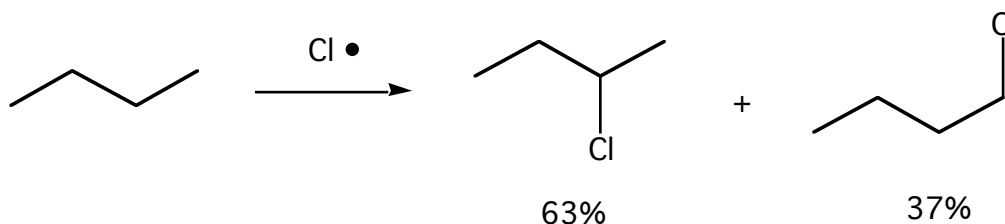<u>Radical Chlorination of 1-Chlorobutane.</u> The purpose of this experiment is to examine a possible polar effect on a free radical chlorination.

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.

$$\text{Cl} \bullet$$

63%   +   37%

Because there are six CH_3 hydrogens and four CH_2 hydrogens in butane, to compare the reactivity at each position, we must convert these results to % attack per hydrogen.

    CH_2 attack: 63%/4 CH_2 hydrogens = 15.8%/CH_2 hydrogen

    CH_3 attack: 37%/ 6 CH_3 hydrogens = 6.2%/ CH_3 hydrogen

This results in a relative reactivity (RR) for CH_2 to CH_3 hydrogens of

$$RR(CH_2/\ CH_3)\ =\ 15.8/\ 6.2 = 2.5$$

This means that under these reaction conditions, a CH_2 hydrogen is 2.5 times more reactive than a CH_3 hydrogen.

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 seeker). Reaction rate will be faster at positions having what characteristic?

<u>Experimental</u>. Turn on the sand bath immediately and begin heating a 30 mL beaker, half filled with water, to about 80°. As this is heating, you can measure out the reagents and set up the apparatus.

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. <u>CAUTION</u>: sulfuryl chloride is caustic and noxious and can react vigorously with HOH (the rate of reaction with water is slowed by its low water solubility - what are the products of reaction of sulfuryl chloride and water?). Weigh the azo compound into a DRY

reaction tube. Measure the chlorobutane in the hood using a graduated pipet and add it to the reaction tube. Measure the sulfuryl chloride in the hood using a syringe <u>without</u> a needle attached and add this to the rection 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.

The reaction and as much other work must be done in the fume hood. Clamp the reaction tube and the trap onto the same ring stand. If you are ready to begin the reaction and the temperature of the water bath has not yet reached about 80°, hot water will be available in a beaker on a hotplate. The water bath should be kept at 77° - 83° C during the reaction by raising or lowering the beaker into or out of the sand bath. The thermometer does not have to be clamped in the HOH bath as described in the book. The temperature can simply be checked occasionally, taking care to not allow the thermometer to be broken. When the bath temp is about 80^OC, the reaction tube should be clamped so that only the solution is in the HOH bath. It is important that the upper part of the tube remains cool so that the vapors will reflux gently and not distill away. The trap should be clamped and tilted as shown in the book so that the open end is pointing downward. This will help to prevent any drops of water from touching the end of the polyethylene tubing. If water touches the tubing, it will get sucked back into the reaction mixture and ruin it. This is also why the cotton should only be damp and not wet. After a 20 minute reaction period, the apparatus should be disassembled in the fume hood to minimize exposure to the HCl and SO_2. The cotton from the trap should be placed into the beaker containing aqueous sodium bicarbonate in the hood.
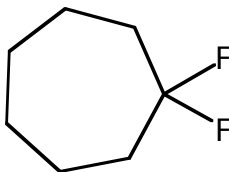
The reaction mixture is worked up by a series of extractions, dried and analyzed by GC. Be careful during the extraction. The density of the organic layer is close to 1, so depending upon the density of the aqueous layer and the extent to which the reaction has gone, the organic layer may be the upper 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 is 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.) Product should be stored in a clean, dry 100 mm (about 4") test tube capped tightly with a cork 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.

<u>GC analysis</u>. There will be five major peaks -- unreacted 1-chlorobutane, 1,1-, 1,2-, 1,3-, and 1,4-dichlorobutanes. The reaction goes to about 50% completion, so the 1-chlorobutane peak will be the largest. Retention times are in the order of the BPs -- mono, 1,1-, 1,2-, 1,3-, and 1,4-.   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_2 to CH_3, for the three CH_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?)