract the aliquot and titrate. If this value is less than 0.2ml different from the last titration, the reaction is done.

Determine the values for the ester and the acid and calculate the equilibrium constant.

Set up the apparatus for fractional distillation with the receiver chilled in an ice bath.

Begin the distillation and collect the distillate until about 20ml has been collected. Isolate the lower layer and determine its volume. Return the upper layer to the distilling flask and continue to collect another 15-20ml fo distillate. Again separate the two layers and record the volume of the lower layer. If the water(lower) layer is as large as the first volume continue the distillation one more time.

Combine the organic materials and wash the apparatus with 20ml of ether and combine with the organic in a separatory funnel.

Wash the ether solution with 10ml of 10% $NaHCO_3$ until no eveidence of acid is obtained from evolving CO_2.

Dry the solution over $MgSO_4$ (anhydrous) and distill off the ether.

Change receivers and distill the ester, recording the boiling range for the ester.

Determine the yield and run an Infrared spectrum.

Requirements for report

Follow the established guidelines for report writing and include the IR spectrum, plus yield data.

Questions

1. What factors effect the value of K?
2. Which of these factors are uncontrollable?

[Reference: **Organic Experiments** by Lindstromberg and Baumgarten, D.C. Heath and Co. publisher]

RATE OF ACID CATALYZED INVERSION

Sucrose, the source of table sugar, is a disaccharide easily hydrolyzed to its two constiuents: glucose and fructose.

These sugars along with their source are all optically active molecules and therefore can be observed utilizing a polarimeter during the course of the hydrolysis.

Sucrose has a specific rotation of plane polarized light of $[\alpha] = 66.5^{\circ}$ where as the combination of the glucose and fructose isomers is $[\alpha] = -20.6^{\circ}$. This is a significant change in optical rotation so it is easily observed.

From the specific rotation values of sucrose and the inverted isomers a factor of -0.31 can be obtained, therefore, if the observed rotation α_o before hydrolysis is known (determined), the rotation at infinity $\alpha_\infty = -0.31\alpha_o$ and the ratio of inversion of the sucrose at any time t is

$$[\text{sucrose}_t]/[\text{sucrose}_o] = \alpha + 0.31\alpha_o / 1.31\alpha_o .$$

Thus if the acid concentration is a constant the rate equation simplifies to

$$\ln[\text{sucrose}_t]/[\text{sucrose}_o] = -kt \text{ or}$$

$$\ln [\alpha + 0.31\alpha_o]/ 1.31\alpha_o = -kt$$

By plotting the time versus the $\ln [\alpha + 0.31\alpha_o]$, the slope of the line equals k.

The values for α_o are found by $[+66.5^{\circ}] \times 0.40\text{g/ml} \times 1$ where 1 is the length of the polarimeter tube in decimeters.
[Review the techniques for use and cleaning of the polarimeter pp 222-226 of CTRRHB.]

Procedure

Prepare a 6.0M HCl solution and have it ready for addition to the sucrose solution. The sucrose is prepared by weighing 20.0g of the sugar into a 50ml volumetric flask and adding about 20ml of water. Dissolve the sugar crystals. When they have gone into solution, quickly transfer a 10ml aliquot of the HCl solution to the flask, make the solution to volume, shake and record the time.

Carefully and quickly transfer the solution to the polarimeter tube.

Record the time and rotation measurements in 5 minute intervals for about 40 minutes.

Prepare a graph of the results as suggested in the discussion section above. Determine the value for k_1 and since this is a second order reaction, also determine k_2 this is simply the value for k_1 divided by the concentration of the acid.

Carefully clean all apparatus utilized in this experiment, specifically the polarimeter tube and its stage.

Requirements for report

Follow the established guidelines for report writing and include your data and calculations and graphs.

Questions

1. Is the concentration of the acid a factor in the reaction?
2. What would be a more controlled experiment, describe the conditions?

[Reference: **Experimental Methods in Organic Chemistry** by Moore,et.al. published by Saunders College Publishing]

RATE OF SAPONIFICATION OF AN ESTER

Esters are the product of an organic acid and an alcohol. The reaction that generates the ester is a reversible reaction and thus has an equilibrium state.

If an ester is placed is a solution containing a base Le Chatelier's Principle applies and the equilibrium will shift to counter the effect of the base (saponification).

The rate of the shift of equilibrium can be measured and is a function of the type of ester we will work with.

The equation for this reaction is:

$$\text{rate} = k[OH^-][\text{ester}] ,$$

which is a 2nd order reaction. If we make the concentration of the base and ester equal we can then write:

$$\text{rate} = k[\text{ester}]^2$$ and the second order

equation becomes

$$1/[\text{ester}]_t = kt + 1/[\text{ester}]_o .$$

Since the value for $[\text{ester}]_o$ is a constant we can simply relate the reciprocal of the ester conc at time t to the time by means of a plot, the slope of which is the value for k.

[Review techniques for titration]

Procedure

Prepare a solution of 0.0100mole of the ester and 60ml of reagent acetone in an Erlenmeyer flask. Clamp the flask to a ringstand and immerse it in an ice bath.

In a separate flask or test tube cool 40.0ml of exactly 0.250M NaOH solution. This solution when cooled will be added to the flask containing the ester and that signals the beginning of the reaction.

In a separate Erlenmeyer flask pipet 10ml of standard 0.100M HCl and to this this pipet 10ml of the reaction solution after about 1 minute.(Note the exact time of transfer). Titrate the solution with a 0.0100M NaOH and phenolphthalein until a stable pink color is observed. Record the volume of the titrant for this represents the quantity of acid generated by the saponification at this point in the reaction. Continue extracting 10ml aliquots from the reaction at sampling intervals such as 4min, 10min, 20min, and 30min or a variety of staggered times.

Plot the the $1/[\text{ester}]_t$ versus time in seconds and selecting points on the line determine the value for k for your ester. Using the equation in the discussion section calculate k also and compare the values, explain any differences.

Requirements for report

Follow the established guidelines for report writing and include all your data.

[Referenc: **Experimental Methods in Organic Chemistry** by Moore et.al. Saunders College Publishing]

pKa OF AN ORGANIC ACID

Organic acids are normally weak acids and therefore have an equilibrium with water. The equilibrium canstant (Ka) is a function of the strength of the acid which in turn is a function of the attached group to the carboxylic carbon. For example, benzoic acid may have a Ka of 3×10^{-6} but by attaching a functional group to the benzene ring the Ka may change to 1×10^{-4} depending on the properties and position on the ring.

This experiment tries to look at this phenomenon to some degree by comparing substituted benzoic acid to the unsubstituted parent. [Review techniques of titration and use of the pH meter.]

Procedure

Weigh out an approximate 0.02g sample of the assigned acids. Dissolve them with 25ml of denatured alcohol in separate 100ml beakers and dilute with 25ml of water.

Prepare to titrate with 0.01N NaOH using the pH meter and a stirring apparatus. Be sure to insulate the beaker from the heat effect of the stirring motor.

Add your titrant in about 1.0ml increments recording both volume and pH measurements. Reduce the size of the addition of titrant when you approach the endpoint. Continue the titration beyond the endpoint by a few ml.

Plot your pH versus volume data and determine graphically the pKa from the 1/2 neutralization volume point of the graph.

Requirements for report

Follow the established guidelines for report writing and include your data and graph of the titration.

Questions

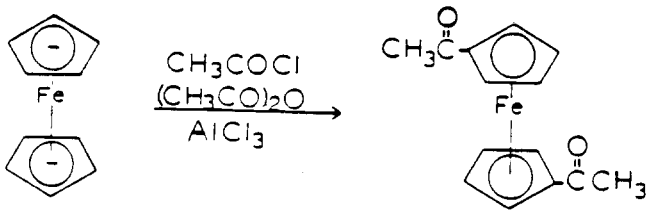
1. Is it necessary to know the concentration of the base exactly?
2. Use your data to generate a mathematical equation for the titration.

[Reference: **Experimental Methods in Organic Chemistry** by Moore, et.al published by Saunders College Publishing]

ACYLATION OF FERROCENE

The ferrocene molecule is a complex metallocene. This "sandwich type" molecule has two aromatic rings surrounding a Fe^{+2} ion. The molecule is electronically neutral and quite stable. It is used quite often as an indicator in iron analysis and redox experiments.

The aromatic cyclopentadienyl rings are subject to electrophilic attack by a suitable agent. The acetyl group is a good reagent to use because of its ease of generation and relative stability during the reaction.



[Review the techniques for column chromatography and vacuum filtration.]

Procedure: In a small Erlenmeyer flask under a **HOOD** place 5ml of acetic anhydride **HOOD** and 0.5g of Ferrocene reagent. To this, add dropwise 1ml of concentrated phosphoric acid. Stir the mixture while the addition of the acid is taking place. The acid is the catalyst for the generation of the acetyl group.

Place a calcium chloride drying tube on the flask and heat the solution for 10 minutes on a steam bath.

Pour the resulting mixture on about 20g of crushed ice and allow the mixture to melt.

Neutralize the solution with solid sodium carbonate and swirling until just about pH 7. Test the solution with pH paper.

Prepare a column of acid washed alumina and introduce a small amount of the precipitate dissolved in a tiny amount of benzene **[use the HOOD and take all precautions]**. Elute the sample with petroleum ether(60-80°) first, then elute with 1:1 mix of petroleum ether and diethyl ether. Collect the two fractions separately and evaporate the solvents in the hood. Determine the melting points of the solid residues.

Collect the solid by vacuum filatration and air dry.

Requirements for report

Follow the established guidelines for report writing and include your melting point data.

PREPARATION OF 1,4-DI-t-BUTYL-2,5-DIMETHOXYBENZENE

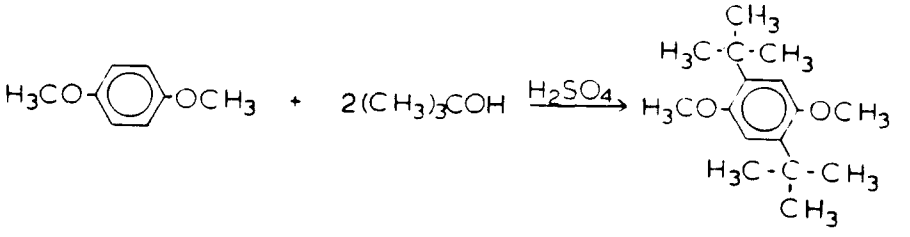
The alkylation by the Friedel-Crafts based reaction of 1,4-dimethoxybenzene is further evidence of this effective technique. Sulfuric acid is the Lewis acid catalyst used in this reaction.

We will again use the more stable trimethylcarbonium ion as the positive electrophilic attacking species.

Since the numbers one and four positions are occupied by activating methoxy groups on the ring, our substitution positions are the two and five cites. This is primarily due to steric hinderance problems after the first substituted group is on the ring the next group must attach at the number five position since the ring is now very active at that cite.

The product formed has a molecular weight of 250.4g with a melting point of 104-105°C.

[Review the techniques for vacuum filtration, Infrared and Ultraviolet spectrophotomery]



Procedure

To a 50ml Erlenmeyer flask add 1g of the p-dimethoxy-benzene and 2ml of t-butyl alcohol and 7ml of acetic acid. Place the flask in an ice bath to cool. In another flask place 7ml of concentrated sulfuric acid and also cool this in an ice bath.

When the 50ml flask is cooled to around 0°C place the sulfuric acid in a small separatory funnel over the ice cooled reaction mixture. (There may be some undissolved solid pieces in the flask but these will dissolve with the reaction.) Over a 2-3 minute period with lots of swirling add the sulfuric acid. The temperature will rise and some solid will separate from the mixture. Continue to swirl the mix after all the catalyst has been added for two to three minutes, then cool and add 7 g of crushed ice to dilute the sulfuric acid and then water to fill the flask.

Filter the precipitate on a Buchner funnel with suction and wash with water. Cool 20ml of methanol and wash in three portions.

Air dry and determine the melting point, Infrared and Ultraviolet spectrums.

Requirements for report

Follow the established guidelines for report writing and include the spectra.

Questions

1. Show the mechnism of reaction for the t-butyl alcohol and sulfuric acid.
2. What is the meaning of steric hinderance?

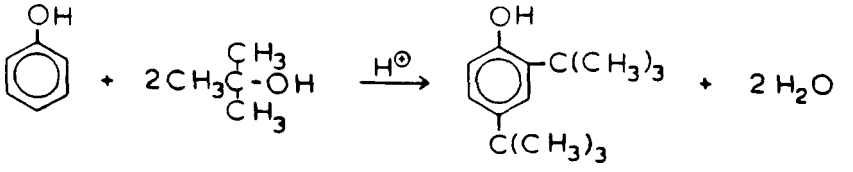
[Reference: **Organic Experiments** by L. Fieser published by Raytheon Education Company]

ALKYLATION OF AN AROMATIC RING

The addition of substituents to the aromatic ring is a difficult reaction without the aid of a catalyst that promotes an electrophilic intermediate. The Friedel-Crafts reaction is the most widely discussed method of addition of an alkyl substituent to the ring. The catalyst normally utilized is anhydrous aluminum chloride. The catalyst strips off the halide from the alkyl halide to be substituted on to the ring making it a carbonium ion. This usually is a good intermediate for attacking the electron rich aromatic compound. Care must be taken to choose an alkyl halide that is stable as the carbonium ion intermediate or expected products will not be forthcoming.

An alternate method for the reaction includes the use of an alcohol and a dehydrating agent such as concentrated H_2SO_4. This works exceptionally well when the alcohol is a secondary or tertiary alcohol such as t-butyl alcohol.

[Review techniques for use of the separatory funnel and recrystallization]



Procedure

Place about 0.02 mole of the aromatic(p-cresol or phenol)a small Erlenmeyer flask with 1ml of glacial acetic acid and 5.6ml of t-butyl alcohol. t-Butyl alcohol has a melting point around room temperature so you may have to warm the flask with a warm water bath to keep the solution liquid. Dissolve the aromatic compound and the alcohol and then cool the mixture to 0°C on an ice bath. You can use a magnetic strirrer under the ice bath for the mixing when the catalyst is added.

Slowly with stirring, transfer 5.0ml of concentrated H_2SO_4. This addition should take a minimum of 4 to 5 minutes or if a pinkish color is noticed longer. If the color appears continue the stirring but stop any further addition of the catalyst until the color fades.

After all the acid has been added, continue the mixing for 20 minutes longer, add a few pieces of ice to dilute the catalyst and then water. Transfer the mixture to a separatory funnel nad rinse the flask with 30ml of ether and add this to the funnel. Shake well and allow to separate. Discard the aqueous layer and wash the organic solution with two 10ml portions of water. Final wash of the organic layer 10ml of a 2% KOH and then dry over anhydrous sodium sulfate.

Transfer the ether solution to a beaker and evaporate on a steam bath until about 10ml is left. Transfer this to a 25 X 100mm test tube with a little ether rinse. Evaporate to as low a volume as possible and then draw a vacuum on the remaining residue to remove any iso-butylene present.

Cool the residue to below zero in a salt-ice bath and scratch the inside of the tube to initiate crystallization. Filter the crystals and recrystallize from methanol.

Determine the yield, melting point and run an Infrared spectrum.

Requirements for report

Follow the established guidelines for report writing.

[Reference: **Introduction to Organic Laboratory Techniques** by Pavia, et.al. Saunders College Publishing]

WILLIAMSON ETHER SYNTHESIS

Ethers can be prepared by various techniques of which we include bimolecular dehydration with H_2SO_4 or alkoxymercuration. Another technique is the use of the alkali salt of an alcohol and an alkyl halide. This method is named for its discoverer, Williamson, and is the most versatile and reliable of the ether preparation techniques..

It can be used to generate a wide variety of ethers with a high degree of success. The reaction is mostly applicable to primary and/or primary-secondary alkyl combinations. The metal alkoxide can usually be prepared by simply refluxing the alkali metal with the desired alcohol and then adding the alkyl halide to this solution. The one problem with this synthesis is the easy of destruction of the alkoxide by moisture.

[Review techniques for reflux, distillation, separatory funnel use and Infrared.]

$$CH_3\text{-}O\text{-}Na \quad + \quad Br\text{-}CH_2CH_3 \quad == \quad CH_3\text{-}O\text{-}CH_2CH_3 \quad + \quad NaBr$$

Procedure

Place 15ml of methanol and 13.5g of anhydrous sodium methoxide in a 250ml round bottom flask. To this solution, add carefully 21.5ml of n-butyl bromide and attach a reflux condenser. Shake the solution to mix and start the initial reaction. When the reaction subsides, begin refluxing the reaction on a steam bath for about one and a half hours.

Cool the reaction mixture to about 40-50°C and add 15ml of water to dissolve the sodium bromide salt that has formed.

Rearrange the apparatus for direct steam distillation and distill over all but about 10-15ml of the solution. The residue in the distilling flask will be mostly NaBr and water and may be discarded. Transfer the distillate to a separatory funnel and wash with 40 to 50ml of 20% NaCl solution. Separate the two layers and dry the organic layer overnight over anhydrous $CaCl_2$.

Decant the liquid to a distilling flask and distill. Collect the fraction boiling between 68-75°C.

Determine the percentage yield and obtain an Infrared spectrum.

Requirements for report

Follow the established guidelines for report writing and include your IR spectrum.

Questions

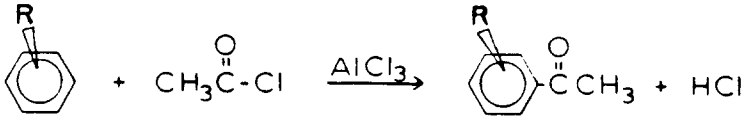
1. What is the other ether synthesis?
2. What are the differences?

[Reference: **Laboratory Experiments in Organic Chemistry** by Adam and Johnson published by MacMillan]

FRIEDEL-CRAFTS ACYLATION

Although the Friedel-Crafts reaction is widely used as an alkylation substitution method for aromatic compounds, it can also be used with suitable acyl groups. In this reaction, we will utilize acetyl chloride as the acyl group to be attached to the aromatic ring to produce the corresponding ketone.

Since the catalyst anhydrous aluminum chloride will be mostly utilized in this reaction, we must make sure of the absolute dryness of our equipment and the atmosphere in contact with our reaction mixture. **[Caution when handling anhydrous aluminum chloride because it reacts violently with water and is caustic to the skin]**.
[Review techniques for reflux, vacuum distillation, gas trapping, Infrared and UV spectrums]



Procedure:

To a 250ml round bottom flask, attach a Claisen head. In the neck directly over the flask place a reflux condenser which has been fitted with a gas trapping arrangement as discussed in the laboratory lecture on techniques. To the other neck of the Claisen head attach a separatory funnel containing a calcium chloride drying tube at its top.

Now working swiftly, weigh out 5.0g of anhydrous aluminum chloride into a 50ml beaker and with a powder funnel transfer it to the 250ml flask. Using 8ml of dichloromethane rinse down any trace of the powder into the flask and reattach the reflux condenser and start the water for cooling. Immerse the flask into an ice bath and swirl the contents of the flask.(If the whole apparatus is attached to one ring stand, carefully agitate by moving the ring stand.)

To this solution slowly add a mixture of 3ml of acetyl chloride in 5ml of dichloromethane over a period of 8 to 10 minutes. Continue the agitation until it is all added and the mixture is cool.

Next, from the separatory funnel, begin a slow addition of 0.025mole of the selected aromatic compound mixed in about 3ml of CH_2CL_2. This should take between 10 and 15 minutes; be careful about excessive foaming due to generation of HCl gas.

When all the addition is completed, the reaction mixture should be allowed to warm to room temperature by removal from the ice bath and let the flask stand for one half hour. Continue occasional gentle agitation during this period.

Transfer the reaction mixture to a beaker with 10g of crushed ice and 10ml of concentrated HCl. Stir the solution for 7 to 8 minutes and separate the organic layer and save it. Extract the aqueous layer with two 5ml portions of CH_2Cl_2 and add these to the organic material. Discard the water layer and back wash the organic layer with 15ml of saturated $NaHCO_3$. Separate the two layers and dry over anhydrous magnesium sulfate.

Decant the dichloromethane mixture into a distilling flask and distill over the CH_2Cl_2 and return it to the reclaimed CH_2Cl_2 bottle.

Save, the residue for later vacuum distillation with other students product.(See instructor)

Determine a rough yield and run an Infrared and Ultra-violet spectrum on the sample.

Requirements for report

Follow the established guidelines for report writing and include your IR and UV spectrum.

Questions

1. What other acylation technique can be used in organic experiments?
2. What is the greatest problem with aluminum chloride?

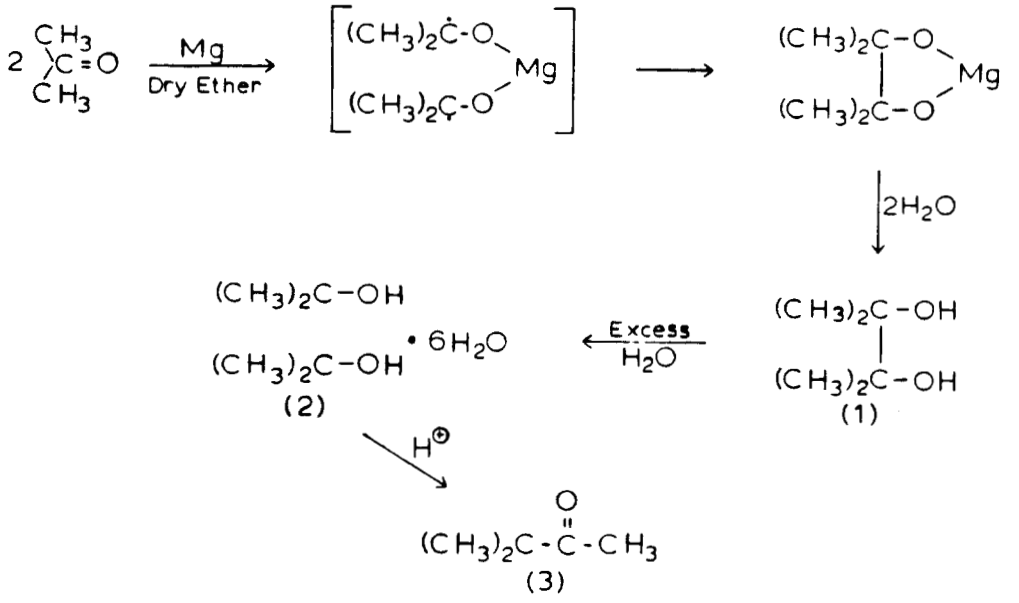
[Reference: **Organic Experiments** by Fieser and Williamson published by D.C. Heath and Co.]

GRIGNARD REACTION
PINACOLONE

The Grignard synthesis is one of the most versatile methods of synthesizing compounds and has a variety of paths by which it can be employed.

Although this reaction is very versatile, it is also very sensitive to decomposition of the most important part of the reaction (the Grignard reagent). It is formed by interacting magnesium metal with a suitable compound such as an alkyl halide to get a reagent with the following structure [R-Mg-X]. The reagent is very susceptible to moisture and the selection of a solvent for the reaction or its quality becomes very important. This also means all the equipment to be used in the reaction must be thoroughly cleaned and dried.

The technique used in this experiment exploits the reduction of acetone by magnesium to generate the bimolecular product pinacol. Pinacol upon dehydration undergoes a tautemeric shift of a methyl group to produce the molecule pinacolone(3,3-dimethyl-2-butanone). [Review the techniques for refluxing, separatory funnel useage and Infrared]



Procedure

Part One: Using a 100ml round bottom flask, place 2.0g of clean dry magnesium turnings inside. To this, add 15ml of dry toluene and attach a reflux condenser.

Attach a vented separatory funnel to the condenser or if this is not available use a Claisen adapter and place the funnel in the side arm of the adapter. In the funnel, place 10ml of dried acetone and a drying tube in neck of the funnel. Allow the acetone to drain slowly into the flask until about 1/4 of the liquid has been added to the flask. Check to see if a spontaneous reaction has begun to occur.

This will be evident by the appearance of small bubbles on the magnesium turnings. If there is no indication of the reaction starting add a tiny crystal of iodine to the mixture. If still no reaction occurs, heat the reaction solution on a steam bath until a noticable reaction is in progress.(Keep an ice bath handy if the reaction gets too vigorous and the acetone begins to escape from the condenser). Once the reaction is in progress, it will be sufficiently exothermic that no further heat will be necessary to continue the reaction. Add the rest of the acetone slowly, and after the reaction subsides, begin heating again on the steam bath for about one hour.

At this time, add 5ml of water through the condenser top and reflux for another 1/4 to 1/2 hour to precipitate the $Mg(OH)_2$ and convert the compound to pinacol.

Filter the hot solution with a Buchner funnel by decantation and return the magnesium precipitate to the reflux flask for further extraction. Add a mixture of 5ml of water and 20ml of acetone and reflux the magnesium salt for a short time, cool, filter and add the filtrate to the first solution. Transfer the combined extracts to a 100ml distilling flask and remove the acetone and toluene as much as possible with a steam bath. Then add 20ml of water and codistill the rest of the toluene using a heating mantle or a sand bath heating source.

Transfer the warm residue to a pre-warmed separatory funnel and extract with a small amount of dichloromethane. Drain off the organic layer and discard it in a waste container designated for this.

Transfer the water solution to a beaker and cool on an ice bath. Scratch the surface of the beaker to initiate precipitation and collect the crystals by vacuum filtration.

Determine the yield at this point and a crude melting point.

Part Two: To a 100ml round bottom flask add 20ml of a sulfuric acid solution prepared by diluting 4ml of concentrated sulfuric acid with 16ml of water (remember always add the acid to the water). To this add about 4g of the hydrate produced in part one and warm the solution to dissolve the hydrate. Set up a reflux apparatus and heat the mixture to reflux temperature for 15 minutes.

After the heating is completed, cool the solution until the boiling has stopped. Then quickly set up a steam generator and distilling apparatus and steam distill the pinacolone(3,3-dimethyl-2-butanone).

Transfer the distillate to a separatory funnel and drain off the water layer. Dry the pinacolone over anhydrous calcium chloride and purify by distillation.

Set up a fractionating column on the distilling apparatus and add to the pinacolone 2 to 4ml of 2-ethoxyethane for a chaser. Distill over the pinacolone saving the fraction that boils from 100 to 106°C.

Determine the yield and Infrared spectrum.

Requirements for report

Follow the established guidelines for report writing and include all pertinent data and results.

Questions

1. What is the by-product of this reaction (side reaction)?
2. Could this be the main product of the sysnthesis?

[Reference: **Organic Experiments** by Fieser and Williamson, D.C. Heath and Co publisher]

SYNTHESIS OF CYCLOHEXYL CHLORIDE CARBOXYLIC ACID BY GRIGNARD REACTION

In this Grignard reaction we are going to utilize the ability of the Grignard reagent to interact with the -(HO)C=O group. To do this we must use CO_2 as our reacting carbonyl containing species. We will supply the CO_2 by using dry ice and bubbling the escaping gas through our reagent containing solution.
[Review techniques for reflux, gas generation and use of the separatory funnel.]

$$(CH_2)_5CH\text{-}Cl + Mg \;==\; (CH_2)_5CH\text{-}Mg\text{-}Cl$$

$$(CH_2)_5CH\text{-}Mg\text{-}Cl + CO_2 \xrightarrow{H_2O} (CH_2)_5CHCO_2H + MgCl_2$$

Procedure

To a 100ml round bottom flask, add 20ml of anhydrous ether and 0.05mole of magnesium turnings. All equipment must be clean and dry. Obtain 0.05mole of cyclohexyl chloride reagent grade and transfer with a pipet about 1/3 of the liquid to the flask. Place the tip of the pipet beneath the surface of the ether close to the magnesium turnings. Attach a reflux condenser and warm the solution with a warm water bath. When the reaction starts(indicated by bubbles and self sustained boiling) begin the flow of the cooling water in the reflux condenser.

Over the next half hour slowly add the remaining cyclohexyl chloride and allow the reaction to reflux with gentle heating from a steam bath if needed. Continue the reaction for another 15-20 minutes and then cool to room temperature.

In a side-arm flask place about 50 to 80g of dry ice. Stopper the flask, and with tubing connected to the side-arm, transfer the gas being formed through a drying tube with anhydrous magnesium sulfate or molecular sieve and then into the flask containing the Grignard reagent. Use the ebulator tube to dispense the CO_2 bubbles below the surface of the solution.(If necessary use a warm water bath to heat the side-arm flask to generate a gentle flow of CO_2 gas - **be very careful not to over pressurize - loosen the stopper so it will relieve any pressure build up**).

When all the CO_2 has evaporated, add 20 ml of ether to the flask and the jello like precipitate. Add 6M HCl with care and in small portions until the precipitate has dissolved.

To isolate the acid, we must first transfer it to a sodium salt form. So transfer the solution to a separatory funnel and drain off the water layer and discard it.

Wash the remaining ether layer with about 10ml of water and then two 15ml portions of 10% NaOH solution and finally 10ml more of water. Collect the water extracts and back wash with a small portion of ether.

Now acidify the water solution with HCl and check to make sure it is decidely acidic. Extract the acidic solution with two 10ml portions of ether. Dry the ether over anhydrous sodium sulfate in an Erlenmeyer flask and carefully evaporate the ether on a steam bath and finally with aspiration.

Determine the yield, melting point and run an Infrared spectrum.

Requirements for report

Follow the established guidelines for report writing and include your IR spectrum.

[Reference: **Introduction to Organic Laboratory Techniques** by Pavia, et.al, Saunders College Publishing]

GRIGNARD SYNTHESIS OF AN ALCOHOL

The Grignard method of preparation (synthesis) of molecules is so versatile that it is used for the preparation of alkanes, alkenes, alkynes - alcohols, ethers, etc.

The main reaction is the organo-metallic reagent and an acidic hydrogen on the reacting group. The fact that acidic hydrogen is active in the Grignard synthesis precludes the use of certain materials in making the reagent itself, but with planning, an individual can arrive at the same desired conclusion.

Although magnesium organics have been known since 1905, the field of organo-metallic compounds in synthesis and catalyst based reactions is an exciting, expanding field.

In this reaction we will be using the typical Grignard reagent and a carbonyl carbon reaction to generate an alcohol.
[Review the techniques for refluxing, separatory funnel useage, distillation and Infrared]

Procedure

Since this experiment can be utilized for a large variety of starting alkyl halides and carbonyl containing compounds, we will relate all quantities of reactants on a mole basis.

All equipment must be clean and very dry because of the Grignard reagents sensitivity to small amounts of moisture.

Starting with a 100ml round bottom flask and 2.0g of Mg(0.08mole), attach a Claisen adapter to the flask. On the side arm, attach a reflux condenser fitted with a drying tube containing anhydrous $CaCl_2$. To the central neck of the adapter, place an additional funnel, with a solution of 0.08mole of the selected alkyl halide and 30ml of absolute ether.(Dry the solutions over anhydrous magnesium sulfate).

Begin the reaction by allowing 3 to 4ml of the alkyl halide solution to run into the 100ml flask. The reaction should start by evidence of boiling in the lower flask.(Be sure to have the cooling water in the condenser on) **NOTE If the reaction does not start reach into the flask with a glass stirring rod and crush a few pieces of magnesium. If it still doesn't start take a piece or two of Mg and a crystal of iodine - grind them together in a mortar and drop them into the solution - but the final solution must be treated with $NaHSO_3$ to remove the I_2.**

Continue the halide addition at a rate to keep the reaction going at a gentle boil.

When all the halide is added to the flask, allow the solution to continue reacting for an additional 15 minutes with occasional agitation of the flask.

After the reacting time is completed, cool the flask and prepare a solution of the carbonyl compound by mixing 0.075 mole of it and 10ml of absolute ether (dried). This is added drop by drop with both cooling and agitation. (It is very exothermic and must be done carefully). When all the solution has been added, allow about 20 minutes for the solution to react at room temperature.

Now pour the reaction mixture onto a solution of ice water and sulfuric acid (3ml H_2SO_4/25g of ice, plus 25ml water). Rinse the flask with some of the solution and transfer it all to a separatory funnel. Separate the ether layer and extract the water with two 10ml portions of ether. Combine all the organic solutions and wash with $NaHSO_3$ if iodine was used, then wash with 10% Na_2CO_3 and finally dry over andhydrous $MgSO_4$.

Distill the ether from the solution using a steam bath and a distilling apparatus. When the ether has been eliminated distill the alcohol. Check with the literature for the boiling point of your prepared alcohol.

Determine the yield, record the boiling point and run an Infrared spectrum.

Requirements for report

Follow the established guidelines for report writing and include all important information.

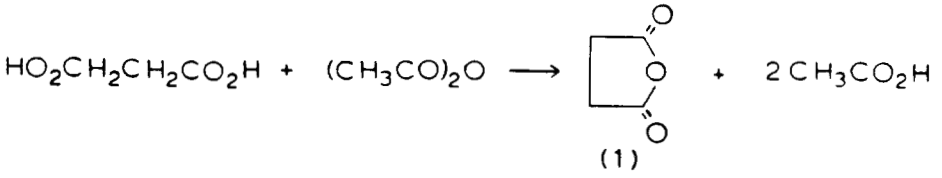
[Reference: **Experimental Methods in Organic Chemistry** by Moore et.al. Saunders College Publishing]

MULTI-STEP SYNTHESIS

Very often desired material (compounds) cannot be obtained easily or inexpensively for an experimental procedure and must be made in the laboratory. This exercise is designated to introduce the student to a multiple step preparation of a compound, not to obtain the compound but to develop confidence in the ability to perform the necessary procedures to generate a final product in sufficient quantity and purity to be of use in further reactions.

We have chosen the synthesis of succinanil for this experiment because of its general ease of preparation and to minimize the need for cyanide compounds for intermediate steps.

The reaction proceeds in three steps from the starting material succinic acid (butanedioic) to succinic anhydride (1), then to succunanilic acid (2) and finally to succinanil (3).
[Review techniques for refluxing, filtration and Infrared]



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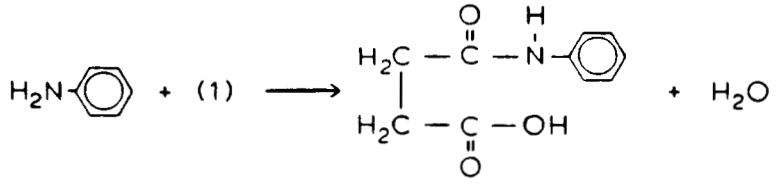

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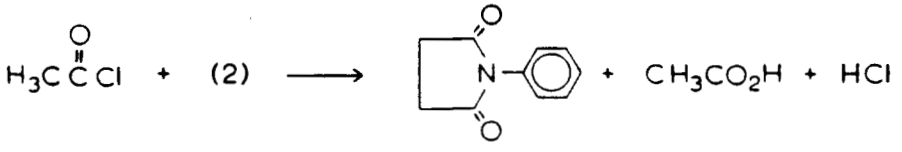

(3)

Procedure

1. Add 15g of succinic acid to a 100 ml round bottom flask. To this add 20ml of reagent acetic anhydride(**HOOD**) and a boiling stone. Reflux the mixture gently until the crystals dissolve and then for another 20 minutes or so. Remove the heating source and allow the flask to stand until it is at room temperature and then cool it in an ice bath.

Filter the crystals formed by aspiration and wash with several small portions of cold ether.

Use a crystal or two and a little cold 5% sodium bicarbonate to check for the absence of the original acid. If there is still some acid present you will dissolve the crystal and see the generation of bubbles of CO_2.

Record the crude yield and melting point.

2. Take 1g of the solid anhydride and dissolve it by heating it with a steam bath in 30ml of toluene in the **Hood.**

Add a prepared solution of 0.9ml of aniline and 5ml of toluene to this solution. **[Both aniline and toluene are extremely dangerous so use proper handling techniques]** You should see an immediate result of the reaction.

Cool the solution and again filter with aspiration in the hood. Wash with cold toluene and air dry. Dispense the filtrate solution into the proper waste container.

Determine yield and melting point and again test with 5% $NaHCO_3$. Note the result of the test- explain.

3. Transfer the succinilic acid to a 100ml round bottom flask plus a boiling chip. Add about 5ml of acetyl chloride to this. **[Extremely corrosive - dispense in HOOD]**. Attach a reflux condenser and begin refluxing. **HCl will be generated as a byproduct so be sure to vent or use the Hood.**

The reaction should be completed in 5 to 6 minutes.

Allow the solution to cool and crystallize. Filter the solution and wash with cold ether as before.

Determine yield, melting point and solubility in 5% $NaHCO_3$. Run an Infrared spectrum on each product and point out the significant differences.

<u>Requirements for report</u>

Follow the established guidelines for report writing and include your sprectrum and melting point data.

[Reference:**Organic Experiments** by Fieser published by Raytheon Education Company]

GAS CHROMATOGRAPHY OF ALCOHOLS

This experiment is an introduction to gas chromatography and the concepts related to the gas chromatograph (GC).

Although this experiment is not designed to be totally qualitative in nature the primary analysis results are to gain an insight to the uses of the gas chromatograph which do apply to quantitative analysis.

Vapor-phase chromatography(VPC) uses a stationary phase consisting of some high boiling liquid dispersed on an inert support material. The liquid coating will have some property such as high or low polarity that allows it to interact with the volatile sample that has been introduced into a flowing mobile phase normally consisting of an inert gas such as helium. The stationary phase and its support material are located in a coiled tube called the column.

The mobile phase is located in a high pressure tank and is delivered through a valve and regulator to the column. Attached to the system before the column is an injector which allows for the introduction of the sample to the mobile phase and then to the column. The last component in the GC is the detector which is the sensing device for the elution process. The types of detectors vary, but we will discuss only the thermal conductivity detector(TCD).

The temperature is an important factor in the performance of the machine and thus needs attention. The temperature can either be held constant(iso-thermal) or can be varied with precision(programmed) to aid in the elution of the sample by the carrier gas(He).

Another factor that affects the results of the chromatogram is the flow rate of the carrier gas. The faster it passes through the column the less interaction the sample has with the stationary phase and thereby the less separation of the components. It is therefore an important variable that must be adjusted and then held constant.

The detector we will use consists of a hot wire that has a constant current flowing under static conditions. The carrier gas has a rather high heat capacity and this keeps the wire cooler with a lower resistance to the electron flow. When a volatile material strikes the detector filament its thermal properties differ from the helium gas and the cooling effect changes on the filament. This creates an electronic unbalancing of the electron flow which is then sensed and transmitted to a recorder. We utilize the response of the recorder to the unbalancing as the method of determining the identity and quantity of material in that particular component.

One other important part of the gas chromatograph is the injector port. Here is the place where the sample is introduced to the column and the carrier gas. It must be held at a temperature that allows the components of the sample to turn to a gas readily, but it must not be so hot as to decompose any of the components. Neither can it be too cool and cause a sample to condense out. Also, it must not be made of a material that could react with one of the sample components. Lastly, it must be sealed so as to prevent any leaking of the sample.

The interaction of the sample and the various parts of the GC must be kept as controlled as possible so that we can obtain reproducible results. If we cannot keep all the variables almost constant our results(analysis) will have little meaning. This means we must start our experiment by setting the parameters according to the instructions in our procedure and then run our samples or unknowns.

Procedure:

A basic introduction to the GC will be given by the instructor. You will then set up the proper sequence for the carrier gas flow, the injector temperature, the oven temperature and the detector temperature. After these have been set and stabilized and the filament current set as prescibed you will establish the baseline on the recorder at the lowest attenuation setting (times 1).

To prepare your known sample mixture you will use volumetric glassware and make a 1:1:1:1:1:1 vol/vol mixture of the following alcohols (t-amyl,2-pentyl,1-pentyl,cyclopentyl,1-hexyl and 1-heptyl) and also individually seal containers of the alcohols.

Run the mixture to check for resolution of the six ingrediants and suitable retention. If there is no chromatogram or if the response is irratic check with the instructor. Now repeat the analysis at least twice more and be aware of the position of the peaks with respect to the air peak and the approximate area of each of the peaks with respect to one another and to the previous runs. If there is a discrepancy repeat the run.

·Next, inject each of the individual alcohols to obtain their retention times for identification of the mixture and the unknown.

The next step is to obtain the chromatogram of the unknown mixture supplied by the instructor. Get at least three reproducible runs. From this you will determine the individual alcohols and the % by weight of each in the mixture.

When all the necessary chromatograms have been obtained you will turn off the filament current to the detector and reduce the flow rate of the carrier gas to conserve the helium. **Do not shut the flow of helium off.** All of the chromatograms should be run on the same day to prevent changes in any variables.

DATA

Now you will analyze the data produced on the chromatograms. The first thing you must do is to check the reproducibility of your work. This is accomplished by determining the peak areas for each peak by multiplying the peak height times the width of the peak half way down from the apex of the peak. The areas of all the peaks are calculated in this fashion. Also, the peaks retention times should agree for each peak relative to the air peak. The correlation between the chromatograms can be checked by summing all the peak areas for a single chromatogram and then dividing each individual peak on that run by the total and multiplying by 100. This is equal to the area %. This is done for each chromatogram and then the values are compared. If there is close agreement the rest of the calculations can be carried out. If not, another series of runs should be **scheduled.**

The next information you need to obtain is the mass to area ratios so that you can determine the detector response factor for each component in the known solution and thus determine the weight % of your unknown solution. This is accomplished by multiplying the volume of each standard alcohol in your mixture by its density and dividing this value by the area corresponding to that alcohol. When all six values are determined, the largest of these values is divided into each of the other units. The results of this are related to the interaction of that molecule with that detector. The name given to these values is detector response factor.

Using the factors and the chromatograms of your unknown you can now calculate the weight % of each of the components in the unknown.

Also, there are characteristic properties that can be calculated that are related to that particular instrument. One of these is a property called resolution R which relates to the effectiveness of separation of two adjacent peaks and is calculated using the formula

$$R = 2d/w_1 + w_2$$

where d is the distance peak to peak between the two adjacent apex and w_1 and w_2 are the widths of the bases of the same peaks.

Another property is called the number of effective plates. If you consider the column to be a fractionating column the ability of the column to isolate fractions of a mixture based on their boiling points is dependant on either its length or the number of trapping sites along its length. This value can be very important in decisions for analysis with GC. The value is calculated using the following formula:

$$n' = 16(Vr/w)^2$$

where $Vr = t_r$ the adjusted retention time relative to air is multiplied by the flowrate of the carrier gas in ml/min. and w is the width of the peak at its base. All of the units must be corrected or adjusted to correspond.

Requirements for report

The final report should include:

1. The response factors of the detector for each alcohol.
2. The weight % of the components in the unknown and the statistics data.
3. The values for R for each of the pairs of adjacent peaks.
4. The value of n' for the first eluted peak after the air peak.

Questions

1. What are some of the variables that must be held constant to get good results in the experiment?
2. What is meant by gas-liquid chromatography?

[Reference: **The Practice of Gas Chromatography** by F. Rowland published by Hewlett-Packard Co.]

THIN LAYER CHROMATOGRAPHY

Chromatography is a method of isolating a component from a mixture. It is more widely used for analytical purposes, but also finds use in preparative work.

The principle of chromatography is to utilize the attraction of a solid adsorbent versus the solubility properties of an eluting liquid to differentiate the materials in the mixture from one another.

Thin layer chromatography (TLC)is just one aspect of many types of chromatography. In this technique, a solid support such as alumina or silica gel, is coated on an inert backing, i.e. glass or plastic. The thickness of the coated material is approximately a fourth of a millimeter. This coating can be done in the laboratory or bought commercially.

The use of the TLC plates is then accomplished by extracting the desired mixture of compounds with a volatile solvent and spotting a tiny portion of the mixture on the lower part of the TLC plate. It is allowed to dry and then placed in a chamber containing an eluting solution.

As the compounds are then continuously dissolved and adsorbed (partitioned) they travel up the TLC plate and separate one from another due to their individual properties. When the solvent gets close to the top of the plate it is removed from the chamber and the position of the solvent front is marked. The solvent is then allowed to evaporate.

The compounds can now be isolated or identified by their R_f value (R_f = distance traveled by the compound/distance traveled by solvent).

[Review the techniques for chromagraphy]

Procedure:

1. **VISUAL TLC**

Chlorophyll, carotene and xanthophyll are present in many plant leaves. To 2g of leaves add a small volume of a solution of acetone and hexane(1:2) and grind this mixture in a mortar. Filter the solution and save it. To the leaves add another portion of the extracting solution and repeat the above procedure.
Combine the extracts and wash in a separatory funnel with three small portions of water then dry over Na_2SO_4(anhydrous).

To a TLC plate spot the extract 1/4 inch above the bottom of the plate. Place the plate in the developing chamber containing slightly less than 1/4 inch of the eluting solvent.[Hexane:Acetone, 7:3] When the solvent front has almost reached the top of the plate (1/4 inch from the top) remove it from the chamber and mark the position of the solvent front. Allow the solvent to evaporate from the plate.

Now determine the R_f values for the various pigments that have been separated by the elution. Can you identify any of the pigments?

2. **ULTRAVIOLET TLC**

To an analgesic (aspirin) add enough methanol to make a solution of about 5 to 10mg/ml concentration.

Place a spot of sample on a TLC plate (Silica gel with flourescent indicator by Eastman) in the appropriate position.

Elute as decribed above using either ethyl acetate or acetone as the eluting solvent.

Again use a developing chamber and follow the progress of the solvent front. When it reaches approximately 1/4 inch from the top of the TLC plate. Remove the plate and immediately mark the position of the solvent front. Allow the solvent to evaporate.

Using a UV light source locate the position of the ingrediants on the TLC plate.

Determine the R_f values and identify the known ingrediants. It is suggested that the experimenter run knowns along with the unknowns.

Requirements for report

Follow the established guidelines for report writing and the identity of your samples.

[Reference: **An Introduction to Modern Experimental Organic Chemistry** by Roberts, Gilbert, Rodewwald and Wingrove published by Holt,Rinehart and Winston]

IODOMETRIC GLYCOL DETERMINATION

Organic molecules containing oxygen are sometimes susceptible to further oxidation in a stoichiometric system that allows for quantitative analysis.

Solutions containing ethylene glycol are examples of this technique when attacked by the periodate ion. By this method, an excess of standard periodate ion is added to a known volume of a sample and allowed to react with the ethylene glycol on a one to one basis. This is done in a slightly acidic media. The solution is then made basic with sodium bicarbonate. Potassium iodide is added to react with the remaining periodate. The tri-iodide ion that is generated is then titrated with standard sodium thiosulfate. The difference is equated to the glycol content in the sample.

$$CH_2OHCH_2OH + IO_4^- = 2H_2CO + IO_3^- + H_2O$$

$$IO_4^- + H^+ + 3I^- = I_3^- + IO_3^- + 3H_2O$$

Procedure

Place a 10ml aliquot of the unknown ethylene glycol(anti-freeze) into a 250ml Erlenmeyer flask. To the flask pipet 10ml of the standard 0.2N sodium metaperiodate into each sample and set aside for twelve minutes. At the end of this time, transfer the solution to the coulometric flask with rinsings and add 5g of sodium bicarbonate. When the bicarbonate has dissolved, add 2g of potassium iodide and allow this to dissolve. Now pipet 25ml of the standard sodium thiosulfate into the reaction flask and when the color has disappeared, add 5ml of the starch indicator.

You are now ready to begin the coulometric titration. Record the time and milliamperes until you see the first perceptable color that stays in the solution for ten seconds. Record the time.

Based on the milliamps and the time in seconds and the value for a Faraday, determine the unreacted periodate. Next, calculate the periodate that reacted with the ethylene glycol. On a one to one basis, calculate the weight of the glycol in the original sample as a weight per volume percentage, also, calculate the weight per liter.

Solutions:
- 0.2N $NaIO_4$ (106.96g/eq)
- 0.1N $Na_2S_2O_3$-$5H_2O$
- 5.0g $NaHCO_3$ per sample
- 2.0g KI per sample
- Starch indicator (1.0g per 100ml boiling H_2O)

Requirements for report

Follow the established guidelines for report writing and include a table of your data for the titration.

[Reference: **Analytical Chemistry Practice** by J. Kennedy page 93, and **Chemical Separations and Measurements** by Peters, Hayes,et.al. p334-7]

FISCHER ESTERIFICATION

This technique for the formation of an ester is widely utilized in the organinc laboratory. This reaction has been used as a vehicle to study both mechanisms and equilibrium for a number of effects on ester reactions.

The acid catalyzed attack of the carbonyl carbon helps to generate the equilibrium status of the reaction, but to increase the yield it is necessary to shift the reaction toward the product side. Normally this is done by isolating one of the by-products or main product through distillation and causing the formation of more product. Another method is to use a Dean-Stark trap on a reflux set up to isolate an immiscible portion or by-product such as water. [Review techniques for refluxing, distillation and use of the separatory funnel.]

$$R\text{-}CH_2OH \;+\; HOOC\text{-}CH_3 \;\overset{H^+}{==}\; R\text{-}CH_2\text{-}O\text{-}\overset{O}{\overset{\|}{C}}\text{-}CH_3$$

Procedure

To a 100ml boiling flask, add 0.10 mole of the alcohol to be reacted,(isopropyl, sec-butyl or others), and 25ml of acetic acid with 3ml of concentrated sulfuric acid. Add a few Hengar granules, a reflux condenser and then heat to reflux for 1 to 2 hours.

Cool the reaction flask and add about 50g of crushed ice and allow it to melt.

Transfer the solution to a separatory funnel and rinse the boiling flask with a small amount of ether. Extract to solution with two 20ml portions of ether, and allow it the layers to separate and discard the aqueous layer. Wash the ether layer with water, two 25ml portions, allow to separate and drain off the water, and then wash with two 25ml portions of 0.5M Na_2CO_3. Draw off the lower layers and discard them. Pour the ether solution into a beaker with anhydrous magnesium sulfate, allow to stand while you set up a distillation apparatus with a steam bath for the heat source. Decant the solution into the boiling flask for distilling of the ether.

After the ether has been distilled over, change the heat source to a heating mantle and distill the ester into a clean tared receiver.

Determine the yield, boiling range and obtain an Infrared spectrum.

Requirements for report

Follow the established guidelines for report writing and include your IR spectrum.

[Reference: **Practical Organic Chemistry** by Kemp, McGraw-Hill, pub.]

METHYL BENZOATE ESTERS

The acid catalyzed preparation of an ester is discussed under Fischer Esterification. The protonation of the carbonyl carbon is necessary for the opening of the carboxylic acid group to attack by the hydroxyl group of the alcohol. This generates an equilibrium situation where the value for Keq is approximately 0.66. Of course, this means that an excellent yield for this reaction is about 70%. To increase this yield it would be necessary to cause some type of shift of the equilibrium.

This can be done by a variety of techniques, but the usual method is to employ a Dean-Stark trap in the reflux step to eliminate water as it is formed in the reaction.

[Review the techniques for reflux, separatory funnel use and Infrared.]

Procedure

To a 100ml round bottom flask, add 0.10 mole of the benzoic acid derivative in about 25ml of methanol with 3ml of concentrated sulfuric acid. Attach a reflux condenser and reflux the solution for about 1 hour.

Cool the reaction mixture and transfer it to a separatory funnel and rinse the flask with about 25ml of ether and add this to the separatory funnel. Add 50ml of water and extract. Discard the water layer and repeat with a smaller quantity of water and again discard the wash. Neutralize the ether layer with a 25ml portion of 5% Na_2CO_3 and discard the lower layer.

Transfer the ether solution to a flask containing some anhydrous magnesium sulfate and allow to dry.

Set up a distillation apparatus with a steam bath heat source and decant the ether solution into the distilling flask. Distill over the ether and then change to a heating mantle for the heat source and distill the ester product. Collect the material that boils above 190°C.

Determine the % yield and obtain an Infrared spectrum.

Requirements for report

Follow the established guidelines for report writing and include the IR spectrum.

[Reference: **Experimental Methods in Organic Chemistry** by Moore, et.al Saunders College Publishing]

ORGANIC UNKNOWN

You will be given an organic compound that you are required to obtain as much information about as is possible utilizing the various instruments and apparatus available to you. You will have an opportunity to obtain an NMR, a IR and a UV-VIS spectrum of your unknown. You will also be able to determine its physical properties such as melting point, boiling point, refractive index, etc.

You are to treat any sample as if it were extremely toxic and hazardous to your health. This is not necessarily the case, but for your own protection it is prudent to follow this procedure in all activities involving chemicals.

Your results and all data and spectra are due at the end of the quarter.

A perfect grade requires absolute identification of the unknown.

GRAVIMETRIC CHLORIDE

The presence of chloride ion in a sample can be readily determined by precipitation as the insoluble silver salt.

$$Cl^- + Ag^+ = AgCl_{(s)}$$

The details of this reaction are widely discussed in most analytical chemistry texts, but it is important to point out that only a slight excess of silver ion is necessary to cause complete precipitation of the chloride ion. Also, digestion is necessary to complete the formation of larger crystals and only washing and drying are then necessary to complete the analysis of the crystalline unknown.

The porcess is enhanced by the fact that the crystals can be dried at 110°C and the use of sintered glass filtering crucibles can then used. AgCl is colloidal in nature so that if filtration is completed immediately after mixing the ions a lot of the material would be lost through the filter and thus create a significant weight error.

Another property of silver chloride is its ease of peptization in a distilled water solution, so the addition of a small amount of dilute nitric acid to the wash and dissolving media reduces this problem.

Lastly, the effect of light on the precipitate causes a small degree of weight descrepancy.

$$AgCl_{(s)} + light = Ag_{(s)} + 1/2Cl_2$$

Reduced light during precipitation and drying helps this problem.

Procedure

Clean and dry threee sintered glass crucibles and bring them to constant weight. (At least three replicate weighings). Also, dry the unkown in a weighing bottle for two hours at 110°C. Cool and place in a dessicator until needed later for the experiment.

Now weigh 3 samples of about 0.4g to the nearest 0.1mg from the dried sample and dissolve in 400ml beakers using deionized water (about 200ml) and add about 5ml of 6M nitric acid. Add a 5% silver nitrate solution slowly while mixing until the precipitate starts to coagulate and then add a few more milliliters. Heat the solution to near boiling and hold for 15 to 20 minutes to allow for precipitate digestion. Finally, check the completeness of precipitation by adding a drop or two of the silver nitrate solution to see if any more AgCl forms. If AgCl is observed add 10% more of the precipitating agent used previously.

Follow the proper procedures and filter the solutions, first decanting the supernatant liquid then transfer the rest of the precipitate to the filter and rinse several times with dilute nitric acid. Test the final rinses for the presence of excess silver ion.

Dry at 110°C for one to two hours and cool in the dessicator. Weigh and redry the crucibles until the weight is constant. Use a change of plus or minus 0.3mg as the guide for consistancy.

Clean the crucibles immediately after completion of the experiment and if necessary soak in 6M ammonium hydroxide to dissolve the silver salt.

Requirements for report

Report the % of chlorine in the original with all the statistical data to justify your answer. Follow the established guidelines for report writing.

Questions

What is the advantage of this analysis over the use of potentiometric or volumetric analysis?

[Reference: **Fundementals of Analytical Chemistry** by Skoog and West, Saunders College Publishing]

THE DETERMINATION OF SULFUR IN A SOLUBLE SULFATE

The sulfate ion forms an insoluble salt with a number of cations, but the salt of barium is the most widely used of precipitating agents for the determination of sulfate containing compounds.

Although the procedure is straight forward, this analysis presents a number of problems due to coprecipitation of a large number of ions and the small size of the crystals. Digestion is required for purifying and increasing the crystalline size. If the procedure as written is followed the results are very favorable.

$$Ba^{+2} + SO_4^{-2} = BaSO_{4(s)}$$

Procedure

Dry the sample for one hour at 110°C. While drying is taking place prepare a 5% solution of $BaCl_2*2H_2O$ of sufficient quantity that you may precipitate a 0.5g sample of about 50% purity.

Weigh out about 0.5g of unknown sample into three 600ml beakers and record the weights to the nearest 0.1mg. Dissolve each in 200ml of distilled water.

Bring this to near boiling and in another beaker heat the barium containing solution you will need for the precipitation. When both are hot, pour the hot, barium solution into the unknown sulfate while stirring. Allow the solutions to digest at about 80°C for two hours.

Prepare three porcelain crucibles by cleaning and heating to constant weight in the muffle furnace at 900 to 1000°C. When they are at constant weight, store them in your dessicator.

Place three 60° funnels and #42 Whatman filter paper in a rack and begin the filtration. The solutions must be decanted while hot and the clear **filtrate** may be discarded so if any precipitate is later passed through the filter paper it may be reclaimed with a minimum of wash liquid in the transfer. When most of the clear liquid is transferred to the funnel, carefully rinse the precipitate into the filter paper and transfer any precipitate clinging to the walls of the beaker with a rubber policeman. Wash the filter paper and the precipitate with hot distilled water until a sample of fresh **filtrate** shows no presence of chloride when tested with a drop of silver nitrate solution.

Now carefully fold the filter paper and the precipitate from the funnel into the crucible and dry the unit. When dry, carefully begin to char the paper with a Meeker burner and a plentiful air supply. [Do not allow an open flame.] When all the filter paper is charred, complete the ashing process in the muffle furnace at 900-1000°C. Cool the crucibles and place them in a dessicator until cool enough to weigh. Repeat the heating, cooling and weighing until the crucibles are at a constant weight.

Clean up all glassware and equipment.

Requirements for report

Calculate the sulfur trioxide content of the unknown sample and justify your results with your data. Follow the established guidelines for report writing.

Questions

1. What is the reason for the abundance of air needed during charring?
2. Write the equation.

[Reference: **Fundementals of Analytical Chemistry** by Skoog and West, Saunders College Publishing]

GRAVIMETRIC DETERMINATION OF IRON

The production of ferric hydroxide as the precipitating species for the gravimetric determination of iron is the usual first quantitative analysis experiment.

The term ferric hydroxide to begin with is misleading and the rest of the experiment is full of pitfalls. Ferric hydroxide in reality is $Fe_2O_3 \cdot xH_2O$ and generally is produced in an ammonical solution.

The precipitate itself is large and bulky and full of impurities, which if not removed will cause great errors in the results.

It must next be redissolved to remove the impurities and then reprecipitated. This involves a lot of time and things can go wrong. A true test of patience and persistence.

The last road block to success is the ashing procedure. If insufficient air is available during the heating you will get reduction by the carbon in the filter paper from Fe_2O_3 to Fe and the magnet test will confirm this.

The equations for the procedure:

$$2Fe + 6HCl == 2FeCl_3 + 3H_2$$

$$2FeCl_3 + 6NH_4Cl == Fe_2O_3 \cdot xH_2O + 6NH_4Cl$$

$$Fe_2O_3 \cdot xH_2O == Fe_2O_3 + xH_2O$$

Procedure

Dry an iron oxide unknown large enough to weigh three samples of about 0.5g each. The sample should be dried overnight at about 150°C.

Place the weighed samples into three clean beakers with 20ml of a 50% hydrochloric acid solution. Cover the beakers with a watch glass and heat near the boiling point and continue to heat until all the dark particles disappear. You may add distilled water or the acid solution in small increments if needed to prevent dryness.

When all the samples have been dissolved, rinse down the walls of the beakers with boiled distilled water and then add 1ml of concentrated nitric acid and boil to expell any oxides of nitrogen.

If there is any residue such as silica, it must be filtered out of the solution at this time or it will be determined as iron. A fast filter paper (#1 or #41 Whatman) may be used and rinsed with dilute hydrochloric acid until no yellow is apparent. Collect all the filtrate in separate 400ml beakers for each sample.

The filtrate is now made basic with the addition of a 30% ammonia solution. A persistant odor of ammonia when heated indicates there is sufficient base present. Continue heating the solution for a period of time and as the precipitate settles, test the solution with more ammonia to check for complete precipitation.

The precipitate is now separated by filtration from its mother liquor by decantation primarily. Leave the bulk of the precipitate in the original beaker, but use a Whatman #41 filter paper to catch any of the precipitate that escapes, and wash the precipitate with a 0.1M ammonium nitrate and pour it through the filter paper. Do not use more than 25ml of the wash solution. Allow the precipitate to settle and decant the wash through the filter. Repeat the washing and again decant the liquid to the filter.

Now discard the washings and the bulk liquid.

Place the funnel over the beaker with the precipitate and carefully pour through the funnel 50ml of 1:10 HCL being sure to dissolve all of the precipitate in the funnel. When all of the solvent has been added, be sure all of the precipitate has dissolved.

Bring the solution up to the same temperature as before and again add ammonia solution to reprecipitate. Heat gently and test for complete precipitation and allow the solid to settle for decantation and filtration. Again wash with 0.1M ammonium nitrate and then transfer all the solid to the filter paper. Wash the precipitate in the funnel with hot ammonium nitrate until a test of the fresh washings gives only a slight test for the presence of chloride ion. (Use a few drops of 5% silver nitrate solution).

Drain the precipitate in the filter as much as possible and then fold it into a preweighed porcelain crucible. Dry the filtered material and then char it as described by your instructor. When it has been charred then ignite the crucible to a bright red heat with a large volume of air available to prevent reduction to the Fe_3O_4 form. Cool and then dessicate before weighing. Repeat the ignition step and weighing until the crucibles are at constant weight.

Clean up all your glassware and any spills of the iron residue.

Requirements for report

Report your results with all the proper statistical verification and follow the established guidelines for report writing.

Questions

1. What is the advantage of this technique over optical or volumetric methods?

[Reference: **Quantitative Analysis** by R.A.Day,Jr. and A.L.Underwood, 5TH Ed. page 120]

NICKEL IN STEEL

Organic precipitates are used in a variety of applications for metal ions. The procedure usually involves the formation of an extremely stable complex ion structure. This experiment uses dimethyl glyoxime and nickel as such a complex. It forms a stable two to one ratio of dimethyl glyoxime to nickel that is quantitative in nature and stable at elevated temperatures. In the presence of iron an interferring ion, the use of tartaric acid excludes the coprecipitation of the iron in the mildly basic solution, thus the iron does not interfer with analysis of the nickel. Quantitatively, the presence of as little as 20mg of nickel is detected by this method thus the sensitivity is as low as 0.2%.

$$Ni^{+2} + C_4H_6(NOH)_2 == Ni(C_4H_6(NOH)_2)_2^{+2}$$

Procedure

Clean and bring three marked sintered glass crucibles to constant weight by alternately heating in an oven at 110°C and cooling and then weighing until two consecutive weights agree within 0.5mg. Set the crucibles aside in a dessicator until needed.

Obtain a steel sample and rinse the sample with a few milliliters of acetone to remove any oils. Dry the sample at a low temperature and dessicate it.

Weigh three separate samples of about 1.0g each into three 400ml beakers. Dissolve the samples in 50ml of 50% HCl,with warming and check for complete dissolution. After, add carefully 10ml of 50% nitric acid and check for oxides of nitrogen evolution. Boil gently until all of the oxides are expelled from the solution.

At this point, dilute the solution with 150ml of distilled water and just bring the solution to the boiling point. Now add 20ml of a 25% tartaric acid solution and readjust the the mixture to neutral with concentrated ammonia. When a slight odor of ammonia persists then add a few milliliters of concentrated ammonia in excess. If the solution is not clear at this time, repeat the acidification and the tartaric acid addition and then readjust the solution to neutral pH.

Now adjust the solution to just on the acid side of neutral and heat again to about 70°C. The addition of 20ml of a 1% solution of dimethyl glyoxime in alcohol is now used to start the precipitation. Slowly add dilute ammonia by stirring until the odor of ammonia again persists and then add an additional 2ml.

Digest the sample for one half to one hour at about 70°C. Allow the solution to settle and test for complete precipitation with a few drops of the dimethyl glyoxime. Cool the solution for about one hour and filter through the prepared crucibles.

Dry to a constant weight at 110°C and use the gravimetric factor 0.2032 to determine the nickel content in the precipitate.
Clean the crucibles with a boiling solution of 6M nitric acid.

Requirements for report

Calculate the % nickel in the original sample and follow the established guidelines for report writing.

Questions

1. List five other complex formation determinations that are stable to gravimetric analysis techniques.
2. Calculate the quantity of nickel present per gram of sample.

[Reference: **Fundementals of Analytical Chemistry** by D. Skoog and D. West, pages 147-8]

GRAVIMETRIC DETERMINATION OF PHOSPHATE

The analysis described in the following discussion is dependent on the formation of the complex salt magnesium ammonium phosphate hexahydrate from an ammoniacal solution. This precipitate can be utilized to determine the quantity of phosphorus in the unknown or can be converted by ignition to the pyrophosphate of magnesium.
The precipitation is carried out by slow neutralization of an acid solution which contains ions of magnesium, ammonium and acid phosphate. While there is acid present in the solution there, is no precipitation, but on neutralization the formation of the hexahydrate slowly forms and the solution must be allowed to stand for several hours.
The formation of the third ionization step of phosphate is strongly dependent on the pH of the solution and a narrow range of concentrations of the ions utilized. Since in general this is very difficult to obtain on the first attempt, the analysis is done by a double precipitation technique.

$$Ksp = [Mg^{+2}][NH_4^{+}][PO_4^{-3}]$$

$$HPO_4^{-2} + H_2O = PO_4^{-3} + H_3O^{+}$$

Due to the predominance of different ion species available to precipitate it is necessary to carry out a double precipitation technique for good purity in the product.

Procedure

Solutions: The magnesia mixture is prepared by dissolving 50g of magnesium chloride hexahydrate and 100 g of ammonium chloride in 500 ml of distilled water. Add a small amount of concentrated ammonia until it is evident that there is an excess present by evidence of a persistent odor. Let the mix stand overnight and filter the next day if it is cloudy. Now carefully add HCl until the solution is slightly acid and dilute to 1000 ml.

The procedure discussed below is primarily for soluble phosphates but may be applied to mineral phosphates or magnesium with proper corrections.

Dry the sample and weigh out three portions of 0.5-0.6 g each, into 400 ml beakers. Dissolve in about 20 ml of 50% hydrochloric acid and dilute to about 100 ml. Place the three beakers in an ice bath and add a few drops of methyl red indicator and 10 ml of the magnesia mixture (See solution preparations) for each 100 mg of P_2O_5 in your sample.(See your instructor). Now slowly add concentrated ammonia that is free of any precipitated matter until the indicator shows its color change. Be sure to stir as the ammonia is added, but avoid any contact with the side or bottom of the beaker with the rod. When the precipitate starts forming, add 5 ml more of the ammonia and allow the beaker to stand in ice for four hours, keeping the level of ice about the same.(It is also possible to allow the solution to sit overnight at room temperature).

Reprecipitation: Filter the cold solution through Whatman #42 or equivalent keeping the precipitate in the beaker. Wash the precipitate by adding 25 ml of chilled 1M ammonia to the beaker and swirling the mix and then decanting the lquid into the filter. Discard the filtrate and the washings.

To redissolve the precipitate, place the beaker with the precipitate below the funnel containing the filter paper and any precipitate that was transferred to the filter and add slowly 50 ml of hot 1M HCl through the filter being careful to wet every area of the filter paper with the acid. Wash the filter paper with a little hot water and catch all the washings in the beaker. Discard the paper and dilute the solution in the beaker to about 100 ml with distilled water. Now reprecipitate and described in the first section. Reduce the quantity of magnesia mixture to 2 ml and again cool as before.

To collect the hexahydrate, the procedure is as follows: Prepare three filtering crucibles by positioning them in suction holders and pass two 15 ml portions of reagent alcohol through then two 15 ml portions of anhydrous ether and allow air the pass through to crucible for five minutes. Wipe dry with a Kimwipe and allow to stand in air for 20 minutes and then weigh. Repeat the above procedure until two consecutive weighings agree to 0.4 mg.

Now decant the solution containing the precipitate through the crucible keeping as much of the solid behind as possible. Wash the precipitate with chilled 1M ammonia as before and again decant the liquid into the crucible. Wash with a little more ammonia solution and check the fresh filtrate for the presence of chloride ion with a drop of silver nitrate solution. If there is no cloudiness then proceed to wash with the reagent alcohol and ether as with the crucibles earlier. Using the vacuum draw air through the precipitate for the five minutes and allow to stand for 20 minutes then weigh.

Requirements for report

Calculate the per cent phosphate in the sample as the hexahydrate precipitate. Follow the established guidelines for report writing.

[Reference: **Applied Inorganic Analysis** by Hillebrand and Lundell, page 556.]

VOLUMETRIC DETERMINATION OF A BASIC MIXTURE

It is possible to analyze a mixture of carbonate, bicarbonate and hydroxide ions in solution by volumetric methods.

Since carbonate ion will react to form an insoluble precipitate with barium, it can be isolated from the analysis and only the soluble hydroxide ion may be titrated.

(1) $CO_3^{-2} + HCO_3^- + OH^- + H^+ = H_2O + CO_2$

(2) $HCO_3^- + OH^- = CO_3^{-2} + H_2O$

(3) $Ba^{+2} + CO_3^{-2} = BaCO_3$

In addition, it is possible to estimate the concentrations of the carbonate and the bicarbonate species by careful titration using phenolphthalien and bromo-cresol green indicators for basic and acidic end point changes.

(4) $CO_3^{-2} + H^+ = HCO_3^-$ **pink**

(5) $HCO_3^- + H^+ = H_2O + CO_2$ **blue-green**

Using the combination of the two titration values, it is possible to determine the concentration of all three ions present.

The first equation will yield the total concentration of all the ions equated to base content. Equation 2 converts all the bicarbonate to carbonate ion and when the barium is added and the mixture titrated, it will give the amount of hydroxide ion present. The results of equations 4 and 5 are then used to determine the bicarbonate and thus the carbonate ion concentrations.

Procedure

Transfer a 50ml aliquot of the unknown solution to a 250ml Erlenmeyer flask. Add 2 drops of phenolphthalien and titrate with standard 0.1N HCl to the endpoint. Record this value and then add 5 drops of bromo-cresol green indicator and titrate to the blue-green end point. At this point, heat the solution just to boiling to drive off the carbon dioxide, continue the titration to the final end point and record this value. Repeat the above analysis with two more trials to verify the results. Also, perform a titration to determine the indicator error.

Next, transfer another 50ml aliquot to a clean Erlenmeyer flask and add 25.00ml of standard 0.1N NaOH. Swirl the solution to mix and add 10ml of 7% $BaCl_2*2H_2O$ solution to precipitate the carbonate ions. Now titrate the solution with bromo-cresol green to the same end point as before with standard HCl and record the result. Since the carbonate and the bicarbonate are now precipitated, it is not necessary to heat the solution.

With these results, it is now possible to calculate the hydroxide concentration and to get a very close estimate of the carbonate mixture present.

Solutions: Standard 0.1N HCl
" 0.1N NaOH
7% $BaCl_2*2H_2O$ made by dissolving 7.0g in 100ml of distilled water
0.1% indicators (see Handbook for specific directions of preparation).

Requirements for report

Follow the established guidelines for report writing and include your % concentration of each species present.

[Reference: **Quantitative Analysis** by Skoog and West pages 252-253]

KJELDAHL ANALYSIS FOR NITROGEN

Nitrogen contained in protein and other organic material can be converted to ammonium salts by sulfuric acid digestion. When the nitrogen has been converted the solution is made basic to help generate the ammonia molecule which is then easily transferred to a receiving flask to be titrated with acid.

Protein + H_2SO_4 == $(NH_4)_2SO_4$ + by-products

$(NH_4)SO_4$ + NaOH == $2NH_3$ + Na_2SO_4 + H_2O

Procedure

Weigh out three 1.0g samples using a piece of filter paper to transfer the sample to the Kjeldahl flask without particles clinging to the neck of the flask. At this time add 20ml of concentrated sulfuric acid plus 7.0 g of potassium sulfate powder and one crystal of copper sulfate as a catalyst. Heat the flask in the **HOOD** being careful to prevent too much foaming. When the foaming has subsided the solution can be heated gently in the hood until the solution becomes clear and pale green or straw colored. The length of time required may be two to t three hours.

When totally digested remove the heat and cool to room temperature and dilute carefully with 250ml of water. Again cool the solution to room temperature.

Now prepare for distillation by pipetting 50.0ml of the 0.1N HCl to a receiver flask and 2 to 3 drops of indicator. Next attach a condenser and a spray trap to the receiver flask and a position to attach the Kjeldahl flask. To the Kjeldahl flask, add the solution of concentrated sodium hydroxide, but add it slowly by pouring it carefully down the wall of the flask to prevent mixing. Add several pieces of zinc granules and a piece of red litmus paper. **IMMEDIATELY** connect the flask to the spray trap. Swirl the solution and bring the solution to a boil. Distill until over half the solution is gone. Disconnect the spray trap and turn off the heat. Rinse down the condenser with distilled water and then titrate the HCl solution with standard sodium hydroxide (0.1N).

A blank should be run in conjunction with the analysis.

Solutions:
0.100N hydrochloric acid
0.100N sodium hydroxide
Bromocresol green indicator
concentrated sulfuric acid
NaOH sol n of 45g/75ml of water
potassium sulfate powder
copper sulfate crystal
granulated zinc

Requirements for report

Report the % nitrogen and follow the established guidelines for report writing.
with all statistical justifications.

[Reference: **Fundementals of Analytical Chemistry** by Skoog and West. p.247&746-7]

COMPLEX ION ANALYSIS

The use of chelating agents for analysis has been known since 1945, when Schwartzenbach first recorded their use as an analytical reagent. The reagent most discussed in literature is the disodium salt of ethylenediaminetetraacetic acid. This material forms some very stable complexes with the typical cations such as zinc, calcium and copper, etc.

The titration we will utilize involves calcium and **EDTA**, but may be extended to any variety of cations listed in the literature.

$$Ca^{+2} + Y^{-4} = CaY^{-2}$$

Procedure

Analysis: Transfer 50 ml of the primary standard by pipet to a 250 ml Erlenmeyer flask and add 5ml of the buffer solution. Also, add 5 drops of the Eriochrome Black T indicator and begin titrating with the **EDTA** solution. The color of the indicator will change from a wine-red to a pure blue (no red). At this point record the volume of the titrant used and repeat the analysis with a new standard solution. When you have 3 equal trials, repeat the above procedure with your unknown.
Using the information from your titration of the standard compute the molarity of the **EDTA** and the titer based on mg of calcium carbonate per milliliter of **EDTA**.

Next compute the concentration of the calcium carbonate in your unknown by multiplying the volume of the titrant times the titer. This will give you the mg of calcium carbonate present in your 50 ml sample. This is then multiplied by the volume of original sample and divided by the aliquot you took to give mg of calcium carbonate in the sample.
If you are to determine the hardness of a water sample, the above procedure is the same except you only add 1 ml of the buffer.

Solutions:

Preparation of titrant and reagents are completed as follows;

Chelating agent, disodium salt of ethylenediamine tetraacetic acid, is made by weighing out 4 g of the salt; plus 0.1 g of $MgCl_2$ and dissolving them in a 400 ml beaker with distilled water. If there is any turbidity, a few drops of 0.1M NaOH can be added to clear this up. Transfer to a 1-L flask and make up to volume. Label this as your titrant.

Buffer is made by weighing out 6.75 g of ammonium chloride and measuring 57 ml of conc. ammonia then diluting to 100 ml of total volume.

Indicator is made by dissolving 0.5g of reagent grade Eriochrome Black T in 100 ml of reagent alcohol and placing it in a clean dry labelled bottle with the preparation date.

Standard is prepared by weighing 0.4 g of primary standard calcium carbonate that has been dried at 100 °C. Place the standard in a small beaker and add 50 ml of distilled water and dropwise add 1:1 HCl until the mixture stops forming bubbles and there is no evidence of solid particles present. Then transfer the solution to a 500 ml volumetric flask and rinse the beaker many times into the flask. Finally make the solution up to volume.

The unknown is prepared for analysis by following the same procedure as the standard. The analysis of the unknown is done as decribed in the standardization of the **EDTA**.

Requirements for report

Follow the established guidelines for report writing and report your results as ppm Calcium.
[Reference: **Fundamentals of Analytical Chemistry** by Skoog and West pages 282-300]

DETERMINATION OF SILVER IN AN ALLOY

The presence of silver in an alloy can be determined by volumetric means using thiocyanate ion and the Volhard method. Since silver must be dissolved in nitric acid and most of the co-metals in the alloy are also below hydrogen on the electromotive series so this presents no problem. The method is acceptable as long as the oxides of nitrogen are completely expelled, because they interact with the thiocyanate ion and will create erroneous results in the analysis. Most of the alloys of silver are able to be analyzed by this method although some containing metals like mercury, cobalt or nickel are difficult to analyze correctly.

$$Ag^+ + SCN^- = AgSCN(s)$$

Procedure

The samples should have about 0.3 to 0.5g of silver per sample so check with the instructor about approximate weights for your samples.

. Weigh out three samples to the nearest 0.1mg and dissolve each in about 15ml of 6M nitric acid in a 250ml Erlenmeyer flask. Using the hood bring each solution to a boil for several minutes after all the sample has been dissolved to expel the oxides. Cool and add 25ml of distilled water.

Titrate the solutions after cooling with standardized 0.1N potassium thiocyanate and 3 drops of iron (III) sulfate indicator.

Add the titrant by swirling until the red indicator color spreads through out the solution and then fades. At this point, begin adding the titrant dropwise until the indicator color remains from thirty to sixty seconds.

Calculate the percentage silver in the alloy using the proper statistical data and procedures.

Solutions:

[The thiocyanate is standardized against reagent grade silver nitrate. The indicator is prepared by dissolving 10g of ferric ammonium sulfate duodecahydrate in 100ml of boiled 6M nitric acid.]

Requirements for report

Follow the established guidelines for report writing and report the % silver in the unknown sample.

ELECTROGRAVIMETRIC

DETERMINATION OF COPPER, COPPER IN BRASS, NICKEL OR LEAD

A number of metallic elements are extremely easily separated by a controlled electrical potential at the platinum cathode. Copper is separated by the plating out at the cathode of an electro-analyzer from an acidic media with a potentail of about +0.34V and an amperage of 2.0 amps.

Nickel on the other hand is at the opposite side of the hydrogen electrode from copper so in an acidic solution the hydrogen ion would underg

o

reduction before the nickel ion, but if the solution is made basic to reduce the hydrogen ion concentration, the nickel then plates out at the cathode under the same conditions.

Some of the cations are complexed, such as silver and iron, with agents that may not be as safe as simple acids and bases.

$$Cu^{+2} + 2e = Cu(s) \qquad E = 0.337V$$

$$Ni^{+2} + 2e = Ni(s) \qquad E = -0.250V$$

$$Pb^{+2} + O_2 = PbO_2 + 2e$$

Procedure

The platinum electrodes must be cleaned by immersion in hot 6N nitric acid plus 1g of potassium nitrite. When the electrodes appear to be cleaned, rinse the electrodes thoroughly with distilled water and then with ethanol or acetone. Place the electrodes in the drying oven at 110°C for a few minutes. When cool, weigh the cathode and place it in the dessicator until needed for the analysis.

A. Weigh a sample containing copper, or other metal, sufficient to contain 100 mg and place the sample to be analyzed in a tall form 150 ml electrolytic beaker. In the hood, add 5ml of 50% nitric acid and heat to dissolve, then add about 6ml of 6M sulfuric acid and dilute to 100 ml.

Preweigh the cathode, (the larger basket type electrode), and the anode if you are working with a lead containing sample.

Prepare the electrodes in the machine as instructed by the teacher. Immerse them into the solution but leave about one fourth of an inch above the surface of the liquid. Turn the stirring motor and check to see that the electrodes are not touching as the electrode spins. Now adjust the voltage knob until the meter reads about two amperes and allow to run for about one half hour. After this time immerse, the electrode totally into the solution and run at 0.5 amps for another 15 minutes. If there is any extra metal plated out, repeat the last step.

When the operation is completed, lift the electrodes carefully from the solution and immerse them into some distilled water. Keep the voltage on but stop the mixer. Finally, rinse with ethanol or acetone, dry and weigh.

B. To analyze for nickel in the solution evaporate until fumes of sulfur trioxide appear then cool and add 25ml of water and neutralize with 6M ammonia to make the solution basic. If any precipitate is formed filter the solution and rinse the precipitate and add this to the filtrate. Adjust the filtrate to about 100ml and than add 15ml more of concentrated ammonia.

Treat the solution as before and again weigh the cathode. The additional weight is due to the nickel.

C. To analyze for lead in a copper or brass sample it is necessary to codeposit the lead on the anode as the dioxide from a 3% nitric acid solution of the mixture. The original solution after dissolving must be neutralized with filtered ammonia until the precipitate of copper hydroxide just persists. Then add nitric acid dropwise until the precipitate just dissolves. At this point, an additional 3ml of concentrated nitric is added per 100ml of solution volume.
The solution is now electrolyzed according to the directions given in part A.
The lead will be plated as a spongy mass on the anode and will, if handled without care, flake off of the anode with rinsing and drying.

Requirements for report

Follow the established guidelines for report writing and include the % concentration of your sample and all pertinent information.

[Reference: **Quantitative Analysis** by Day and Underwood pages 379-86]

DISSOLVED OXYGEN BY WINKLER METHOD

The Winkler method of dissolved oxygen for water samples is a well documented technique using manganese(II) salts and iodometric techniques. Manganese undergoes a two step reaction with oxygen and iodide ion releasing iodine. The method is very good but require precise handling techniques where the introduction of oxygen or its loss is minimized. Using BOD bottles helps to eliminate some of the problems of extraneous introduction of oxygen to the samples.

$$4Mn(OH)_{2s} + O_2 + 2H_2O == 4Mn(OH)_3$$

$$2Mn(OH)_3 + 2I^- + 6H^+ == 2Mn^{+2} + 3H_2O + I_2$$

Procedure

Place the sample into a BOD bottle by siphoning it from the sample source and allow the bottle to overflow. At this point, deliver one ml of a manganese sulfate reagent Prepared by dissolving 48g of the tetrahydrate salt of manganese sulfate and diluting to 100ml. The reagent must be delivered below the surface. Next add one ml of a KI/NaOH solution prepared by dissolving 15g of KI to which 25ml of water and 66ml of a 50% NaOH is added and then dilute to 100ml.

Place a stopper in the bottle eliminating any source of air and turn the bottle over to disperse the precipitate that is formed.

Allow the precipitate formed to settle. When the precipitate has settled slightly below the stopper introduce one ml of concentrated sulfuric acid again below the surface, and agitate to dissolve the precipitate. Transfer 200ml of the solution to a 500ml Erlenmeyer flask using a graduated cylinder.

Titrate the solution using standard 0.025N thiosulfate until the iodine color is pale yellow then add 5ml of starch indicator solution and resume the titration.

Requirements for report

The results are reported as milliliters of oxygen at STP per liter of sample. Follow the established guidelines for report writing.

[Reference: Fundementals of Analytical Chemistry by Skoog and West page 772]

POTENTIOMETRIC ACID-BASE TITRATION

Potentiometric titrations are based on the change in potential of an electrode immersed in the solution being titrated. For acid-base titrations, an electrode which will respond to changes in hydrogen ion concentration is necessary. The electrode most commonly used for this purpose is the glass electrode. The hydrogen ions can diffuse through the membrane of the glass electrode and the potential developed is a function of the hydrogen ion concentration in the solution surrounding the electrode. The potential of the calomel electrode, which is used as the reference electrode, remains constant. Thus, the measured potential is a function of the acidity of the solution.

The measurement of the potential developed by the glass electrode is difficult because of the high resistance of this electrode. The pH meter, commonly used to measure this potential, is a vacuum tube voltmeter of high sensitivity. Such a meter can measure a potential while drawing a current in the range of 10^{-12} to 10^{-14} amperes.
This experiment will consist of two titrations, one to standardize the base against potassium acid phthalate, the other to determine the concentration of an unknown phosphoric acid solution.
The second titration will pass through two end points and the result will be based on the second endpoint as the two-thirds concentration point.

$$H^+ + OH^- = H_2O$$

Procedure

Prepare a 500ml quantity of approximately 0.1N NaOH and standardize this solution against a dried, weighed sample of potassium acid phthalate.

Set up the pH meter and a stirring motor so that they are accessible to the buret containing the base. At this point the pH meter should be calibrated with a buffer of pH 7.0.
Place the beaker with the standard KHP on the stirring motor and add a magnet to the beaker. Immerse the electrodes into the solution being careful not to strike the electrode tip with the spinning magnet. Begin the titration with a small addition of the base to the beaker and read the pH. Record the results and continue the titration as above. When the pH change to volume added begins to rise, reduce the volume of the additions so that the end point can be determined easily by graphic methods. Titrate to at least a pH of 11.0. When finished, rinse the electrodes and place them in a beaker containing distilled water or buffer until the next titration of the unknown.

Proceed with the unknown phosphoric acid titration by pipeting 25ml of the unknown into a 400ml beaker and add the magnet. Place the beaker on the stirring motor and begin the titration as before. Again titrate through the two end points being careful to obtain data points so that the graph will give a good representation of the end points.

Clean up the glassware and store the electrodes properly. Turn the pH meter to standby and leave it for the next student.

Solutions:

2 g of NaOH dissolved in 500 ml distilled H_2O

Requirements for report

Graph your results and report the concentration of the unknown in moles per liter. Follow the established guidelines for report writing.

SPECIFIC ION ANALYSIS

In the present age of technological advances, it is now possible to use a pH meter along with a specific ion or gas sensing electrode to determine trace concentrations of sought after analyte.

The typical electrode system consists of a sealed tube containing either a standard solution or gel with a specific electrolyte and some type of half cell that is compatible with the electrolyte. Since the electrode consists of a basic half cell and the analyte system, in general, constitutes a concentration cell with the nonreacting reference electrode as the other component in the system, we are in fact working with the Nernst Equation for a concentration difference.

$$E = \text{constant} + \frac{RT}{F} \ln[\ (Cl^-)int\ /\ (Cl^-)ext\ ] \qquad (1)$$

The pH meter or potentiometer just reads the E value for our compared system. The constant includes all of the incorporated values such as liquid junction potential, reference electrode, internal junction potentials, etc.

The system utilized in the following experiment consists of a liquid type chloride sensing electrode working in the concentration range of 10^{-1} to 10^{-5}M versus a double junction reference electrode. These electrodes are highly susceptible to contamination, therefore, they must <u>never be touched by your fingers</u>.

A - Chloride Analysis

<u>Procedure</u>:
[Due to the sensitivity of the electrodes, all of the solutions must be prepared in deionized water and all glassware thoroughly cleaned and rinsed with deionized water.]

Chloride Analysis: Prepare the following solutions : Ionic Strength Adjustor (ISA) to keep a constant ionic background for samples of 0.1M total ionic strength. Prepare 5M $NaNO_3$ by dissolving 42.5g of reagent in 100ml of deionized water, 2ml of this solution will be added to each 100ml of sample.
Standard Chloride is prepared by placing 1.6500g of reagent NaCl in a 1-L volumetric flask and diluting to the mark. This is a 1000 ppm standard to be used in the calibration curve and checking the electrode performance.

Electrode Check: When the electrode is ready then connect the reference electrode and the sensing electrode into the appropriate jacks. Place 100 ml of deionized water and 2 ml of ISA in a 250 ml beaker. Turn the switch to mV position with the electrodes in the solution and pipet 1 ml of the standard into the beaker, mix well and take the reading. Next add 10 ml of the standard, stir thoroughly and again take the reading in mV. The difference between the readings should be 53 to 59 mV at a temperature of 20-25°C. If the reading is not in this range there is a problem, check with the instructor.

Experimental Procedure: Prepare by serial dilution, standards of 1000, 100 and 10 ppm for measurement. To each 100 ml of the standard dilutions add 2 ml of ISA before the final dilution then make up to volume. Now take the mid-range standard (100 ppm) and place the electrodes in the solution and switch to REL MV (relative millivolts). Set the meter to 000.0 using the calibration control. If it will not zero just record the millivolt reading and proceed. Rinse the electrodes and blot dry then place in 1000 ppm solution, stir thoroughly, wait for a stable reading and record. Again rinse, blot dry and place in the 10 ppm standard and repeat the procedure. Finally, using a 50 to 100 ml aliquot add 2 ml of ISA per 100 ml of sample and measure the mV as before .
Taking the values for the two standards plot the millivolts reading on the linear axis of semi-log paper and the concentration on the log axis. Place the mV reading of the unknown on the proper axis and convert the reading to concentration.

B - **Fluoride Analysis**:
Procedure: Using equipment for this experiment as designated by your instructor, complete the following directions.
This analysis uses a research grade instrument to determine the potential developed by the change in concentration of the fluoride ion. Arrange the electrodes as described in the instruction manual(Fluoride electrode to **Asense** and the reference electrode to **Aref**) Be sure the **B** settings are shorted with a strap. Immerse the electrodes in a few mls of distilled water.
Using a graduated cylinder, place 100 ml of the 1 ppm standard in a 150 ml beaker and add a teflon coated stirring bar. Transfer the electrodes after blotting with tissue, to the solution. Turn the meter mode switch to **concn** and set the std value to 1.00 and the slope switch to -56.00. Press the **Clear/Read** switch and allow the signal to stabilize, then press the **set concn** button.
Next, transfer 100 ml of the 10 ppm standard to a clean 150 ml beaker and again set the electrodes into the solution. Stir until a stable response is obtained. Now adjust the slope switch to 10.00 ppm.
Prepare the unknown by weighing out 1.000 g of fluoride containing toothpaste and transferring it to a Nalgene beaker with 30 ml of distilled water. Stir the unknown solution swith a stirring motor and bar for two minutes, then transfer to a 100 ml Volumetric flask and rinse the beaker with 50 ml of ISA (ionic strength adjusting) solution (TISAB II) #940909 and dilute to 100 ml with distilled water. Place the solution into a beaker and after blotting the electrodes, immerse them into the solution. Stir and take the reading when it stabilizes. When finished dry the electrodes and place them in a little distilled water until the next operator is ready or ask the instructor for further instructions.

C - Sodium Analysis

Experimental Procedure: Using equipment as prescribed by the instructor proceed as directed in the following section.

Prepare the standard solutions by placing 100 ml of the 100 ppm standard sodium stock solution in a 250 ml beaker and add 2 ml of the proper ISA solution and a clean stirring bar. Next add 100 ml of the 10 ppm sodium standard and 2 ml of the ISA and a stirring bar to another clean beaker. Now place 100 ml of the unknown (a soft drink) to be analyzed in another 250 ml beaker, add the ISA and the stirring bar. The following is the procedure for the analysis using the functions on the equipment you have been assigned.

Rinse the electrodes in the electrode rinse solution made by diluting 20 ml of ISA to 1 L and place them in the 10.0 ppm standard. Stir with the magnetic stirrer. Turn the **Mode** switch to **CONCN** and set the **STD VALUE** switch to 10.0 and the **SLOPE** switch to -56.00 with the sign switch at plus. If the **SET BLANK** switch is on press to turn it off. Press the **CLEAR/READ MV** and wait until a stable reading is noted and then press the **SET CONCN** switch to set.

Rinse the electrodes with rinsing solution and set them into the 100 ppm standard, stir, and wait for a stable reading. Adjust the **STD VALUE** switch until 100.0 is displayed. Now after rinsing with the rinse solution place the electrodes into the unknown soft drink. Stir and when a stable reading is obtained, record the reading directly as ppm sodium.

When the analysis is complete, store the electrodes in the proper storage solution for the next analysis.

Requirements for report

Follow the established guidelines for report writing and include the graphical determination of your analysis.

[Reference: **Fundamentals of Analytical Chemistry** by Skoog and West, Saunders College Publishing, pg 396-420]

VOLUMETRIC DETERMINATION OF IRON BY OXIDATION-REDUCTION

Cerium(IV) is a very good oxidizing agent when used in acidic solution. It is monovalent in its oxidation change so the reagent forms a monoequivalent relationship to its reductant. This makes calculations of results easier to manage and the reaction proceeds quickly to completion. Also, its hazard to the environment is low in comparison to some other oxidizing agents such as dichromate ion. The formal potential for a 1 M solution in sulfuric acid is +1.61V and thus the potentiometric titration of the Ce(IV)-Ce(III) couple proceeds from a starting potential to a more positive mV potential. It is not important where the first potential reading is as long as it is stable and there is adequate potential expansion left to complete the titration.

The Fe(II)-Fe(III) couple being titrated is only stable in acid media and must be made up in sulfuric acid also to eliminate any oxidation-reduction reactions that may compete with the cerium-iron reaction. This reaction can be done by either the use of a redox indicator or by potentiometric method.

$$Fe(II) + Ce(IV) = Fe(III) + Ce(III)$$

Procedure

As this reaction takes place in sulfuric acid solution, the precautions for handling acids are to be reviewed. Also, the directions for this experiment are given for the potentiometric method, but the use of ferroin indicator or barium benzenesulfonate indicator allows for a simple volume-volume titration.
Prepare the solution of Ce(IV) as described in the section on solutions. The cerium solution is then standardized against a weighed quantity of ferrous ammonium sulfate (Mohr's salt) using a platinum electrode versus a glass electrode attached to a pH meter. The preparation of the Mohr's salt is decribed in the solutions section

Place the standard in a 400ml beaker on a stirring motor and add a magnet to the beaker. With slow agitation and the electrodes immersed in the solution, turn the mode selector switch on the pH meter to mV and record the reading,(it is not important what it is just that you know where you started and that its stable).

Now place the Ce(IV) solution in a buret so that you can make 1ml additions to the beaker and wait until the meter stabilizes and record the reading. Continue adding increments of Ce(IV) to the beaker carefully, but do not rinse the tip of the buret with distilled water. When a small addition of the Ce(IV) causes the meter reading to jump, reduce the additions to 0.1ml or drops to collect the maximum data points during this part of the titration. When further addition of small increments of titrant seem to cause no change in the mV reading, the titration is completed.

Repeat this determination with your unknown Mohr's salt following the same directions for preparation of the unknown salt and titration as you followed for the standardization. Plot both the standardization and the unknown titration using mV versus volume and determine the end points.

Using the value from the standardization, calculate the iron content of the unknown.

Clean up the electrodes by rinsing with distilled water and immerse them in a beaker of distilled water for the next analysis .

Solutions: Dissolve 63.0g of $(NH_4)_4Ce(SO_4)_4 \cdot 2H_2O$ in a solution of 28ml of conc. sulfuric acid in about 500ml of water and then dilute to 1 L.
Standardize with 1.2000g of $Fe(NH_4)_2(SO_4)_2 \cdot 6H_2O$ dissolved in 30ml of 0.5M sulfuric acid.

Requirements for report

Follow the established guidelines for report writing and report your concentration values.

[Reference: **Quantitative Analysis Lab Manual**by Day and Underwood p76-80]

SPECIFIC ION HALIDE ANALYSIS

A metal electrode placed in a solution of its ions will have a tendency to lose electrons and go into solution. There is an opposing tendency for the ions in solution to gain electrons and deposit on the metal surface. The potential which results will depend on the particular metal and the concentration of the ions in solution. Since the potential is a function of metal ion concentration, the concentration of the metal ion may be followed potentiometrically in a precipitation titration.

A silver electrode will be used in this experiment to follow the concentration of the silver ion in the titration of silver nitrate with potassium iodide. The reference electrode is the calomel electrode and ammonia will be used to prevent the precipitation of silver chloride. Chloride ions are introduced into the solution by diffusion from the calomel electrode.

The silver electrode has a relatively low resistance. A potentiometer could be used for measurement of the electrode potential, but a pH meter will be used in this experiment. The voltage measurements in the experiment will only be relative since the pH meter will not be standardized against silver solutions of known concentration. These potential measurements will have no meaning compared to the E° value for the system.

It is possible to replace the reference electrode with a glass electrode since the readings we will be using are only relative.

$$Ag^{+} + X^{-} == AgX_{(s)}$$

Procedure

Meter preparation: Obtain a pH meter that reads in mV and connect a silver billet electrode to the sensing jack and a glass electrode to the reference jack. [A calomel may also be used but may introduce a slight error in the analysis]. Immerse the electrodes in distilled water and turn the meter to **standby**. Allow it to warm up for a few minutes while you prepare the solutions for analysis.

Analysis of a silver containing unknown is done as follows: Standardize a 0.1 M KI solution by preparing 200 ml of silver nitrate of 0.1000M concentration and transfer by pipet 25.00 ml of the solution to a 250 ml beaker. Add 5 ml of concentrated ammonia and a stirring bar to the beaker. Lower the rinsed electrodes into the ammoniacal solution and adjust the stirrer to moderate speed.

Set the meter to read the potential in mV and record the first reading when stable. Begin to add the 0.1M KI solution prepared by dissolving about 16 g of dried reagent grade KI per liter of titrant. Record the potential and the volume after each addition. Continue this process until there is no appreciable change in potentialwith a new addition. At this point, the titration is complete. Calculate the concentration of the KI solution by plotting the potential versus the volume and relating it to the molarity of the silver nitrate solution.

Now dissolve the unknown in 5 ml of 6M nitric acid. If necessary, add small amounts of acid to complete the dissolution of the sample. Next, carefully neutralize the solution with concentrated ammonia and then add 5 ml in excess. Dilute the solution with 25 ml of distilled water and repeat the analysis as above.

B. Analysis of a halide containing unknown is done as follows. Prepare a solution of the unknown by dissolving it in 25 ml of distilled, deionized water and add 5 ml of concentrated ammonia. Place the silver nitrate solution in the buret and proceed as above with the pH meter and the electrodes. Continue the titration until the potential does not change with volume addition and then determine the concentration of the halogen in the unknown by plotting the potential versus volume of silver nitrate and relating it to the molarity of the silver nitrate titrant.

When finished, rinse the electrodes with distilled water and allow them to stand in a beaker of distilled water. Turn the meter to standby and wash all glassware used in the experiment.

Requirements for report

Follow the established report writine guidelines and report your concentration of halide, including graphs.

Questions

1.Does the presence of ammonia introduce any error by dissolving the silver iodide precipitate? Use 1.0×10^{-16} for the Ksp of AgI and 1.0 M for the concentration of the ammonia, where Ki for $Ag(NH_3)_2^+$ equals 7.0×10^{-8}.

[Reference: **Fundementals of Analytical Chemistry** by Skoog and West pages 178-190]

IODOMETRIC GLYCOL DETERMINATION

Organic molecules containing oxygen are sometimes susceptible to further oxidation in a stoichiometric system that allows for quantitative analysis.

Solutions containing ethylene glycol are examples of this technique when attacked by the periodate ion. By this method, an excess of standard periodate ion is added to a known volume of a sample and allowed to react with the ethylene glycol on a one to one basis. This is done in a slightly acidic media. The solution is then made basic with sodium bicarbonate. Potassium iodide is added to react with the remaining periodate. The tri-iodide ion that is generated is then titrated with standard sodium thiosulfate. The difference is equated to the glycol content in the sample.

$$CH_2OHCH_2OH + IO_4^- = 2H_2CO + IO_3^- + H_2O$$

$$IO_4^- + H^+ + 3I^- = I_3^- + IO_3^- + 3H_2O$$

Procedure

. Place a 10ml aliquot of the unknown ethylene glycol(anti-freeze) into a 250ml Erlenmeyer flask. To the flask pipet 10ml of the standard 0.2N sodium metaperiodate into each sample and set aside for twelve minutes. At the end of this time, transfer the solution to the coulometric flask with rinsings and add 5g of sodium bicarbonate. When the bicarbonate has dissolved, add 2g of potassium iodide and allow this to dissolve. Now pipet 25ml of the standard sodium thiosulfate into the reaction flask and when the color has disappeared, add 5ml of the starch indicator.

You are now ready to begin the coulometric titration. Record the time and milliamperes until you see the first perceptable color that stays in the solution for ten seconds. Record the time.

Based on the milliamps and the time in seconds and the value for a Faraday, determine the unreacted periodate. Next, calculate the periodate that reacted with the ethylene glycol. On a one to one basis, calculate the weight of the glycol in the original sample as a weight per volume percentage, also, calculate the weight per liter.

Solutions: 0.2N $NaIO_4$ (106.96g/eq)
0.1N $Na_2S_2O_3$-$5H_2O$
5.0g $NaHCO_3$ per sample
2.0g KI per sample
Starch indicator (1.0g per 100ml boiling H_2O)

Requirements for report

Follow the established guidelines for report writing and include a table of your data for the titration.

[Reference: **Analytical Chemistry Practice** by J. Kennedy page 93, and **Chemical Separations and Measurements** by Peters, Hayes,et.al. p334-7]

Polarimetry- Refractrometry
Determination of Sucrose in Syrup

The purpose of this experiment is to show how analyses may frequently be performed by use of physical properties which have specific rather than general applicability. Sucrose solutions can be analyzed by measurement of the index of refraction or by the rotation of plane polarized light. Either method will give precision with solutions of pure sugar in water. If the solutions contain other carbohydrates along with the sucrose, either or both of the porperties may be altered. All carbohydrates affect the refractive index to approximately the same degree, but the specific rotation is highly unique, being zero in some cases and either positive or negative with other substances.

We shall use a standard polarimeter and an Abbe' refractometer. The theory and description of these instruments are found in their respective manuals or in most references such as the **CHEMICAL TECHNICIAN HANDBOOK**. To calculate the specific rotation, we must know the density of the solution. This will be determined as a function of the refractive index of our solution from a table of specific gravities.

Procedure

Prepare a series of standards by making solutions of 7.500g, 10.000g and 20.000g of sucrose per 100 ml of solution. Next place 25 ml of the unknown sugar solution in a preweighed weighing bottle, seal the bottle and weigh.(Use a pipet to determine the 25 ml volume). Transfer the unknown solution to a 100 ml volumetric flask, rinsing the weighing bottle frequently with distilled water and adding this to the flask. Add one drop of concentrated ammonia and dilute to the mark. Now determine both the refractive index and the optical rotation(a) of each of the solutions. Record the temperature and determine the percent sucrose by weight(p) from the table referred to in the following references. Using the value (p), determine the specific gravity (s) from the next table referenced. Now using the values of p and s and the length of the tube in decimeters(d) plus the observed rotation(a) calculate the specific rotation $[a]_D$ from the equation:

$$[a]_D = 100\ a/dps$$

Using the specific rotation, compute the % sucrose by weight for the unknown. Also, compare the result with the value determined by the refractive index for (p) for the unknown and estimate the difference in carbohydrate content.

Requirements for report

Follow the established guidelines for report writing and include your calibration graphs.

[References: **Optical Methods of Chemical Analysis** by T.R.P.Gibb Jr., Chap 7 & 8]
Tables: D-261 **CRC HANDBOOK**
E-248 **CRC HANDBOOK**

GEL PERMEATION CHROMATOGRAPHY
SIZE EXCLUSION CHROMATOGRAPHY

Gel permeation or size exclusion chromatography has been used by the analyst to estimate molecular weight. The principle of GPC is based on the fact that large molecules are excluded from a network of pores in the separating column and thus flow directly through the column to the detection device. As the size of the particle decreases it is entrapped more effectively in the pores of the column and therefore take longer to elute. There is a linear correlation between the elution volume (V_e) and the Log Mw. If the column packing has the ability to fractionate the molecules and you have reliable reference standards you would be able to determine the molecular weight of an unknown polymeric sample.

The ability of this method to differentiate varying molecular weights depends on the exclusion limit of the stationary phase (the smallest particle which is too large to enter the pores of the stationary phase) and the relationship of the standards to the unknown.

There are some deviations from the differentiation, if the standards are linear molecules and the polymer is a branched molecule, it is difficult to correlate the elution volumes to the same molecular weights.

Another problem with separations of molecular weights is those particles with molecular weights below the minimum pore size would all be retained and elute together as the stationary phase volume V_s.

The above facts can be used to obtain some very useful information about the column and predicting the elution times for some of the polymers. Using the equation:

$$V_r = V_m + KV_s$$

where V_m = void volume - elution time of a nonheld standard or known

K = distribution coefficient of the molecules between the mobile phase and the stationary phase.

V_s = stationary phase volume - retention time of a totally retained molecule.

$V_r = V_e$ = retention volume of the species

and with retention volume (flowrate {ml/min} times time{min}) we can relate V_r to Log Mw.

Both V_r and K are necessary to the evaluation of columns. V_r helps determine the range of molecular weights the column will isolate and K helps in determining the efficiency of the method being used. It may suggest a slight change in the solvent for better mobility in the column or for more retention on the column packing.

There are other factors that can be determined also with further information but for this experiment we will look only at the molecular weight distribution for an unknown polymer.

Procedure

All samples and unknowns must be water soluble for this experiment. They must also be filtered after preparation and before injection into the GPC columns.

The order of events for this experiment starts with the optimization and calibration of the equipment.

1. Prepare the mobile phase as per instruction by the teacher. The solution must be pure so all glassware and utensils are to be cleaned and dried. Before the addition of the mobile phase to the reservoir, it should be rinsed thoroughly with the filtered solution. The mobile phase should be filtered through a 0.5micron filter to eliminate any contaminants and to degass the solvent. The filtering is done with vacuum and stirring.

2. The next portion requires the attachment of the solvent reservoir to the pump and then start up of the instrument. Before any of the solvent is passed through the columns, it must be checked for any air bubbles in the line. If there are bubbles and they get to the detector cell there will be irratic responses on the recorder and will lead to erroneous results. The bubbles are removed by opening the bleed valve and pumping solvent until no bubbles appear. When this has been accomplished the valve is closed and the solvent is pumped through the system. The flow rate that was selected is now checked with a volumetric flask and a stopwatch.{Flowrate is usually set at 1.0 ml/min.} After the flowrate is known, the recorder baseline is adjusted until a flat stable response is obtained. It is now ready to inject the standards and unknown.

3. All of the standards and unknown are made at a 0.5% concentration(0.05g/10ml) level. They are first weighed and then dissolved in the mobile phase solvent. Then they are filtered with a 0.5 micron disposable filter. When preparation is complete the sample and standards are injected sequentially from the highest molecular weight to the lowest, thus there will be no interferring co-elution of the standards and the unknown sample. The unknown may be run separately, but not on differing laboratory periods.(Why?)

4. Using the data generated from the recorder and the flowrate you will now calculate the retention volumes of all the standards and plot them versus the Log Mw (molecular weight). Then using the graph of this plot determine the Mw of the unknown polymer. It will also be necessary to know the void volume and the pore volume to calculate the K value for your polymer.

Requirements for report

Follow the established guidelines for report writing and include your calculations and graphs where appropriate.

[Reference: **"Pratical Liquid Chromatography** by Yost, et.al. and pages 743-67 from your C.T.R.R.H.]

DIFFERENTIAL SCANNING CALORIMETRY

Changes that are accompanied by corresponding changes in the heat content of a compound can be monitored on the differential scanning calorimeter(DSC). There may be changes in temperature due to the melting energy of the crystal lattice, or the softening of a plastic material during the glass transition. There may also be an energy change when a hydrate converts to the anhydrous form and so on. Knowledge of these changes is important for the chemist and the manufacturer because it can lead to continued good products and prevent problems in the manufacturing process.

The DSC uses a closely controlled programmed temperature on a sample and a reference. When there is a transition in the sample there is heat added or subtracted to maintain a constant temperature relation between the reference and sample. The energy that is absorbed or evolved is directly equivalent to the heat the instrument maintains and we can obtain direct calorimetric information.
The glass transition and melting points are physical properties that can be used to identify and monitor polymeric reactions and the DSC is used for this purpose. A compound such as polyethylene would have a melting temperature of Tm = 110-130°C where as polystyrene has a Tg = 100°C. The properties relating to these two different temperatures are the polyethylene would be hard-wax like and strong and the polystyrene would be an amorphous hard material. This type of information can be obtained and used through out the polymer industry.

Procedure

The first part of your experiment is to acquaint yourself with the DSC. With the help of the instructor set the parameters of the instrument to obtain the information you will need. Next run a calibration using the indium sample already prepared in the machine. [Be sure to have a flow of nitrogen gas for all of your analysis]. When this is done, weigh out about 10 mg of your polymer and obtain a trial run. You can reset whatever parameters you will need. Rerun your sample or a new sample. When you have obtained the graph of the run and the needed data consult with your instructor.
[Techniques: Weighing procedures- operation of the DSC- graphical methods].

Requirements for report

Follow the established guidelines for report writing and include your plot of the temperature runs made.

COULOMETRIC TITRATION

It is documented that using an anodic generation of triiodide ion can be used for coulometric titration. By use of the back titration method, the concentration of an oxidant can be determined. A sample such as household bleach or the hypochlorite ion can be determined by such a technique. The starch/iodine end point is reached as the titration comes to completion. The experiment is started by adding an excess of standard sodium thiosulfate and then an aliquot of the bleach. The excess thiosulfate is then determined by coulometric generation of triiodide at the anode. The equations for this reaction are as follows:

$$OCl^- + 3I^- + 2H_3O^+ = Cl^- + I_3^- + 3H_2O$$

$$2S_2O_3^{-2} + I_3^- = 3I^- + S_4O_6^{-2}$$

At the end point, the meq of oxidant are equal to the meq of reductant or the sum of the meq of bleach plus the meq of triiodide are equal to the meq of the thiosulfate. Since the thiosulfate concentration is known and the triiodide concentration is known the bleach can be easily calculated.

Procedure

Place a 5ml aliquot of the bleach into a 250ml volumetric flask and dilute to the mark. This will be your unknown sample for the analysis.

The electrodes for the titration are cleaned with warm 6M nitric acid for a few minutes and then placed into the circuit. The anode will be connected to the positive terminal and the cathode will be at the negative terminal. The current used for this analysis should be about 50mA.

Place the two electrodes into the two arms of the reaction vessel. Place a stirring bar into the reaction vessel through the center neck and place the flask over the stirring motor. Next, add the KI solution made by dissolving 3g of KI in 100ml of distilled water and 10ml of gl. acetic acid and 1ml of starch solution[this should be fresh]. The volume should cover the electrode surface. Start the stirring motor and turn on the switch until a faint blue tinge persists in the solution.

Next, transfer 5ml of the thiosulfate by volumetric pipet to the electrolysis cell and standardize it with the cell until the same blue color is observed. Note the times and then add a 5ml aliquot of the bleach and another aliquot of the thiosulfate. Titrate to the end point as before.

The procedure can be repeated without changing the solution in the cell until the volume prohibits further additions.

Be careful of the speed of the stirrer, because a vortex will bring oxygen into the flask from the air and could cause some error in the analysis.

Calculate the normality of the thiosulfate from the first titration and then calculate the concentration of the bleach. Report the results as the percent sodium hypochlorite by weight in the original bleach solution.

Solutions:
[The thiosulfate is prepared by dissolving 5g of the sodium thiosulfate pentahydrate in 1 liter of freshly boiled water and 0.1g of sodium carbonate.]

Requirements for report

Follow the established guidelines for report writing and report the concentration of the unknown bleach.

[Reference: **Analytical Chemistry Practice** by J. Kennedy, Harcourt, Brace Jovanovich, Publishers]