

Vacuum Line Synthesis of a Boron Trifluoride Trimethyl Amine Adduct

Introduction

This laboratory will give you experience using a vacuum line (“Schlenk line”), a mercury U-tube manometer, and working with noxious gases. Boron trifluoride (BF_3) will be purified by trap-to-trap distillation under reduced pressure, and its adduct with trimethylamine (Me_3N) prepared. We will put the $PV = nRT$ relationship to good use. The Hg U-tube manometer will supply the “P” measurement, and you will use it along with a known amount of CO_2 to measure the various volumes in the system. With this information, you will know the number of moles of the two reactants, which controls the stoichiometry of the reaction you will run.

Before entering the lab, you should familiarize yourself with the use of vacuum line systems by reading the handout and references 1-3.

Equipment

- Vacuum rack in A105
- Mel-Temp melting point determination apparatus
- Thermo-Nicolet IR200 Fourier-transform infrared spectrometer with an attenuated total reflectance (ATR) head & PC data system
- Bruker AXR 500 MHz NMR

Some important definitions:

There are two types of vacuum valves in the system that come in two different types and each type appears in two different forms:

- 1) One form is the “L” or “T” shaped form where gas will enter the valve via the inlet tube and exit the valve at 90° via the outlet tube. In this configuration, the body of the valve runs parallel to inlet line. Such a configuration can be found in the reservoirs. None of the ground-glass valves are of this type.
- 2) The other form is a “straight through” or “+” form. The gas enters and exits in a straight line, but the valve body is perpendicular to the inlet/outlet lines (hence the “+”). There is only one valve of this type.

Please note these different configurations before starting the lab.

- 3) The primary valve-type used has a **Teflon- or glass-plug** with O-rings.
 - a) The two O-rings near the top of the plug keep atmosphere from leaking into the system, even when the valve plug is being turned to open or close it. **Do not open these valves so much that the back O-ring no longer seals.**
 - b) The O-ring at the bottom forms the internal seal when compressed between the 2-halves of the valve. **To close the valve you only have to close it just enough to cause the bottom O-ring to compress against the glass. You do not need to “honk” down hard to seal the valve shut.**
 - c) The O-rings have previously received a very light coat of lubricating grease and do not need any further attention by you.
- 4) The other valve type is a **ground-glass “high” vacuum valve**.

- a) The definition “high” in this case means that ground-glass plug is hollow and the back of the valve body has a “bulb” on it. The purpose of the hollow plug and the “bulb” is to reduce leaks. When the valve-plug is evacuated, outside atmosphere pushes passively on the glass plug, keeping it seated with more force. See the APPENDIX for more information about this valve type. You won’t have to manipulate one valve of this type in the rack.
- 5) There is an Hg U-tube manometer in the system that will be used to measure pressure in the “mm” range. However, you must exercise extreme caution using the system with this manometer in place. The common problem is that one side of the manometer is evacuated and closed and the other side is open to the system. When you let gas into the system, the Hg on the system side will go down and the Hg on the evacuated side will rise. **HOWEVER, if you let too much gas into the system, The Hg may go up to several hundred torr (mm Hg). That means that the “high-pressure” will cause the Hg on the other side to go up like a freight train.** Guess what boys & girls: the fast rising Hg column will slam into the top of the manometer with the same force as a freight train, and the result is often some form of broken glass, disconnected fitting and Hg spraying out in all directions (along with the glass shards). **We do not need this kind of display of Hg excitement.**

On the other hand, if you have both sides of the Hg manometer open to the manifold and you pressurize the line, nothing happens. Why? Because both sides of the manometer see the same pressure simultaneously. The key to using the system is **do not allow a sudden differential pressure to exist across one leg of the Hg manometer.**

Before you turn a valve:

- a. **Think!!**
- b. Be sure you know at all times which valves are open and where the gas will go.
- c. Look at the configuration of the various valves to confirm they are as you think they should be.
- d. Think again.

Finally, you will be working with noxious gases, and if you break the line toxic fumes (e.g., BF_3 , Me_3N) may exit the system (along with the flying glass and Hg).

Experimental

You MUST wear safety glasses at ALL times!

Preparation of the high-vacuum line:

- 1) Remember the hazards of working with a vacuum line, column of Hg and noxious gases. Approach this experiment with care and thought. Always think about which portions of the line are evacuated and which parts contain gases. Remember to support the stopcocks and turn them slowly and steadily. **Be careful** and **THINK**.
- 2) Be sure that the 2 reaction tubes and the calibration trap are properly attached to the rack and that clamps are holding the tubes tightly in place.
- 3) Note that during the following discussion that the BF_3 and Me_3N reservoir valves are **closed** and are to remain **closed**.

- 4) Valve **A** should be closed and will stay closed.
- 5) Valve **K** should be closed and will stay closed.
- 6) If valve **B** is **closed** and the rest of the rack is up to atmospheric pressure:
 - a) Check to make sure that both legs of the Hg manometer are connected to the manifold (valves **H, I, J** are open) and that the calibration trap **DD** is connected. Then you can **open B**.
- 7) Evacuate the line, opening one piece at a time from the manifold towards the far ends. Be careful that the Hg manometer legs have a common path. The pump will become silent when it is not pumping a load of gas, i.e. when it is “pulling against a vacuum.”
- 8) There is an electronic pressure gauge located off valve **C**. It should read <0.1 torr once a vacuum is achieved in the whole system. Now you have a *dynamic* vacuum: vacuum with the pump pumping the system. If the pressure does not go down sufficiently, begin closing off the system from the far end inward. Watch the gauge and see if it goes down. If so, you know where your leak is. Fix it.
- 9) Because we will use the manifold to move gases, we need a *static* vacuum in the manifold (i.e. with valve **B** closed).
 - a) Close **C** and watch the pressure. If the pressure rises, you have a leak at valve **C**—fix it.
 - b) Open **C**, and close **B** (all the other valves need to be open). Does the pressure remain low? If so, we are ready to go. If it rises, try to find the leak. Test for leaks by isolating all the valves but **C**.
 - c) Systematically check the other seals and valves throughout the line until you get a good static vacuum (valve **B** closed, valve **C** and the other valves open). You may need to clean (degrease with a Kimwipe and hexane) the attachment of the calibration trap **DD** using Apiezon M vacuum grease.
- 10) Take great care to keep the Hg manometer either evacuated or with both sides in common during this process.
- 11) When you think that the vacuum line is ready, have the instructor inspect the line.
- 12) *If you have not already done so*, you should now put liquid nitrogen (LN₂) in the cold trap **AA** at the outlet from the manifold to the pump.

Calibration of trap volume using CO₂:

To measure the volumes of the traps, a quantity of CO₂ at a known pressure and temperature, is placed into the calibration trap **DD**. The trap is weighed to determine the amount of gas in moles present. Using the ideal gas law, the volume of the calibration trap can be determined. Likewise, expanding this quantity of CO₂ into the other traps permits the determination of their volumes.

An important point to note is that the Hg manometer has volume and that volume is dependent upon the height of the Hg column connected to the sample side, i.e. valve **I**. **Therefore**, you must measure not only the difference in heights of the two sides of the Hg reservoir, but also the height of the left side *period*. The easiest thing to do is to record at the start of the lab (*right now*), the height in mm of the bottom of the bulb of the left side of the Hg manometer. The height is relative and is most simply defined as what the meter-stick scale says. Once you know the height of the bottom of the bulb, then you can calculate volumes in the left side as long as you always record the height of both the left and right sides of the Hg manometer

columns. The difference of the height of the left and right sides gives you the pressure in mm of Hg (on the left side because the right side will always be kept under vacuum). The difference of the height of the bottom of the bulb on the left side from the height of the Hg on the left side will give you the volume from the bottom of the bulb to the present Hg. *If this point does not make sense, try working an imaginary example through on paper. If it still does not make sense, ask your TA to explain.*

Notes: The i.d. of the Hg manometer glass tube is **3.8 mm**. The volume of the bulb on the left side of the Hg manometer is ~20 ml.

- 1) Confirm from the vacuum gauge that the whole system is evacuated and stable.
- 2) **Close J** to create the evacuated end of the manometer. *Note: if the Hg meniscus bows downward rather than sticks up, you have a leak in this part of the system.*
- 3) **Close D; E & G.**
- 4) Get the initial weight of the calibration trap:
 - a) **Close I.**
 - b) If you did not previously open **L**, then **open L** and wait until the vacuum gauge comes down to be sure you have a good vacuum in trap **DD**.
 - c) **Close L & H.**
 - d) Remove trap **DD**; degrease the joint completely, and weigh it on an analytical balance (to 0.1 mg).
 - e) Regrease the fitting, and place the trap back on the vacuum line.
 - f) **Open H**; wait for the vacuum in the manifold to return; **open L** and finally **I**.
- 5) Put CO₂ into trap **DD**:
 - a) Remove trap **BB** (valves **D & E** are **closed**).
 - b) Weigh trap **BB** (you will need this weight much later).
 - c) Place a piece of dry ice (obtain from the walk-in freezer on the 3rd floor) about the size of a lima bean in the reaction tube **BB**.
 - d) Reconnect **BB** to the vacuum line.
 - e) **Close H**, and then **open D** for ~15 sec. Note the pressure on the vacuum gauge. This step removes any air from the trap, leaving only CO₂ in the trap.
 - f) **Close D**, and wait for the pressure to fall.
 - g) **Open H & G**. Check for vacuum at the pressure gauge.
 - h) **Open E**, then **close H**. Monitor the pressure at the Hg manometer. When the pressure (read as the difference in the height of the Hg columns) is ~600 mm, **close G**, and open **D**. Record the pressure in the Hg manometer. **Close L**.
 - i) **Close D & E**. Remove trap **BB**, and remove the dry ice from the trap. Put the trap back on the line, and **open D & E**. Be sure the trap is clean and free of moisture. The pressure in the manifold should return to a vacuum. If it does not you may have to gently heat trap **BB** with a heat gun to remove residual moisture.
- 6) Measure trap volume **DD**:
 - a) **Close I**. Remove, degrease fitting, and weigh the calibration trap **DD** on an analytical balance. Calculate the amount of CO₂ in the trap as moles. The thermometer suspended

in the hood will give you the temperature. Calculate the trap volume in ml. *Note:* the ideal gas constant is $R = 6.24 \times 10^4$ torr $\text{cm}^3/\text{mole}^\circ\text{K}$, where 1 torr = 1 mm Hg.

- b) Regrease and replace the calibration trap **DD** on the vacuum line.
- 7) Measure the other volumes:
- a) Carefully **open H** (wait for vacuum to return) and **I**, then **close H** after vacuum has returned (again) in the manifold.
 - b) **Open L** (gently) to expand the CO_2 in trap **DD** into the volume enclosed by valves **G, H**, and the Hg manometer.
 - c) Record the heights of the Hg columns; calculate the pressure, and calculate the total volume.
 - d) Calculate the volume of the space from the bottom of the bulb to the present Hg height on the left side of the manometer. Subtract it from the "total volume".
 - e) Subtract the volume you measured for trap **DD**. Now you have the volume bounded by valves **G, H, L**, & **I** plus the volume from valve **I** to the bottom of the bulb on the left side of the Hg manometer. *Define this volume as volume XXX.*
 - f) **Close E & L.**
 - g) **Open G** to expand the CO_2 from volume **XXX** into trap **CC**. Record the Hg column heights and calculate the new volume.
 - h) Calculate the new dead volume from the bottom of the bulb to the top of the Hg level, and subtract from the new volume. Subtract volume **XXX**; now you have the volume bounded by valves **E, F & G** plus trap **CC**.
 - i) **Close D**; **open E** to expand the CO_2 into trap **BB**. Record the Hg heights, and calculate the volume bounded by valves **D & E** plus trap **BB**.
- 8) **Open D, E, G, H & J** to evacuate the entire line. **Open L.**

Isolation and purification of BF_3 :

- 1) *During the following steps, BF_3 and Me_3N will be in the line.*
- 2) With the entire line evacuated, **close L, D, E, & J.**
- 3) Put BF_3 into trap **CC**:
 - a) Valves **H, I, & G** are **open**. **Close B**; confirm the pressure does not rise in the gauge, and then **close C** (BF_3 and Me_3N will damage the pressure gauge). If the pressure rises in the pressure gauge, you have a leak in the manifold or above trap **DD** that must be fixed.
 - b) Place an LN_2 trap under the nipple of the BF_3 reservoir for ~1 min. Slowly **open** the BF_3 reservoir valve. **Open B** to remove the non-condensable gas from the system. When the Hg manometer pressure returns to zero, **close B**.
 - c) Remove the LN_2 Dewar and wait for the BF_3 in the trap to warm. When the Hg pressure reaches ~400 mm, **close** the BF_3 valve and **close H**.
 - d) Record the Hg-column heights. **Close G**.
 - e) Recover the excess BF_3 by placing a Dewar of LN_2 under the nipple of the BF_3 reservoir, wait 30-60 sec, and then **open** the BF_3 valve and valve **H**. After the pressure falls in the Hg manometer, wait ~1 min; **close** the BF_3 valve, and remove the Dewar.
 - f) **Open B** to clean the line. **Open D**.

- 4) Move the BF_3 to trap **BB**:
 - a) **Close D**.
 - b) Place the LN_2 Dewar under trap **BB** (don't freeze the joint to **BB**). **Open E**. Wait ~1 min; **close E**, and remove the Dewar.
 - c) **Close I**; **open G**, then **reopen I** to evacuate the trap and manometer. Also **open C** to confirm vacuum.

Preparation of trimethylamine:

- 1) Put Me_3N into trap **CC**:
 - a) Valves **H, I, & G** are **open**. **Close B**, confirm the pressure does not rise in the gauge, and then **close C**.
 - b) Place the Dewar of LN_2 under the nipple of the Me_3N reservoir, wait ~1 min. **Open** the Me_3N valve & then valve **B**. After the pressure falls to zero in the Hg manometer, **close B**.
 - c) Remove the LN_2 Dewar and wait for the Me_3N in the trap to warm. When the Hg pressure reaches ~400 mm, **close** the Me_3N valve and **close H**.
 - d) Record the Hg-column heights. **Close G**.
 - e) Recover the excess Me_3N by placing a Dewar of LN_2 under the nipple of the Me_3N reservoir, wait 30-60 sec, and then **open** the Me_3N valve and valve **H**.
 - f) After ~1 min, **close** the Me_3N valve, and remove the Dewar.
 - g) **Open B** to clean the line. Then **open C & J**, and confirm vacuum.
 - h) **Close C**.

Combine the reactants:

- 1) Put the Dewar of LN_2 under trap **CC**; wait ~1 min. Remove the Dewar.
- 2) Put the LN_2 just under the bottom tip of trap **BB** to condense the BF_3 at the very bottom.
- 3) Put about $\frac{1}{2}$ of trap **BB** under the LN_2 . Gently **open E** to condense the Me_3N into the **BB** reaction tube while warming trap **CC** to room temperature.
- 4) After ~2 min, **close E, open G**.
- 5) Remove the Dewar from trap **BB** and let the reactants come to room temperature and react. The product should be a stable white solid.
- 6) Remove any residual reactants from the reaction tube by **closing H & J** and **opening D** for ~15 sec, then closing **D** (opening **D** for a longer time will remove product because of its appreciable vapor pressure).
- 7) **Open** valves **H & J**. After ~1 min, **open C**.
- 8) Remove trap **BB** from the line. Weigh the tube; scrape the product from the reaction tube to a sample container, and re-weigh the tube.
- 9) Calculate (from your pressure readings and volume calculations) how much of each reactant you used, your product amount and yield.
- 10) Clean and replace trap **BB**.

Vacuum line shutdown:

- 1) **Open D**.
- 2) The vacuum in the manifold should be restored in 1-2 min. If not, fix the leak.

3) Close C & B.

Product characterization:

- 1) Measure the melting point.
- 2) Get an IR spectrum as a KBr pellet.
- 3) Get an ^1H NMR spectrum in CDCl_3 .
Characterization should be done promptly because the product is (slightly) moisture sensitive.

Lab Report Guidelines

Introduction:

- Why are vacuum line techniques used?
 - Discuss the important parts of the line.
- Discuss the reaction that *will take* place (follow up in the Discussion).

Experimental:

- Describe the vacuum line and the techniques used to perform the experiment, but do not reproduce the minute details. Give the bigger picture of what and how it was accomplished.
- Define how the calculations will be made and any constants that you will need for the calculations.

Results:

- Provide a data table showing mm Hg measurements & volumes calculated.
- Give calculations of reactant amounts and theoretical & actual product yields.
- Give product characterization data:
 - melting point,
 - IR spectrum as a figure with major peaks labeled
 - NMR spectrum as a figure with peaks identified

Discussion:

- Discuss whether the volumes you calculated in the system seem appropriate.
- Discuss your product yield.
- Compare the melting point, IR, and NMR data you obtained for your product with published values (i.e. did you get the correct product?)
- What can you say about the chemistry, bonding, etc. of the adduct?

Handouts

1. D.P. Shoemaker, C.W. Garland, & J.W. Nibler, Chap 27: Vacuum techniques, *Experiments in Physical Chemistry*, 5th ed, McGraw-Hill, NY, 1989, pp 677-714.
2. R.J. Angelici, Expt 19: $(\text{CH}_3)_3\text{N}:\text{BF}_3$, *Synthesis and Technique in Inorganic Chemistry*, 2nd ed, W. B. Saunders: Philadelphia, 1977, pp. 188-97.

References

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2. B Benton-Jones, MEA Davidson, JS Hartman, JJ Klassen & JM Miller: Trimethylamine and 4-methylpyridine adducts of the mixed trihalides of boron: Exchange reactions and nuclear magnetic resonance spectra. *J. Chem. Soc. Dalton*, 2603-7, 1972.
3. MJ Bula, DE Hamilton & JS Hartman: Donor-acceptor adducts of the mixed boron trihalides: Adducts of dimethyl ether. *J. Chem. Soc. Dalton*, 1405-12, 1972.
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5. AR Katritzky: Infrared absorption of heteroaromatic and benzenoid six-membered monocyclic nuclei. Part VI. Pyridine-boron complexes. *J. Chem. Soc.*, 2049-2051, 1959.
6. R.L. Amster and R.C. Taylor, *Spectrochim. Acta* **20A**: 1487-1502 (1964).
7. A. Derek and D. Clague, *Spectrochim. Acta*. **23A**: 2359-69 (1967).
8. K. Nakamoto, *Infrared Spectra of Inorganic and Coordination Compounds*. John Wiley: New York, 1963.
9. D.F. Shriver, *The Manipulation of Air-Sensitive Compounds*. McGraw-Hill: New York, 1969. pp. 1-57 (Chaps 1-4) – (DEM: can't find in the Cook Library 2/2001)

APPENDIX: High-vacuum ground glass plug valves:

This type of valve has a funny plug with 3 holes in it.

- i) Two of the holes in the valve plug connect via the glass tube that runs through it. When these two holes are lined up with the holes in the valve body, the valve is in the OPEN position. The **open** position is **when the valve handle is parallel to the inlet/outlet tubes**. *Caution: there are two configurations where the valve handle is parallel; see the next point.*
 - ii) The 3rd hole in the valve plug connects the inside of the hollow plug and the bulb of the valve to the outlet side of the valve. However, the inlet side of the valve is blocked and no gas can flow from inlet to the outlet, i.e. the valve is **closed**. The purpose of this configuration is to allow the valve to be closed and to keep the inside EVACUATED. Hence why we refer to this position as **closed**, but **evacuated**. The **evacuated** position is the normal “**valve closed**” position because the valve is closed, but the plug is still connected to the manifold, which remains at vacuum.
 - iii) Note that when the valve is in the **evacuated** position, the handle is parallel to the inlet/outlet tubes, but 180° opposite to its position in the **open** position. Confused? Well get rid of any and all confusion before you start this lab!! Look at the valves and with the help of your TA turn the valve and test their configuration. Be sure you know what you are doing at this point.
 - iv) The final position of the valve is **closed** with the valve handle turned perpendicular to the inlet/outlet tubes. In this position, none of the 3 holes in the plug is connected to anything. We will use this position to isolate the valve plugs when the gases are in the line on the outlet side. This position is not the normal position for anything but shorter periods of time because gas can leak into the plug over time, reducing the push of atmosphere down on the valve and its ability to act as a high vacuum valve.
- b) The ground-glass valves and the other ground-glass fittings require grease. We use Apiezon M, which will dissolve in hexane. You do not need “two fingers” of grease to make a seal, just a little bit on the tip of your little finger. Your TA can demonstrate how to grease and degrease fittings and valve plugs.
 - c) A properly greased valve will turn very easily. However, to be safe, always grip the valve body with one hand while turning the handle with the other. Test the turning of all valves in the system **BEFORE YOU START**. If a valve is hard to turn, see your TA and get it regreased. A heat-gun is helpful for setting the grease once the valve has been reassembled.