# Experiment 6

## General Safety Considerations

1. Wear gloves and goggles for all operations.
2. 1-Chlorobutane is toxic and irritating. Avoid all contact with this compound 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 fifteen minutes. If a large spill occurs, contact your instructor.
3. Sulfuryl chloride is a lachrymator and in its lachrymator activity decomposes to form two very corrosive acids in the presence of water or aqueous sodium hydroxide. What acids would form? The compound itself is toxic and irritating, the products are very corrosive to skin and mucous membranes. Avoid all contact. If you have any exposure, flush the exposed area with cold water for fifteen minutes. Avoid exposing the reagent to water or aqueous base in an uncontrolled way. Please notify your instructor of any exposure to this compound.
4. AIBN also known as azo-bis-isobutyronitrile is toxic and unstable (it produces nitrogen gas and radicals upon heating. This means it is potentially explosive. Rest

assured, the reagent will be measured for you in a vial in very small quantity. But,

if you have any exposure, let your instructor know and rinse the exposed area for fifteen minutes with cold water.

# Flip-flops, open toed shoes and shorts are strictly prohibited.

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| **Name****Chemistry 211-212 Investigative Experiments** | **TA Name:** |
| **Experiment** # 6 | **Lab Day:** |
| **Unknown** # |
| Section 1 (Pre-lab) | (20 points) |
| Section 2 (Intro) | (10 points) |
| Section 3 (E and R) | (30 points) |
| Section 4 (Disc.) | (40 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 prefab.**

# Experiment 6Free-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 ally/lc 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 that will bring about this reaction is chlorine in the presence of light. Please review your text on this subject. You should look up halogenation of alkanes in the index of your text . Another reagent combination that can bring about this reaction is *sulfuryl chloride*, SO2Cl2 in the presence of *AIBN*. Though it has safety issues, as indicated earlier in this text, they are easier to handle as they are a liquid and solid, respectively.

**Prelab Questions**

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

 AIBN, heat

 1-chlorobutane + SO2Cl2  dichlorobutanes + HCl + SO2

2. Write chemical equations that explain why the aqueous layer eventually becomes basic during the extraction process. (Hint: Na2CO2 – 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 is present to “salt out”. See safety page.) (b) Write an equation defining the chemistry occurring in the step described in part (a) of this question.

When butane is subjected to free-radical chlorination, two mono-chioro products are obtained: 1-chlorobutane and 2-chlorobutane (di- and higher substitution can be minimized-how?). 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-

CH2CI-CH2-CH2CH3

1 2 3 4

substituted products. Second, we might expect that the CI 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 CI 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 and Lab Writeup**

1. Assemble **in the hood** the apparatus pictured below, 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 septum cap, to a 250 or 500 mL filter flask functioning as a water trap to dissolve the gaseous HCl and SO2 produced 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 OR INSTRUCTOR CHECK YOUR APPARATURS BEFORE YOU ADD THE REACTANTS. NOTE: THE DIAGRAM BELOW DOES NOT SHOW THE TRAP ADAPTOR OR THE SEPTUM CAP.



1. Detach your 50 mL roundbottom 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 a lachrymator!!!), and ca. 0.05 g of azo-bis-isobutyronitrile (AIBN) (0.05 g samples of AIBN will be provided in small vials which you should return without washing to your intstructor without washing at the end of lab). Cork the flask at once in the hood. Transport the corked flask to the balances and measure the total mass of the flask, stopper and contents. Why does the flask have to be corked at the balances? Record this mass in your notebook. Please record all lab data in your laboratory notebook.
2. Get ahead tip, with your flask heater sitting on the bench – not touching the flask- preheat it at 20 volts.
3. Take the massed flask back to your hood, remove the stopper, and reconnect the flask to the reflux apparatus. Heat the mixture under gentle reflux for twenty minutes. This would require a voltage setting of about 40-50 volts. Note, the twenty minutes is from the beginning of reflux, not from the beginning of heating. See the Youtube linked into the course schedule that explains how to build a reflux apparatus. You may have to adjust the voltage. You do not want to heat your reaction mixture too vigorously or you may inadvertently distill out some reagents and products and consequently be misled into thinking that you have achieved the theoretical weight loss before all the sulfuryl chloride has reacted. After the twenty minute reflux, remove the heater and coll the flask while attached to the apparatus with an ice bath (bring the ice bath to the flask while attached). It will take about five minutes for it to cool. Detach the cooled flask from the condenser, **replace the stopper**, and measure the total mass once again. Compare the actual mass loss with the theoretical calculated before lab and consult your instructor or TA as to how to proceed. Sometimes more AIBN is added and additional reflux is carried out, but this is rare. A wide range of mass losses will work.
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 (cup sinks) **in the hood**. Then leave all 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 being cooled in the ice-water bath. This is the last of the operations in this experiment that must be carried out in the hood, though you should try to work in the hood whenever possible.
6. Transfer the two-layer mixture resulting from step 6 into a 125 mL separatory funnel and separate the two layers. (If you obtain an emulsion consult your instructor or TA.) Determine which layer is organic (you should be a pro at this by now) and set aside the layer that you ascertain to be aqueous (do not discard yet!!!). With the organic layer in the separatory funnel, wash it with a 10 mL portion of 0.5 M aqueous sodium carbonate solution. Test the sodium carbonate, aqueous layer with pH paper to see if it is basic. If it is not basic, continue to wash the organic layer with fresh, 10 mL portions of sodium carbonate until the wash is basic. What are you trying to do here? Finally wash the organic layer with aqueous NaCl. Do not throw any aqueous layers out until your are sure you have the organic layer in hand.
7. Transfer the washed organic layer 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. Alternatively, you can dry the organic liquid by passing through a micro drying pipet filled with about a 1-1.5 cm of anhydrous magnesium sulfate. Please see the Youtube regarding this subject on the schedule for this course linked in with this experiment.
8. Analyze the dried organic product directly by gas chromatography. You will be injecting 1 microliter of your material into the GC. If you have any questions please ask your instructor. There is a Youtube on operating the GCs linked into this experiment on the the chem 211 schedule. 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:
	1. The area of each peak.
	2. The percentage fo each product obtained (excluding the huge 1-chlorobutane peak). Yes, that means you have to recalculate the ratio.
	3. 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.
	4. Calculate the secondary/primary rations 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.

	1. A comparison/contrast of 2o/1o rations for C-2 and C-3 of 1-chlorobutane with the

2o/1o ratio of butane. Explain what the differences mean in terms of relative reactivity.

* 1. An evaluation of any trends in reactivity along the carbon chain.
	2. A physical explanation of the trends in reactivity and relative reactivity observed. (Possibilities: think about electronic, resonance and steric effects (they may not all be applicable, they are just possibilities)
1. Answer the following questions at the end of your lab report.
	1. Given the following equations for initiation, using the arrow formalism write a complete mechanism (include propagation and termination steps) for the reaction your carried out in lab.



 Please note that the above is the initiation sequence without arrows. To write the

 complete mechanism, you must include all propagation steps and one termination

 step with the arrows.

* 1. What are less than stoichiometric amounts of SO­2Cl2 and AIBN used in this reaction

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# 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**

Pre-Lab Exercises *(20 points total)*

Point breakdown:

1. 6 points
2. 4 points
3. 4 points
4. 6 points
5. Introduction *(10 points total)*
6. 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

1. 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

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

Point breakdown:

* 1. 10 points
	2. 10 points
1. Quality of Results *(20 points total)*