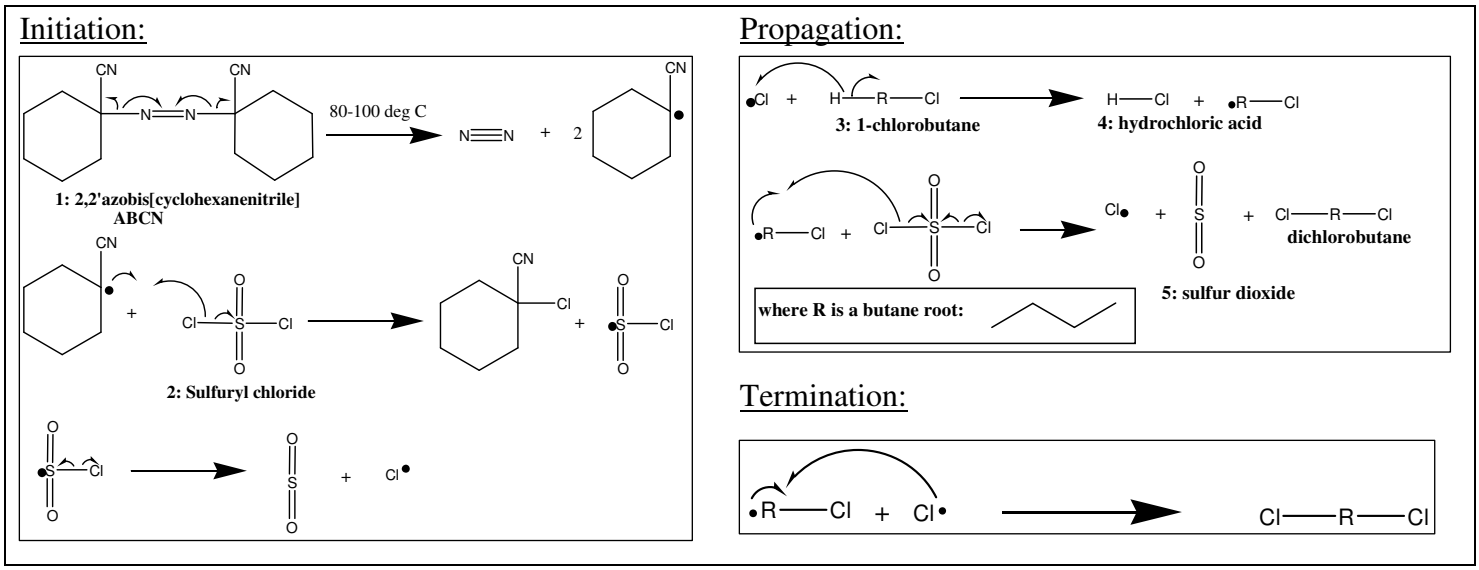
1. EXPERIMENT #3 GRACE KIM
7/16/07 MIKE HALL
ALKANE CHLORINATION

2. INTRODUCTION AND PURPOSE

1-chlorobutane will be halogenated to produce dichlorobutane using sulfuryl chloride via a free-radical chain reaction mechanism. The ratio of the different dichlorobutane isomers produced will be determined by gas chromatography, and the relative reactivities of each type of hydrogen on the 1-chlorobutane calculated.

3. MAIN REACTION & MECHANISMS



OVERALL REACTION: $C_4H_9Cl + SO_2Cl_2 \xrightarrow{ABCN} C_4H_8Cl_2 + SO_2 + HCl$

4. TABLE OF REACTANTS & PRODUCTS

Table of Reagents

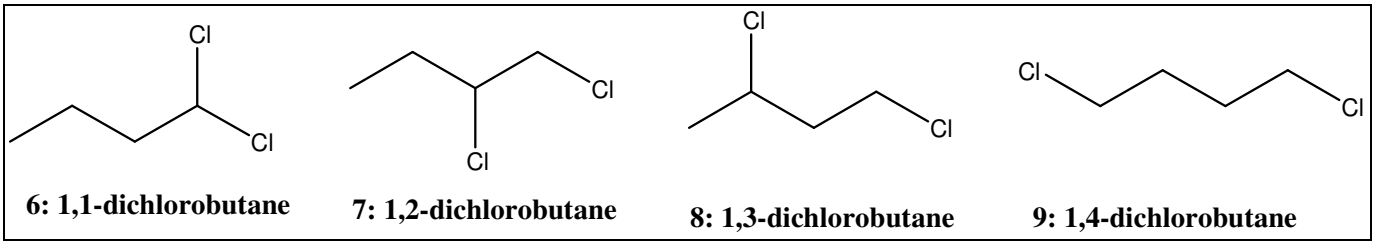
Compound	structure #	MW (g/ mol)	Amounts used		Moles theoretically		Physical properties
			mL	grams	used	required	
2,2'azobis[cyclohexanenitrile]	1	244.0	-	0.2	0.00082	-	initiator for radical formation
NaCl solution, saturated	-	-	40.0	-	-	-	brine for extraction
Na2CO3 , 0.5 M solution	-	-	10.0	-	-	-	base to extract/ neutralize acid
Sulfuryl chloride	2	134.9648	2.0	3.334	0.0247	0.0247	density = 1.667 g/ mL
1-chlorobutane	3	92.5681	5.0	4.43	0.0479	0.0247	density = 0.886 g/ mL b.p. = 77-78 degrees C

Limiting reagent = sulfuryl chloride

Table of Products

Compound	structure #	MW (g/ mol)	Theoretical yield		Theoretical Physical properties
			grams	moles	
1,1-dichlorobutane	6	127.0132	3.137	0.0247	b.p. = 114-115 degrees C
1,2-dichlorobutane	7	127.0132			b.p = 121-123 degrees C
1,3-dichlorobutane	8	127.0132			b.p. = 131-133 degrees C
1,4-dichlorobutane	9	127.0132			b.p. = 161-163 degrees C
sulfur dioxide	5	64.0588	1.58	0.0247	acid anhydride, gas
hydrochloric acid	4	36.4609	0.90	0.0247	acidic gas

Isomers of dichlorobutane:



6: 1,1-dichlorobutane **7: 1,2-dichlorobutane** **8: 1,3-dichlorobutane** **9: 1,4-dichlorobutane**

5. YIELD DATA

THEORETICAL CALCULATIONS:

Before rxn: (mass) 4.43 g + 3.33 g = 7.76 g total

C_4H_9Cl (l) + SO_2Cl_2 (l) ➔ $C_4H_8Cl_2$ (l) + SO_2 (g) + HCl (g)

Before	0.0479 mol	0.0247 mol	0	0	0
Change	-0.0247 mol	-0.0247 mol	+0.0247 mol	+0.0247 mol	+0.0247 mol
After	0.0232 mol (ER)	0 mol (LR)	0.0247 mol	0.0247 mol (g)	0.0247 mol (g)

After rxn: (mass) 2.15 g + 3.14 g = 5.29 g total

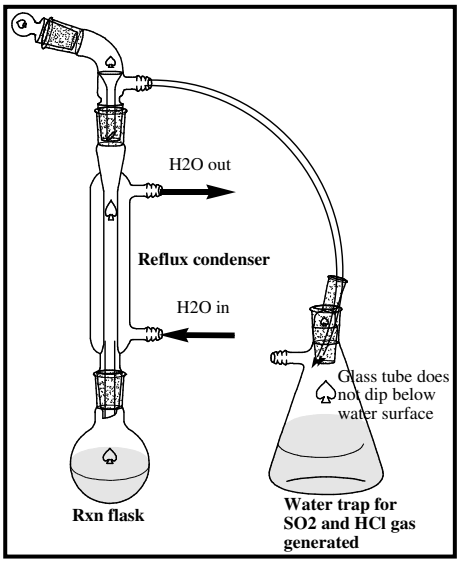
Theor. % comp: of total mass 40.6% 59.4%

ER = excess reagent; LR= limiting reagent

OBSERVED YIELD (masses corrected for addition of ABCN)**:**

Initial mass, 1-chlorobutane + SO_2Cl_2	7.55 g
Mass of flask contents after 20 min	5.73 g
Mass of flask contents after 30 min	4.88 g (92.2% mass yield)
Mass of isolated organics, after extraction	1.51 g (28.5% mass yield)

6. EXPERIMENTAL PROCEDURE AND RESULTS



Reaction under gentle reflux

The reaction apparatus was set up as shown in the figure to the left with a 25-mL florence flask and a 500-mL filtration flask. The tube transferring the SO_2 and HCl gas into the water trap was not allowed to dip below the water surface to ensure that no water would be sucked back into the reaction flask. The sidearm of the filtration flask was left open to vent into the fumehood.

0.1-g ABCN, 5-mL 1-chlorobutane, and 2-mL sulfuryl chloride was placed into a tared, stoppered 25-mL florence flask, and weighed.

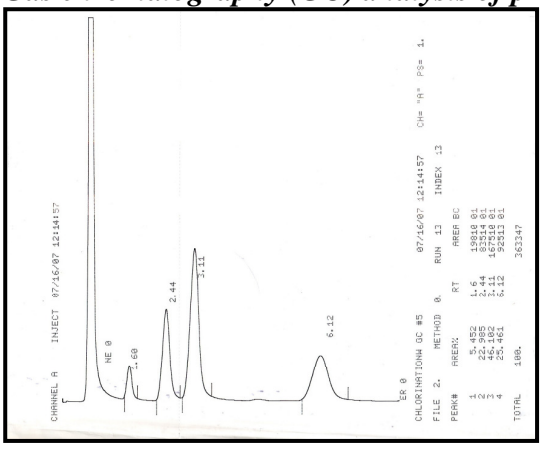
The reaction flask was heated under gentle reflux for 20-min., cooled, and weighed. Since the flask did not lose 90% of the expected weight, another 0.1-g portion of ABCN was added, and the reaction flask was heated under gentle reflux for an additional 10-min., cooled, and weighed.

Mass, empty rxn flask, stopper, & stir bar	39.33 g
Mass, rxn flask, stopper, & stir bar PLUS 1-cyclobutane, ABCN, and SO_2Cl_2	46.98 g
Mass of rxn flask after 20-min. reflux	45.16 g (additional 0.1 g ABCN added after weighing)
Mass of rxn flask after 30-min. reflux	44.41 g
Observation of rxn flask contents	Contents of flask: a clear and colorless liquid mixture

Workup and isolation

The reaction flask was cooled in an ice-water bath, and purified using a bicarbonate and brine extraction (Please see the flowchart in Section 9).

Gas chromatography (GC) analysis of products



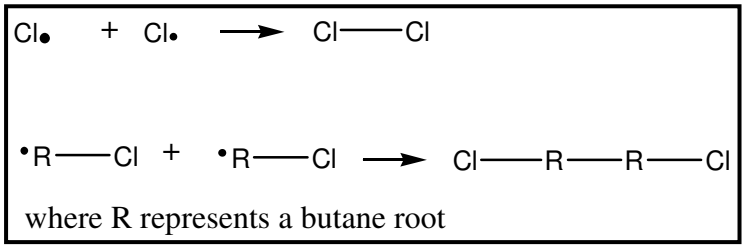
After extraction, the organic mixture of 1-chlorobutane and dichlorobutane isomers was analyzed via gas chromatography to determine the percentage of each dichlorobutane isomer produced. The peak for 1-chlorobutane was "off-scale." The percentages were then used to determine the relative reactivity of each type of hydrogen on the 1-chlorobutane.

Dichlorobutane isomer	% of product	# of H on 1-chlorobutane that yield this product:	% product produced PER hydrogen:	Relative reactivities
1,1-dichlorobutane	5.452 %	2	2.726%	1
1,2-dichlorobutane	22.985 %	2	11.4925%	4.22
1,3-dichlorobutane	46.102%	2	23.051%	8.46
1,4-dichlorobutane	25.461%	3	8.487%	3.11

7. OBSERVED PHYSICAL PROPERTIES OF PRODUCTS OBTAINED

The product obtained, a liquid mixture of the dichlorobutane isomers and 1-chlorobutane, was slightly cloudy whitish in appearance after extraction, most likely due to the formation of an emulsion with water during the extraction process.

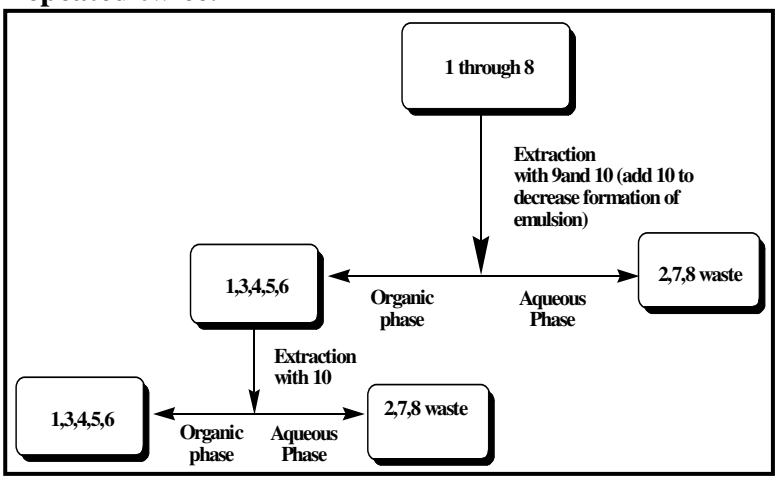
8. SIGNIFICANT SIDE REACTIONS

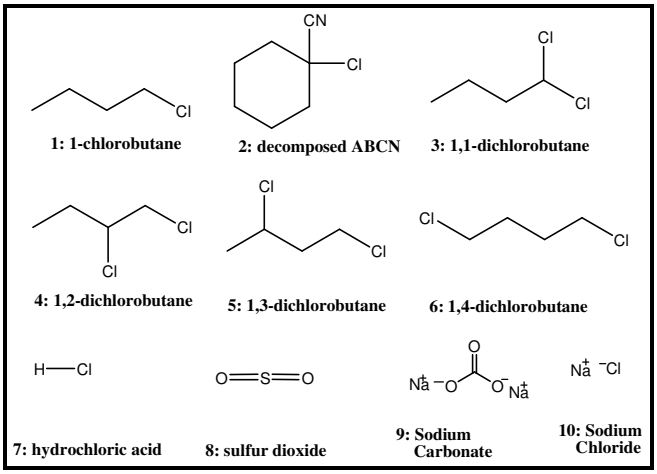


Because the amount of sulfuryl chloride was so small relative to the amount of 1-chlorobutane, the concentration of chlorine radicals and chlorobutane radicals would be low compared to the concentration of 1-chlorobutane molecules. Therefore, there would not have been a significant number of side reactions (i.e. termination reactions not resulting in product formation). However, if the amount of sulfuryl chloride were greater, the side reactions shown would have been observed.

9. METHOD OF PURIFICATION

Repeated twice.





10. CONCLUSIONS

The GC analysis showed that in the free-radical chlorination of 1-chlorobutane, the secondary C-H bonds (i.e. those producing 1,2-dichlorobutane and 1,3-dichlorobutane when substituted) were more reactive than primary C-H bonds (i.e. those producing 1,1-dichlorobutane and 1,3-dichlorobutane when substituted). These results support the idea that secondary C-H bonds will be more easily substituted than primary C-H bonds because of the greater stability of a secondary alkyl radical.

Between the two secondary C-H bonds, the more reactive C-H bond was the one farthest away from the electron-withdrawing chloro-group (i.e. the one producing 1,3-dichlorobutane). Between the two primary C-H bonds, the more reactive C-H bond was also the one farthest away from the electron-withdrawing chloro-group (i.e. the one producing 1,4-dichlorobutane). These results support the observation that the presence of an electron-withdrawing group, such as the chloro-group, stabilizes the C-H bonds closest to it, reducing their reactivity.

ERROR ANALYSIS

The percentage yield of product may have been overly low for a variety of reasons. During the additional 10-min of reflux, some 1-chlorobutane, which has the lowest boiling point, most likely evaporated (was not condensed) and was lost. Some small amount of the product may have escaped as well.

During extraction, a cloudy white emulsion formed, resulting in a difficult separation of the organic and aqueous layer and some product loss in the aqueous layer. In an attempt to obtain a better, non-emulsified organic layer, the extraction was performed twice, resulting in an even greater product loss. After extraction, in an attempt to "dry" the emulsion, several spatula scoops of sodium sulfite were used. Because the amount of dessicating agent used was relatively large compared to the volume of the product mixture, a significant quantity of the product mixture would have remained in the flask with the clumped sodium sulfite after decanting.

11. ANSWERS TO ASSIGNED QUESTIONS

2. The amount ot SO_2Cl_2 is LESS than the amount theoretically required to convert all the starting material to more substituted product because this minimized the formation of polysubstituted products (what happens when there is an excess of halogen).

9.

Dichlorobutane isomer	**% of product**	**# of H on 1-chlorobutane that yield this product:**	**% product produced PER hydrogen:**	**Relative reactivities**
1,1-dichlorobutane	5.452 %	2	2.726%	1.0
1,2-dichlorobutane	22.985 %	2	11.4925%	4.22
1,3-dichlorobutane	46.102%	2	23.051%	8.46
1,4-dichlorobutane	25.461%	3	8.487%	3.11

H	**Hydrogen off of C-1**	**Hydrogen off of C-2**	**Hydrogen off of C-3**	**Hydrogen off of C-4**
1^0 or 2^0	1^0, near Cl	2^0, near Cl	2^0	1^0
Rel. react.	1.0	4.22	8.46	3.11