CH241 Experiment #5, Week of November 5, 2018

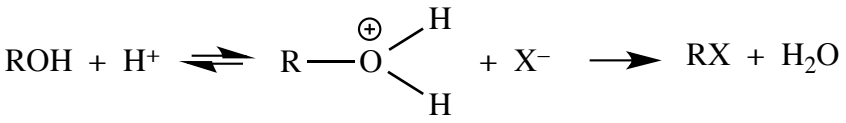
Nucleophilic Substitution Reactions (S_N1 and S_N2)[1]

Background

In this experiment you will determine the importance of the nucleophile under S_N1 and S_N2 conditions. You will allow an equimolar mixture of competing nucleophiles, Br^- and Cl^-, to react under S_N1 conditions with 2-methyl–2-propanol (*tert*-butyl alcohol) and under S_N2 conditions with 1-butanol. The alkyl halide products of the S_N1 and the S_N2 reactions will be analyzed by gas chromatography to determine the relative amounts of the components in the product mixtures. You will also for the first time become familiar with the technique of heating at reflux.

Experimental

You will be running the following reaction, where X^- is either Br^- or Cl^-:



First prepare the equimolar mixture of Br^- and Cl^- in concentrated sulfuric acid. **CAUTION: Concentrated sulfuric acid is a very strong, corrosive acid. Be very careful handling it.** Carefully add 38 mL of concentrated H_2SO_4 to 50 g of ice in a 250-mL Erlenmeyer flask. Set aside. Weigh 9.5 g of ammonium chloride and 17.5 g of ammonium bromide. Thoroughly crush any lumps, and then transfer these salts into a 500-mL Erlenmeyer flask. Slowly add the sulfuric acid, a little at a time, and swirl to dissolve the salts. The mixture may have to be gently heated and/or as much as 5 mL of additional water may have to be added to get the salts into solution. Allow the solution to cool slightly while you prepare the apparatus for the S_N1 and S_N2 reactions.

S_N2: Assemble an apparatus for reflux using a 500-mL round-bottomed flask, a condenser, and a gas trap. A demonstration set up will be available for you to see. Sketch the apparatus in your notebook and/or take a photograph of it with your electronic device.

S_N1: Pour 35 mL of your acidic nucleophile mixture into a 125-mL separatory funnel and replace the stopper.

S_N2 reaction (start first, then while your reaction is refluxing, complete the S_N1 reaction)

Pour the remainder of the nucleophile mixture into the 500-mL round-bottomed flask, add a boiling stone, and replace its stopper. Add 5 mL of 1-butanol (*n*-butyl alcohol) to the reflux apparatus by pouring it down the condenser. Replace the gas trap and reflux gently for 60 minutes, making sure that the reflux ring does not rise more than a quarter of the way up the condenser.

At the end of the reflux period, discontinue heating and lower the heating mantle to allow the flask to cool undisturbed (at this point, shaking the reaction flask may cause violent boiling and loss of product). Allow the flask to cool at least 5 minutes in the air before putting it into an ice-

water bath. Cool for a few minutes, and then begin to swirl the mixture to facilitate more rapid cooling. Transfer the cooled solution to a 125-mL separatory funnel leaving any solid material behind, and then separate the layers. Be sure to check which is the organic layer and which is the aqueous layer. Wash the organic layer with 10 mL of water and then with 10 mL of saturated aqueous sodium bicarbonate solution. The bicarbonate neutralizes any remaining acid to produce CO_2, so remember to release the pressure build-up in the separatory funnel often (vent…vent…vent). Dry the organic layer with anhydrous Na_2SO_4 and decant or pipet the clear solution into a small, dry vial. Cap the vial immediately to avoid loss of product. Analyze your products by gas chromatography.

S_N1 reaction

Add 5 mL of 2-methyl-2-propanol to the separatory funnel containing the nucleophile mixture. Since the melting point of 2-methyl-2-propanol is 25 °C, use a warm graduated cylinder to measure it. Swirl the mixture gently, and then vent the separatory funnel. Keep swirling and venting the funnel until the pressures are equalized, then shake the funnel vigorously, with occasional venting, for 2 minutes. Allow the layers to separate for about a minute, and then drain the lower layer. Wait 10-15 seconds longer, then drain another small portion, this time including a bit of the upper, organic layer into the stopcock, just to be sure that the remaining organic layer is not contaminated with water. Pour the organic layer out of the top of the separatory funnel into a small beaker containing 1 g of solid sodium bicarbonate. Stir, and as soon as the bubbling stops, decant the clear solution into a dry vial. Cap the vial immediately to avoid loss of product. Analyze your products by gas chromatography.

All derived experimental data that are unique to your experiment, such as the gas chromatograms in this lab, should be carefully labeled immediately after you acquire them. The label minimally should include your names, the compound or reaction, and the date and time collected.

Pre-laboratory Assignments

In addition to the exercises below, read about and take notes on the techniques of (a) heating a reaction under reflux and (b) gas chromatography. Use an organic laboratory text and/or the internet, and be sure to cite your sources!

1. Which is a better nucleophile in aqueous solution, Br^- or Cl^-? Why?
2. What are the products of the S_N1 and S_N2 reactions to be done in this experiment? Find the boiling points of the organic products.
3. Write mechanisms, with correct arrow formalism, for these S_N1 and S_N2 reactions.
4. What is the limiting reagent for each reaction? Show your calculations to support the answers.

What Should Be In Your Notebook?

1. The usual items: an entry of the title, date, and page number in your table of contents and the title, date, and partner's name all pages of your experiment.
2. Masses and/or volumes of all materials that you used in this experiment.
3. A sketch of the reflux apparatus for the S_N2 reaction.
4. Brief description of the procedures you followed for S_N1 and S_N2 reactions.
5. Calculations showing the relative amounts (in units of mole percent) of the products in S_N1 and S_N2 reactions.

What Should Be In Your Laboratory Report?

Use the **Experiment 5 Report Form** to write your lab report.

Remember to:

1. Submit an electronic copy to CH241Lab@colby.edu by the date your report is due.
2. Submit a hardcopy in lab on the due date (start of lab).

[1] This experiment was adapted from *Introduction to Organic Laboratory Techniques*, 3rd edition, 1999 by Donald L. Pavia, Gary M. Lampman, and George S. Kriz.