

Experiment 6

General Safety Considerations

1. Wear gloves and goggles for **all** operations.
2. SO_2Cl_2 = Sulfuryl Chloride is really NASTY. It is highly toxic and corrosive. The fumes are extremely irritating. When SO_2Cl_2 contacts water, it reacts very vigorously producing two very strong acids (try to predict which ones). Please be super careful with it. It must be destroyed before it is discarded. Dump it into cold H_2O in the hood to destroy it. The resulting aqueous solution must be dumped down the hood drain. Be especially careful of the trap water. Dump it down the hood drain.
3. AIBN is extremely toxic. This is why it has been preweighed for you. Wearing gloves, take the lid off the vial, dump the contents and give the vial back to your TA. **DO NOT WASH THE VIAL.**
4. Use care with the Na_2CO_3 washes. There may be a lot of pressure (why?). Vent often and swirl the flask in a very conservative fashion.
5. Chlorobutane and SO_2Cl_2 are toxic and irritating. Avoid all contact with these compounds by always wearing gloves and goggles and by working in the hood. If you should get any on your skin, flush the contaminated area with cold water for at least ten minutes. If a large spill occurs, contact your instructor.

/institutional research/

Chemistry 211-212**Investigative Experiments**

Name _____

TA Name: _____

Experiment # 6

Lab Day: _____

Section 1 (Pre-lab)	_____	(20 points)
Section 2 (Intro)	_____	(10 points)
Section 3 (E and R)	_____	(40 points)
Section 4 (Disc.)	_____	(30 points)
Section 5 (Post-lab)	_____	(20 points)
Quality of results	_____	(20 points)
TOTAL	_____	(140 points)
SCORE	_____	(percent)

This is your report cover. Please fill it out and attach it to your prelab.

Experiment 6

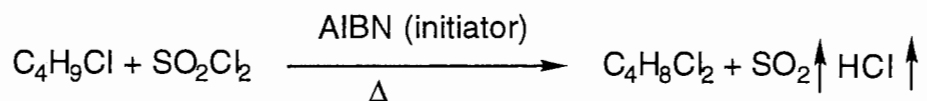
Free-Radical Substitution: Chlorination of 1-Chlorobutane

Quantification as such has no merit except insofar as it helps to solve problems. To quantify is not to be a scientist, but goodness, it helps.

P. B. Medawar, *Advice to a Young Scientist*

In this experiment you will use a gas chromatographic analysis to investigate the influence of molecular structure on reactivity in a free-radical reaction. You have learned about free-radical brominations brought about by N-bromosuccinimide. With this reagent, the most susceptible positions on a molecule are the *allylic* positions of alkenes and the *benzylic* positions of aromatic compounds. It is possible, in addition, to halogenate saturated carbon atoms that occupy no special position in a molecule. A reagent for bringing about such chlorination reactions is *sulfuryl chloride*, SO_2Cl_2 . As part of your preparation for this lab, study pp. 197-200 and 371-373 in Loudon and answer the following prelab questions.

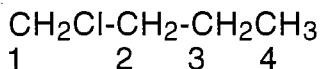
1. Given the following balanced chemical reaction describing the chemistry of this experiment, calculate the weight expected to be lost during the reflux step. (Hint: this is a simple yield calculation. Weight losses are due to any gases formed).



2. Write chemical equations that explain why the aqueous layer eventually becomes basic during the extraction process. (Hint: Na_2CO_3 - how does it react with water)
3. a) Why is the chlorination reaction mixture cautiously poured into an ice cold, saturated NaCl solution. (Hint: the only reagent here is the water. NaCl has its usual function. See safety page.)
b) Write an equation defining the chemistry occurring in the step described in question 3.

When butane is subjected to free-radical chlorination, two mono-chloro products are obtained: 1-chlorobutane and 2-chlorobutane (di- and higher substitution can be minimized by making the sulfuryl chloride limiting). Two factors influence the proportion of products obtained from a free-radical chlorination: the number of replaceable H atoms at each position, and the intrinsic reactivity per H atom at each position. On the basis of number of H atoms, we expect the ratio of 2-chloro- to 1-chlorobutane to be 4:6, or 2:3, or 1:1.5. The observed ratio, however, is 1:0.4 (a higher ratio). Thus the intrinsic reactivity of the secondary position of butane is greater than that of the primary by a ratio of $1.5/0.4$, or 3.75. In other words, the secondary position of butane is 3.75 times more reactive than the primary position. This is because a secondary alkyl radical is more stable than a primary one. Since the transition states for the formation of the radicals have some radical character (Hammond postulate), the secondary radical is formed faster than the primary.

What if the reactant, instead of being butane itself, already has one chlorine atom in it, as in 1-chlorobutane (below)? First, there will be **four** different dichloro-

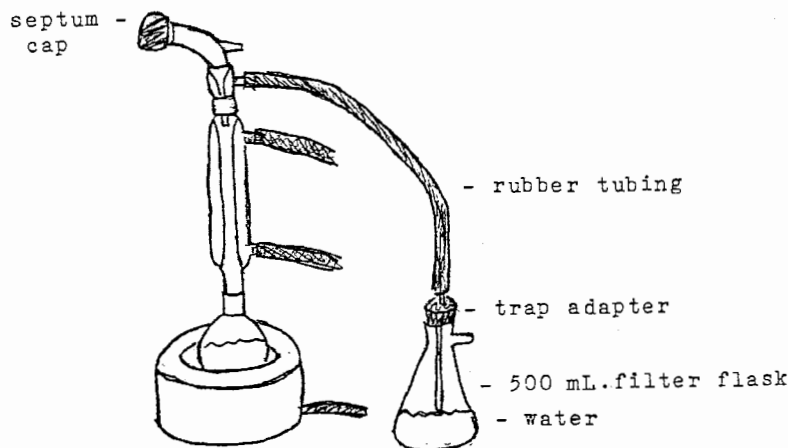


substituted products. Second, we might expect that the Cl atom already present, because it is electron-withdrawing, ought to have some effect on the reactivity of this molecule. What this effect is, whether it increases or decreases reactivity, will be examined in this experiment. Furthermore, whatever the effect, we expect it to fall in strength with increasing distance from the chlorine atom. Thus we predict that the four C atoms of 1-chlorobutane ought to be different in their reactivity toward chlorination, and that there should be a trend (in one direction or the other) in moving from C-1 to C-4. You will carry out the free-radical chlorination of 1-chlorobutane and analyze the products by GC. After mathematically correcting for the different number of replaceable hydrogens at different positions, you will be able to see whether there is a trend in reactivity as predicted, and if so in which direction.

Our computational approach is as follows: we determine the area under each peak in the GC and calculate the percentage of each isomeric product formed. We divide each percentage by the number of hydrogens at the position where the second Cl atom added. This gives us the intrinsic reactivity at each position. We then make an assumption: that the C-4 position is so far from the Cl atom originally present in the molecule that it is not affected by it. Granting this assumption, we must recognize that C-4 is a primary carbon, whereas C-3 and C-2 are secondary. To correct for this difference, we recall that the ratio of reactivities of secondary to primary positions in **butane** is 3.75. We now calculate the ratio of reactivity at C-3 of 1-chlorobutane to that at C-4 to obtain the secondary/primary ratio for the C-3 position of this molecule. Then, by comparing this ratio to 3.75, the ratio for unsubstituted butane, we will see whether the reactivity at C-3 has been increased or diminished by the Cl at C-1. We then do the same for reactivity at C-2. Finally, we simply compare the intrinsic reactivity of C-1 with that of C-4 in 1-chlorobutane, since they are both primary positions.

Procedure

1. Assemble IN THE HOOD the apparatus pictured on the next page, consisting of a flask heater and a 50 mL round-bottomed flask fitted with a reflux condenser which in turn is connected, through a curved adapter fitted with a serum cap, to a 500-mL filter flask functioning as a water trap to dissolve the gaseous HCl and SO₂ given off during the reaction. Leave the side-arm of the filter flask open. Be sure to leave about 4 inches of space under the flask heater.



CAUTION: Great care must be taken to avoid having any water from the trap getting sucked back into the reaction flask, because sulfuryl chloride reacts **violently** with water. The glass tube must **not** dip below the surface of the water in the trap. **HAVE YOUR TA CHECK YOUR APPARATUS BEFORE YOU ADD THE REACTANTS.**

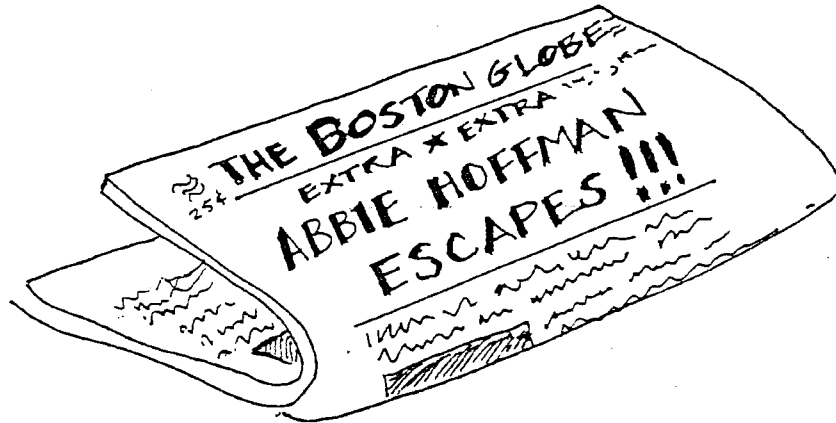
2. Detach your 50-mL round-bottom flask from the apparatus and place in it 5 mL (4.5 g, 0.05 mole) of 1-chlorobutane, 2 mL (3.4 g, 0.025 mole) of sulfuryl chloride (CAUTION: sulfuryl chloride is corrosive, toxic, and lachrymatory!), and ca. 0.05 g of azobisisobutyronitrile (AIBN) (0.05 g samples of AIBN will be provided in small vials). Cork the flask at once, (write your initials on your cork to avoid confusion and resulting error in weight.) Measure the total weight of the flask, stopper, and contents.
3. Take the weighed flask to the hood, remove the stopper, and reconnect the flask to the reflux condenser. Heat the mixture under gentle reflux for 20 minutes. (Do not heat your reaction mixture too vigorously or you may inadvertently distill out some 1-chlorobutane and consequently be misled into thinking that you have achieved the theoretical weight loss before all of the sulfuryl chloride has reacted.) Then remove the heater and cool the flask in an ice bath. Detach the cooled flask from the condenser, **replace the stopper**, and measure the total weight once again. Compare the actual weight loss with that expected theoretically. (You should have calculated the theoretical weight loss before coming to the laboratory.) If the measured loss is significantly less than the theoretical loss, add another 0.05 g portion of AIBN and heat the mixture under reflux for an additional 10 minutes. If your reaction mixture has still not lost the appropriate weight at this stage, consult your TA.
4. When you are finished with your reflux condenser and gas trap, disassemble the apparatus completely and pour the contents of the filter flask into one of the small drains **in the hood**. Then leave all of the disassembled equipment in the hood for about 15 minutes to allow the residual gaseous HCl and SO₂ to be swept out. The object here is to minimize the extent to which these noxious gases escape into the laboratory when you clean up your glassware at one of the main sinks.
5. After your chlorination reaction is complete, as judged by the loss of weight, cool the reaction mixture in an ice-water bath and then **cautiously** pour it into 12.5 mL of a saturated solution of sodium chloride in water in an Erlenmeyer flask that is

also being cooled in the ice-water bath. This is the last of the operations in this experiment that needs to be carried out in a hood.

6. Transfer the two-phase mixture resulting from step 5 to a 125-mL separatory funnel and separate the two layers. (If you obtain an emulsion, consult your TA or instructor.) Set aside the water layer (to be discarded eventually). Wash the organic layer in the separatory funnel with a 10 mL portion of 0.5 M aqueous sodium carbonate solution. Test the aqueous layer to be sure it is basic to litmus paper. If it is not, repeat the washing until the aqueous wash is basic to litmus. Be careful to vent the funnel frequently during these sodium carbonate washes. Why? Finally, wash the organic layer with one 10 mL portion of saturated aqueous NaCl.
7. Transfer the washed organic layer from the separatory funnel to a 50-mL Erlenmeyer flask and dry it over anhydrous magnesium sulfate. Filter the dried solution into another dry 50-mL Erlenmeyer flask or a dry vial.
8. Analyze the dried organic product directly by gas chromatography. The instructions and conditions for the gc analysis and a representative trace are posted near the gas chromatographs. Note that the unreacted 1-chlorobutane is **not** included in your calculations; the gc peak for this major component of the mixture should be "off-scale" in order for the peaks for the dichloro products of interest to be of sufficient size to enable a reasonably accurate analysis of their relative areas.
9. Include the following in your lab report:
 - a. The area of each peak.
 - b. The percentage of each product obtained (excluding the huge 1-chlorobutane peak). Yes, this means that you have to recalculate the ratio.
 - c. Calculate **reactivity per H atom** position. This is the percent of a given product calculated in "b" divided by the number of hydrogens at the position before substitution.
 - d. Calculate the **secondary/primary ratios** at positions 2 and 3. This is calculated by dividing the numbers obtained for positions 2 and 3 by the number obtained for position 4 (why do you think you use position 4?) in part "c" above.
10. Include the following points in your discussion.
 - a. A comparison/contrast of $2^\circ/1^\circ$ ratios for C-2 and C-3 of chlorobutane with the $2^\circ/1^\circ$ ratio of butane. Explain what the differences mean in terms of relative reactivity.
 - b. An evaluation of any trends in reactivity along the carbon chain.
 - c. A physical explanation of the trends in reactivity and relative reactivity observed. (Possibilities: think about electronic, resonance and steric effects.)

Everything should be made as simple as possible, but not simpler.

Albert Einstein



"Free Radical" by Liza Donlon/Heather Campbell

Specific Point Breakdown for Experiment 6

I. Pre-Lab Exercises (*20 points total*)

Point breakdown:

1. **6** points
2. **4** points
3. **4** points
4. **6** points

II. Introduction (*10 points total*)

III. Experiments and Results (*40 points total*)

Point breakdown:

- 8** points for GC trace with peaks identified and parameters recorded
- 8** points for the retention times for the four dihalide peaks
- 8** points for the calculation of the percent of each product in mixture from GC areas
- 8** points for the calculation of the reactivity per hydrogen atom
- 8** points for the calculation of the secondary/primary ratio for each of the two methylene positions

IV. Conclusions (*30 points total*)

For this experiment, this section should include:

- 10** points for the points for the discussion of the trend in reactivity and comparison of the two secondary/primary ratios with the secondary/primary ratio of butane (3.75)
- 10** points for the physical explanation of the effect of the chlorine atom on reactivity in chlorobutane
- 10** points for a discussion of errors

V. Answers to Exercises (*20 points total*)

Point breakdown:

- a. **10** points
- b. **10** points

VI. Quality of Results (*20 points total*)