Chem 2219: Exp#7 Relative Rates of SN1 & SN2 Reactions

Objective: In this experiment, you will determine the effect on the reaction rate for SN1 and SN2 reactions that occurs when the substrate structure and leaving group are changed. Specifically, you will compare the relative rates of SN1 and SN2 reactions as a function of the substrate structure: 1°, 2° 3° and leaving group (Br or Cl). In order to ensure that the reactions occur within acceptable time limits, temperature baths will be used.

Reading Assignment: Solomons "Organic Chemistry, 12th ed.", Chapt. 6, Nucleophilic Reactions
"Organic Lab Techniques, 2nd ed. (online pdf lab book), pp.341+ (Alkyl Halides);
pp. 341, 343 & 357 (Silver Nitrate Test); and, pp. 341, 343 & 358 (Sodium Iodide / Finkelstein Test)

Concepts:
aprotic solvent, carbocation, leaving group, nucleophile, precipitate, protic solvent, rate of reaction, SN1 reaction, SN2 reaction, substrate

Chemicals:
1-bromobutane, 2-bromobutane, t-butyl bromide, 1-chlorobutane, 2-chlorobutane, t-butyl chloride, acetone, ethanol, silver nitrate, sodium iodide

Safety Precautions:
Wear chemical splash-proof goggles and appropriate attire at all times.
Alkyl halides are irritants and inhalation hazards.
Silver nitrate ($AgNO_3$) will stain skin and clothing black.
Hot glassware looks just like cold glassware.
Be careful when working with hot glassware! Do not to touch it!

Materials:
Two sets of 6 test tubes in a test tube rack, a set of reagents (listed above), 0.1M AgNO3 in EtOH, 15% NaI in acetone, hot water bath (~125 ml water in a 250 ml beaker on a hotplate with a kitchen thermometer ~40°C), ice water bath (~100 ml ice water in a 150 ml beaker with a kitchen thermometer)

Background Information:

Nucleophilic substitution reactions are classified as SN1 and SN2. A SN1 reaction involves a two step reaction mechanism in which a leaving group is lost to form a carbocation intermediate, which is then followed by attack from a weak nucleophile with loss of stereochemistry. A SN2 reaction involves a single step displacement of a leaving group by a nucleophile with inversion of configuration. In this experiment we will look at how changing the structure of the substrate and the nature of the leaving group affects the relative rates for SN1 and SN2 reactions.

The test reagents in this experiment involve production of a precipitate which can be timed to compare relative rates. For SN1 reactions, $AgNO_3$ in EtOH is chosen because nitrate ion is a weak nucleophile and EtOH is a polar protic solvent favoring a SN1 mechanism. The AgBr and AgCl formed in this reaction are insoluble in EtOH, so that the time to produce a cloudy solution can be compared.

For SN2 reactions, NaI in acetone is chosen as iodide ion is a good nucleophile and acetone is a polar aprotic solvent, favoring a SN2 mechanism. The NaBr and NaCl formed in this reaction are insoluble in acetone, so that the time to produce a cloudy solution can be compared as a measure of relative rates.

Summary of SN1 and SN2 Reactions

	SN1	**SN2**
Rate Law	Unimolecular (substrate only)	Bimolecular (substr. & nuc.)
Energy Barrier	carbocation stability	steric hindrance
Alkyl halide structure	3° > 2° >> 1°	1° > 2° >> 3°
Nucleophile	weak (generally neutral)	strong (generally neg. charged)
Solvent	polar protic	polar aprotic
Stereochemistry	mix of retention & inversion	inversion only

****Note: You will be working in pairs for this experiment.****

I. SN2 Procedure Using a 15% Sodium Iodide in Acetone Test Reagent:

1. At your station there should be a hot water bath: a 250 ml beaker with ~125 ml of water on a hotplate set at ~100°C. Insert a digital kitchen thermometer and when the temperature reaches 40°C, reduce the hotplate to 65°C. The bath needs to be maintained at ~40 °C.* (*Make adjustments to the hotplate temperature as needed to maintain the temperature range of the bath.*)

> **Note:** Acetone boils at 56°C, and 2-chlorobutane boils at 68 °C, so you do NOT want the temperature on the kitchen thermometer to be above 40°C when you add the test tubes to the bath.

2. While the bath is adjusting, confirm that the green-taped test tubes labeled 1-bromobutane (1B), 2-bromobutane (2B) and t-butyl bromide (TB) have ~1 ml of 15% NaI/acetone test reagent in them.

3. Using the test tube clamps, lower the three test tubes into the ~40 °C water bath. Wait 3 minutes to allow the solutions to come to temperature.

> **Note:** Make sure stopwatch on your phone is ready to use. Sample Tables are provided on page 5. These may be used for data collection, scanned and added to your report or rewritten in your lab notebook.

4. Locate 1-B test tube in the bath. (*Be sure to start the timer as soon as the 1-bromobutane is added.*) Add **8** drops of 1-bromobutane to the 1B test tube. Start timer on your stopwatch. Shake to mix. In Table 1, record the time in minutes to the nearest second at which visible cloudiness appears. Remove the test tube from the bath once the solution is visibly cloudy or after 10 minutes whichever comes first. Place the test tube in the test tube rack.

5. Repeat step #4 for 2 bromobutane (2B test tube) and predict t-butyl bromide (TB test tube).

6. Repeat steps #2-4 using the blue-taped test tubes for 1-chlorobutane (1C), and 2-chlorobutane (2C). Record the times in Table 2.

7. Clean the test tubes* and place the rack on the cart near the hood on the east side near the lab entrance. Leave the hot water bath (250 ml beaker) on the hot plate for the next section.

> ***Note:** NaX ppts are water soluble, so rinse test tubes with water first. When clean, rinse the test tubes with acetone to remove any residual water. Turn the test tubes upside down to dry on the rack.

> ***Note:*** Once the test tubes are clean, place them in the test tube rack. Place the rack on the cart near the waste hood on the east end of the lab.

II. SN1 Procedure Using a 0.1M Silver Nitrate in Ethanol Test Reagent:

1. Make an ice bath. Using your 250 ml beaker, add ~125 ml of ice, then add cold water until volume is ~125 ml. Insert a digital kitchen thermometer into the ice bath. The temperature of the bath should be 0 °C to 5 °C.

2. While the bath is adjusting, confirm that the orange-taped test tubes labeled 2-bromobutane (2B) and t-butyl bromide (TB) have ~1 ml of 0.1M $AgNO_3$/EtOH test reagent in them.

3. Using test tube clamps, lower the t-butyl bromide (TB) and 2-bromobutane(2B) test tubes into the ~5 °C ice water bath. Wait 5 minutes for the solution to come to temperature. (Proceed to 4.)

Note: In order to see the test tubes in the ice bath, you may need to use a Kim wipe to wipe any fog off the outside of the 250 ml beaker.

4. Add **8** drops of t-butyl bromide (TB) to the TB test tube. (*Be sure to start the timer as soon as the t-butyl bromide (TB) is added.*) Shake to mix. In Table 3, record the time in minutes to the nearest second at which visible cloudiness appears. Remove the test tube from the bath once the solution is visibly cloudy or after 10 minutes whichever comes first. Place the test tube in the test tube rack.

5. Repeat step #4 for 2-bromobutane (2B).

6. Repeat steps #2-6 using the yellow-taped test tubes for 2-chlorobutane (2C) and t-butyl chloride (TC). (i.e., The t-butyl chloride (TC) test tube should be placed in the ice bath Record the times in Table 4.

7. Clean the test tubes** and place the rack on the cart near the hood on the east side near the lab entrance. Return your 250 ml beaker to your drawer.

****Note:** AgX ppts are insoluble, so rinse test tubes with water while scrubbing with a test tube brush. When the test tubes are clean, rinse them with acetone to remove residual water. Turn the test tubes upside down to dry on the rack.

Note: Once the test tubes are clean, place them in the test tube rack. Place the rack on the cart near the waste hood on the east end of the lab.

Post Lab Questions

SN2 Rate Trends Based on the Data in Tables 1 & 2:

1. Determine what the effect of the substrate structure is on the SN2 rate.
   a. Compare the rates in Table 1 for the brominated compounds. Explain the trend.
   b. Compare the rates in Table 2 for the chlorinated compounds. Explain the trend.
   c. Do both sets of data show the same trend? Why is this the case?
      Explain this trend in terms of the substrate structure of the compounds.

2. Determine what the effect of the leaving group is on the SN2 rate.
   a. Compare the rate for 1-bromobutane to 1-chlorobutane. Which is faster?
   b. Compare the rate for 2-bromobutane to 2-chlorobutane. Which is faster?
   c. Compare the rate for t-butyl bromine to t-butyl chlorine. Which is faster?
   d. Do all of the comparisons show the same trend? Why is this the case?
      Explain this trend in terms of the leaving group of the compounds.

SN1 Rate Trends Based on the Data in Tables 3 & 4:

3. Determine what the effect of the substrate structure is on the SN1 rate.
   a. Compare the rates in Table 3 for the brominated compounds. Explain the trend.
   b. Compare the rates in Table 4 for the chlorinated compounds. Explain the trend.
   c. Do both sets of data show the same trend? Why is this the case?
      Explain this trend in terms of the substrate structure of the compounds.

4. Determine what the effect of the leaving group is on the SN1 rate.
   a. Compare the rate for 1-bromobutane to 1-chlorobutane. Which is faster?
   b. Compare the rate for 2-bromobutane to 2-chlorobutane. Which is faster?
   c. Compare the rate for t-butyl bromine to t-butyl chlorine. Which is faster?
   d. Do all of the comparisons show the same trend? Why is this the case?
      Explain this trend in terms of the leaving group of the compounds.

Other:

5. What was the temperature effect on the SN1 & SN2 reactions?
   a. Why was it necessary to heat the SN2 reactions?
      Would the reaction have been faster or slower at room temperature? Explain.
   b. Why was it necessary to chill the SN1 reaction?
      Would the reaction have been faster or slower at room temperature? Explain.

In your conclusion:

1. Be sure to note whether the experiment successfully demonstrated what it was supposed to or not. That is, did the reactions that you observed followed the expected trends or not? Explain.

2. Make suggestions for what could be done differently in order to improve the experiment.

Name: ______________________________

Partner's Name: ______________________________

Course/Section Number: ______________________________

Day/Date: ______________________________

Chem 2219: Exp#7 Relative Rates of SN1 & SN2 Reactions Datasheet

Record the time in minutes to the nearest second.

Table 1: SN2 (NaI/acetone) Data for Bromine compounds. (Green Taped Test Tubes)

Substrate	Compound	Time (to cloudy) at 40 °C
primary	1-bromobutane (1B)	
secondary	2-bromobutane (2B)	
tertiary	t-butyl bromide (TB)	(predicted)

Table 2: SN2 (NaI/acetone) Data for Chlorine compounds. (Blue Taped Test Tubes)

Substrate	Compound	Time (to cloudy) at 40 °C
primary	1-chlorobutane (1C)	
secondary	2-chlorobutane (2C)	
tertiary	t-butyl chloride (TC)	(predicted)

Table 3: SN1 ($AgNO_3$/EtOH) Data for Bromine compounds. (Orange Taped Test Tubes)

Substrate	Compound	Time (to cloudy) at ~5 °C
primary	1-bromobutane (1B)	(predicted)
secondary	2-bromobutane (2B)	
tertiary	t-butyl bromide (TB)	

Table 4: SN1 ($AgNO_3$/EtOH) Data for Chlorine compounds. (Yellow Taped Test Tubes)

Substrate	Compound	Time (to cloudy) at ~5 °C
primary	1-chlorobutane (1C)	(predicted)
secondary	2-chlorobutane (2C)	
tertiary	t-butyl chloride (TC)	