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Free-Radical Chlorination

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PURPOSE OF THE EXPERIMENT

Using gas chromatography, determine the relative reactivities of different hydrogen atoms in 1-chlorobutane toward free-radical substitution by chlorine atoms.

BACKGROUND REQUIRED

You should be familiar with microscale extraction and quantitative gas chromatography.

BACKGROUND INFORMATION

Chlorination occurs by a free-radical chain reaction mechanism. The reaction is initiated by the formation of chlorine radicals, as shown in Equation 1. Because the chlorine atoms are quite reactive, their concentration is always small.

$$\mathrm{Cl{-}Cl} \xrightarrow{\text{light}} \mathrm{Cl\cdot} + \mathrm{Cl\cdot} \qquad \text{(Eq. 1)}$$

Propagation steps for the process involve the abstraction of a hydrogen atom from a hydrocarbon by a chlorine atom (Cl•), followed by reaction of the resulting hydrocarbon radical with molecular chlorine (Cl_2), as shown in Equations 2 and 3.

$$\mathrm{R{-}H} + \mathrm{Cl\cdot} \longrightarrow \mathrm{R\cdot} + \mathrm{H{-}Cl} \qquad \text{(Eq. 2)}$$

$$\mathrm{R\cdot} + \mathrm{Cl{-}Cl} \longrightarrow \mathrm{R{-}Cl} + \mathrm{Cl\cdot} \qquad \text{(Eq. 3)}$$

Each chlorine atom consumed in the first step is replaced in the second step. Consequently, the generation of even one chlorine atom in the reaction mixture can lead to the production of as many as 10,000 molecules of the chloroalkane product.

Radicals are removed from the reaction mixture by termination reactions, as shown in Equations 4–6.

$$\mathrm{R\cdot} + \mathrm{Cl\cdot} \longrightarrow \mathrm{R{-}Cl} \qquad \text{(Eq. 4)}$$

$$\mathrm{Cl\cdot} + \mathrm{Cl\cdot} \longrightarrow \mathrm{Cl{-}Cl} \qquad \text{(Eq. 5)}$$

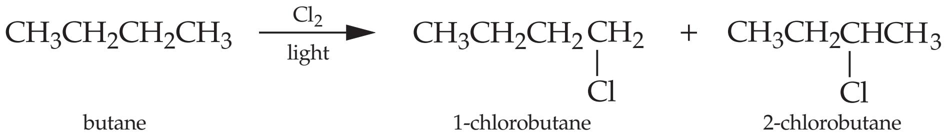
$$\mathrm{R\cdot} + \mathrm{R\cdot} \longrightarrow \mathrm{R{-}R} \qquad \text{(Eq. 6)}$$

These radicals are very reactive and readily combine with each other. However, the reactions occur slowly in the reaction mixture because the radicals collide with one another very infrequently due to their very low concentrations.

03 02 01 00 — 15 14 13 12 11 10 9 8 7 6 5 4 3 2 1

The formation of alkyl chlorides by the direct chlorination of hydrocarbons is an important industrial process. The products formed are widely used as solvents, among other applications. However, mixtures of isomeric products are commonly formed, so chlorination is not generally useful for the laboratory synthesis of specific alkyl chlorides.

For example, the chlorination of butane yields a mixture of 1-chlorobutane and 2-chlorobutane, as shown in Equation 7.


$$\mathrm{CH_3CH_2CH_2CH_3} \xrightarrow[\text{light}]{\mathrm{Cl_2}} \mathrm{CH_3CH_2CH_2}\underset{\underset{\displaystyle \mathrm{Cl}}{|}}{\mathrm{CH_2}} + \mathrm{CH_3CH_2}\underset{\underset{\displaystyle \mathrm{Cl}}{|}}{\mathrm{CH}}\mathrm{CH_3} \qquad \text{(Eq. 7)}$$

The resulting chlorobutanes can undergo further reaction to produce di- and tri-chlorobutanes. If monochlorination is desired, the reaction is conducted using a large excess of the hydrocarbon so that the chlorinating agent is the limiting reagent.

When a reaction produces more than one product, the relative amounts of each product obtained may be either thermodynamically controlled or kinetically controlled. Reactions are **thermodynamically controlled** if the product molecules are rapidly interconverted under the reaction conditions. In this case, an equilibrium mixture of the product molecules is formed and their relative potential energies or thermodynamic stabilities determine the relative amount of each product obtained. Lower energy, thermodynamically more stable molecules are obtained in larger amounts under these conditions.

Reactions in which the product molecules are not interconverted under the reaction conditions used are said to be **kinetically controlled.** In this case, the relative amount of each product is determined by how rapidly it is formed from the reactants. Those product molecules that are formed faster are present in the product mixture in larger amounts. The difference between thermodynamic control and kinetic control is illustrated in Figure 1.

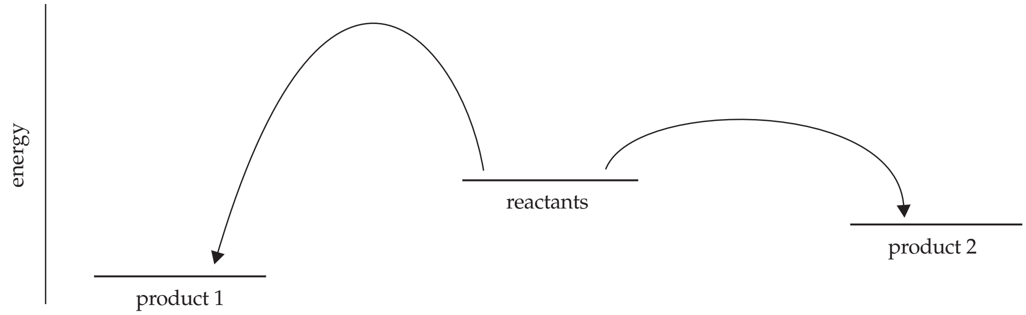


Figure 1 Kinetic versus thermodynamic control of product composition

Product 2 molecules are formed faster because the activation energy leading to them is lower. With kinetic control, if nothing further happens, more molecules of product 2 will be found in the product mixture. With thermodynamic control, however, products 1 and 2 are interconverted under the reaction conditions and equilibrium may be reached or approached. Under equilibrium conditions, the relative amount of the more stable product 1 will increase and more of product 1 will be found in the product mixture.

Free-radical chlorination is kinetically controlled. The relative amount of each product formed is determined by how rapidly that it is produced from the reactants. The identity of the product is determined when the hydrogen atom is initially removed from the hydrocarbon. Therefore, the ease with which the hydrogen atom is abstracted determines the rate of each product's formation. The reaction occurs most rapidly at those sites with the weakest carbon–hydrogen bonds. These sites produce the most stable free-radical intermediates. Tertiary radicals are more stable than secondary radicals; secondary radicals are more stable than primary radicals.

In simple alkanes, then, tertiary hydrogen atoms react faster than secondary hydrogen atoms and secondary hydrogen atoms react faster than primary hydrogen atoms. This pattern is illustrated by the chlorination of butane, as shown in Figure 2.

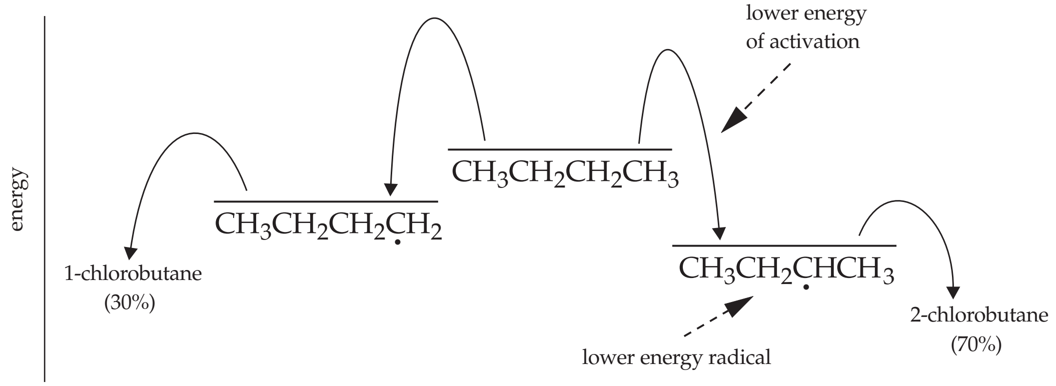
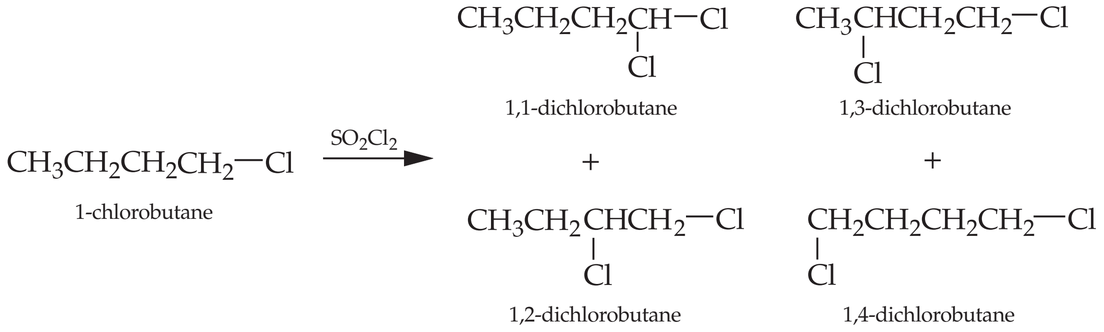


Figure 2 Kinetic control favors the production of 2-chlorobutane

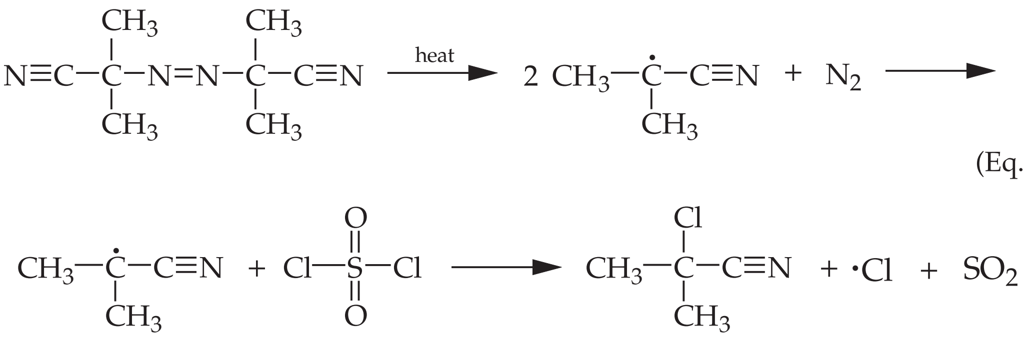
More 2-chlorobutane than 1-chlorobutane results, even though there are six primary (1°) hydrogen atoms that can be removed to yield 1-butane and only four secondary (2°) hydrogen atoms that can be removed to yield 2-chlorobutane.

In this experiment, you will investigate the chlorination of 1-chlorobutane. The reactant already contains one chlorine atom. Four isomeric dichlorobutanes are produced, as shown in Equation 8.



$$CH_3CH_2CH_2CH_2{-}Cl \xrightarrow{SO_2Cl_2} CH_3CH_2CH_2CH(Cl){-}Cl + CH_3CH(Cl)CH_2CH_2{-}Cl + CH_3CH_2CH(Cl)CH_2{-}Cl + CH_2(Cl)CH_2CH_2CH_2{-}Cl \quad \text{(Eq. 8)}$$

An excess of 1-chlorobutane will be used to minimize the formation of trichlorobutanes. Sulfuryl chloride (SO_2Cl_2) will be used as the source of chlorine atoms. 2,2′-Azobisisobutyronitrile(ABIN), a free-radical initiator that decomposes at temperatures only slightly above room temperature, will be used to generate the necessary chlorine radicals, as shown in Equation 9 on the next page.



$$N{\equiv}C-\overset{CH_3}{\underset{CH_3}{C}}-N{=}N-\overset{CH_3}{\underset{CH_3}{C}}-C{\equiv}N \xrightarrow{\text{heat}} 2\ CH_3-\underset{CH_3}{\dot{C}}-C{\equiv}N + N_2 \longrightarrow$$

(Eq. 9)

$$CH_3-\underset{CH_3}{\dot{C}}-C{\equiv}N + Cl-\overset{O}{\underset{O}{S}}-Cl \longrightarrow CH_3-\overset{Cl}{\underset{CH_3}{C}}-C{\equiv}N + \cdot Cl + SO_2$$

You will analyze the product mixture quantitatively by gas chromatography. The components in the mixture elute from the gas chromatography column in order of their boiling points, with the lowest boiling component eluting first. You will determine the relative amounts of the product molecules by measuring the areas of their chromatography peaks.

Equipment

250-mL beaker*
boiling chip
cotton†
graph paper
hot plate
2 Pasteur pipets, with latex bulb
rubber septum,
  fitted with teflon tubing†

support stand
13 × 100-mm test tube
18 × 150-mm test tube†
thermometer, 110 °C
toothpick†
utility clamp
1 to 2-dram vial

*for hot-water bath
†not needed if fume hood is available for reaction

Reagents and Properties

substance	*quantity*	*molar mass (g/mol)*	*bp (°C)*	*density (g/mL)*
2,2′-azobisisobutyronitrile (ABIN)	0.004 g	164.21		
calcium chloride, anhydrous	0.5 g			
1-chlorobutane	1.0 mL	92.5	78	0.886
1,1-dichlorobutane*		127	114	1.09
1,2-dichlorobutane*		127	124	1.11
1,3-dichlorobutane*		127	134	1.12
1,4-dichlorobutane*		127	162	1.14
sulfuryl chloride	0.16 mL	135		
5% sodium hydrogen carbonate	0.5 mL			

*product

Preview

- Assemble a reaction tube with gas trap
- Add 1-chlorobutane, sulfuryl chloride, and ABIN
- Heat the reaction mixture at 80 °C for 15 min

- Wash the reaction mixture with distilled water, then 5% $NaHCO_3$, then distilled water again
- Dry the product mixture with anhydrous $CaCl_2$; transfer the product to a tared vial
- Obtain a gas chromatogram of the product mixture

PROCEDURE

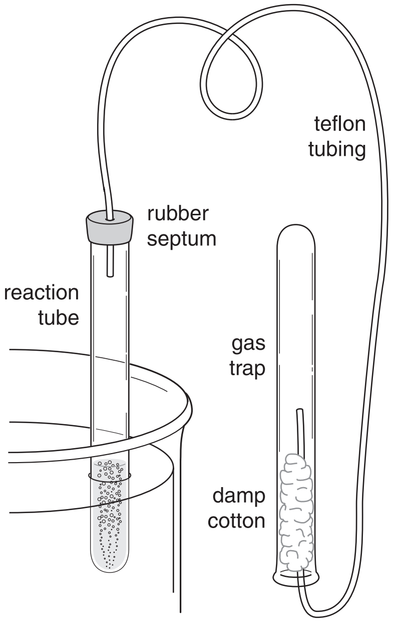
Caution: Wear departmentally approved safety goggles at all times while in the chemistry laboratory.

Always use caution in the laboratory. Many chemicals are potentially harmful. Prevent contact with your eyes, skin, and clothing. Avoid ingesting any of the reagents.

1. Setting Up the Apparatus

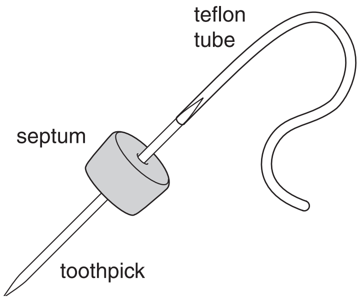
Set up the chlorination apparatus shown in Figure 3. If a ***fume hood*** is available for the reaction, omit the septum–tubing assembly and gas trap and simply use the reaction tube.

Figure 3 Apparatus for free-radical chlorination



Using a toothpick, thread teflon tubing through a rubber septum, as shown in Figure 4. Fit the septum over the mouth of a 13 × 100-mm test tube. Insert the open end of the tubing into an 18 × 150-mm test tube that contains a damp plug of cotton to absorb the SO_2 and HCl generated by the reaction.

Figure 4 Technique for threading tubing through a rubber septum



2. Conducting the Reaction

Caution: 2,2′-Azobisisobutyronitrile (ABIN) is flammable and toxic. 1-Chlorobutane is flammable. Keep away from flames and other heat sources. Sulfuryl chloride (SO_2Cl_2) is toxic and corrosive.

Prepare a hot-water bath by placing ~200 mL of water into a 250-mL beaker. Heat the water to 80 °C.

Remove the rubber septum from the reaction tube. Place 1.0 mL of 1-chlorobutane, 0.16 mL of SO_2Cl_2, and 0.004 g (4 mg) of ABIN into the reaction tube. Add a small boiling chip. Replace the rubber septum over the mouth of the reaction tube.

Clamp the reaction tube so that only the bottom 1 cm is immersed in the hot-water bath. Heat the reaction mixture for 15 min. [NOTE 1]

NOTE 1: Avoid overheating; the liquid should boil and re-condense on the sides of the reaction tube. Make certain the bath is not hotter than 80 °C.

Remove the reaction tube from the hot-water bath and allow the tube to cool to room temperature.

Remove the septum from the reaction tube. Carefully add 0.5 mL of distilled or deionized water dropwise. Mix thoroughly by repeatedly drawing the mixture into a Pasteur pipet.

Draw off the aqueous layer with the Pasteur pipet. [NOTE 2] Discard the aqueous layer.

NOTE 2: The density of 1-chlorobutane is less than that of water, while the densities of the dichlorobutane products are greater than that of water (see table of Reagents and Properties). Therefore, the product mixture density will depend on how long the reaction has run. During extractions, the product layer may be the top or bottom layer, depending on the extent to which your reaction has occurred. Add a few drops of water to the layer you suspect is the aqueous layer and observe whether or not they mix.

Wash the product with 0.5 mL of 5% $NaHCO_3$. Use the Pasteur pipet to mix the layers. Draw off the aqueous layer and discard it.

Wash the product with 0.5 mL of distilled or deionized water. Mix as before and discard the aqueous layer.

Dry the organic product layer that remains with a few particles of anhydrous $CaCl_2$. Once the liquid product is clear, transfer it to a vial.

Obtain a gas chromatogram of the product mixture, as directed by your laboratory instructor.

3. Cleaning Up

Use the labeled collection containers provided by your laboratory instructor. Clean your glassware with soap or detergent.

Caution: Wash your hands thoroughly with soap or detergent before leaving the laboratory.

Post-Laboratory Questions

1. Based on the boiling points of the reactant and the products given in the Reagents and Properties table, identify each of the peaks in your chromatogram.
2. Measure the area of each of the product peaks as directed by your laboratory instructor. Do not measure the area of the 1-chlorobutane reactant peak.
3. Determine the percent of each product formed by dividing the area of each product peak by the total area of all product peaks. Assume that the detector response is the same for each of the products. Show your calculations.
4. Determine the percent product per replaceable hydrogen atom by dividing the percent of each product by the number of hydrogen atoms that may be removed to yield that product. This number is a measure of the reactivity of the hydrogen atom removed from 1-chlorobutane to form this product. Show your calculations.
5. Determine the *relative reactivity* at each position in the reactant molecule by dividing each of the values calculated in Question 4 by the smallest of those values. The slowest reaction will have a relative reactivity of 1. Show your calculations.
6. Use a molecular modeling computer program to calculate the energy contents of 1,2-dichlorobutane and 1,3-dichlorobutane. Is the product molecule obtained in larger amount by your reaction the one with lower energy? Based on your answer, does this reaction appear to be kinetically or thermodynamically controlled? Briefly explain.
7. Use a molecular modeling computer program to determine the relative energy contents of the free-radical intermediates leading to 1,2-dichlorobutane and 1,3-dichlorobutane. Is the product molecule obtained in larger amount by your reaction the one with the lower-energy free-radical intermediate? Based on your answer, does this reaction appear to be kinetically or thermodynamically controlled? Briefly explain.
8. On a piece of graph paper, use the results of your experiment and the modeling studies to sketch energy coordinate diagrams for the formation of 1,2-dichlorobutane and 1,3-dichlorobutane from 1-chlorobutane.
9. (a) How did the yield of 1,1-dichlorobutane compare to that of the other products?

   (b) What do these results indicate about the effect of the chlorine atom in 1-chlorobutane on the stability of the free radical formed?

   (c) Did the electron-withdrawing power of the chlorine atom in 1-chlorobutane make a free radical more or less stable? Briefly explain.
10. Compare the relative reactivities of the hydrogen atoms on carbons 3 and 4 of 1-chlorobutane. What do these results indicate regarding the relative stability of the primary radical that yields 1,4-dichlorobutane and the secondary radical that yields 1,3-dichlorobutane?

NAME SECTION DATE

REAC 741/Free-Radical Chlorination

Pre-Laboratory Assignment

1. What hazards exist in handling:

   (a) 1-chlorobutane?

   (b) sulfuryl chloride?

2. What happens to the SO_2 and HCl that are generated as by-products in this reaction?

3. Why is an excess of 1-chlorobutane used in this reaction?

4. Why is only a very small amount of ABIN required for this reaction?

5. Explain why the organic compound that elutes from the end of the gas chromatograph most quickly in this experiment is the unreacted starting material.

6. What are the structures and names of the possible monochlorination products of 2-methylbutane? Ignore any stereoisomerism.

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