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Chemistry 502
July 29, 2005

LAB #3

Chlorination of 1-chlorobutane

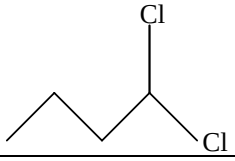
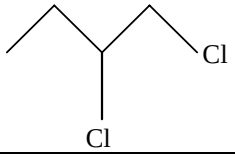
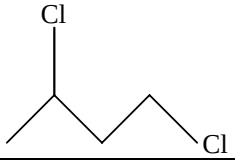
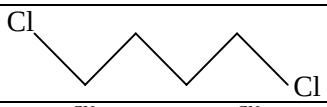
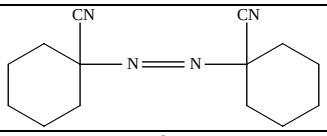
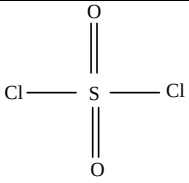
Introduction and Procedure

In order to chlorinate an alkane, chlorine free-radicals must be provided from some source. One source of chlorine free-radicals is chlorine gas. The bond between the two chlorine atoms can be broken using UV light. A draw-back to this approach is that chlorine gas is dangerous. The source of free-radicals in this laboratory procedure is sulfuryl chloride. Caution must be exercised when using this compound as it will produce sulfuric acid and hydrochloric acid when mixed with water. Also, HCl gas and SO_2 gas are produced when the chlorine free-radical is produced.

In order for the free-radical to be released into the system, the reaction must be initiated. The initiator in this reaction is 2,2'-azobis[cyclohexanenitrile] (ABCN). A small amount of this compound will be needed because once the reaction starts, it will propagate until it is complete. Four dichlorinated alkanes will be produced in this reaction: 1,1-dichlorobutane; 1,2- dichlorobutane; 1,3- dichlorobutane; 1,4-dichlorobutane. In order for these compounds to be produced, the solution must be refluxed for at least 20 minutes. After the first 20 minutes of reflux, the mass of the solution must be determined. If at least 90% of the expected mass loss has occurred (as SO_2 and HCl gas) the reaction is considered complete and should be stopped. If less than 90% of the mass loss has occurred, add more ABCN initiator and continue refluxing for 10 minutes. The products of this chlorination reaction will be washed with salt water and sodium carbonate and dried over anhydrous sodium sulfate prior to analysis by GC. The final dichlorobutanes should be clear and colorless.

In this reaction, sulfuryl chloride (SO_2Cl_2) is the limiting reagent and will determine the molar amounts of the four dichlorobutanes produced. As long as there is sulfuryl chloride in the solution, chlorination of the alkanes will occur. When this compound has been consumed in the reaction, termination of the process will begin. The mechanism for this reaction will be shown in this report.

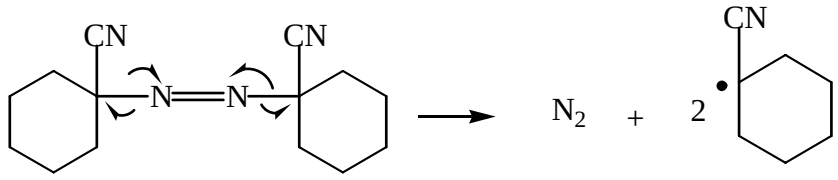
Table of Reactants and Products

Compound	Structure	Molecular Weight	Physical Properties
1-chlorobutane		92.57 g/mol	Boiling point =78.4ºC Density = 0.886g/mL Colorless and volatile
1,1-dichlorobutane		127.01 g/mol	Boiling point = 112ºC Colorless and volatile
1,2-dichlorobutane		127.01 g/mol	Boiling point = 124ºC Colorless and volatile
1,3-dichlorobutane		127.01 g/mol	Boiling point = 134ºC Colorless and volatile
1,4-dichlorobutane		127.01 g/mol	Boiling point = 154ºC Colorless and volatile
ABCN		244 g/mol	White crystal Initiator
SO_2Cl_2		134.96 g/mol	Density = 1.667g/mL Corrosive Yellow liquid Pungent odor LACHRYMATOR
Sodium Carbonate	Na_2CO_3	105.99 g/mol	Hygroscopic Neutralizer
Sodium Sulfate	Na_2SO_4	142.00 g/mol	Hygroscopic Drying agent

Main Reaction and Mechanism

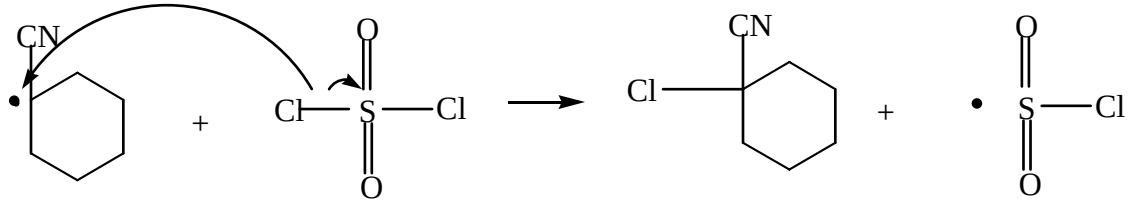
Initiation reactions

Adding heat to the solution causes the formation of the free radical which is involved in starting the propagation reactions. The amount of initiator is negligible in the overall reaction.



(1) **(2)**

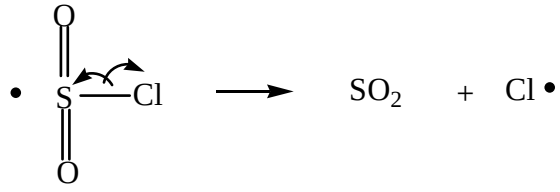
The Free radical attacks the SO_2Cl_2 to create a chlorinated cyclohexanenitrile and the free-radical ($SO_2Cl\cdot$) which will contribute to propagation.



(2) **(3)** **(4)** **(5)**

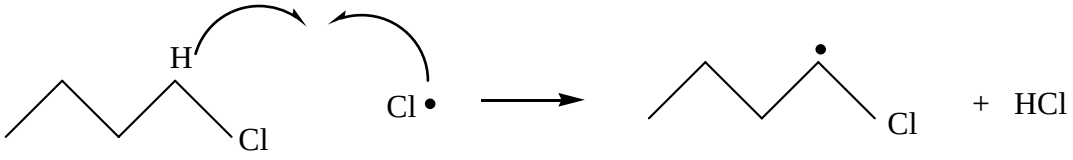
Propagation Reactions

The free-radical ($SO_2Cl\cdot$) begins the propagation reaction by providing the $Cl\cdot$ free-radical.



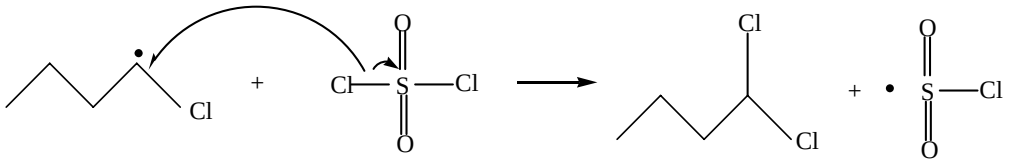
(5) **(6)** **(7)**

The $Cl\cdot$ free-radical will attack the 1-chlorobutane to produce the chlorinated butane radical and HCl gas.



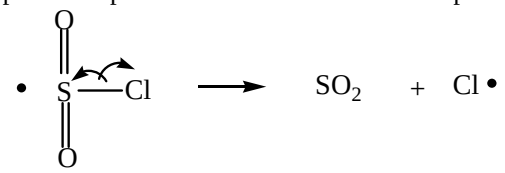
(8) **(7)** **(9)** **(10)**

The chlorinated butane radical attacks the SO_2Cl_2 molecule to produce the $SO_2Cl\cdot$ free-radical and the dichlorobutane.



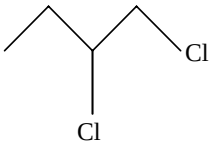
(9) **(3)** **(11)** **(5)**

The free-radical ($SO_2Cl\cdot$) continues the propagation reaction by creating the $Cl\cdot$ free-radical and SO_2 gas. The process repeats until no $Cl\cdot$ free-radical is produced.

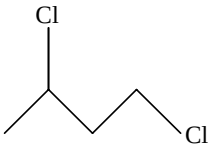


(5) **(6)** **(7)**

The other dichlorinated compounds produced are:



(12)
1,2-dichlorobutane

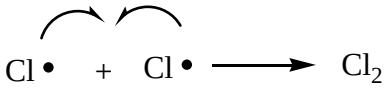


(13)
1,3-dichlorobutane

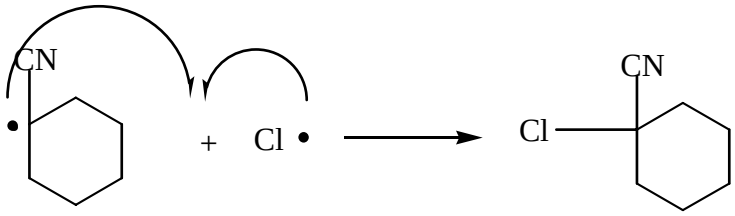
(14)
1,4-dichlorobutane

Termination Reactions

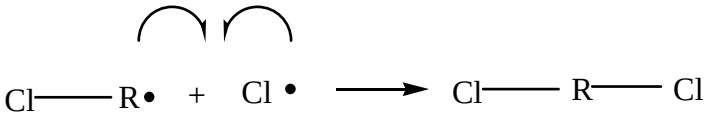
Results when the free-radicals begin to combine to create other compounds and consume free-radicals which will slow the reaction rate;



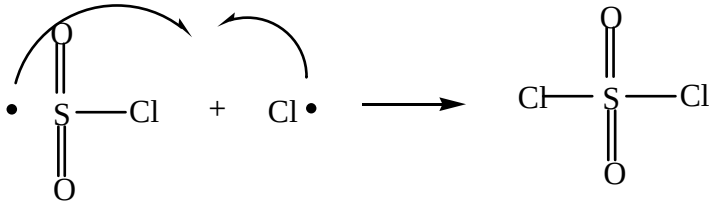
(Leaves the system as a gas)



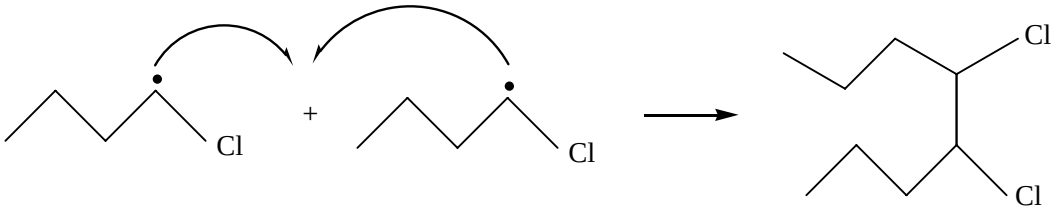
(Initiator is terminated)



(This represents the four different possible dichlorobutanes; **11 - 14**)



(This reaction is not likely if initiator and 1-chlorobutane are still present)



(This reaction is possible and represents only one of several dichloroctanes which were not tested for using GC analysis)

Stoichiometry of the Reaction

$$C_4H_9Cl_{(l)} + SO_2Cl_{2(l)} \longrightarrow C_4H_8Cl_{2(l)} + SO_{2(g)} + HCl_{(g)}$$

Theoretical Data

Mass of ABCN initiator = **0.10 g**

Mass of C_4H_9Cl = (5 ml * 0.886g/ml) = **4.43 g**

Mass of SO_2Cl_2 = (2 ml * 1.667g/ml) = **3.33 g**

Moles of C_4H_9Cl = 4.43 / 92.57 = **0.0479 mol**

Moles of SO_2Cl_2 = 3.33 / 134.96 = **0.0247 mol** (limiting reagent)

Total mass of compounds in solution = 4.43 g + 3.33 g + 0.10 g = **7.86 g**

Moles of SO_2 = **0.0247 mol**

Moles of HCl = **0.0247 mol**

Mass of SO_2 = 0.0247 mol * 64 g/mol = **1.58 g**

Mass of HCl = 0.0247 mol * 36.4 g/mol = **0.90 g**

Total mass lost as gas = 1.58 g + 0.90 g = **2.48** g (predicted)

Total mass in system after reaction = 7.86 g – 2.48 g = **5.38 g** (predicted)

Moles of 1-chlorobutane unreacted = 0.0479 mol – 0.0247 mol = **0.0232 mol**

Theoretical mass of unreacted 1-chlorobutane = 0.0232 mol * 92.57 g/mol = **2.15 g**

Theoretical mass of dichlorobutanes produced = 5.38 g – 2.15 g = **3.23 g** (predicted)

Theoretical yield of dichlorobutanes = (3.23 g / 5.38 g) * 100 = **60.0 %**

Experimental data:

Mass of flask + stir bar = **37.70 g**

Mass of solution in flask before reaction = **45.56 g**

Mass of solution = 45.56 g – 37.70 g = **7.86 g**

Mass of solution in flask after reaction = **42.63 g**

Mass of solution after reaction = 42.63 g – 37.70 g = **4.93 g** (experimental)

% of solution lost as SO_2 + HCl gas = ((7.86 g – 4.93 g) / 7.86 g)* 100 = **37.3 %**

Moles of 1-chlorobutane unreacted = 0.0479 mol – 0.0247 mol = **0.0232 mol**

Mass of 1-chlorobutane unreacted = 0.0232 mol * 92.57 g/mol = **2.15 g**

Mass of dichlorobutanes produced = 4.93 g – 2.15 g = **2.78 g*** (experimental)

% yield of dichlorobutanes = (2.78 g / 4.93 g) * 100 = **56.4 %** *(experimental)

Data Summary Table

Compound	MW (g/mol)	Vol. (mL)	Mass (g)	Moles Used	Moles Required	Density (g/mL)	Mass Unreacted (g)
ABCN	244	-	0.10	-	-	-	-
1-Chlorobutane	92.57	5.0	4.43	0.0479	0.0247	0.886	2.15
SO_2Cl_2	134.96	2.0	3.33	0.0247	0.0247	1.667	-
HCl + SO_2	-	-	2.93	-	-	-	-
Dichlorobutanes	127.01	-	2.78*	-	-	-	-

* - Mass prior to washing with NaCl brine and sodium bicarbonate and drying with anhydrous sodium sulfate. The purified product was discarded prior to obtaining an actual mass.

% Composition Using Peak Areas from the Gas Chromatograph

Mass of 1,1 – dichlorobutane = 2.78 g * 6.04 % = **0.17 g***

Mass of 1,2 – dichlorobutane = 2.78 g * 23.07 % = **0.64 g***

Mass of 1,3 – dichlorobutane = 2.78 g * 46.03 % = **1.28 g***

Mass of 1,4 – dichlorobutane = 2.78 g * 24.86 % = **0.69 g***

* - Mass prior to washing with NaCl brine and sodium bicarbonate and drying with anhydrous sodium sulfate. The purified product was discarded prior to obtaining an actual mass.

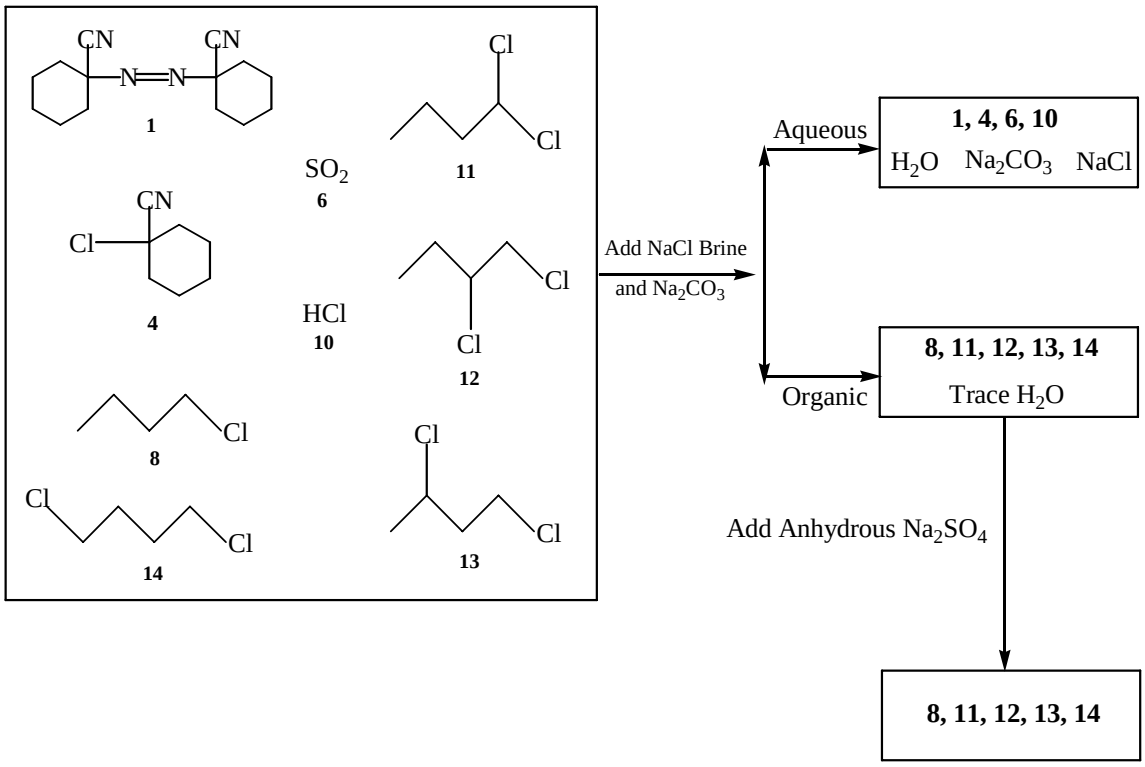
Method of Purification and Observations

During the heating process the solution was boiling without foaming. But, as the reflux continued, foaming was noticed, although slightly. The vapors were entering the cooling column and refluxing nicely for most of the reflux process. Approximately 10 minutes into the reflux a white vapor was noticed rising through the column. It was surmised that this vapor was the sulfur dioxide and hydrochloric acid gasses mixing with water vapor to produce the hydrated gasses which can be seen as white vapor. This phenomenon ended and the boiling of the solution became more "foam-like" in nature. After 20 minutes the reflux was terminated and the solution was cooled in an ice bath. The mass of the solution was calculated and it was determined that more than 90% of the expected mass loss (due to gassing and product evaporation) had occurred. At this point, it was determined that the reaction had gone to completion and was terminated.

The organic solution was combined with a saturated "brine" solution of sodium chloride and shaken in a separatory funnel. The result of this process was that the organic layer, which contained the dichlorinated alkanes, became milky-white. The aqueous layer was drained and dilute sodium carbonate was added to the dichlorobutanes to remove any excess hydrochloric acid and sulfur dioxide. After shaking this mixture the organic layer was still milky-white. The sodium carbonate was drained and tested using red litmus paper. The aqueous layer proved to be basic, which indicates that all of the HCl was removed from the organic layer.

The milky-white organic layer was combined with sodium sulfate to remove any excess moisture from the solution. After several minutes of vigorous stirring, the solution became clear. The organic solution was decanted into a sample bottle and analyzed by GC. The results of the gas chromatograph showed that the 1,3 – dichlorobutane (**13**)was the most prominent compound and 1,1 – dichlorobutane (**11**) was the least prominent.

Purification Flow Chart



Conclusion

The chlorination of 1-chlorobutane produced four isomers of dichlorobutane. There were higher amounts of the 1,3-dichlorobutane than any of the other three isomers. From the relative reactivities, 1,3-dichlorobutane is more than 7 times more likely to be produced than the 1,1-dichlorobutane isomer. Two of the reasons behind the explanation to this phenomenon are steric hindrance and free-radical stability.

The 1,3-dichlorobutane has low steric strain compared to the 1,1-dichlorobutane and the 1,2-dichlorobutane. This is because the large chlorine atom requires space in order to bond efficiently with the 1-chlorobutane. So then why does the 1,4-dichlorobutane not exist at higher percentages? This is because the stability of the free-radical is higher when the location of the unpaired electron is situated between two alkyl groups. In this case, the 1,3-dichlorobutane has the best of both worlds. It allows space for the large chlorine atom (reducing the steric strain in the molecule), and it has a free-radical conformation that maximizes the number of alkyl groups that flank the location of the lone electron where the chlorine will bond.

Answers to Questions in Gilbert and Martin (p. 260 – 261)

2) Why is the amount of sulfuryl chloride used *less* than the amount theoretically required to convert all the starting material to monosubstituted (dichlorinated) products?

If all of the 1-chlorobutane has been converted to dichlorobutanes, then unwanted byproducts will begin to form. The byproducts are trichlorobutanes and tetrachlorobutanes. These byproducts will form because the dichlorinated butane is easily chlorinated until steric strain becomes a factor.

9) Based on your calculation of the percentage of the various dichlorobutanes formed in the reaction, determine the values for the relative reactivity for the various types of hydrogen atoms in 1-chlorobutane.

The relative reactivity is determined by dividing the percent of a synthesized compound by the number of chances of forming that particular compound.

1,1-dichlorobutane – 6.04 / 2 = **3.02**

1,2-dichlorobutane – 23.07 / 2 = **11.54**

1,3-dichlorobutane – 46.03 / 2 = **23.02**

1,4-dichlorobutane – 24.86 / 3 = **8.29**

Relative Reactivities

1,1-dichlorobutane – 3.02 / 3.02 = **1.00**

1,2-dichlorobutane – 11.54 / 3.02 = **3.82**

1,3-dichlorobutane – 23.02 / 3.02 = **7.62**

1,4-dichlorobutane – 8.29 / 3.02 = **2.74**

The 1,3-dichlorobutane is 7.62 times more likely to be produced than the 1,1-dichlorobutane.