# Experiment 6

## General Safety Considerations

1. Wear gloves and goggles for all operations.
2. Chlorobutane and bleach 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 fifteen minutes. If a large spill occurs, contact your instructor.
3. Hydrochloric acid is very corrosive and gives off corrosive, noxious fumes. 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. Do not breath the vapor.

#  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. Chlorine can be generated from ordinary household bleach in the presence of hydrochloric acid as outlined in the equation below. As part of your preparation for this lab, study pp. 338 and 749-750 in your textbook, Loudon, and answer the following prelab questions.

NaOCI + HCI Cl2 + NaOH

light

 1-chlorobutane + Cl2  dichlorobutanes + HCl

**Prelab Questions**

1. If you are using 3 mL of chlorine bleach (bleach is 5 grams of NaOCI per 100 mL of water) and 3 mL of 1-chlorobutane, how many moles of each reagent are you using in the reaction. (5 points)
2. What is the limiting reagent in the reaction and why do you believe this is so. (5 points)
3. Propose a mechanism for the formation of chlorine (Cl2) from sodium hypochlorite in the presence of hydrochloric acid. (10 points)

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 dicholoro-

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-' with that of C-4 in 1-chlorobutane, since they are both primary positions.

**Procedure and Lab writeup**

The Chlorination of 1-Chiorobutane using Chlorine Bleach

1. To a 50 mL round bottom flask from your kit, add 3 mL of 1-chlorobutane, 3 mL of chlorine bleach (5 % NaOCI in water) and 1.5 mL of 3M hydrochloric acid .
2. Add asmall stir bar to the flask and clamp your flask at an angle on the monkey bars over a stir plate. Rapidly stir the reaction, lightly stopper under the provided lamp with a clear bulb for 15-20 minutes. The reaction should turn a green color after addition of the HCI solution and that green color should gradually dissipate with time. Do not stop the reaction until the green color has dissipated.
3. Throughout the reaction and at the end there should be two layers in the flask (why?). When the reaction is complete, add 300 mg of sodium bicarbonate until the aqueous layer is neutralized. Measure the pH of the aqueous layer with pH paper. Do not dip the paper. What is the proper technique? How will you determine which layer is aqueous and which is organic?
4. When the pH of the aqueous layer has been adjusted, transfer the two layer reaction mixture to your smallest separatory/addition funnel ( from your kit). Separate the layers and isolate the organic layer. Do not throw anything away any layers until you are absolutely sure you have isolated the organic layer.
5. Dry the organic layer over sodium sulfate. One way to dry such a small amount of liquid is to add a small amount of glass wool to a Pateur pipet and then add a two to three cm of sodium sulfate to the pipet. Using another pipet slowly allow your wet organic layer to percolate through the bed of sodium sulfate into another small container (i.e., a vial).
6. Analyze your reaction mixture by injecting 3-4 microliters onto the GC. You will need the identity and percent areas of the peaks.
7. Include the following in your lab report (or prepare the following for your conference).

**Experiments and Results**

* 1. The GC and the area of each peak. ( 8 points)
	2. The percentage of each product obtained (excluding the huge 1-chlorobutane peak). Yes, this means that you have to recalculate the ratio. (6 points)
	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. (8 points)
	4. 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. ( 8 points)

**Discussion**

* 1. A comparison/contrast of 2°/1 ° ratios for C-2 and C-3 of chlorobutane with the 2°/1 ° ratio of butane. Explain what the differences mean in terms of relative reactivity. (8 points)
	2. An evaluation of any trends in reactivity along the carbon chain. (8 points)
	3. A physical explanation of the trends in reactivity and relative reactivity observed. (Possiblities: think about electronic, resonance and steric effects.)

Interpret the results. Focus on the two secondary sites. On a molecular/ mechanistic level, can you explain why you are seeing the reactivities/hydrogen that you have for the secondary sites. (24 points)

**Post Lab Questions**

* 1. The mechanism for the entire reaction. ( 20 points)

After you are finished working on these issues, you will either complete a normal investigative write up (see introductory pages of lab manual) or groups of three or four will present this data in a conference with your instructor.

# 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)*