



# Studying $S_N1$ and $S_N2$ Reactions: Nucleophilic Substitution at Saturated Carbon

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**PURPOSE OF THE EXPERIMENT** Convert a primary alcohol to an alkyl bromide using an  $S_N2$  reaction. Investigate some factors that influence the rate of  $S_N1$  reactions.

**EXPERIMENTAL OPTIONS** Synthesizing 1-Bromobutane Using Microscale Techniques . . . . . 4  
Synthesizing 1-Bromobutane Using Macroscale Techniques . . . . . 6  
Factors Affecting the Rates of  $S_N1$  Reactions . . . . . 9

**BACKGROUND REQUIRED** You should be familiar with techniques used to dispense small amounts of liquid reagents and with techniques used to conduct microscale extractions. You should be familiar with reflux, distillation, and codistillation. You should know how to measure boiling points, refractive index, and density. You should be familiar with infrared spectroscopy. You should also be familiar with the nature of  $S_N1$  and  $S_N2$  reactions.

**BACKGROUND INFORMATION** **Substitution reactions**, in which one atom or group of atoms replaces another, are commonly observed for organic compounds. Many substitution reactions involve a kind of reacting group called a nucleophile. A **nucleophile** contains an unshared pair of electrons that reacts with a site in an organic molecule that has a deficiency of electrons. Nucleophilic substitution reactions share several characteristics with acid–base reactions, as shown in Figure 1 on page 2.

Groups that are good leaving groups in nucleophilic substitution reactions are weak bases in acid–base reactions. Strong bases are typically good nucleophiles in substitution reactions. In an acid–base reaction, a proton is transferred from the conjugate acid of a weak base to a strong base. In a similar fashion, nucleophilic substitution reactions often involve the transfer of a carbon group from a weak base, the leaving group, to a stronger base, the nucleophile.

**Figure 1** Comparison of an acid–base reaction and a nucleophilic substitution reaction

**Acid–base reaction:**

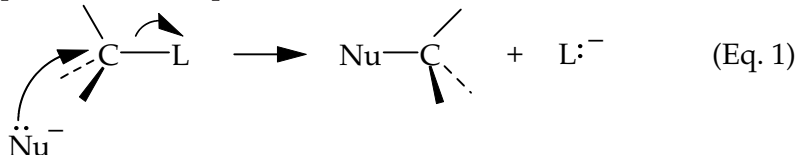


**Nucleophilic Substitution:**



Nucleophilic substitution reactions may occur by one of two common mechanisms, designated S<sub>N</sub>2 and S<sub>N</sub>1.

**S<sub>N</sub>2 Mechanism** The S<sub>N</sub>2 mechanism derives its designation from the fact that *two* chemical species—the organic reactant and the nucleophile—participate in the rate-determining step of the reaction. This mechanism has only one step, as shown in Equation 1.



The reaction is initiated by an attack of the nucleophile on the carbon bonded to the leaving group. This *back-side* attack produces a product in which the configuration of the carbon atom is inverted.

Some factors that can have a significant effect on the rate of S<sub>N</sub>2 reactions include:

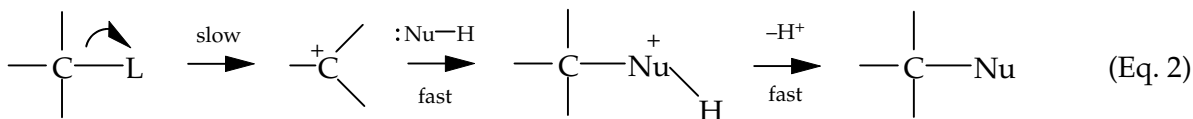
(1) The leaving group: Leaving groups are invariably weak bases. The presence of a good leaving group in the organic compound is essential for a nucleophilic substitution reaction to occur.

(2) The carbon group: An S<sub>N</sub>2 reaction occurs fastest when the approach of the nucleophile to the carbon is unhindered by the presence of bulky groups. For example, the reaction occurs faster at primary carbon atoms than at secondary carbon atoms.

(3) The nucleophile: For nucleophiles in which the attacking atoms are of comparable size, nucleophilicity parallels basicity. That is, stronger bases are better nucleophiles than weaker bases. When nucleophiles differ in size, however, the larger, more polarizable atoms are more nucleophilic, even though they are weaker bases.

(4) The solvent: Reactions involving negatively charged nucleophiles occur much more rapidly in *polar-aprotic* solvents; that is, solvents in which anionic nucleophiles are poorly solvated. Dimethylsulfoxide (DMSO) is an example of a polar-aprotic solvent.

**S<sub>N</sub>1 Mechanism** Nucleophilic substitution reactions may occur via an S<sub>N</sub>1 mechanism, in which *only* the organic reactant is involved in the rate-determining step, as shown in Equation 2. The nucleophile reacts in a fast step.



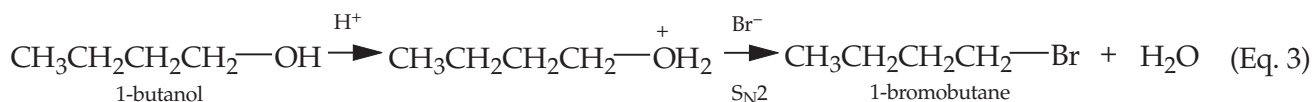
$S_N1$  reactions occur when conditions favor ionization of the organic reactant. Such conditions include:

(1) The leaving group: The leaving group (L) must be a weak base.

(2) The carbon group: The rate-determining step involves production of a carbocation. This step will occur faster for those compounds that yield more stable carbocations. For example, tertiary compounds react faster than secondary compounds. Primary compounds react extremely slowly. Carbocation intermediates are also stabilized by dispersal of the positive charge through delocalization of electrons.  $S_N1$  reactions that produce such resonance-stabilized carbocation intermediates are also quite fast. For example,  $S_N1$  reactions occur readily with molecules that form allyl or benzyl carbocations.

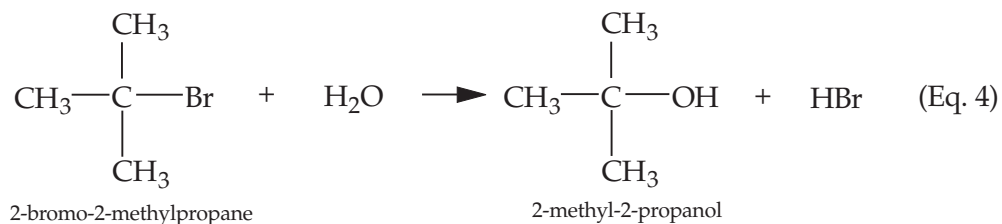
(3) The solvent: Ionization processes are facilitated by polar solvents. Because the rate of an  $S_N1$  reaction is directly dependent on such an ionization, the reaction occurs faster in more polar solvents.

In the first part of this experiment, you will convert 1-butanol to 1-bromobutane as an example of an  $S_N2$  reaction. Because the OH group of the alcohol is not a weak base and, therefore, not a good leaving group, you will conduct the reaction in a strongly acidic solution. In an acidic environment, the alcohol exists as its conjugate acid, and the leaving group is a water molecule, a weak base, as shown in Equation 3.



The relatively uncrowded primary carbon atom is open to back-side attack by an appropriate nucleophile. Most nucleophiles are strong bases and could not exist in this acidic environment because they would be rapidly protonated. Bromide ion, however, is a very weak base that is strongly nucleophilic due to its very large size. Bromide ion is an effective nucleophile even in a very acidic medium.

In the second part of this experiment, you will study factors affecting the rates of  $S_N1$  reactions. In  $S_N1$  reactions, solvent molecules often serve as the nucleophile. Such reactions are called **solvolysis** reactions. The reaction of 2-bromo-2-methylpropane with water is shown in Equation 4.



The HBr formed as a byproduct is a strong acid and is completely ionized in the solution. As the reaction occurs, the acidity of the solution increases, providing a convenient means for monitoring the rate of the reaction. In this experiment, monitoring is initiated by placing a measured quantity of base into the solution. As the  $S_N1$  reaction proceeds, the generated acid neutralizes the base. An acid–base indicator added to the reaction solution changes color at the point when all of the base has been neutralized. The shorter the time period required for this neutralization, the faster the  $S_N1$  reaction has proceeded.

You will investigate three factors that affect the rate of S<sub>N</sub>1 reactions: the identity of the leaving group, Br<sup>-</sup> versus Cl<sup>-</sup>; the structure of the alkyl group, 3° versus 2°; and the polarity of the solvent, 40 percent 2-propanol versus 60 percent 2-propanol.

## SYNTHESIZING 1-BROMOBUTANE

### USING MICROSCALE TECHNIQUES

#### Equipment

2 beakers, 100-mL	2.0-mL pipet
2 boiling chips, acid-resistant	sand bath*
15-mL centrifuge tube	support stand
125-mL Erlenmeyer flask	13 × 100-mm test tube <sup>†</sup>
glass stirring rod	18 × 150-mm test tube
25-mL graduated cylinder	2 vials, 5-mL <sup>†</sup>
6 Pasteur pipets, with latex bulb	utility clamp
1.0-mL pipet	

\*sand in crystallizing dish on electric hot plate or sand in electric heating well with heat controller

<sup>†</sup>extra equipment for optional procedure, 3. **Distilling the Product**

#### Reagents and Properties

substance	quantity	molar mass (g/mol)	bp (°C)	density (g/mL)	$n_D^{20}$
1-bromobutane*		137.0	102	1.276	1.4390
1-butanol	1.00 g	74.1	118	0.810	1.3990
calcium chloride, anhydrous	0.4 g				
hydrobromic acid, 48%	2.0 mL	80.9		1.49	
sulfuric acid, concentrated	1.0 mL	98.1		1.84	
sodium hydrogen carbonate, 5% aqueous	2 mL			1.04	

\*product

#### Preview

- Place a boiling chip, 1-butanol, and HBr solution into a test tube
- Slowly add concentrated H<sub>2</sub>SO<sub>4</sub>
- Heat at reflux for 1 hr
- Allow the reaction mixture to cool, then separate the acid layer
- Wash the organic layer with water, aqueous NaHCO<sub>3</sub>, then water again

- Dry the organic layer with anhydrous  $\text{CaCl}_2$
- Purify the product by distillation
- Characterize the product by boiling point, refractive index, density, or IR spectroscopy

## PROCEDURE **Chemical Alert**

1-bromobutane—*flammable and irritant*

1-butanol—*flammable and irritant*

48% hydrobromic acid—*toxic and corrosive*

sulfuric acid—*toxic and oxidizer*

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

### 1. Conducting the Reaction

**Caution:** Hydrobromic acid (HBr) is toxic and corrosive. Concentrated sulfuric acid ( $\text{H}_2\text{SO}_4$ ) is toxic and oxidizing. HBr and  $\text{H}_2\text{SO}_4$  can cause severe burns. In case of spill, notify your laboratory instructor immediately.

1-Butanol is flammable and irritating. Do not use near flames or other heat sources. Prevent eye, skin, and clothing contact. Avoid inhaling fumes and ingesting these compounds.

**NOTE 1:** As the reaction occurs, you should note the production of a second liquid layer. One layer contains the water and acid; the other contains 1-bromobutane produced by the reaction.

**NOTE 2:** Once the liquid in the test tube reaches a steady reflux condition, proceed with the section “Factors Affecting the Rates of  $\text{S}_{\text{N}}1$  Reactions” on page 9.

Insert an  $18 \times 150$ -mm test tube into a 125-mL Erlenmeyer flask. Place the flask on a balance and tare the balance. Add 1.00 g of 1-butanol to the test tube. Add 2.0 mL of 48% HBr and an *acid resistant* boiling chip. Then *slowly* add, with mixing, 1.0 mL of concentrated  $\text{H}_2\text{SO}_4$ .

Remove the test tube from the Erlenmeyer flask. Clamp the test tube vertically to a support stand with *only the very bottom* of the tube in a sand bath. Heat the mixture to boiling using a low setting.

Avoid loss of HBr; do not allow the condensation ring to rise more than 2 cm in the test tube. Reflux the solution for 1 hr. [NOTE 1] [NOTE 2]

### 2. Washing the Reaction Mixture

**Caution:** 1-Bromobutane is flammable and irritating. Do not use near flames or other heat sources. Prevent eye, skin, and clothing contact. Avoid inhaling fumes and ingesting 1-bromobutane.

Label two 100-mL beakers “Acid Layer” and “Washes”, respectively. Place 25 mL of distilled or deionized water into the beaker labeled “Acid Layer”.

After the reflux is complete, remove the test tube from the sand bath. Allow the test tube to cool.

Transfer the contents of the test tube to a 15-mL centrifuge tube. Use a Pasteur pipet to remove the bottom acid layer. Place the acid layer into the beaker labeled “Acid Layer”.

To wash the 1-bromobutane layer, add 2 mL of water to the test tube and mix well. Then use a Pasteur pipet to remove the upper water layer. Place the water into the beaker labeled “Washes”.

Wash the 1-bromobutane again, first with 2 mL of 5% aqueous sodium hydrogen carbonate ( $\text{NaHCO}_3$ ), then with a second 2 mL of water. Each time, use the Pasteur pipet to remove the aqueous layer and place the layer into the beaker labeled “Washes”.

**NOTE 3:** As the solid anhydrous CaCl<sub>2</sub> removes water from the liquid 1-bromobutane, the liquid layer will become clear. Swirling the mixture will facilitate the process.

### 3. Distilling the Product (optional)

**NOTE 4:** Use the product characterization techniques designated by your laboratory instructor.

### 4. Characterizing the Product [NOTE 4]

**NOTE 5:** The refractive index at 20 °C is calculated by using the following equation, where  $T$  is the ambient temperature in degrees Celsius, and  $n_D^T$  is the refractive index measured at ambient temperature.

$$n_D^{20} = n_D^T + 0.00045 (T - 20 \text{ } ^\circ\text{C})$$

### 5. Cleaning Up

After the final washing with water, allow the two layers to *completely* separate. Use a clean Pasteur pipet to transfer the 1-bromobutane layer to a clean, dry 5-mL vial.

Add 4–5 granules of anhydrous CaCl<sub>2</sub> to the vial to dry the product. Allow the product to dry for 5–10 min. [NOTE 3]

If you do not conduct the optional distillation in Part 3, measure and record the mass of your product.

Tare a 5-mL vial. Use a clean, dry Pasteur pipet to transfer the product to a clean, dry 13 × 100-mm test tube. Add a boiling chip. Clamp the test tube vertically in a sand bath and heat the product until the liquid refluxes in the test tube.

Submerge the tip of a clean, dry Pasteur pipet into the 1-bromobutane vapors, as shown in Figure 2. Draw the vapors into the pipet, where they will condense. Transfer the condensed 1-bromobutane to the tared 5-mL vial.

Repeat this process until no more vapors are obtained. Measure and record the mass of the 1-bromobutane collected.

Characterize the product by measuring its boiling point, density, or refractive index. Record the temperature when measuring the refractive index. Make a temperature correction for the refractive index. [NOTE 5] Compare your experimental values with the literature values given under Reagents and Properties.

Obtain an infrared spectrum of your product. Compare your product spectrum with a spectrum of the 1-butanol used as the reagent. Pay particular attention to the regions at 3500 cm<sup>-1</sup> and 1050 cm<sup>-1</sup>.

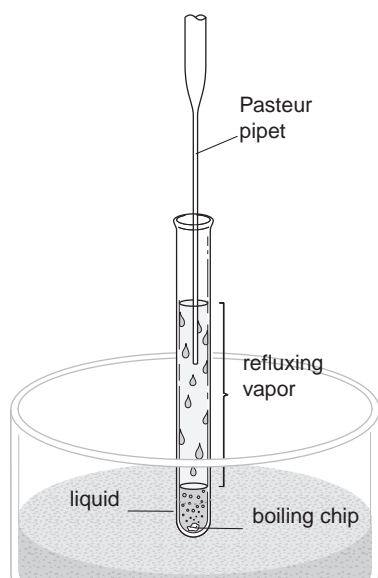
Place your recovered materials in the appropriate labeled collection containers as directed by your laboratory instructor. Clean your glassware with soap or detergent.

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

## SYNTHESIZING 1-BROMOBUTANE USING MACROSCALE TECHNIQUES

### Equipment

50-mL beaker	standard taper glassware:
400-mL beaker*	condenser, with tubing
boiling chip, acid-resistant	distilling head
15-mL centrifuge tube	10-mL round-bottom flask <sup>†</sup>
100-mL flask heater, with heat controller	100-mL round-bottom flask
10-mL graduated cylinder	thermometer, -10–260 °C, with adapter
2 Pasteur pipets, with latex bulb <sup>†</sup>	vacuum adapter
product vial <sup>†</sup>	support ring
rubber stopper, one-hole	2 support stands
rubber tubing	18 × 150-mm test tube
*for ice bath	2 utility clamps
<sup>†</sup> extra equipment for optional procedure, 4. Distilling the Product	Y-tube or T-tube <sup>‡</sup>
<sup>‡</sup> for gas trap	



**Figure 2** Test-tube distillation apparatus

### Reagents and Properties

substance	quantity	molar mass (g/mol)	bp (°C)	density (g/mL)	$n_D^{20}$
1-bromobutane*		137.0	102	1.276	1.4390
1-butanol	5.0 g	74.1	118	0.810	1.3990
calcium chloride, anhydrous	1.0 g				
hydrobromic acid, 48%	10.0 mL	80.9		1.49	
sulfuric acid, concentrated	4.0 mL	98.1		1.841	
sodium hydrogen carbonate, 5% aqueous	5.0 mL			1.04	

\*product

### Preview

- Place a boiling chip, 1-butanol, and HBr solution into a round-bottom flask
- Slowly add concentrated  $H_2SO_4$  to the cooled reaction mixture
- Heat the mixture at reflux for 1 hr
- Codistill the product with water
- Wash the organic layer with water, 5%  $NaHCO_3$ , then water again
- Dry the organic layer with anhydrous  $CaCl_2$
- Purify the product by distillation
- Characterize the product by boiling point, refractive index, density, or IR spectroscopy

### PROCEDURE **Chemical Alert**

1-bromobutane—*flammable and irritant*

1-butanol—*flammable and irritant*

48% hydrobromic acid—*toxic and corrosive*

sulfuric acid—*toxic and oxidizer*

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

#### 1. Conducting the Reaction

**Caution:** Hydrobromic acid (HBr) is toxic and corrosive. Concentrated sulfuric acid ( $H_2SO_4$ ) is toxic and oxidizing. HBr and  $H_2SO_4$  can cause severe burns. In case of a spill, notify your laboratory instructor immediately.

1-Butanol is flammable and irritating. Do not use near flames or other heat sources. Prevent eye, skin, and clothing contact. Avoid inhaling fumes and ingesting these compounds.

**NOTE 1:** As the reaction occurs, you should note the production of a second liquid layer. One layer contains the water and acid; the other contains 1-bromobutane produced by the reaction.

**NOTE 2:** Once the liquid in the flask reaches a steady reflux condition, proceed with the section "Factors Affecting the Rates of S<sub>N</sub>1 Reactions" on page 9.

## 2. Codistillation of the Product

**NOTE 3:** You will observe two layers in the test tube because the 1-bromobutane will codistill with water. Once you collect 10–15 mL of distillate, only water should remain in the pot.

## 3. Washing the Product

**NOTE 4:** The liquid layer becomes clear as the solid anhydrous CaCl<sub>2</sub> extracts water from the liquid 1-bromobutane.

## 4. Distilling the Product (optional)

Use the 400-mL beaker to prepare an ice-water bath. Place an *acid resistant* boiling chip, 5.0 g (6.2 mL) of 1-butanol, and 10 mL of 48% HBr into a 100-mL round-bottom flask. Cool the mixture in the ice bath. *Slowly* add to the round-bottom flask, with stirring, 4 mL of concentrated H<sub>2</sub>SO<sub>4</sub>.

Fit the flask with a condenser for reflux, as shown in Figure 3. Fit the top of the condenser with a rubber stopper equipped with a Y-tube. Use rubber tubing to connect one arm of the Y-tube to the water aspirator. Leave the other arm open. Turn on the water to the aspirator to draw the acid fumes generated by the reaction.

Heat the mixture to boiling. Reflux the mixture gently for 1 hr. [NOTE 1] [NOTE 2]

**Caution:** 1-Bromobutane is flammable and irritating. Do not use near flames or other heat sources. Prevent eye, skin, and clothing contact. Avoid inhaling fumes and ingesting 1-bromobutane.

Once the reflux is complete, remove the heater from the flask and allow the flask to cool. Add 10 mL of distilled or deionized water and an additional boiling chip.

Arrange the apparatus for distillation, as shown in Figure 4. Distill the mixture into an 18 × 150-mm test tube until you collect 10–15 mL of distillate. [NOTE 3]

Place the pot residue in the container labeled "Recovered Pot Residue", provided by your laboratory instructor.

Label a 50-mL beaker "Washes". Use a Pasteur pipet to remove the upper aqueous layer from the distillate. Place this layer into the labeled beaker.

To wash the 1-bromobutane layer, add 5 mL of water to the test tube and mix well. Use a Pasteur pipet to remove the water layer and transfer the water to the labeled beaker.

Wash the 1-bromobutane again, first with 5 mL of 5% aqueous sodium hydrogen carbonate (NaHCO<sub>3</sub>), then with a second 5 mL of water. Each time, use the Pasteur pipet to remove the aqueous layer and place the layer into the labeled beaker.

After the last water wash, remove as much of the water as possible with the Pasteur pipet. Transfer the contents of the test tube to a centrifuge tube to facilitate the removal of the water. Again, remove as much water as possible.

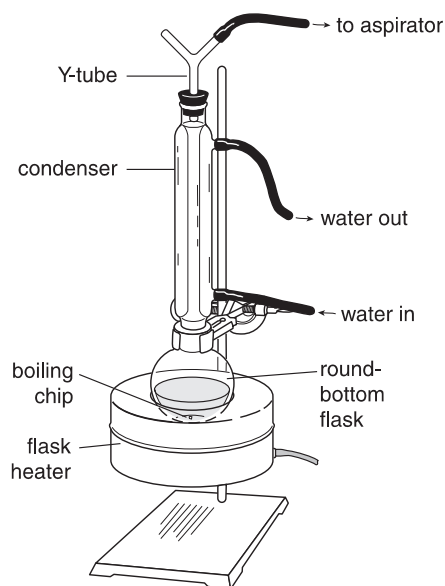
Add approximately 1 g of anhydrous CaCl<sub>2</sub> to dry the product. Allow the product to dry for 5–10 min. [NOTE 4]

If you do not conduct the optional distillation in Part 4, measure and record the mass of your product.

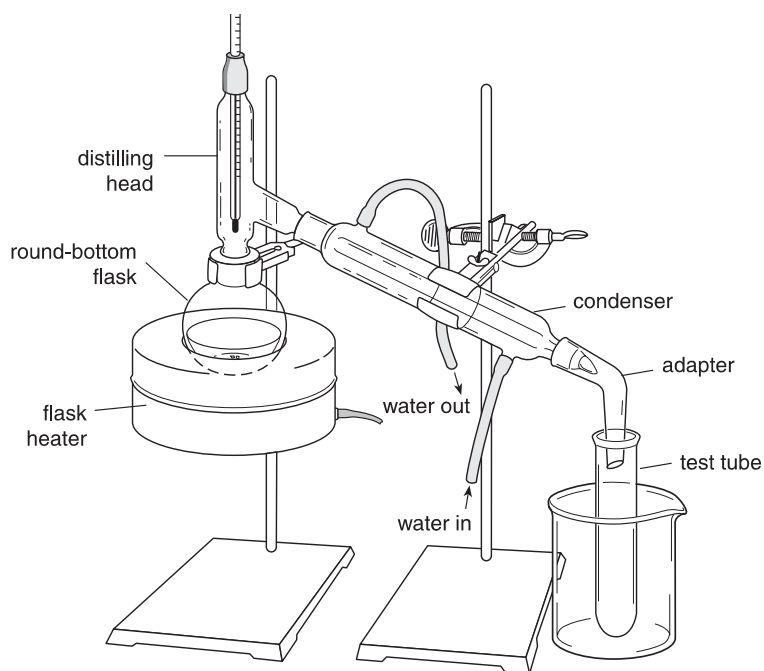
Tare a product vial. Use a clean, dry Pasteur pipet to transfer the dried 1-bromobutane into a 10-mL round-bottom flask. Assemble a distillation apparatus using the 10-mL round-bottom flask. Make certain the distillation apparatus is clean and dry.

Distill the product into the tared vial, collecting the portion that distills from 99–103 °C. Measure and record the mass of the 1-bromobutane collected.





**Figure 3** Reflux apparatus for macro scale preparation



**Figure 4** Apparatus for codistillation

## 5. Characterizing the Product

[NOTE 5]

**NOTE 5:** Use the product characterization techniques designated by your laboratory instructor.

## 6. Cleaning Up

**NOTE 6:** The refractive index at 20 °C is calculated by using the following equation, where  $T$  is the ambient temperature in degrees Celsius, and  $n_D^T$  is the refractive index measured at ambient temperature.

$$n_D^{20} = n_D^T + 0.00045(T - 20 \text{ } ^\circ\text{C})$$

Characterize the product by measuring its boiling point, density, or refractive index. Record the temperature when measuring the refractive index. Make a temperature correction for the refractive index. [NOTE 6] Compare the experimental values with the literature values given under Reagents and Properties.

Obtain an infrared spectrum of your product. Compare your product spectrum with a spectrum of the 1-butanol used as the reagent. Pay particular attention to the regions at  $3500 \text{ cm}^{-1}$  and  $1050 \text{ cm}^{-1}$ .

Place your recovered materials in the appropriate labeled collection containers as directed by your laboratory instructor. Clean your glassware with soap or detergent.

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

# FACTORS AFFECTING THE RATES OF S<sub>N</sub>1 REACTIONS

## Equipment

2 Erlenmeyer flasks, 125-mL  
50-mL graduated cylinder  
100-mL graduated cylinder  
marking pen

50- $\mu$ L micropipet  
100- $\mu$ L micropipet\*  
timer

\*or adjustable micropipet set to 200- $\mu$ L

*Reagents and Properties*

<i>substance</i>	<i>quantity</i>	<i>molar mass (g/mol)</i>	<i>bp (°C)</i>	<i>density (g/mL)</i>	<i>n<sub>D</sub><sup>20</sup></i>
2-bromopropane	50 μL	123.0	59	1.31	1.4250
2-propanol	150 mL	60.1	82	0.79	1.3770
0.5M sodium hydroxide	1.2 mL				
phenolphthalein	30 drops				
2-bromo-2-methylpropane	200 μL	137	73	1.19	1.4279
2-chloro-2-methylpropane	50 μL	92.6	52	0.85	1.3848

*Preview***Measuring the Effect of the Leaving Group on Reaction Rate**

- Prepare a 50% 2-propanol/water solvent mixture
- Divide the mixture into two portions
- Add phenolphthalein indicator and NaOH solution
- Add alkyl halides and measure the time required for discharge of the indicator color

**Measuring the Effect of the Alkyl Group Structure on Reaction Rate**

- Prepare a 50% 2-propanol/water solvent mixture
- Divide the mixture into two portions
- Add phenolphthalein indicator and NaOH solution
- Add alkyl halides and measure the time required for discharge of the indicator color

**Measuring the Effect of Solvent Polarity on Reaction Rate**

- Prepare 40% and 60% 2-propanol/water solvent mixtures
- Add phenolphthalein indicator and NaOH solution
- Add 2-bromo-2-methylpropane and measure the time required for discharge of the indicator color

**PROCEDURE** *Chemical Alert*2-bromopropane—*flammable and irritant*2-bromo-2-methylpropane—*flammable*2-chloro-2-methylpropane—*flammable*2-propanol—*flammable and irritant*sodium hydroxide—*corrosive and toxic*

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

### 1. Measuring the Effect of the Leaving Group on Reaction Rate

**Caution:** 2-Bromo-2-methylpropane, 2-chloro-2-methylpropane, and 2-propanol are flammable and irritating. Do not use near flames or other heat sources. Prevent eye, skin, and clothing contact. Avoid breathing fumes and ingesting these compounds.

To prepare a 50% mixture of 2-propanol in water, place 50 mL of 2-propanol into a 100-mL graduated cylinder and add enough distilled or deionized water to make 100 mL. Mix well. Place 50 mL of the mixture into each of two 125-mL Erlenmeyer flasks.

NOTE 1: The phenolphthalein should be bright pink in this slightly basic solution.

Add 5 drops of phenolphthalein indicator and *exactly* 200  $\mu\text{L}$  of 0.5M NaOH to each of the flasks. Mix well. [NOTE 1]

Add 50  $\mu\text{L}$  of 2-bromo-2-methylpropane, with swirling, to one of the flasks. Measure and record the time required for the solution to become colorless.

Add 50  $\mu\text{L}$  of 2-chloro-2-methylpropane, with swirling, to the second flask. Again measure and record the time required for the solution to become colorless.

### 2. Measuring the Effect of the Alkyl Group Structure on Reaction Rate

**Caution:** 2-Bromopropane, 2-bromo-2-methylpropane, and 2-propanol are flammable and irritating. Do not use near flames or other heat sources. Prevent eye, skin, and clothing contact. Avoid breathing fumes and ingesting these compounds.

Prepare 100 mL of a 50% mixture of 2-propanol in water as described in Part 1. Divide the mixture equally between two 125-mL Erlenmeyer flasks.

Add 5 drops of phenolphthalein and *exactly* 200  $\mu\text{L}$  of 0.5M NaOH to each of the flasks. Mix well.

Add 50  $\mu\text{L}$  of 2-bromo-2-methylpropane, with swirling, to one of the flasks. Measure and record the time required for the solution to become colorless.

Add 50  $\mu\text{L}$  of 2-bromopropane, with swirling, to the second flask. Again measure and record the time required for the solution to become colorless. If the solution does not become colorless within 15 min, stop the reaction and record the time as >15 min.

### 3. Measuring the Effect of Solvent Polarity on Reaction Rate

**Caution:** 2-Bromo-2-methylpropane and 2-propanol are flammable and irritating. Do not use near flames or other heat sources. Prevent eye, skin, and clothing contact. Avoid breathing fumes and ingesting these compounds.

To prepare 50 mL of a 40% mixture of 2-propanol in water, place 20 mL of 2-propanol into a 50-mL graduated cylinder and add enough water to make 50 mL. Place the mixture into a labeled 125-mL Erlenmeyer flask.

To prepare 50 mL of a 60% mixture of 2-propanol in water, place 30 mL of 2-propanol into a 50-mL graduated cylinder and add enough water to make 50 mL. Place the mixture into a labeled 125-mL Erlenmeyer flask.

Add 5 drops of phenolphthalein and *exactly* 200  $\mu\text{L}$  of 0.5M NaOH to each flask. Mix well.

Add 50  $\mu\text{L}$  of 2-bromo-2-methylpropane, with swirling, to each flask. Measure and record the time required for each solution to become colorless.

4. **Cleaning Up** Place all alcohol–water reaction mixtures in the container labeled “Recovered Alcohol–Water Mixtures”, provided by your laboratory instructor. Clean your glassware with soap or detergent. [NOTE 2]

**NOTE 2:** If you conducted this section of the experiment during the reflux time for Section I or II, return to that section.

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

## Post-Laboratory Questions

1. Calculate the percent yield of 1-bromobutane obtained in your experiment.
2. What experimental evidence can you provide that the product isolated in your synthetic experiment is 1-bromobutane?
3. Which compound, 2-bromo-2-methylpropane or 2-chloro-2-methylpropane, reacted faster in your  $S_N1$  experiment? What were the relative rates of the two reactions?
4. Based on your answer to question 3, which is the better leaving group,  $Br^-$  or  $Cl^-$ ? Are these results consistent with the relative basicities of these two ions? Briefly explain.
5. Which compound, 2-bromo-2-methylpropane or 2-bromopropane, reacted faster in your  $S_N1$  experiment? How are the reactivities of 2-bromo-2-methylpropane and 2-bromopropane related to the stabilities of the carbocations produced as intermediates in the reaction? Briefly explain.
6. Which of the two solvent mixtures, 40% 2-propanol or 60% 2-propanol, is more polar? Briefly explain.
7. In which of the two solvent mixtures did 2-bromo-2-methylpropane react faster? Account for your results in terms of the effect of solvent polarity on the rate-determining step in this  $S_N1$  reaction.
8. Use your results to explain which variable—leaving group, alkyl structure, or solvent polarity—has the greatest impact on the rate of an  $S_N1$  reaction.



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NAME

SECTION

DATE

*REAC 714/Studying S<sub>N</sub>1 and S<sub>N</sub>2 Reactions: Nucleophilic Substitution at Saturated Carbon*

**Pre-Laboratory Assignment**

1. Why should care be exercised in handling concentrated acids such as H<sub>2</sub>SO<sub>4</sub> and HBr?
  
2. Why do primary alkyl halides typically undergo S<sub>N</sub>2 substitution reactions more rapidly than do secondary or tertiary alkyl halides?
  
3. Why should reflux of the microscale reaction mixture be gentle, with the condensation ring remaining close to the surface of the liquid in the test tube?
  
4. By observing the reaction mixture, what visual evidence can be gained to indicate that 1-butanol is being converted to 1-bromobutane?
  
5. What is the function of anhydrous CaCl<sub>2</sub> in this experiment?

