EXPERIMENT THREE

THE CANNIZARO REACTION:
THE DISPROPORTIONATION OF BENZALDEHYDE

\[
\begin{align*}
2x \text{H} &\quad \rightarrow \\
\text{C} &\quad \text{O} &\quad \text{HO} &\quad \text{C} &\quad \text{O} &\quad \text{H} &\quad \text{C} &\quad \text{OH} \\
\end{align*}
\]

DISCUSSION

In planning the laboratory schedule, it should be observed that this experiment requires materials to be mixed and allowed to stand for 24 hr or longer.

In the presence of strong alkalis, benzaldehyde (like formaldehyde) undergoes disproportionation to form the corresponding primary alcohol and a salt of the carboxylic acid: the Cannizzaro reaction.

The process involves addition of hydroxyl ion to the carbonyl group of one molecule and transfer of hydride anion from the adduct to a second molecule of benzaldehyde, accompanied by proton interchange to form the benzoate anion and benzyl alcohol. If the reaction is effected under anhydrous conditions with the sodium derivative of benzyl alcohol as catalyst, the product is the ester, benzyl benzoate.

EQUIPMENT

18 g KOH
20 mL Benzaldehyde
125 mL Erlenmeyer/stopper
100 mL methylene chloride
Steam bath
125 mL separatory funnel
10 mL 20% sodium bisulfite
4 g anhydrous magnesium sulfate
100 mL round bottom flask
Thermometer (0-250°C)
Bunsen burner
40 mL conc. HCl
Chipped ice
Blue litmus paper
Side arm flask
Buchner funnel

EXPERIMENT: In a small beaker dissolve 0.27 mole (18 g of 85% pure solid) of solid
potassium hydroxide in 18 mL of water and cool the solution to about 25°C. Place 0.2 mole (21 g, 20 mL) of benzaldehyde in a 125-mL Erlenmeyer flask (or narrow-mouth bottle) and to it add the potassium hydroxide solution. Cork the flask firmly and shake the mixture thoroughly until an emulsion is formed. Allow the mixture to stand for 24 hr or longer. At the end of this period, the odor of benzaldehyde should no longer be detectable.

Isolation of Benzyl Alcohol

To the mixture add just enough distilled water to dissolve the precipitate of potassium benzoate. Shake the mixture thoroughly to facilitate solution of the precipitate. Extract the alkaline solution with three or four 20-mL portions of methylene chloride to remove the benzyl alcohol and traces of any unconverted benzaldehyde. Combine the methylene chloride extracts for isolation of benzyl alcohol and reserve the aqueous solution to obtain the benzoic acid.

Concentrate the methylene chloride solution of benzyl alcohol by distillation on a steam bath using a water-cooled condenser, until the volume of the residual liquid has been reduced to 15-20 mL. A steam bath is just a beaker of boiling water into which the distillation flask is emersed. Cool the remaining liquid, transfer it to a small separatory funnel (using 2-3 mL of methylene chloride to rinse the distilling flask), and shake it thoroughly with two 5-mL portions of 20% aqueous sodium bisulfite to remove any benzaldehyde. Wash the methylene chloride solution finally with two 10-mL portions of water and dry it with 3-4 g of anhydrous magnesium sulfate. Filter the solution into a small dry distilling flask and carefully distill off the methylene chloride. Attach a short air-cooled condenser and distill the benzyl alcohol, by heating the flask directly with a luminous flame kept in motion. Collect the material boiling at 200-206°C. The yield is 4-5 g.

Isolation of Benzoic Acid

To free the acid, pour the aqueous solution of potassium benzoate (from which the benzyl alcohol has been extracted) into a vigorously stirred mixture of 40 mL of concentrated hydrochloric acid, 40 mL of water, and 40-50 g of chipped ice. Test the mixture with indicator paper to make sure that it is strongly acidic. Collect the benzoic acid with suction and wash it once with cold water. Crystallize the product from hot water, collect the crystals, and allow them to dry thoroughly. The yield is about 8g.
I.R. SPECTROSCOPY

Setup Instructions

1. Remove the cover from the machine.

2. The "ON" switch is located to the rear on the right side of the machine. Switch the machine on. The spectrometer will take about a minute to warm-up. When it is ready for use it will beep twice.

3. Running the machine involves several simple steps. The machine can scan at two rates, a three minute and a twelve minute scan. A three minute scan will give you all of the major spectroscopic peaks, but none of the details. The twelve minute scan will give you the details that the three minute scan missed. Set the machine to a three minute scan.

4. There are several kinds of chart paper that can be used for plotting the output. We use the shortest sheets. Set the machine for short paper output.

5. Before a plot can be made a pen must be placed into the slide bar located near the center of the machine. The pens are located on a shelf next to the spectrometer (several colors are available). Slide one of the pens (any color) into the pen holder on the slide bar.

6. Occasionally the edge of the chart paper becomes misaligned with the pen position. The chart can be moved by pressing the Chart button (either the UP or the DOWN button) to move the chart into the proper position.

The spectrometer is now ready to accept a sample.

Sample Preparation

Infrared spectroscopy can be done on either liquid or solid samples. The preparation of these samples differ dramatically. Follow these general guidelines.

Liquid Samples

Liquid samples are loaded into "cells". What this means is that the liquid will be sandwiched between two plates. Each plate has a shallow indentation in it's surface that holds a small amount of sample. When the plates are put together the sample is trapped in this indentation producing a thin film of sample which can be analyzed by the spectrophotometer.

The process is very simple. Locate the cell and it's holder. It should be found in a small white box on a shelf adjacent to the machine. The cell holder is a round piece of white plastic with a hole in the center and should be found together with small piece of protective cloth which contains the cells themselves. The cells are small round disks of what appear to be plastic but they are really made of solid AgCl so be careful with them.
You will notice that the cell holder unscrews. Unscrew the cell holder and inside you will see a black rubber "O" ring. Take one of the two cells and place it, shallow side up, on top of the "O" ring. Place two or three drops of sample onto the cell surface and quick place the other half cell and place it on top (shallow side down). Now screw the top of the cell holder back onto the cell. The cell should be snug but not overly tight. Overtightening can warp or even break the AgCl cells. Please be careful.

Now that the sample is in the cell you are ready to mount the cell into the spectrometer and take a spectrum of the sample.

**Solid Samples**

Solid samples can be prepared by mixing (actually grinding) the solid together with KBr. You will do this using an agate mortar and pestle. It is usually wise to use about two to three times more KBr than the amount of solid sample (eye-ball it). Use very small amounts of each, 1 gram of KBr and 0.3 grams of solid are more than enough (usually). After the sample has been well mixed place a small amount in the KBr wafer press and make a thin, nearly transparent wafer of this mixture. Small cracks in the sample are alright. Mount the pellet in the IR and run the sample.

**Problem**

Write equations for the preparation of benzaldehyde from

(a) benzene
(b) toluene
(c) benzoic acid
### REACTIONS OF AROMATIC ALDEHYDES WORKSHEET

#### Results: Benzyl Alcohol

<table>
<thead>
<tr>
<th>Mass of Benzyl Alcohol</th>
<th>Ref. Index of Benzyl Alcohol</th>
<th>Boiling Point Benzyl Alcohol</th>
<th>Theoretical Yield (grams)</th>
<th>Actual Yield (Percent)</th>
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</thead>
<tbody>
<tr>
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#### Results: Benzoic Acid

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<tr>
<th>Mass of Benzoic Acid</th>
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Attach your spectra to this sheet and locate the following peaks by circling and labeling them.

**Benzyl Alcohol**

- OH stretch
- CH stretch
- Benzene C=C stretch
- C-O stretch

**Benzoic Acid**

- OH stretch
- CH stretch
- Benzene C=C stretch
- C-O stretch
- C=O stretch