RECITATION NOTES FOR EXPERIMENT # 13

# PREPARATION OF ISOPENTYL ACETATE (BANANA OIL)

*Have your lab textbook available for quick reference to specific pages, indicated in **red**.*

## LEARNING OBJECTIVES

This experiment is intended to illustrate the following concepts and techniques:

- Heating under **reflux**
- Theory, technique, and use of **simple distillation**
- **Boiling point determination** techniques
- **Microscale assembly** of a simple distillation apparatus

This manuscript will refer you to the following pages and figures from your textbook. You may want to mark them beforehand.

- **p. 600 – 603, section 7.2 and the following figures:**
  - Fig. 7.6 – *Reflux apparatus*
  - Fig. 7.7 – *Reflux ring*
  - Fig. 7.8B – *Microscale magnetic spin vane*
- **p. 694 – 696, section 13.1 and 13.2 and the following figure:**
  - Fig. 13.3 – *Macroscale method of determining the boiling point*
- **p. 703 – 710, and the following figures:**
  - Fig. 14.2 – *Three types of temperature behaviour during a simple distillation*
  - Fig. 14.4 – *The Hickman head*
  - Fig. 14.5 – *Microscale distillation apparatus*
  - Fig. 14.6 – *Removing the distillate from the Hickman head*
- **p. 103 – 108 (exp. 13)**

## INTRODUCTION

This is the first experiment in this course that involves a chemical reaction rather than a physical operation. You are expected to include the chemical equation in your lab report, including the amounts of starting materials used (in grams and moles). Please refer to the manuscript *Guidelines for Writing Lab Reports* for examples.

## HEATING UNDER REFLUX

Running organic reactions is a lot like cooking. There are periods when you should heat “the soup” in the pot, covered with a lid, for long periods. If you use a crock pot with a glass lid, you’ll be able to see the following process very clearly (refer to the picture below). Water boils and evaporates by the action of heat, but the lid keeps it from escaping into the atmosphere. Since the lid is usually cooler than the bottom of the pot, and the concentration of vapor is very high at the top, water condenses on the lid wall and falls back into the pot. This state of dynamic equilibrium prevents large losses of water while allowing time for the vegetables and spices to cook for as long as needed (getting hungry yet?).

According to the *Webster's* college dictionary, the word **reflux** comes from the Latin *refluxus*, meaning "**a flowing back**." The reflux process in chemistry is similar to that taking place in the crock pot. After mixing the "ingredients" (starting materials) in a reaction flask, the solvent is allowed to boil for a period of time until the reaction is "done." The difference is that instead of using a lid to keep the solvent from escaping into the atmosphere, a condenser is used. The condenser cools the solvent vapor and causes it to revert back to liquid. The liquid then falls back into the reaction flask, or "cooking pot." A typical microscale reflux apparatus is shown in **fig. 7.6, p. 601** of your textbook. In the lab we'll use this same apparatus, but will substitute a sand bath for the aluminum block.

**Page 602** gives some guidelines for efficient refluxing. First, the **rate of heating** should be adjusted in a manner similar to the way you do it when you cook soup. First, you bring the temperature to a high setting just to start the water boiling. Once it's boiling, you lower the temperature to a minimum, just enough to keep the water boiling (simmering). Likewise, in a reaction which calls for reflux, you bring the temperature to a high value first, to get the solvent boiling. Then you lower the temperature to the minimum value that will sustain the boiling process.

The formation of a "**reflux ring**" (**fig. 7.7**) is a good way to monitor the rate of heating. An indication that you are about to form a reflux ring is the formation of liquid droplets above the boiling liquid that look like sweat. As the droplets become more numerous, a well defined borderline forms where the vapor condenses, resulting in a "reflux ring." The ring will not form unless the solvent is boiling at a steady rate and not too fast. The point at which the rate of evaporation equals the rate of condensation determines is the ideal rate of heating.

**Fig. 7.8 B on p. 603** shows a microscale magnetic spin vane, which is used to stir liquids. **Stirring is very important to avoid** "**bumping**" **any time a liquid is heated**. In the event that a magnetic spin vane is not available, use boiling stones, or a boiling (wooden) stick. If you heat a liquid without stirring it can bump, which can result in accidents such as burns. If you use a magnetic spin vane, **the reaction flask must be positioned in the center of the hot plate/stirrer**. If it's not, stirring will be difficult, erratic, or even impossible.

## THE BOILING POINT

The definition of boiling point is given on **p. 694**. **The boiling point is the temperature at which the vapor pressure of the liquid equals the external pressure**. In an open system, like in most laboratory setups, the external temperature is the atmospheric pressure. The **normal boiling point** is defined for an external pressure of **1 atm, or 760 mm Hg**.

The above also means that the boiling point of a substance under vacuum is lower than the boiling point of the same substance in an open system. For example if diethyl ether, which has a normal boiling point of 35-36$^{o}$C, is exposed to vacuum, it can boil at room temperature. A system under vacuum is sometimes said to be under **reduced pressure**.

**Fig. 13.3 on p. 696** shows **the method that will be used in the lab for determining boiling point**. The student takes a small test tube, about the size of an average little (or "pinky") finger. Place about 1 mL of liquid in the test tube and start heating. When the liquid boils and a reflux ring forms above it, insert the thermometer **deep enough for the tip to be inside the refluxing vapor, but without touching the boiling liquid**. Allow for temperature stabilization. When the temperature reading becomes constant, record the boiling point.

## THE TECHNIQUE OF SIMPLE DISTILLATION

Technique 14 on **p. 703** defines distillation. This process is much like reflux, but instead of allowing the condensing liquid to fall back into the same pot, it is routed into a separate container and collected. This technique is useful for separating liquid mixtures when the components have different boiling points. There are different types of distillation for different purposes. **Simple distillation is used to separate liquids whose boiling points are at least 100 degrees apart**.

**Fig. 14.2 on p. 705** shows the behaviour of three different liquid mixtures during a simple distillation. **Panel A** is straightforward: a pure liquid boils at constant temperature during the distillation. The temperature stays at the boiling point of the liquid without any variations over time until all the liquid has evaporated.

**Panel B** shows the behaviour of a mixture of two liquids whose boiling points are less than 100$^{o}$C apart. At first, the mixture boils at the boiling point of the lowest boiling component, but the temperature increases gradually until it reaches the boiling point of the highest boiling component. The vapors coming out of this mixture always contain the two components in varying proportions. Therefore the resulting distillate is very similar in composition to the original liquid, giving no effective separation.

**Panel C** shows the behaviour of a mixture of two liquids whose boiling points are 100$^{o}$C apart or more. At first, the mixture boils at the boiling point of the lowest boiling component, but the temperature **remains constant** until most of this component boils off. Then **the temperature increases sharply** until it reaches the boiling point of the highest boiling component. The vapors coming out during the first stage are therefore richer in the lowest boiling component, and the vapors coming out during the second stage are richer in the highest boiling component. This gives two distinct distillation fractions that can be collected in separate containers, resulting in efficient separation of the mixture.

**Fig. 14.5 on p. 708** shows a **microscale setup for simple distillation**. The only difference between this setup and the reflux apparatus is the presence of a **Hickman head** (**fig. 14.4, p. 707**), positioned between the boiling pot and the condenser. The drying tube at the top is optional. It is mostly intended for labs where hoods are not available, or for use in reactions where water is to be excluded. **A sand bath will be used instead of the aluminum block for heating**.

In order to make the distillation more efficient, **the boiling pot and the neck of the Hickman head can be loosely wrapped with two or three layers of aluminum foil**. This minimizes heat loss from the sand bath into the atmosphere. If you do this, take care **not to wrap the bulb of the Hickman head**, or the condensation process might be less efficient.

**The bulb of the Hickman head is a reservoir** where the condensate collects before it falls back into the boiling pot. When this reservoir is full, the distillate is drawn out with a Pasteur pipette (**fig. 14.6, p. 709**).

The next two pages give guidelines for setting up a simple distillation apparatus properly. **Have a copy handy when you first attempt this**, as will be the case in experiment 13.

**SETTING UP A SIMPLE DISTILLATION APPARATUS**
**AND AVOIDING COMMON PITFALLS**

USE THESE GUIDELINES THE FIRST TIME YOU SET UP A DISTILLATION APPARATUS
AND HAVE YOUR INSTRUCTOR PERFORM THE CHECK IN STEP 9.

1. First of all, **make sure the reaction vial is not chipped, starred, or cracked**. If it is, do not use it. Have the stockroom manager replace it. Next, mix the reactants in the reaction vial according to instructions, and you are ready to go. You should start the distillation at least one hour before the end of the lab session, or you will not have time to finish. If you are working in an afternoon section, remember the stockroom closes at 5 pm.

2. Set up a hot plate/stirrer near the sink inside the hood. Place a sand bath in the center of the plate and start heating by turning the heating knob to a setting of about 6. **It is important that the sand bath be in the center of the plate** for efficient stirring of the reaction mixture.

3. Attach the Hickman Head to your reaction vial, **making sure that there is an O-ring under the screw cap**. The O-ring should not be wrapped around the ground glass part of the joint, but just over it. The ground glass part should be free to sit inside the reaction vial and make a good seal. Make sure the connection is secure and tight. Students have lost their products because they did not use an O-ring, or it was in the wrong place, or the connection was loose.

4. Place a small clamp at the neck of the Hickman Head and attach the clamp to a solid support rod.

5. Lower the setup until the reaction vial is buried in the sand as much as possible, but without pressing too hard against the bottom. Do not use any aluminum foil at this point. **Make sure the setup is as upright as possible** and that it doesn't wiggle.

6. Attach a water-jacketed condenser **to the top of the Hickman Head**, again making sure the connection is secure. Do not use any more clamps. If your clamp is secure and the connections are tight, that should hold the entire setup in place.

7. Attach hoses to the condenser for water cooling, making sure that they are secure. Remember, water goes in at the bottom and out at the top. Open the water flow **to a little more than a trickle**. Do not open the faucet to full flow, or you will risk a flood.

8. Set the stirring speed knob to about mid range. The spin vane should spin freely without freezing or jumping. If either of these occurs, turn the knob to the off position and then try a lower setting. If your vial is centered on the plate, stirring should proceed without problems.

9. **Have your instructor check the setup**. The instructor will check that:

    a. All the ground glass connections are secure,
    b. The condenser is above the Hickman Head, and not the other way around,
    c. The reaction vial is centered on the plate as much as possible,
    d. The setup is solid and upright, and doesn't wiggle,
    e. Hoses are securely attached to the condenser and to the water outlet,
    f. The cooling water is set to flow as a trickle, not in full force,
    g. The spin vane stirs smoothly, without freezing or jumping, and
    h. The temperature knob is set to about 6.

10. Wait until the mixture starts to boil, then lower the temperature knob to about 5 (midrange). Make sure that the mixture is boiling steadily before proceeding with the next step. Make adjustments to the rate of heating as needed to keep the mixture boiling steadily.

11. Careful to not burn your fingers, **loosely** wrap two or three layers of aluminum foil around the reaction vial and the neck of the Hickman Head. **Do not cover the collecting reservoir** (the bulb part of the Hickman

head). The aluminum foil keeps the sand from losing heat to the atmosphere and allows for more efficient heating of the reaction vial. If you don't use foil, your distillation will take much longer, or it may not happen at all.

12. Notice that no mention has been made of thermometer use. You don't need to monitor the temperature anywhere at this point. As long as your mixture is boiling smoothly, **the temperature should remain constant at the boiling point of the lowest-boiling component of the mixture**. You will measure the boiling point at a later time.

13. If your setup is correctly assembled, you will observe some fogging inside the Hickman Head after about 10-15 min. of heating. Then the fogging will get thicker and turn into droplets. Finally liquid will start falling down into the collecting reservoir until it reaches a steady rate. At this point you are observing a successful simple distillation at work.

14. Because you're working with small amounts, consider yourself lucky if your reservoir fills up with distillate. You may stop heating as soon as you get a half to a full reservoir of product, depending on how you're doing with time. You may not have the time or enough material to go for a second fraction (which would be less pure anyway). Do not worry about yields. At this point we are more concerned with learning the technique than with maximizing yields.

15. If after 10-15 min. into boiling you notice that no distillate is coming out, or even fogging occurring on the walls of the Hickman head, remove the aluminum foil wrapping and check for the following potential trouble spots:

    a. **Is there still liquid inside the reaction vial and is it boiling?** If there is liquid but it is not boiling, move the temperature knob to the next higher setting and wait until boiling starts to resume the distillation. If there is no liquid, it is probably because of a leak in your system, as discussed next. In this case, stop the experiment immediately.
    b. **Is there a leak in the connection between the condenser and the reaction vial?**. If there is, it is probably due to either the absence of an O-ring, improper positioning of it, or a loose screw cap. Have your instructor check the setup and correct the situation. A leak can also happen if the rim of the reaction vial is chipped or cracked. In this case have the stockroom attendant replace the defective vial.

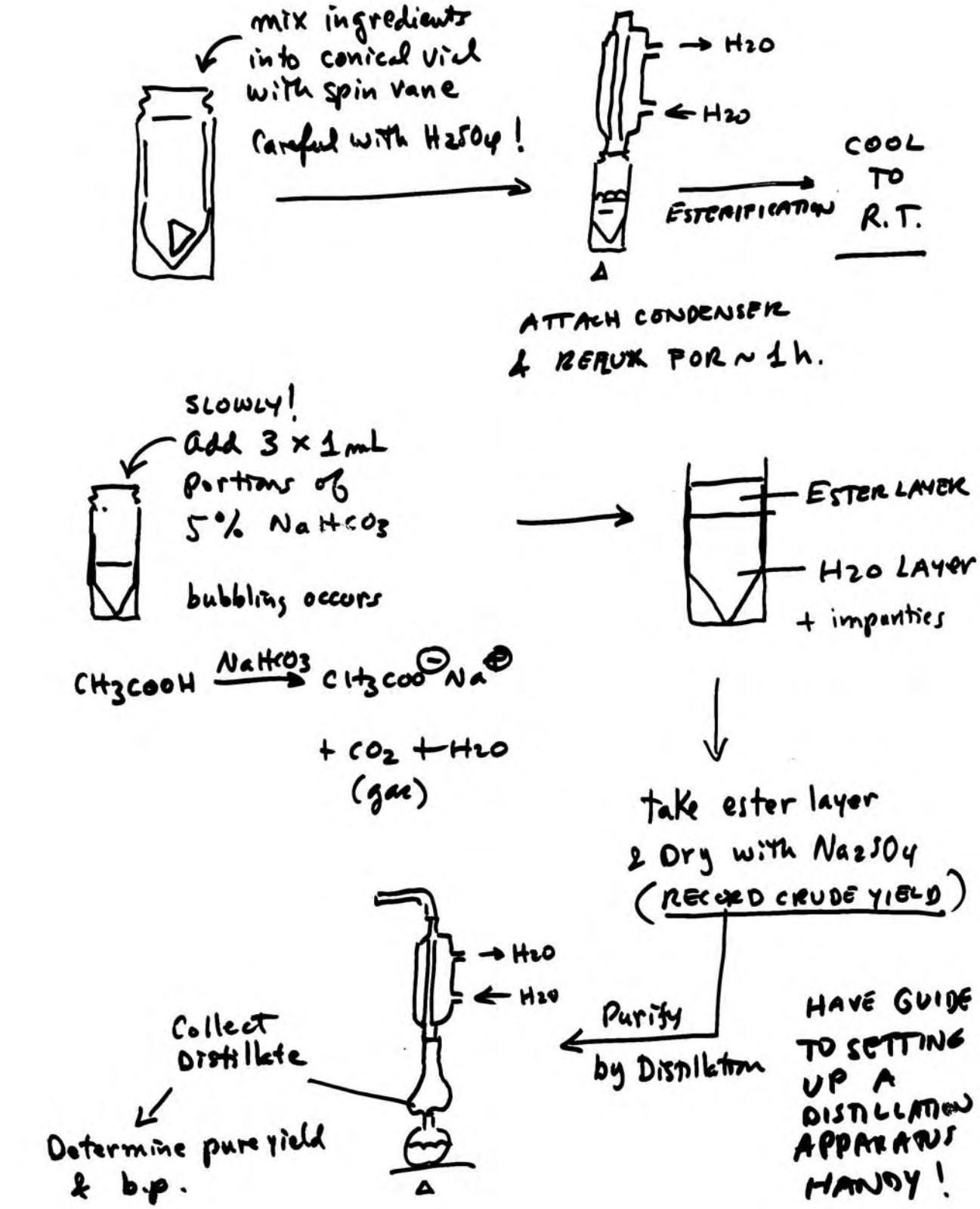
16. Transfer the distillate to a previously weighed container and record the yield. As an optional step, save a small amount of product (2 or 3 drops) in a sealed container for IR analysis in the upcoming week.

17. Measure the boiling point of the distillate using the technique previously discussed, with the setup shown in **fig. 13.3, on p.696**.

**PLEASE CONSULT WITH YOUR INSTRUCTOR IF YOU HAVE ANY QUESTIONS OR PROBLEMS.**

**FLOWCHART FOR EXP. 13**

Please refer to the textbook for details



**DETAIL OF REACTION POT WITH ALUMINUM FOIL SHIELD**
**TO SPEED UP THE DISTILLATION PROCESS**