Justin Barry
Professor Bill Dailey
Chemistry 502

Experiment #3, Alkanes: Chlorination

Experimental Organic Chemistry: A Miniscale and Microscale approach by Gilbert and Martin, Section 9.1-9.2

7-17-06

TA: Mike and Carolyn

INTRODUCTION:

In this experiment the reactivity of alkanes will be understood with free-radical chlorination. Gas chromatography will be used to examine the products of the reaction of sulfuryl chloride with 1-chlorobutane. The purpose of this lab is to produce four isomers of dichlorobutane and determine the percent composition of each. To perform this lab, chlorine will be reacted with 2,2`-azobis[cyclohexanenitrile] to produce a chlorine free radical. Then, the free radical will be reacted with sulfuryl chloride, which is the limiting reagent. A theoretical yield of the combined isomers can be obtained using the sulfuryl chloride as the limiting reagent. Gas chromatography will aid in dertermining the % composition of the dichlorobutanes.

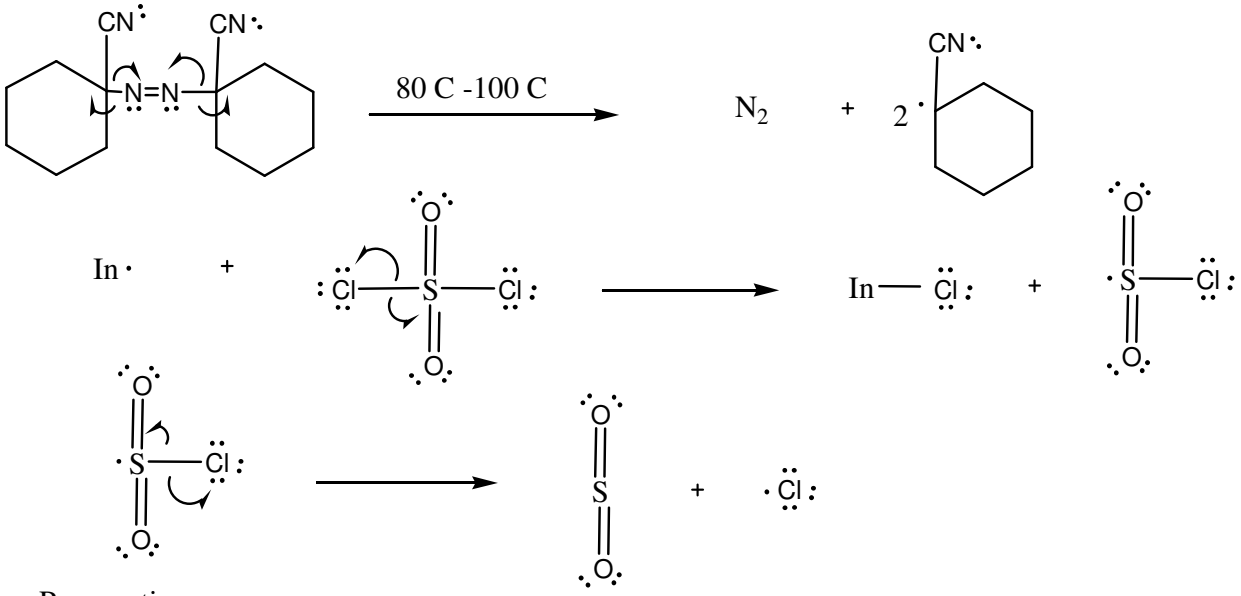
PROCEDURE

- Use a thermowell with a variable transformer and magnetic stirbar.
- Assemble the apparatus as shown in picture (p 258 in G&M) under the hood. Be sure the glass tube does not dip below the water.
    - Make sure all connections are air tight
    - Do not use a water aspirator
    - Tubing must be fire-polished on both ends
    - Lubricate hole in stopper with glycerine
- Add a stirbar and 0.1g of 2,2`-azobis[cyclohexanenitrile] (ABCN) to a 25-mL tarred round bottom flask.
- Add 5-mL of 1-chlorobutane and 2-mL of sulfurylchloride into the flask.
- Stopper and weigh flask. Attach to condenser quickly.
- With stirring, heat solution under gentle reflux for 20 min and allow mixture to cool below the reflux temperature.
- Add a second 0.1g ABCN and heat under reflux for another 10 min.
- Weigh flask and make sure mixture has lost 90% of expected weight.
- Cool the mixture in an ice-water bath and cautiously pour it with stirring into 15 mL of ice-cold saturated aqueous sodium chloride (brine) in an Erlenmeyer flask if the two layers form an emulsion.
- Separate the layers in a separatory funnel.
- Wash the organic layer in the funnel with 10-mL of 0.5 sodium carbonate solution, venting the funnel frequently.

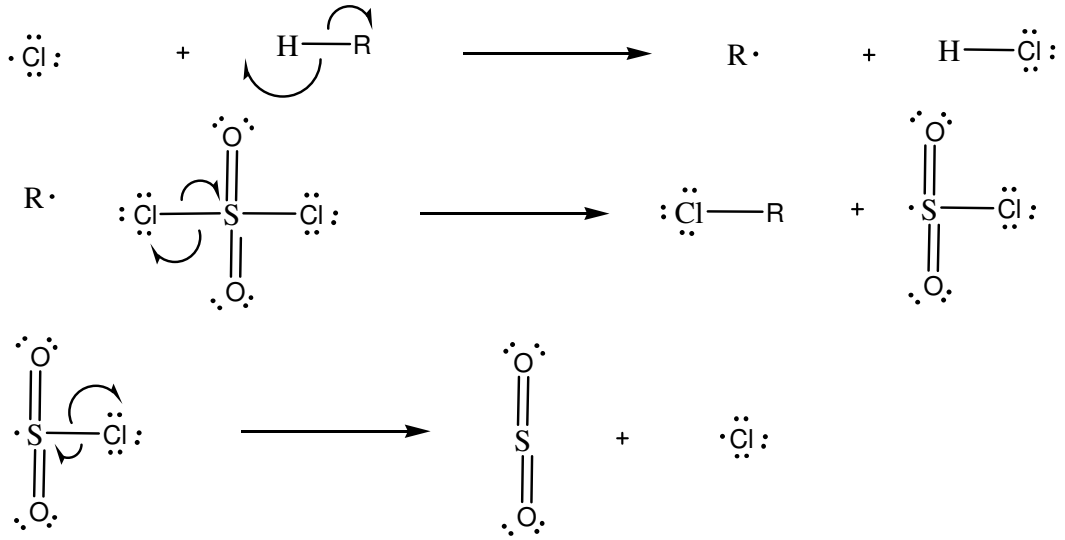
- Using pH paper, determine whether or not the aqueous layer is basic. If not, repeat washing the organic layer with 10-mL portions of sodium carbonate solution until the aqueous washes are basic.
- After washing the reaction mixture with 15-mL of brine, transfer the organic layer to an Erlenmeyer flask containing several spatula-tips full of anhydrous sodium sulfate. Let the mixture stand for 10-15 minutes, swirling occasionally. Make sure the mixture is clear.
- Decant the organic layer into a tarred container.
- Calculate the material isolated
- Determine the theoretical yield and actual weight obtained and % yield.
- Analyze the organic mixture by GC (the peak for 1-chlorobutane should be "off scale" in order for the product peaks to be of sufficient size to enable an accurate analysis.
- Determine the % composition of the mixture of the 4 isomeric dichlorobutanes (see figure 9.1 on p. 259 of G&M for identification of various peaks)

REACTION AND MECHNAISM

Initiation



Propagation



Termination

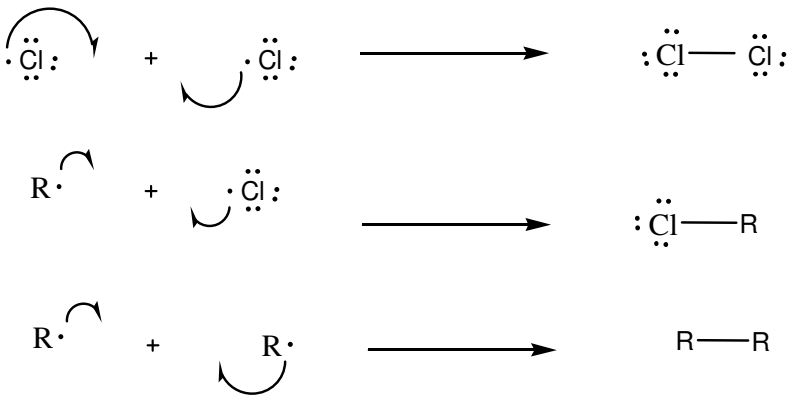


TABLE 1: REACTANTS

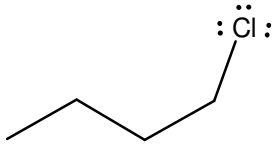
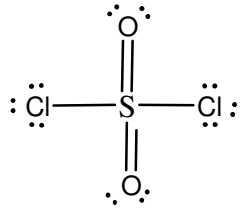
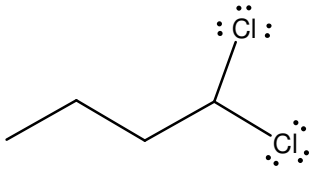
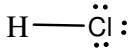
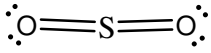
Compound Number	Compound	Theoretical Amt used/required (g)	Molecular Weight (g/mol)	Physical Properties
1	 1-chlorobutane	2.33	92.54	Denstiy: 0.89 g/mL Flammable
2	 Sulfuryl Chloride	3.34 “All used up”- limiting reagent	134.97	Density: 1.68 g/mL Toxic, corrosive, lachrymatory

TABLE 2: PRODUCTS

Compound Number	Compound	Theoretical Yield (g)	Molecular Weight (g/mol)	Physical Properties
3	 Dichlorobutane (one of 4 structures)	3.20	127	Denstiy: 1.086 g/mL b.p. 112 ° C
4	 Hydrochloric Acid	.919	36.46	Dissolves in Water b.p. -85.06ºC Corrosive
5	 Sulfer Dioxide	1.61	64.07	b.p. -10.06ºC Antioxidant

YIELD DATA: Theoretical and Observed

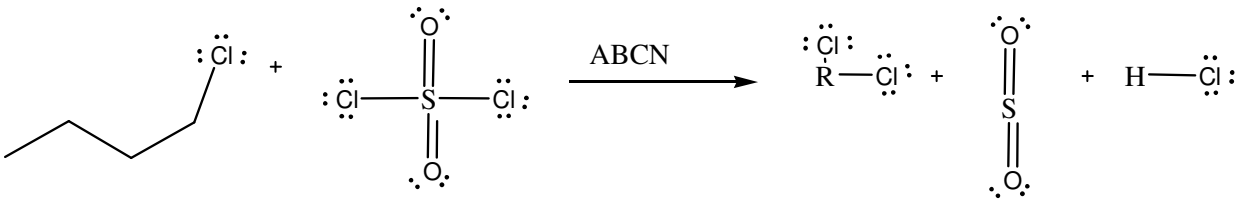
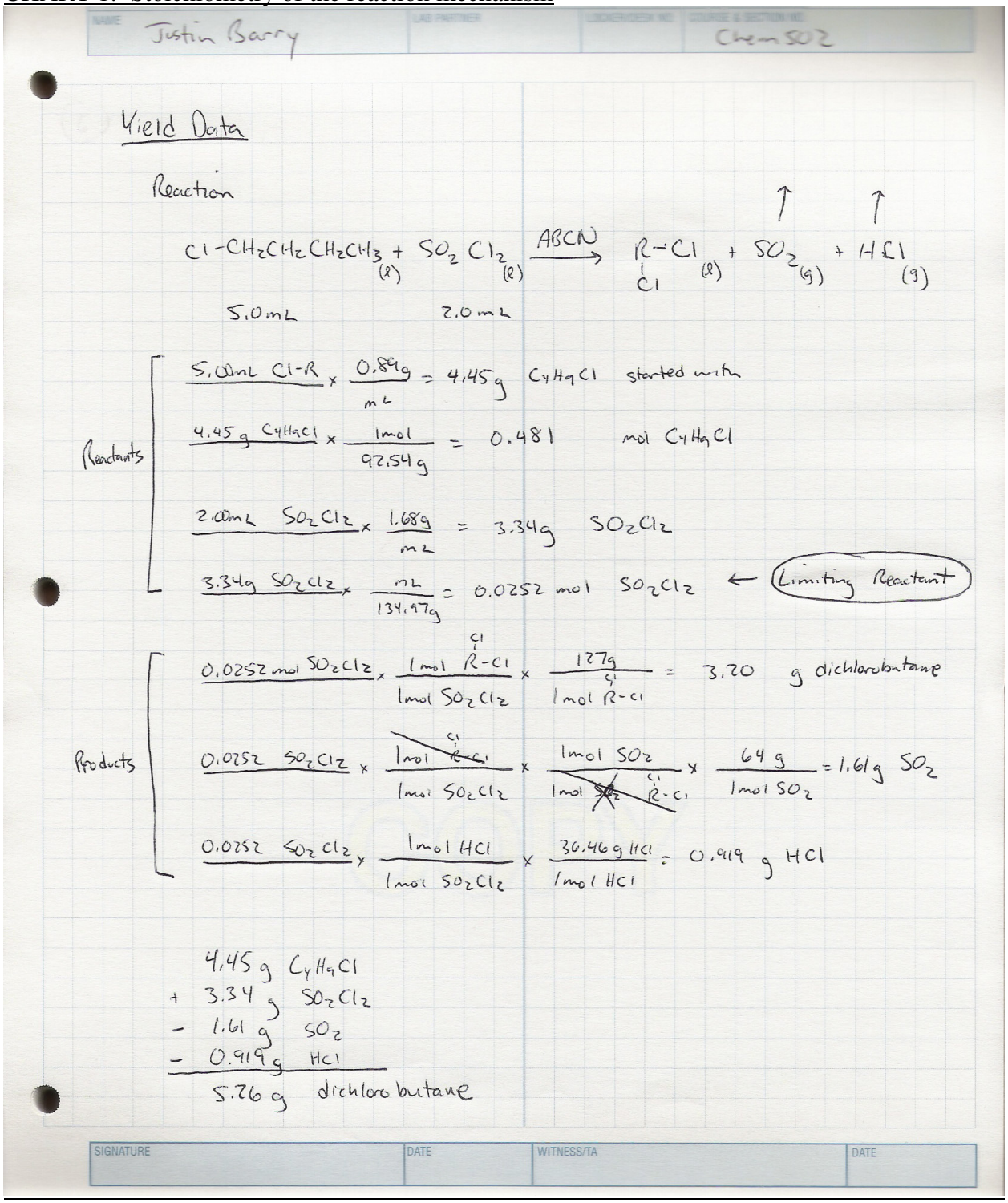


CHART 1: Stoichiometry of the reaction mechanism



As shown above, sulfuryl chloride was the limiting reactant. In addtion the sulfur dioxide and hydrochloric acid was lost as gas. Therefore, the total weight that should have been lost was 1.61 g sulfur dioxide + 0.919g hydrochloric acid. The total theoretical weight loss was 2.52 g of product. After weighing my reaction, I had 2.24g of product lost. This was approximately 89% of product lost.

5.26 g of dichlorobutane (and remaining 1-chlorobutane) is the amount of product the should have been retrieved. The percent yield is shown in Table 3 below.

TABLE 3: % Yield data of Dichlorobutane

Compound	Theoretical	Observed	% Yield
Dichlorobutane	5.26 g	1.19g	22.6 %

Table 3 shows the theoretical value of dichlorobutane in its various forms. The math for the reaction can be found in Chart 1 above. The observed value of 22.6% was relatively low. This could be from dichlorobutane left with the hydrous sodium sulfate and left in the separatory funnel. Another possible cause of low % yield could be from loosing some of the organic layer in the discarded aqueous layer. I suspect the latter because after adding sodium bicarbonate, only a small amount of venting was needed. This suggests that there was hardly any water in the organic layer. When separating, the organic layer might have been deposited slightly in the aqueous layer, hence the very small amount of aqueous layer in the sodium bicarbonate wash.

Gas Chromatograph Data

- GC #7
- Column A
- 2.5 µL
- Polarity (+)
- Current: 100 mA
- Column T = 128 ºC
- Detector = 150 ºC
- Injector = 130 ºC

CHART 2: % Composition from the Gas Chromatography of dichlorobutane (peaks labeled)

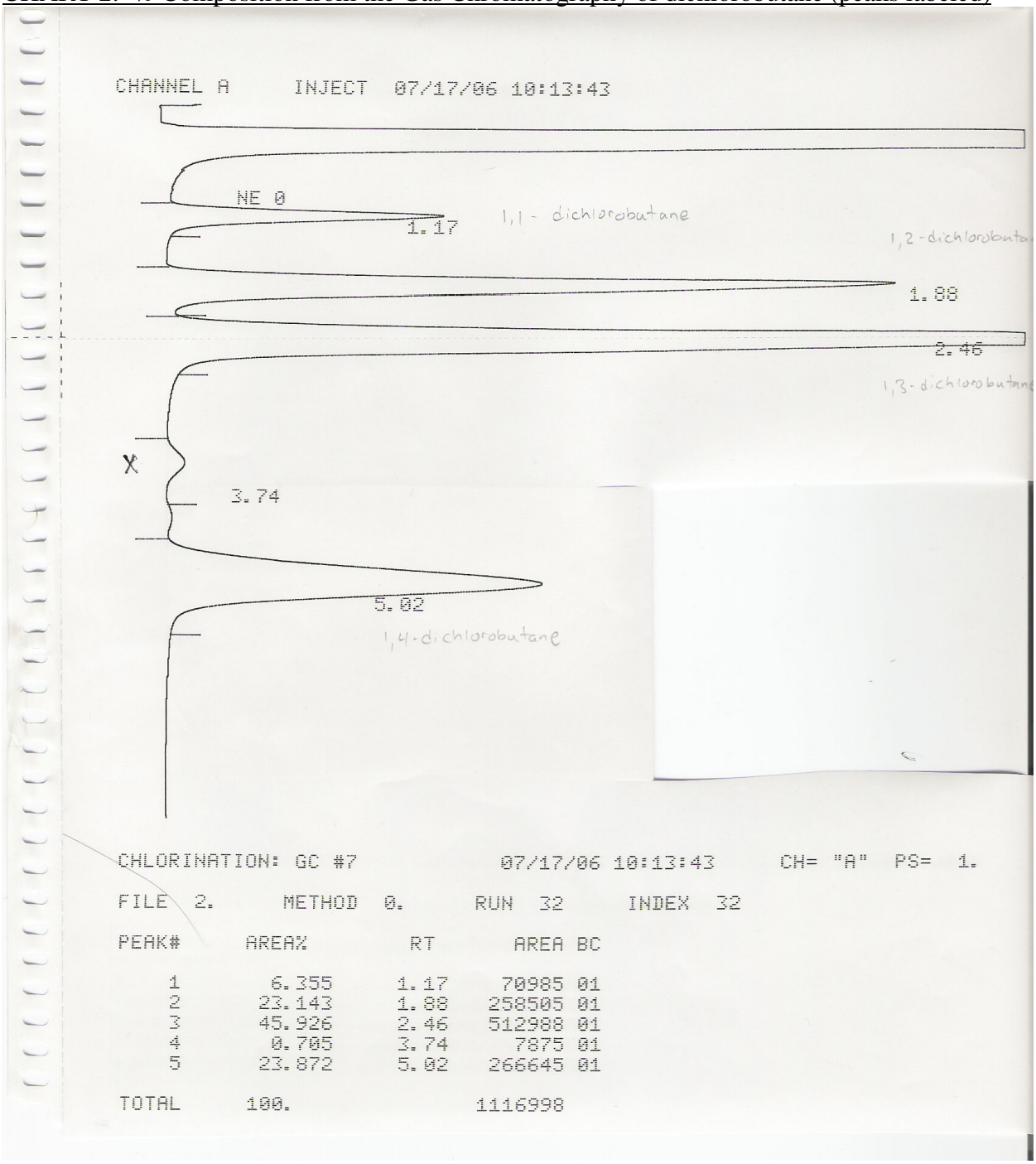


TABLE 4: % Composition of Dichlorobutane and Relative Reactivity

Compound	% Composition from GC	Relative Reactivity
1,1-dichlorobutane	6.355	1.00
1,2-dichlorobutane	23.143	3.64
1,3-dichlorobutane	45.926	7.22
1,4-dichlorobutane	23.872	2.50

Table 4 consists of the % composition of each of the four dichlorobutanes. After the % was obtained from the GC, it was divided by the number of hydrogens that the chlorine could have bonded to (2,2,2, &3 respectively). After making the least reactive compound have a relative reactivity of 1 (1,1-dichlorobutane), the rest of the reactivates were calculated.

TABLE 5: Results from Reaction

	Weight (g)		Weight
Flask and Reagents before	67.62	Flask and Organic Products	47.30
Flask and Reagents after reflux	65.38	Flask	46.11
Reagents	2.24	Organic Products	1.19

Table 5 shows the results of the experiment after weighing reactants and products. 1.19g of dichlorobutane was retrieved from the experiment. Table 3 shows the % yield of the reaction.

SYNOPSIS OF AND NOTES ON EXPERIMENTAL PROCEDURE-RESULTS

According to the data only 22% of the overall product was retrieved. Despite this poor result, the Gas-Liquid Chromatograph had plenty of liquid to use to get a solid result. After running the GLC, Table 4 above indicated the percent composition for each of the dichlorobutanes. As stated in the purpose of the lab, our intention was to see what the relative reactivity of each of the carbons; primary and secondary. From our data, one can see that the primary carbons on the 1,1-dichlorobutane and 1,4-dichlorobutane had a relative reactivity of 1.00 and 2.50 respectively. 1,4-dichlorobutane was slightly more reactive because of the additional place for the hydrogen to attach (3 positions as opposed to 2 positions). In addition, the secondary hydrogens were more reactive; 3.64 and 7.22 respectively. The data supports the prediction that secondary hydrogens are more reactive.

TABLE 4: % Composition of Dichlorobutane and Relative Reactivity

Compound	% Composition from GC	Relative Reactivity
1,1-dichlorobutane	6.355	1.00
1,2-dichlorobutane	23.143	3.64
1,3-dichlorobutane	45.926	7.22
1,4-dichlorobutane	23.872	2.50

OBSERVED PHYSICAL PROPERITES OF THE PRODUCTS OBTAINED

After the extraction of the aqueous layer on the bottom of the separatory funnel, the top organic layer was what was left as the product. Dichlorobutane was originally cloudy but cleared up after adding anhydrous sodium sulfate in several spatula additions. Also, the organic layer was slightly viscous.

SIGNIFICANT SIDE REACTIONS

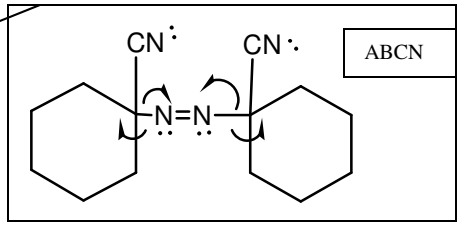
All of the significant side reactions are located in the Reaction and Mechanism above. The initiation, propagation, and termination steps all have very important side reactions that enable us to produce the four different forms of dichlorobutane.

METHOD OF PURIFICATION

Flow Chart of Lab (The numbers in the following flow chart are derived from Table 1: Reagents and Table 2: Products). The dichlorobutane was purified using separation of the aqueous and organic layer. This method proved to be successful despite the low percent yield in my particular experiment. The flow chart below details this procedure of separation.

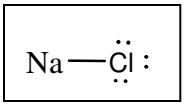
Mixture of 1, 2

Add ABCN and place mixture in a 25-mL round bottom flask in a reflux setup.

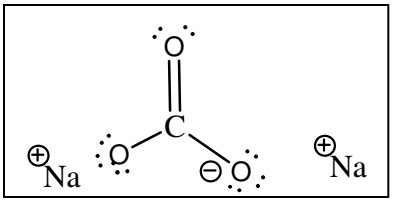


Mixture refluxed 20 min. Add 0.1 g ABCN and reflux 10 min more.

Cool the mixture and add 15-mL cold NaCl to form emulsion

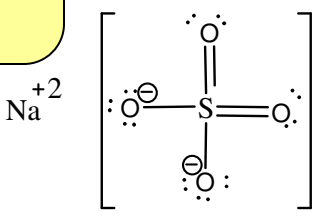


Separate layers and wash organic layer with 10 mL sodium carbonate, venting frequently.



Test to make sure the aqueous layer is basic. If not wash with sodium carbonate again.

Transfer the organic layer to Erlenmeyer and add anhydrous sodium sulfate to produce a clear liquid. Decant and weigh the clear organic liquid.



Determine the % yield. Run the sample in the CG machine.

CONCLUSIONS

In this experiment, the reactivity of alkanes was seen after reacting sulfuryl chloride and 1-chlorobutane and then analyzing theresulting product, dichlorobutane, in the Gas-Liquid Chromatograph. The percent composition of each dichlorobutane was determined to aid in determining the reactivity of hydrogens. From our data, one can see that the primary carbons on the 1,1-dichlorobutane and 1,4-dichlorobutane had a low relative reactivity and the secondary hydrogens were more reactive; 3.64 and 7.22 respectively. The data supports the prediction that secondary hydrogens are more reactive.

ANSWERS TO ASSIGNED QUESTIONS

2) *Why is the amount of sulfuryl chloride used less than the amount theoretically required to convert all the starting material to mono-substituted products?*

The amount of sulfuryl chloride used is less than the amount theoretically required to convert all the starting material to mono-substituted products because our main objective was to produce a di-substitued product. SO_2Cl_2 was the limiting reactant in this experiment. It was used in the initiation and in the propagation step. It was an important reactant to produce a mono-chlorinated radical, which would react with another chlorine radical to produce our desired product, dichlorobutane. If all the SO_2Cl_2 was used up, the remaining Cl radicals will bond with the mono-chlorinated reactant. In addition, if you had excess sulfuryl chloride you could produce tri-chlorinated products.

9) *Based on your calculation of the percentage of the various dichlorobutanes formed in the reaction, determine the values for the relative reactivity for he various types of hydrogen atoms in 1-chlorobutane. Assign the relative reactivity of the methyl hydrogens as 1.0.*

TABLE 4: % Composition of Dichlorobutane and Relative Reactivity

Compound	% Composition from GC	Relative Reactivity
1,1-dichlorobutane	6.355	1.00
1,2-dichlorobutane	23.143	3.64
1,3-dichlorobutane	45.926	7.22
1,4-dichlorobutane	23.872	2.50

Table 4 consists of the % composition of each of the four dichlorobutanes. After the % was obtained from the GC, it was divided by the number of hydrogens that the chlorine could have bonded to (2,2,2, &3 respectively). After making the least reactive compound have a relative reactivity of 1 (1,1-dichlorobutane), the rest of the reactivates were calculated.