

CHEM 100L Lab 2: Alcohol Oxidations

Purpose: In this virtual experiment, you will be performing two oxidation reactions of benzyl alcohol, a primary alcohol. Primary alcohols can be oxidized to aldehydes or carboxylic acids, depending on the reagents used. You will be setting up oxidation reactions using chromic acid (H_2CrO_4) and pyridinium chlorochromate (PCC), and comparing the products of the two reactions. You will be monitoring the reactions using thin-layer chromatography (TLC) and comparing key signals in the IR spectra of the reactants and products.

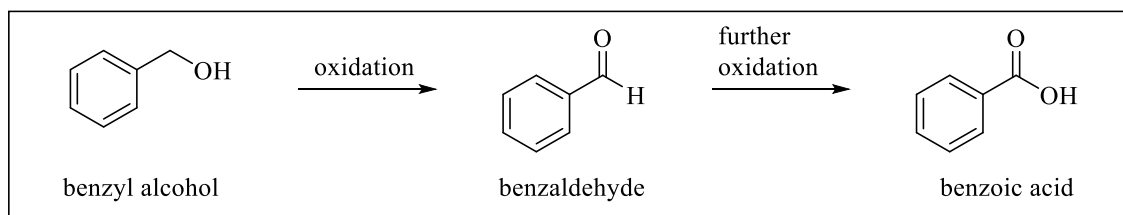


Figure 2.1 Oxidations of benzoic acid

Introduction: Primary alcohols can be oxidized to aldehydes or carboxylic acids, depending on the reagents used. For many years, chromium reagents were commonly used for alcohol oxidations. Because of the toxicity of chromium-based reagents, many safer oxidizing agents have been developed and are more commonly used. As this lab is virtual, we can safely explore the reactivity trends for the older, chromium-based reagents. The two reaction conditions we will be exploring in this virtual experiment are:

- *Jones oxidation:* This reaction uses chromic acid (H_2CrO_4) as the oxidizing agent. Chromic acid can be formed by dissolving sodium dichromate ($\text{Na}_2\text{Cr}_2\text{O}_7$) or chromium trioxide (CrO_3) in aqueous sulfuric acid (H_2CrO_4).
- *PCC oxidation:* This reaction uses pyridinium chlorochromate (PCC) in an anhydrous solvent, typically dichloromethane (CH_2Cl_2). The virtual lab does not give us CH_2Cl_2 as an option for a solvent, so we will substitute diethyl ether ($\text{CH}_3\text{CH}_2\text{OCH}_2\text{CH}_3$, or Et_2O).

Once your two virtual experiments are complete, you will decide which set of conditions oxidizes primary alcohols to aldehydes, and which oxidizes primary alcohols to carboxylic acids.

IR spectroscopy:

We can identify functional groups using infrared (IR) spectroscopy. IR radiation is in the same range of frequencies ($4000\text{-}600\text{ cm}^{-1}$) as the stretching and bending vibrations of bonds in organic molecules. When the frequency of the radiation exactly matches the frequency of the bond, the molecule absorbs energy, resulting in an absorption peak in the IR spectrum. Most functional groups show absorption bands in the region of $4000\text{-}1400\text{ cm}^{-1}$.

You will use the Beyond Labz virtual platform to record the IR spectrum for the benzyl alcohol starting material. Look for the broad absorption that is characteristic of the O-H bond of the alcohol ($\sim 3650\text{-}3200\text{ cm}^{-1}$).

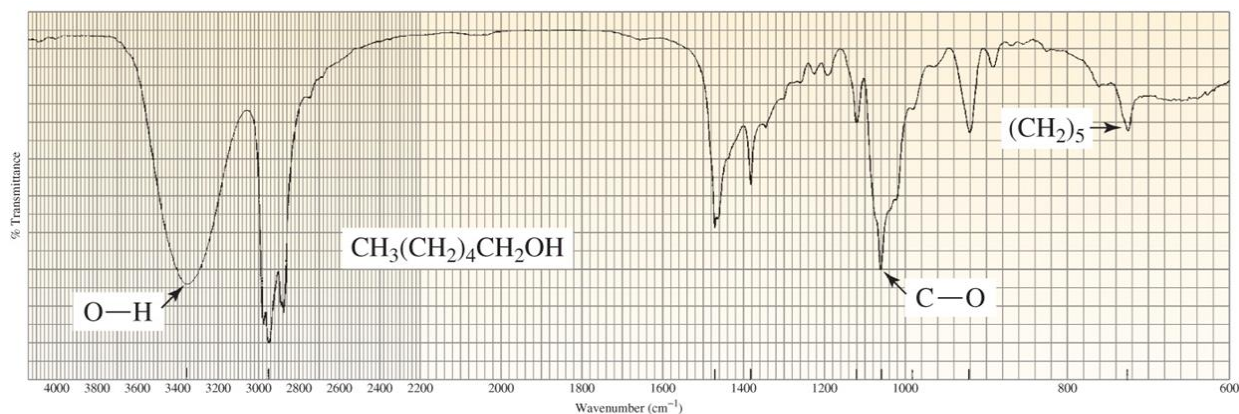


Figure 2.2 IR spectrum of 1-hexanol. (From Organic Chemistry by Bruice, 8th Ed.)

When your reaction is complete, you will use the Beyond Labz virtual platform to record the IR spectra for the oxidized products. You should observe that the characteristic alcohol absorption (broad, O-H stretch of the alcohol at $\sim 3650\text{-}3200\text{ cm}^{-1}$) is absent. If the product is an aldehyde, you should observe the C-H stretches for the aldehyde (~ 2820 and 2720 cm^{-1}) and the C=O at $\sim 1680\text{-}1715\text{ cm}^{-1}$ for the conjugated carbonyl.

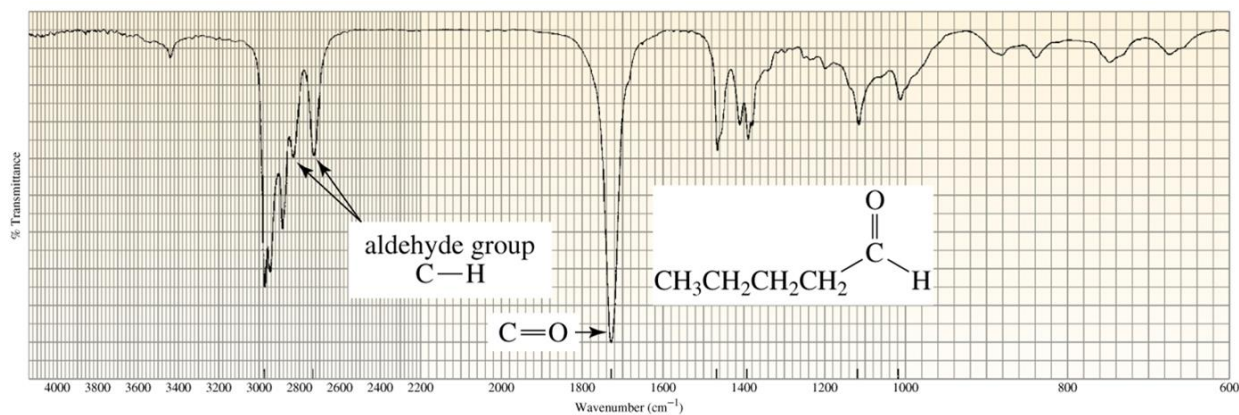


Figure 2.3 IR spectrum of pentanal. (From Organic Chemistry by Bruice, 8th Ed.)

If the product is the carboxylic acid, you should observe the broad O-H of the carboxylic acid ($\sim 3300\text{-}2500\text{ cm}^{-1}$). This signal is lower and broader than an alcohol O-H and is not smooth because of the overlap with the C-H stretching absorption peaks. Like the spectrum for the aldehyde product, C=O at $\sim 1680\text{-}1715\text{ cm}^{-1}$ for the conjugated carbonyl.

Reference spectra for the benzyl alcohol, benzaldehyde, and benzoic acid are provided at the end of this handout with the key absorptions clearly labeled.

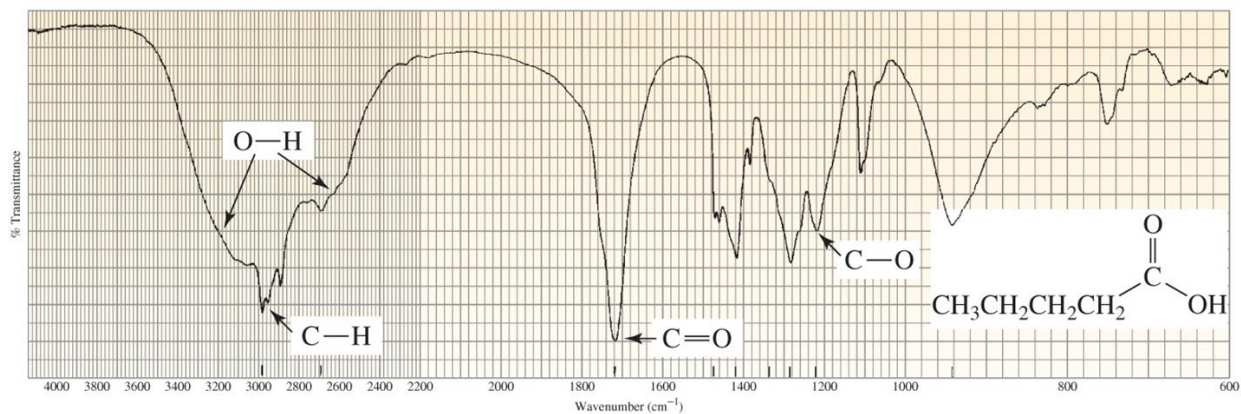


Figure 2.4 IR spectrum of pentanoic acid. (From Organic Chemistry by Bruice, 8th Ed.)



Figure 2.5 Synthesis virtual lab.

Virtual Lab Instructions (video instructions also available). Help is available by clicking on the bell on the stockroom counter. *Note: Reference spectra for the benzyl alcohol, benzaldehyde, and benzoic acid are provided at the end of this handout with the key peaks clearly labeled.*

Part 1: Starting Material IR

1. Open the organic chemistry lab on the Beyond Labz platform. Select “Qualitative Analysis” at the top left of the screen to open the Qualitative Analysis virtual lab.
2. Select “**Alcohols**” from the chalkboard, then click and drag (or double-click) the reagent bottle for the **benzyl alcohol** to add it to the flask.
3. Drag the flask to the cork ring support on the lab bench.
4. Record the IR spectrum by clicking on the IR spectrometer and dragging the salt plate icon to the flask. This will display the IR spectrum on the screen. You can type the name of the compound on the spectrum and click save to save it to your lab notebook. Click ok to close the spectrum.
5. Leave the qualitative analysis lab by clicking on the exit sign.

Part 2: Chromic acid oxidation:

6. Select “Synthesis” at the top left of the screen to open the Synthesis virtual lab.
7. On the chalkboard (top right) mouse over “Alcohol Oxidation”, and you will see the available chemicals. You will notice that there are 3 different alcohols available from the “stockroom”, so be sure to select the correct alcohol for the oxidation experiment!
8. Clicking and dragging adds reagents into the flask. Click on the benzyl alcohol and drag it into the flask. The simulation doesn’t allow us to weigh the reagents. Assume that 2.00 mL of benzyl alcohol was added- you will need this number for calculations!
9. Click on the water and add it to the flask, assume that a volume of ~ 10.0 mL was added.
10. Check to see that the reagent and the solvent have been added to the flask by hovering your mouse over the flask. The contents of the flask will display on the chalkboard.
11. Drag the flask over to the clamp above the stirring hot plate.
12. You still need to add the chromic acid/sulfuric acid oxidizing agent. Find it on the bench top (labeled $\text{H}_2\text{Cr}_2\text{O}_7$) and click and drag to the flask. Note the color change in your observations! Assume that you have added enough to completely react with the benzyl alcohol.
13. Check the chalkboard and verify that your flask contains the correct alcohol, the water, and the chromic acid/sulfuric acid oxidizing agent.
14. This reaction is fairly slow, so you will need to apply heat. Drag the heating mantle under the flask.
15. To prevent the solvent from evaporating, add a reflux condenser to the flask.
16. Notice that the top of the condenser is sealed with a rubber septum. If we heat a closed system, it will explode! Click and drag the nitrogen line to the top of the condenser.
17. Before starting the reaction, check the initial (total reaction time = 0 minutes) TLC by clicking on the TLC chamber and dragging the plate to the flask. The TLC plate will always have two lanes- one that shows the starting materials (left), and one that shows what was in the flask at the time you measured the TLC (right). Since this is before the reaction has started, the two lanes should look identical because they both contain just the

- alcohol starting material. Sketch the plate or save it to your lab notebook by clicking save. Close the TLC plate by clicking OK.
18. Start the reaction by clicking the right knob on the stirring hotplate.
 19. Advance the clock 10 minutes (total reaction time = 10 minutes). Check the TLC as before, you should notice now in the right lane that the starting material spot is getting smaller, and a new spot (the product!) has appeared. We want to continue the reaction until the starting materials are consumed. Sketch the plate or save it to your lab notebook by clicking save. Close the TLC plate by clicking OK.
 20. Advance the clock 20 more minutes (total reaction time = 30 minutes). Check the TLC as before, sketch the plate or save it to your lab notebook by clicking save. Close the TLC plate by clicking OK. The reaction should now be complete.
 21. The reaction should now be complete.
 22. Stop the reaction by dragging the separatory funnel over to the flask. The chalkboard will display what is in the flask, which should be the water, the chromous sulfate by-product, and your product.
 23. Add water by clicking and dragging the water to the separatory funnel. To extract an organic product, an organic solvent is required. After you have added the additional water to your aqueous reaction solution, you will see two layers of liquid in the funnel. There is clearly an assumption that diethyl ether has been added as the organic solvent to extract the product. Recall that the less dense ether layer (“organic layer”) will float on top of the aqueous layer. If you hover your mouse over the layers, it will display if the layer is organic or aqueous and the chalkboard will display the chemicals contained within the layer.
 24. Remove the lower aqueous layer and discard it into the waste container by clicking and dragging it first into the cork ring support, and then into the red waste container. Make sure it only contains water and the chromous sulfate by-product before throwing it away!
 25. Click and drag the ether layer to the cork ring support. You will notice when you do this that the ether disappears from the flask. This step assumes that you evaporated the solvent using a rotatory evaporator leaving you with just the product in the flask.
 26. The product of this reaction is a solid. Organic solids are often purified by recrystallization. “Recrystallize” your solid product by clicking and dragging the flask to the crystallization dish, you should see a white solid appear in the dish.
 27. Record the melting point by clicking on the Mel-Temp and dragging the capillary tube icon to the crystallization dish.
 28. Hover your mouse over the display on the Mel-Temp to view the melting point of the product and record this value in your notebook.
 29. Record the IR spectrum of the product by clicking on the IR spectrometer and dragging the salt plate icon to the flask. This will display the IR spectrum on the screen. You can type the name of the compound on the spectrum and click save to save it to your lab notebook. Click ok to close the spectrum.
 30. Your virtual oxidation of benzyl alcohol is now complete!
 31. Reset the synthesis lab by clicking on the waste container to “clear lab”.

Part 3: PCC oxidation:

32. On the chalkboard (top right) mouse over “Alcohol Oxidation”, and you will see the available chemicals. You will notice that there are 3 different alcohols available from the “stockroom”, so be sure to select the correct alcohol for the oxidation experiment!
33. Clicking and dragging adds reagents into the flask. Click on the benzyl alcohol and drag it into the flask. The simulation doesn’t allow us to weigh the reagents. Assume that 2.00 mL of benzyl alcohol was added- you will need this number for calculations!
34. Click on the diethyl ether and add it to the flask, assume that a volume of ~ 10.0 mL was added. *Note: The typical solvent for a PCC oxidation is dichloromethane, CH₂Cl₂, but unfortunately that is not available to us in the virtual lab.*
35. Check to see that the reagent and the solvent have been added to the flask by hovering your mouse over the flask. The contents of the flask will display on the chalkboard.
36. Drag the flask over to the clamp above the stirring hot plate.
37. You still need to add the pyridinium chlorochromate oxidizing agent. Find it on the bench top (labeled PCC) and click and drag to the flask. Assume that you have added enough to completely react with the benzyl alcohol.
38. Check the chalkboard and verify that your flask contains the correct alcohol, the water, and the PCC oxidizing agent.
39. This reaction is fairly slow, so you will need to apply heat. Drag the heating mantle under the flask.
40. To prevent the solvent from evaporating, add a reflux condenser to the flask.
41. Notice that the top of the condenser is sealed with a rubber septum. If we heat a closed system, it will explode! Click and drag the nitrogen line to the top of the condenser.
42. Before starting the reaction, check the initial (total reaction time = 0 minutes) TLC by clicking on the TLC chamber and dragging the plate to the flask. The TLC plate will always have two lanes- one that shows the starting alcohol (left), and one that shows what was in the flask at the time you measured the TLC (right). Note that in addition to the alcohol starting material spot in the reaction mixture lane, there is a lower spot- this is the PCC reagent spot. Sketch the plate or save it to your lab notebook by clicking save. Close the TLC plate by clicking OK.
43. Start the reaction by clicking the right knob on the stirring hotplate.
44. Advance the clock 60 minutes (total reaction time = 60 minutes, or 1 hour). Note the color change! Check the TLC as before, you should notice now in the right lane that the starting material spots (alcohol and PCC) are getting smaller, and new spots (the product, and the pyridine by-product) have appeared. We want to continue the reaction until the starting materials are consumed. Sketch the plate or save it to your lab notebook by clicking save. Close the TLC plate by clicking OK.
45. Advance the clock 60 more minutes (total reaction time = 120 minutes, or 2 hours). Check the TLC as before, sketch the plate or save it to your lab notebook by clicking save. Close the TLC plate by clicking OK.
46. Advance the clock 60 more minutes (total reaction time = 180 minutes, or 3 hours). Check the TLC as before, sketch the plate or save it to your lab notebook by clicking save. Close the TLC plate by clicking OK. The reaction should now be complete.

47. Stop the reaction by dragging the separatory funnel over to the flask. The chalkboard will display what is in the flask, which should be the diethyl ether, the pyridine by-product, and your product.
48. Separate the pyridine by-product from the product by extracting with aqueous HCl- this converts the pyridine into water-soluble pyridinium chloride. Add the HCl solution by clicking and dragging it to the separatory funnel. Recall that the less dense ether layer ("organic layer") will float on top of the aqueous layer. If you hover your mouse over the layers, it will display if the layer is organic or aqueous and the chalkboard will display the chemicals contained within the layer.
49. Remove the lower aqueous layer and discard it into the waste container by clicking and dragging it first into the cork ring support, and then into the red waste container. Make sure it only contains water and the pyridinium chloride by-product before throwing it away!
50. Click and drag the ether layer to the cork ring support. You will notice when you do this that the ether disappears from the flask. This step assumes that you evaporated the solvent using a rotatory evaporator leaving you with just the product in the flask.
51. Record the IR spectrum of the product by clicking on the IR spectrometer and dragging the salt plate icon to the flask. This will display the IR spectrum on the screen. You can type the name of the compound on the spectrum and click save to save it to your lab notebook. Click ok to close the spectrum.
52. Your virtual experiment is complete!

Lab 2 Assignment:

Points (total = 50)

- 12 pts Prelab question
- 4 pts Part 1 Results
- 10 pts Part 2 Results
- 10 pts Part 3 Results
- 14 pts Postlab questions

Prelab Question (12 pts total)

(12 pts) Before working with compounds in the laboratory, it is important to look up key physical properties and hazards for the chemicals that you are working with. For benzyl alcohol, benzaldehyde, and benzoic acid, look up the formula weight (FW), boiling point (b.p.), density, and hazards and complete the table below. A good place to look up information is a company that sells chemicals for laboratory use, try: www.sigmaaldrich.com.

	FW (g/mol)	b.p. (°C)	m.p. (°C)	Density (g/mL)	Hazards
benzyl alcohol					
benzaldehyde					
benzoic acid					

Results (22 pts total)

Part 1 Results (4 pts)

Sketch (or screen capture) the IR spectrum you recorded using Beyond Labz for the benzyl alcohol starting material. Circle the characteristic alcohol O-H absorption peak.

Part 2 Results (10 pts total)

(4 pts) Sketch (or screen capture) the IR spectrum you recorded using Beyond Labz for the product of the chromic acid oxidation. Circle the and label characteristic peaks (aldehyde C-H and C=O if product is benzaldehyde; carboxylic acid O-H and C=O if product is benzoic acid).

(3 pts) TLC Observations: Sketch (or screen capture) the TLC plates at 0 minutes, 10 minutes, and 30 minutes for the chromic acid oxidation.

(2 pts) Describe any color changes you observed during this reaction.

(1 pt) Record the product melting point.

Part 3 Results (10 pts)

(4 pts) Sketch (or screen capture) the IR spectrum you recorded using Beyond Labz for the product of the PCC oxidation here. Circle the and label characteristic peaks (aldehyde C-H and C=O if product is benzaldehyde; carboxylic acid O-H and C=O if product is benzoic acid).

(4 pts) TLC Observations: Sketch (or screen capture) the TLC plates at 0 minutes, 60 minutes, 120 minutes and 180 minutes for the PCC oxidation.

(2 pts) Describe any color changes you observed during this reaction.

Postlab Questions (14 pts total):

1. (2 pts) Identify the product of the chromic acid oxidation. From this result, complete the following statement: Chromic acid can be used to oxidize primary alcohols to form _____.

2. (2 pts) Identify the product of the PCC oxidation. From this result, complete the following statement: PCC can be used to oxidize primary alcohols to form _____.

3. (4 pts) Predict the major organic product of the following reactions.



4. (2 pts) The procedure mentions that the starting amount of benzyl alcohol is 2.00 mL. How many moles does 2.00 mL of benzyl alcohol contain? Show calculation with units for full credit.

5. (2 pts) If 2.00 mL of benzyl alcohol reacts with enough of the appropriate oxidizing agent, calculate the theoretical yield of the benzoic acid product. Show calculation with units for full credit.

6. (2 pts) The by-product of the PCC oxidation is pyridine. The pyridine is separated from the organic solution by reaction with hydrochloric acid solution to form the water-soluble salt, pyridinium chloride. Draw the curved arrows for this acid-base reaction.



IR Spectra: Benzyl alcohol, benzaldehyde, benzoic acid.

