

FREE-RADICAL CHAIN CHLORINATION OF 1-CHLOROBUTANE

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Introduction: The purpose of this experiment is to synthesize a mixture of dichlorobutane isomers starting with 1,1'-azobis(cyclohexanenitrile), also known as ABCN; sulfuryl chloride; and 1-chlorobutane. The percentage of each dichlorobutane isomer will be analyzed using gas-liquid chromatography, GC, since each isomer has a unique boiling point and response time. The actual isomer percentages will be compared to the statistical percentages calculated based on probability. The relative reactivity of each type of hydrogen on 1-chlorobutane will be calculated based on the actual isomer percentages.

Main Reaction and Mechanism: The first step of a free-radical chain reaction is initiation, where a reactive intermediate radical is produced. Initiation often needs heat or light to get the reaction started. The chlorination of 1-chlorobutane has three initiation steps as shown in Figure 1. First, heat is used to break ABCN down into two radicals and nitrogen gas. The radicals produced react with sulfuryl chloride to produce a new radical. Lastly, the sulfuryl chloride radical decomposes to produce sulfur dioxide and a chlorine radical.

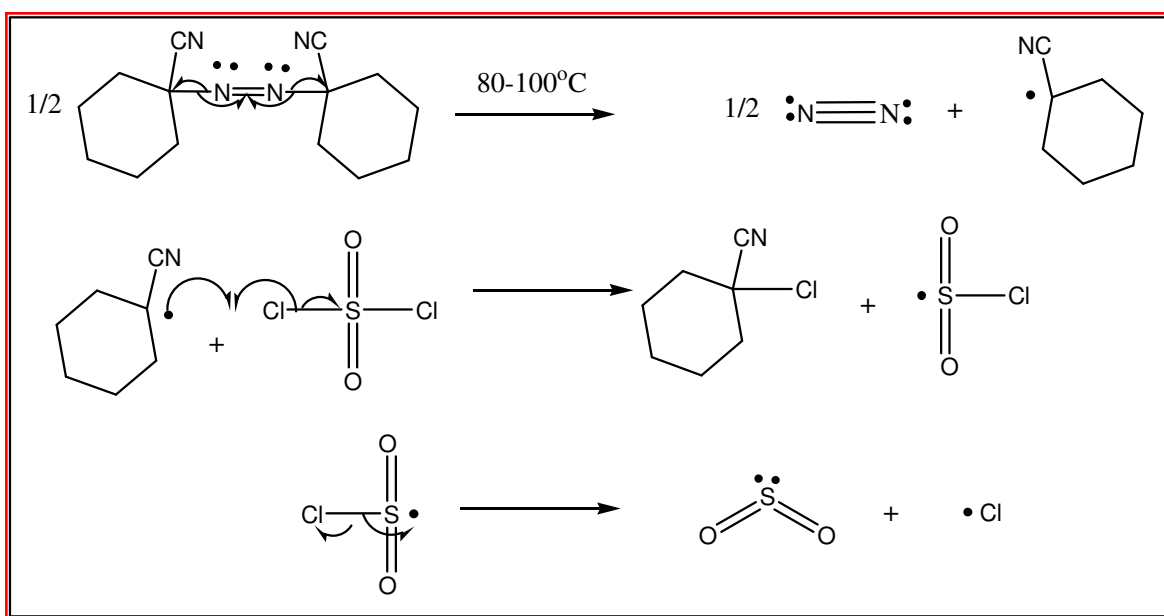


FIGURE 1 The three initiation steps for the free-radical chain reaction.

The second step of a free-radical chain reaction is propagation, where the radical produced during initiation reacts with another molecule to produce a different radical. The new radical can proceed through another propagation step producing yet another radical. The chain is complete when the initiator radical is regenerated. The chlorine radical produced during initiation reacts with 1-chlorobutane to produce a 1-chlorobutane radical. This new radical reacts with sulfuryl chloride to produce a dichlorobutane isomer and a sulfuryl chloride radical. As in initiation, the sulfuryl chloride radical decomposes to produce sulfur dioxide and a chlorine radical which can start propagation again. All three steps of propagation are shown in Figure 2.

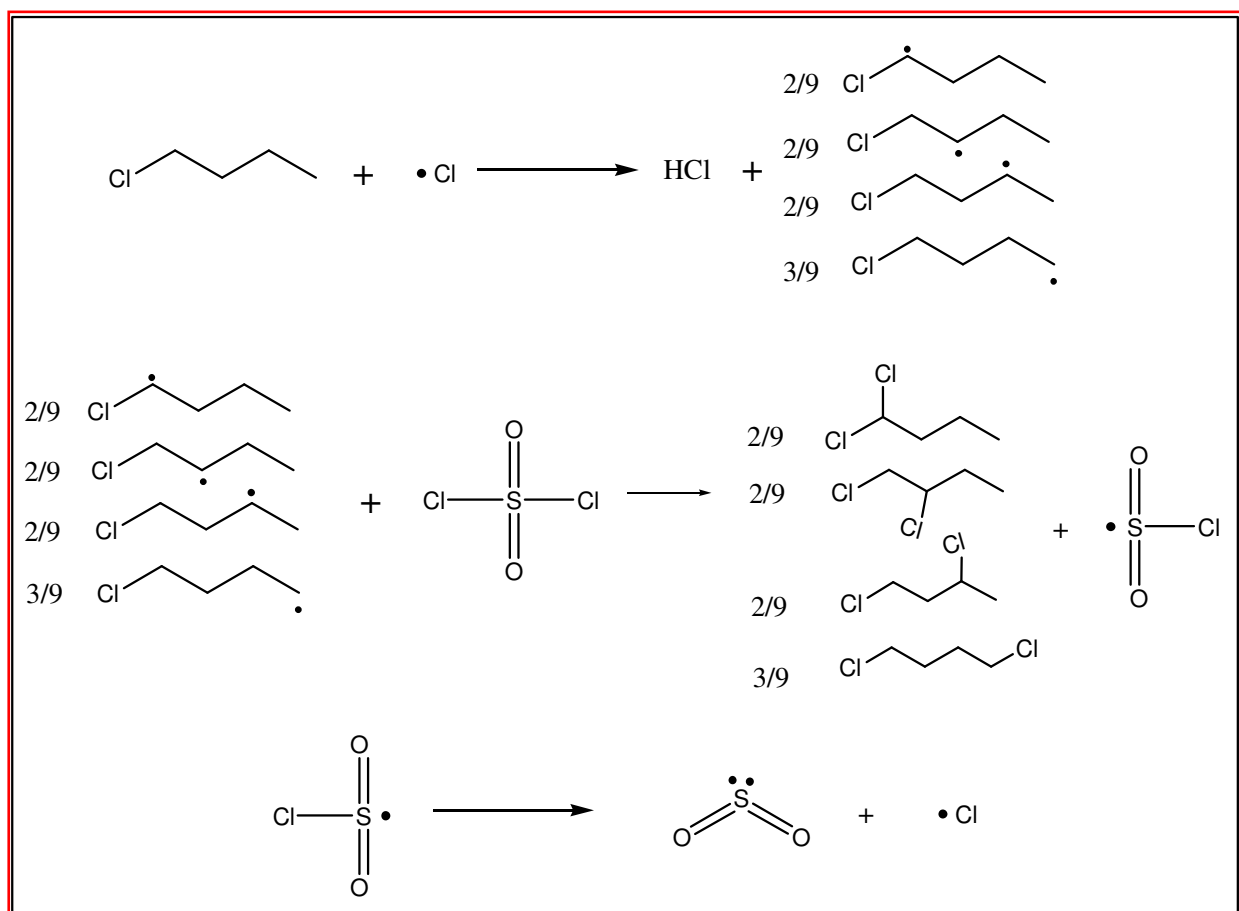


FIGURE 2 The three propagation steps for the free-radical chain reaction.

The third and final step of a free-radical chain reaction is termination, where side reactions destroy radicals. These side reactions often involve the bonding of two radicals to form a relatively stable molecule. A radical may also be bound to the wall of the reaction flask, which inhibits that radical from being used to start propagation. Termination slows or stops the chain reaction. For this reason, additional ABCN may need to be added after 20 minutes of refluxing to ensure that enough dichlorobutane isomers are produced.

Table of Reactants:

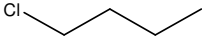
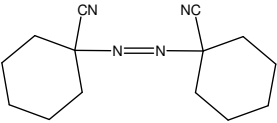
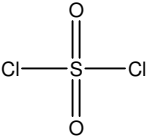
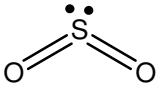
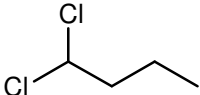
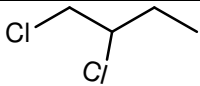
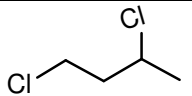
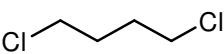
Reactant	Structure	Mol. Wt. (amu)	Vol. Mass Moles	Stoich. Required	Properties
1-chlorobutane C ₄ H ₉ Cl		92.5681	5.0mL 4.43g 47.8mmol	1	Colorless liquid ρ = 0.886g/mL f.p. = -6°C b.p. = 78.4°C P _{vap,20°C} = 80.1mmHg Sol.=0.07g/100mL H ₂ O
ABCN C ₁₄ H ₂₀ N ₄		244.3388	-- 0.12g 0.49mmol	0.5	
sulfuryl chloride SO ₂ Cl ₂		134.9648	2.0mL 3.33g 24.7mmol	1, L.R.	Colorless liquid ρ = 1.667g/mL b.p. = 69.1°C P _{vap,20°C} = 110mmHg Decomposes in H ₂ O

Table of Products:

Product	Structure	Mol. Wt. (amu)	Theor. Yield	Stoich. Required	Properties
sulfur dioxide SO ₂		64.0588	24.7mmol 1.58g	1	Colorless gas ρ _{vap} = 2.26 b.p. = -10.06°C P _{vap,20°C} = 2 539mmHg Sol.=10g/100mL H ₂ O
hydrogen chloride HCl	H—Cl	36.4609	24.7mmol 0.90g	1	Colorless gas ρ _{vap} = 1.27 b.p. = -85.06°C sol.= 62g/100mL H ₂ O
1,1-dichlorobutane C ₄ H ₈ Cl ₂		127.01	5.4mmol 0.69g	2/9	ρ = 1.086g/mL b.p. = 112°C
1,2-dichlorobutane C ₄ H ₈ Cl ₂		127.01	5.4mmol 0.69g	2/9	ρ = 1.112g/mL b.p. = 125°C
1,3-dichlorobutane C ₄ H ₈ Cl ₂		127.01	5.4mmol 0.69g	2/9	ρ = 1.115g/mL b.p. = 134°C
1,4-dichlorobutane C ₄ H ₈ Cl ₂		127.01	8.2 mmol 1.04 g	3/9	ρ = 1.141g/mL b.p. = 153.9°C

Yield Data: Ninety-percent completion of the reaction would produce 22.2mmol of both SO₂ and HCl, 1.42g and 0.81g, respectively (Eq. 1). Since these gases were not being condensed, a total of 2.23g would be lost from the reaction mixture. After one 20-minute reflux, the reaction flask lost 2.18g, or 21.7mmol of each product, which corresponds to 87.8% completion.

$$0.90 \times \frac{24.7\text{mmol SO}_2}{1} \times \frac{64.0588\text{g}}{\text{mol}} = 1.42\text{g SO}_2 \quad (1)$$

$$0.90 \times \frac{24.7\text{mmol HCl}}{1} \times \frac{36.4609\text{g}}{\text{mol}} = 0.81\text{g HCl}$$

Assuming 100% completion, the contents of the reaction flask should have weighed 5.29g, 3.14g from the dichlorobutane isomers and 2.15g from the excess 1-chlorobutane (Eq. 2).

The actual mass of the contents was 2.12g. The percent yield for the reaction was 40.1%. Part of the low yield may have resulted from the 1-chlorobutane evaporating. The Erlenmeyer flask was not stoppered during the drying process with sodium sulfate.

$$\frac{24.7 \text{ mmol dichlorobutanes}}{\text{mol}} \times \frac{127.1 \text{ g}}{\text{mol}} = 3.14 \text{ g dichlorobutanes} \quad (2)$$

$$\frac{47.9 \text{ mmol chlorobutane} - 24.7 \text{ mmol chlorobutane}}{\text{mol}} \times \frac{92.5681 \text{ g}}{\text{mol}} = 2.15 \text{ g excess 1-chlorobutane}$$

Experimental Procedure: A reflux apparatus with a magnetic stir bar was assembled and connected to a 500mL-Erlenmeyer-flask gas trap as shown in Figure 3. ABCN (0.12g), 1-chlorobutane (5.0mL), and surfuryl chloride (2.0mL) were added, respectively, to a 25mL round bottom flask. The mass of the stoppered reaction flask and its contents was 40.13g.

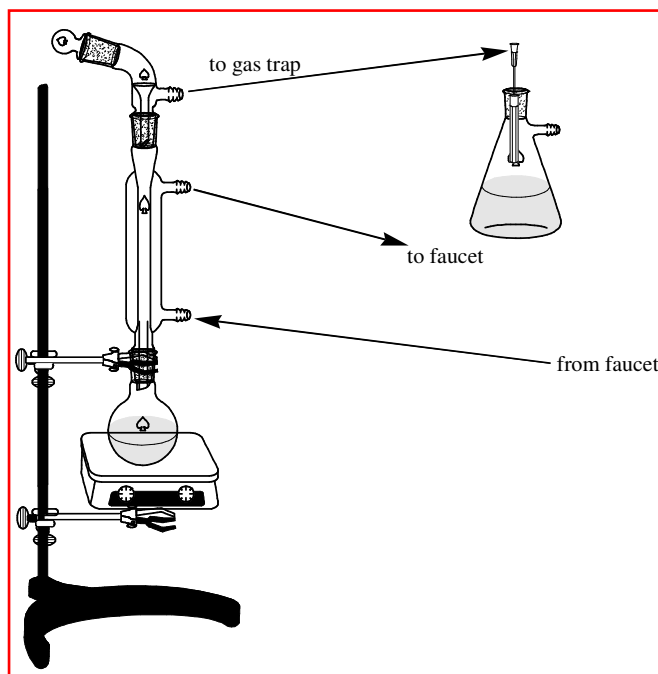


FIGURE 3 Reflux apparatus connected to an Erlenmeyer-flask gas trap.

The reaction flask was gently refluxed with stirring for 20 minutes. The voltage to the Thermowell heater was set at 50V and the reaction was refluxing at a rate of 1 drop every 3 seconds within 20 minutes. After the 20-minute reflux, the reaction flask was cooled and weighed. The mass of the stoppered reaction flask and contents after one refluxing period was 37.95g. The reaction flask lost 2.18g. Since 90% completion would have resulted in a loss of 2.23g, a second reflux for 20 minutes was unnecessary.

The reaction flask was cooled in an ice-water bath. The contents were poured into an Erlenmeyer flask containing 15mL of ice-cold saturated brine solution. The reaction mixture separated into two layers upon adding the brine solution. The top organic layer was cloudy-white, and the bottom aqueous layer was clear. The two layers were poured into a separatory funnel and isolated. The top organic layer was washed with 10mL of 0.5M sodium carbonate. The separatory funnel was frequently vented, and the two layers were separated. The top organic layer was again washed with 15mL of brine solution. The organic layer was still cloudy-white. The top organic layer was transferred to an Erlenmeyer flask with several spatula scoops of sodium sulfate. The solution was swirled occasionally for 10 minutes. The clear, organic solution was decanted into a dry, tared Erlenmeyer flask. The mass of the Erlenmeyer flask with a stopper was 64.88g. The mass of the flask with products was 67.00g, a 2.12g yield of products and excess reactants.

The products were analyzed using GC #7. A 2.5 μ L sample was injected into column A which was set at the following conditions: + polarity, 100mA current, 126 $^{\circ}$ C column temperature, 150 $^{\circ}$ C detector temperature, and 130 $^{\circ}$ C injector temperature.

Properties of Products: The dried product was a colorless, homogenous solution of 1-chlorobutane and dichlorobutane isomers. The sample was analyzed using GC. A GC trace is shown in Figure 4 and a summary of the results is shown in Table 1 along with the expected statistical percentages. Ignoring the excess 1-chlorobutane, the product consisted of 48% 1,3-dichlorobutane; 24% 1,2-dichlorobutane; 22% 1,4-dichlorobutane; and 6% 1,1-dichlorobutane.

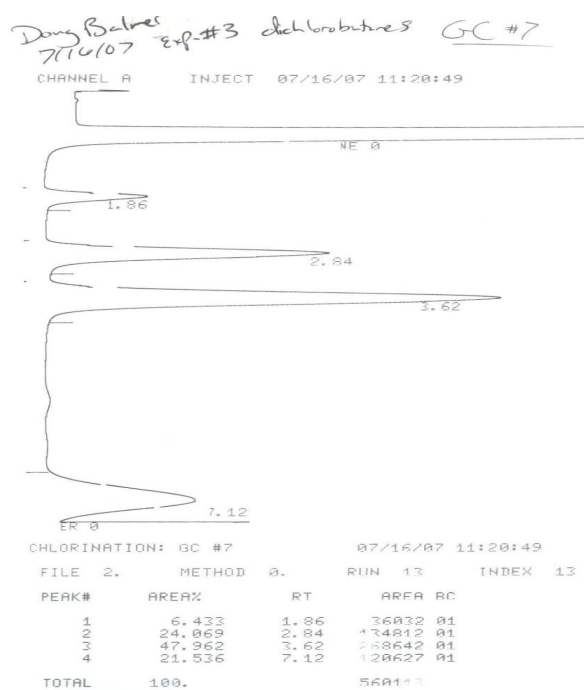


FIGURE 4 A GC trace of dichlorobutane products.

Compound	Statistical Expected %	GC Area %	GC Area
1,1-dichlorobutane	(2H's/9H's) 22.2%	6.433%	36 032
1,2-dichlorobutane	(2H's/9H's) 22.2%	24.069%	134 812
1,3-dichlorobutane	(2H's/9H's) 22.2%	47.962%	268 642
1,4-dichlorobutane	(3H's/9H's) 33.3%	21.536%	120 627

TABLE 1 GC data of dichlorobutane products.

Significant Side Reactions: The radicals necessary to keep the chain reaction going are consumed during the termination steps as shown in Figure 5. More importantly, tri- and possibly tetra-chlorobutanes could possibly form if enough sulfuryl chloride is present. As the concentration of dichlorobutane isomers increases, there is an increasing chance that the chlorine radical will react with the product and not the 1-chlorobutane as shown in Figure 6. The 1-chlorobutane was used in excess to limit the formation of tri- and tetra-chlorobutanes.

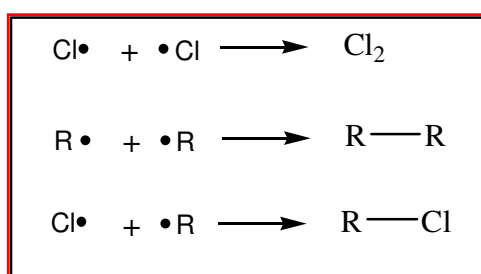


FIGURE 5 Possible termination steps.

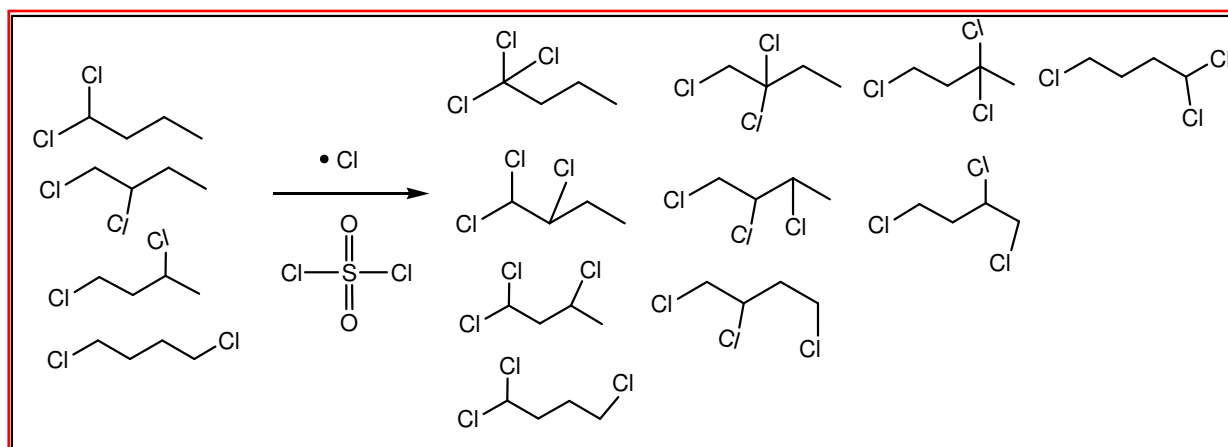


FIGURE 6 Chlorination of dichlorobutane isomers to form trichlorobutane isomers.

Method of Purification: The product was purified according to Figure 7. The reaction mixture was washed with a brine solution to remove any dissolved HCl gas. The organic layer was washed with sodium carbonate to remove any unreacted sulfuryl chloride. The organic layer was washed with a brine solution a second time. Lastly, the organic layer was dried with sodium sulfate and decanted.

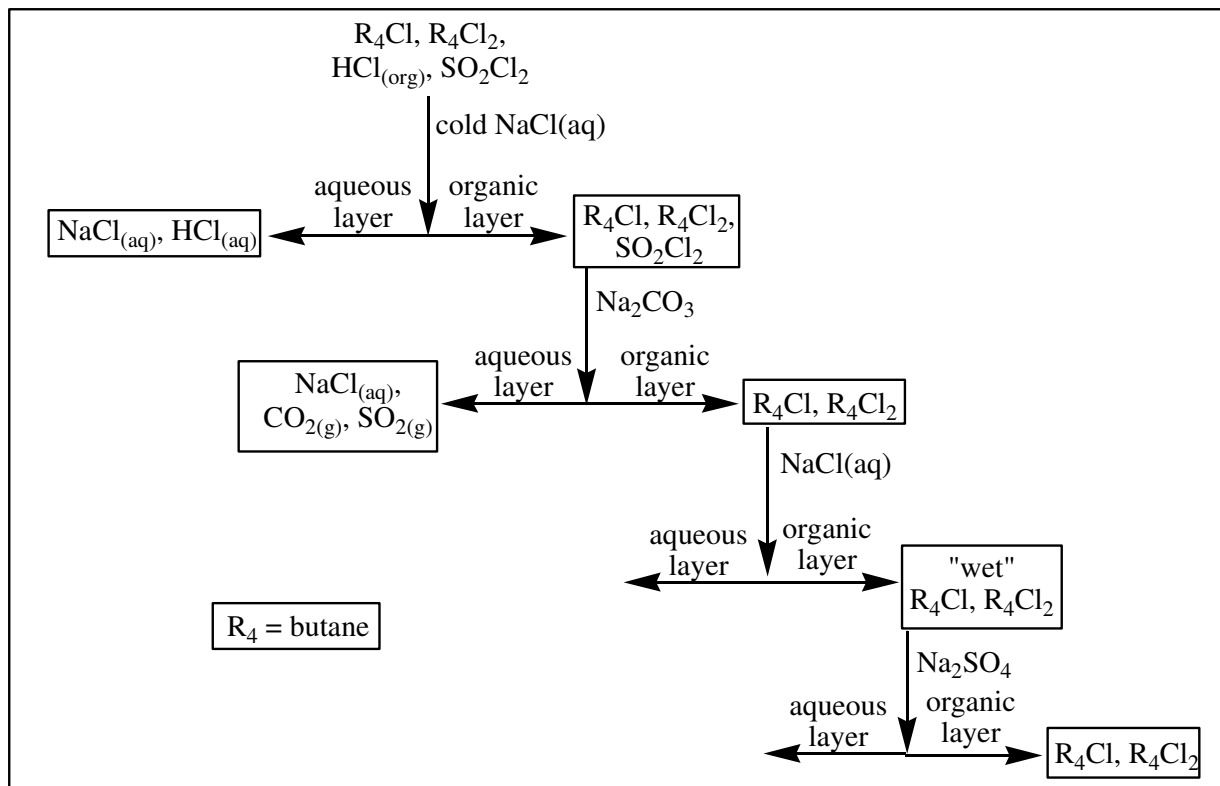


FIGURE 7 Purification of chlorinated butane.

Conclusions: As expected, four dichlorobutane products did form. They did not form in the same ratio as statistically expected based on the number of hydrogens on each carbon. You would expect 1,1-dichlorobutane; 1,2-dichlorobutane ; and 1,3-dichlorobutane to each make 22.2% of the product and 1,4-dichlorobutane to make 33.3% of the product. The GC traces showed that the product consisted of 48% 1,3-dichlorobutane; 24% 1,2-dichlorobutane; 22% 1,4-dichlorobutane; and 6% 1,1-dichlorobutane. The 1,3 and 1,2 isomers predominate because the intermediate carbon radical is secondary and therefore more stable. The chlorine atom is more electronegative, so it pulls electron density away from the carbon chain and makes C₁ partially positive. This strengthens the carbon-hydrogen bonds closer to the C₁ atom. This explains why the 1,3 isomer is more prominent than the 1,2 isomer. This also explains why the 1,4 isomer is more prominent than the 1,1 isomer.

Answers to Assigned Questions: Page 261 (2,9)

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

Only 24.7 mmol of sulfuryl chloride was used, when 47.8mmol would have been needed to stoichiometrically react all of the 1-chlorobutane. The likelihood of producing trichlorobutane and tetrachlorobutane isomers increases as the amount of sulfuryl chloride and the dichlorobutane isomers increases. The fact that sulfuryl chloride is the limiting reactant reduces the chances for unwanted side reactions as shown in Figure 6.

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. Assign the relative reactivity of the methyl hydrogens as 1.0.

$$\mathbf{C_1:} \quad \frac{6.433\%}{2 \text{ C}_1 \text{ H's}} = 3.217\% \text{ per H} \quad 3.217\% / 7.1787\% = 0.4481$$

$$\mathbf{C_2:} \quad \frac{24.069\%}{2 \text{ C}_2 \text{ H's}} = 12.035\% \text{ per H} \quad 12.035\% / 7.1787\% = 1.6765$$

$$\mathbf{C_3:} \quad \frac{47.962\%}{2 \text{ C}_3 \text{ H's}} = 23.981\% \text{ per H} \quad 23.981\% / 7.1787\% = 3.3406$$

$$\mathbf{C_4:} \quad \frac{21.536\%}{3 \text{ C}_4 \text{ H's}} = 7.1787\% \text{ per H} \quad 7.1787\% / 7.1787\% = 1.0000$$

The relative reactivity of each hydrogen with respect to the methyl hydrogens is

0.4481 : 1.6765 : 3.3406 : 1.0000 (C₁: C₂: C₃: C₄)