Radical Chlorination of 1-Chlorobutane (rev 6/2019)  The purpose of this experiment is to examine a possible polar effect on a free radical chlorination.

When butane is chlorinated at 75° in the liquid phase, one observes 63% attack at the secondary hydrogens and 37% attack at the primary hydrogens (see reaction1 below). Because there are six CH₃ hydrogens and four CH₂ hydrogens in butane, to compare the reactivity at each position we must convert these results to % attack per hydrogen.

**Reaction 1. The non-selective chlorination of butane.**

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\text{CH}_3\text{CH}(_2)\text{CH}(_2)\text{CH}_3 + \text{Cl}_2 \rightarrow \text{CH}_3\text{CH}(_2)\text{CH}(_2)\text{Cl} + \text{CH}_3\text{CH}(_2)\text{Cl} \]

63% 37%

2° (CH₂) hydrogen abstraction: \(63%/4\) secondary hydrogens = 15.8%/secondary hydrogen

1° (CH₃) hydrogen abstraction: \(37%/6\) primary hydrogens = 6.2%/primary hydrogen

This results in a relative reactivity (RR) for 2° to 1° hydrogens of:

\[
\text{RR (2°/1°)} = \frac{15.8}{6.2} = 2.5:1
\]

This means that under these reaction conditions, secondary hydrogens are 2.5 times more reactive than primary hydrogens.

In the chlorination of 1-chlorobutane by sulfuryl chloride (assume that the attacking radical is Cl•), you will measure the % attack at each of the four non-equivalent positions by an analysis of the gas chromatogram of the product mixture. The results will be discussed in terms of a possible polar effect on the reaction.

Hint: the chlorine atom is a powerful electrophile (electron lover). Reaction rate will be faster at positions having what characteristic?

**Experimental.** We will be heating with a steam bath, not the heater stirrer.

We will be using new techniques and equipment with this experiment. A separatory funnel and a water-jacketed condenser. Remember, when using a water cooled condenser, that water goes in the bottom inlet and drains through the top inlet. The proper use of a separatory funnel will be demonstrated by your TA. Take note of proper venting techniques.

The experimental procedure is quite simple, but care must be taken in working with the hazardous sulfuryl chloride. The 1-chlorobutane is used in large excess, and the azo compound is used in a catalytic amount, so quantities do not have to be measured with great accuracy. The data that we wish to obtain is the product distribution (ratio of isomeric dichlorides) - small
differences in amounts of reagents will have no effect on the ratios. The apparatus must be free of water. **CAUTION:** sulfuryl chloride is caustic and noxious and can react vigorously with water (the rate of reaction with water is slowed by its low water solubility - what are the products of reaction of sulfuryl chloride and water?). Follow the procedure in the lab text making sure that all equipment (RBF, condenser) is free of water droplets. Measure the chlorobutane in the hood using a graduated pipet and add it to the RBF. Measure the sulfuryl chloride in the hood using a syringe without a needle attached and add this to the reaction mixture. Again, use extreme caution when working with this reagent- goggles must be worn and if accidental contact with the skin occurs, wash with soap and water immediately and inform the TA. After measuring the sulfuryl chloride, wash out the syringe in the hood by drawing acetone into the syringe and emptying it into the labeled container in the hood. Do this twice. At your bench, wash the syringe thoroughly with soap and water to remove any remaining sulfuryl chloride.

As always, any work in the organic lab must be done in the fume hood. Clamp the apparatus and to the ring stand. Make sure to attach gas trap as in the lab text. After a 20-minute reaction period (this means actively refluxing for 20 minutes, not time spent on the steam bath) the apparatus should be disassembled in the fume hood to minimize exposure to the HCl and SO2.

The reaction mixture is worked up by a series of extractions, dried over anhydrous CaCl\textsubscript{2} and analyzed by GC. Be careful during the extraction. The density of the organic layer is close to 1.0 g/mL, so depending upon the density of the aqueous layer and the extent to which the reaction has gone, the organic layer may be the upper or lower layer. Be certain that you know which layer is which. To help make the layers separate better, add several drops of saturated aqueous sodium chloride to the first water washing and use saturated aqueous sodium chloride in place of water for the last wash. The amount of product can be rather small. Add drying agent in small amounts, a couple of granules at a time. Too much will soak up the product. However, be sure that the product is dry (not cloudy and no visible signs of water). The product should be stored in a clean, dry Erlenmeyer flask and then analyzed by GC on the same day. A reaction tube should not be used for storage of the product mixture because the GC syringe cannot fit into a reaction tube. Purify the dried product via a fractional distillation. You should only separate any unreacted 1-chlorobutane. When this has finished collecting, switch collection vessels until the next drops come over, then switch again. Stop the distillation when the flask contains about 10% of the original volume.

**GC analysis.** There should be four peaks (you got rid of unreacted 1-chlorobutane in the distillation) 1,1-, 1,2-, 1,3-, and 1,4-dichlorobutanes. Retention times are in the order of the BPs of the 1,1-, 1,2-, 1,3-, and 1,4-dichlorides. After each use of the GC syringe, rinse it with acetone a few times and then dry it by removing the plunger and sucking air through it with an aspirator. If this is not done, the plunger will become stuck.

**Calculations.** Determine the % conversion = area of total dichlorides/(area of total dichlorides + area of 1-chlorobutane). The % of each dichloride isomer represents the % attack at each position. Because there are different numbers of H's at some positions, divide the % attack at each position by the # of H's at that position to get the % attack per H at each position. Divide the % attack per H at each position by the % attack per H at the primary position to obtain the relative reactivity of CH\textsubscript{2} to CH\textsubscript{3}, for the three CH\textsubscript{2} positions. Results then would be reported.
for example, as follows: "At 80° C and XX% conversion, the relative reactivities were v, x, y, and z for the 1,2, 3 and 4 positions of 1-chlorobutane." These four values can then be compared to the value of 2.5 for butane and the numbers discussed in terms of a possible polar effect.

Postlab Exercises.

1. Propose an experiment, or experiments, to further test any conclusions that you draw from this experiment. Explain your proposal in some detail and evaluate it critically. In other words, try to shoot holes in it and see if it can take the heat.

2. Draw structures of the products that would result from radical monochlorination of the following compound. What would be the relative product distribution (relative amounts only – e.g., most, least, etc)?

3. In your experiment, a large excess of 1-chlorobutane is used. This was done for the purpose of having a low conversion of 1-chlorobutane to the dichloro compounds. How might your results and conclusions be changed by using a 1:1 molar ratio of sulfuryl chloride and 1-chlorobutane? (Hint: in your gas chromatogram, if you allowed the sample to run for a longer time, you would notice that several other smaller peaks show up at longer retention times. What might these compounds be, what would the GC look like at a higher conversion, and how might this relate to this question?)