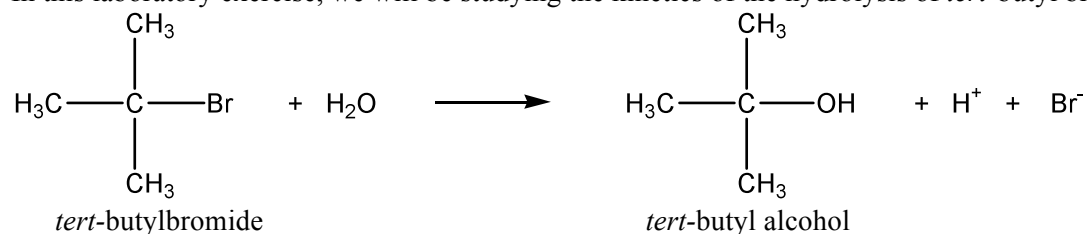


Determination of the Order, Rate Constant, Half-Life, and Activation Energy for the Hydrolysis of *tert*-Butyl Bromide

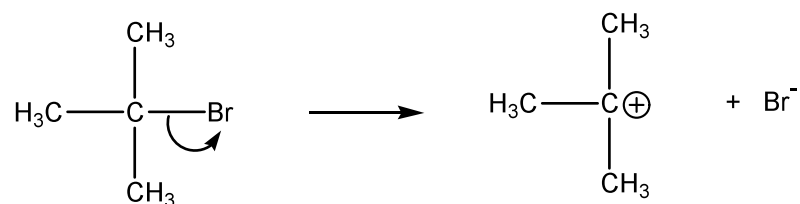
INTRODUCTION

In this laboratory exercise, we will be studying the kinetics of the hydrolysis of *tert*-butyl bromide:

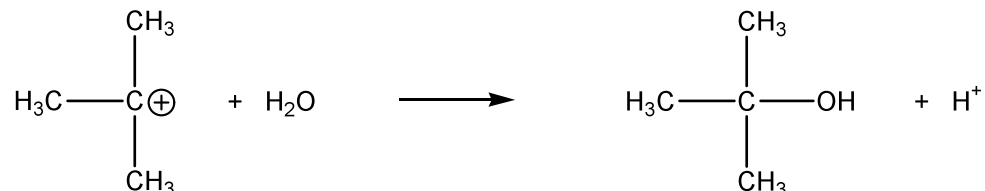


The above equation provides information about the overall stoichiometry of the reaction, but does not provide any information about the pathway or mechanism of the reaction. However, similar reactions have been shown to proceed in two steps:

Step 1 - Slow ionization of *t*-butyl bromide



Step 2 - Fast reaction of the carbocation with water



The first step is slow and determines the overall rate of the reaction. It is the **rate determining step**.

We would like to be able to describe the rate of the reaction in terms of the concentrations of the reactants. We could express this relationship in terms of the rate law equation:

$$\text{Rate} = k[\text{HOH}]^m[\textit{t}\text{-BuBr}]^n$$

We will study this reaction in solution that has a 50/50 isopropyl alcohol/water solvent mixture. The small amount that is used up in the reaction is negligible compared to the amount present. Therefore, [HOH] may be considered constant and factored into the k value, where $k' = k[\text{HOH}]^m$, the rate expression may be simplified to:

$$\text{Rate} = k'[\textit{t}\text{-BuBr}]^n$$

Another feature of most chemical reactions is the need for a little energy “boost” to get the reaction going. For example, placing a match to a piece of paper gets a combustion reaction going; however, once burning, the assistance of the match is no longer needed. Such a necessary boost in energy to initiate or activate a reaction is called the energy of activation, E_a , for that reaction. For many reactions, including the one we are studying, the heat energy available from the surroundings is sufficient to provide the necessary E_a . By determining the rate constant of a reaction at two different temperatures, it is possible to calculate the value of E_a for a reaction from the Arrhenius equation (see below).

Our experiment will involve several determinations. You will first find the order of the reaction with respect to $[t\text{-BuBr}]$ by measuring the concentration of $t\text{-BuBr}$ remaining at various times in the reaction at room temperature, and plotting the appropriate data to find the order of the reaction in a graphical integrated rates analysis. After determining whether the reaction is zero, first, or second order, you will use a linear regression and appropriate calculations to find the rate law constant k' , and the half-life of the reaction $t_{1/2}$, for the reaction at room temperature. Additionally, you will perform similar determinations near 0°C , and by evaluating k' versus the temperature of the reaction, determine the activation energy.

Reaction, titration, and the determination of the order of the reaction for $[t\text{-BuBr}]$

We will determine the order of the reaction for $t\text{-butyl}$ bromide by monitoring the $t\text{-BuBr}$ concentration remaining at various times in the reaction. As the hydrolysis reaction proceeds, the amount of remaining $t\text{-BuBr}$ will constantly diminish. As there is less reactant, the reaction will slow. Eventually, the reaction would stop when all the $t\text{-BuBr}$ was consumed.

We will plot the concentration of $t\text{-BuBr}$ remaining as a function of time. If the plot of the unreacted $[t\text{-BuBr}]$ vs. time is a straight line, the reaction is zero order. If it is a curve, however, we must make additional plots to determine the order. If a plot of the natural log of unreacted $t\text{-BuBr}$ vs. time yields a straight line, we determine the reaction is first order. However, if this is also a curve, we can then plot the inverse of the unreacted $t\text{-BuBr}$ concentration ($1/[t\text{-BuBr}]$) vs. time. If that yields a straight line, we determine the reaction to be second order in $t\text{-butyl}$ bromide. Because the data we will get in the lab will have some uncertainty, it is good practice to prepare all three plots to make the best determination of the order of the reaction.

The principle challenge in designing an experiment for this type of determination is to find a convenient means of determining the concentration of a reactant or product at various times in the reaction. If one of the reactants or products is brightly colored, we could use spectrophotometry to measure concentrations at various times in the reaction. However, all of our reactants and products are clear, colorless liquids or solutions.

Devising an experiment which would allow us to directly measure the amount of unreacted $t\text{-BuBr}$ at various time intervals is difficult. However, we can measure the quantity of H^+ ions produced at various time intervals. In the reaction, one H^+ ion is produced for each $t\text{-BuBr}$ which is hydrolyzed. Therefore, if we titrate the reaction solution at various time intervals with standardized NaOH solution, the amount of NaOH required to neutralize the H^+ produced by the reaction must be equal to the amount of $t\text{-BuBr}$ which has undergone reaction. If we know the amount of $t\text{-BuBr}$ which has reacted, we can subtract that amount from the initial amount and calculate the amount of $t\text{-BuBr}$ which remains unreacted – the concentration at the measured time.

The challenge is to titrate the reaction solution at various time intervals. Because we want to measure the concentration at several points in the reaction, we cannot simply halt the reaction and titrate the H^+ ions thus far produced. Instead, we will add 1.0, 2.0, or 3.0-mL aliquots of NaOH to the reaction mixture itself and measure the time points at which enough H^+ ions have been produced to completely react with the NaOH in the solution. Phenolphthalein will act as an indicator for the reaction. When the sodium hydroxide is in excess, the indicator will be pink. When enough of the H^+ has been produced to fully react with the sodium hydroxide in the reaction pot, the indicator will turn to clear. At that point, we will mark the time, add an additional aliquot of NaOH , and wait for the next pink \rightarrow clear color change.

A detailed overview of the reaction & titration:

We will prepare a reaction flask containing water, isopropyl alcohol, phenolphthalein, and a magnetic stir bar. This flask will be placed in a water bath to control the temperature of the reaction. The water bath will be placed over a magnetic stirrer. Above the flask, we will mount a burette filled with NaOH solution. A small amount (3.0-mL) of NaOH solution will be added to the flask before any of the $t\text{-BuBr}$ is added. The reaction solution will be pink. Then, a precise volume of $t\text{-BuBr}$ will be introduced into the flask. At this point, the hydrolysis reaction begins and the stopwatch started. The reaction is rapid at room temperature, but not instantaneous.

After a brief time, the pink color will suddenly disappear, indicating that enough H⁺ ions have been produced to just neutralize the NaOH which had been added. You will note the time at the color change, but will NOT stop timing. You must then quickly add another aliquot of NaOH. The solution will become pink once again. As the reaction continues, when enough additional H⁺ has been produced to neutralize the added NaOH, the pink color will again disappear at which point you will want to note time, again NOT stopping the timer. You will repeat this procedure several times – until you have the initial concentration and 8 additional data points to work with.

Once these incremental data points have been taken, it is necessary to determine how much NaOH would be required to titrate all of the H⁺ ions produced by the hydrolysis of the *t*-BuBr. In order to drive the reaction to completion, we will heat the solution. By finding the ratio of the total amount of NaOH added at any time interval to this final titration value, you can determine the percent of the NaOH reacted at each time interval. Because sodium hydroxide is reacted at the same rate *t*-butyl bromide is used up, you can subtract that percentage from 100% to determine the percent of *t*-BuBr remaining at each measured time interval.

Determination of rate constant, k, and the half-life, t_{1/2} for the reaction:

You will determine the order of the reaction based on which of the graphs gives you a straight line. From that same graph you will be able to determine the rate constant *k* from the slope of the line. By rearranging the integrated rate expressions, it is simple to determine the amount of time which will be required to have 1/2 of the remaining reactant consumed.

Determination of the activation energy for the hydrolysis reaction.

The activation energy can be calculated from the Arrhenius equation provided the values of *k* are known for two different temperatures. The Arrhenius equation is:

$$\ln \frac{k_2}{k_1} = -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right)$$

where *k*₁ and *k*₂ are the values of the rate constant at temperatures T₁ and T₂ respectively. R is the constant 8.3145 J/K·mol and *E*_a is the activation energy.

EXPERIMENTAL PROCEDURE

A. Preparation of the NaOH-solvent mixture:

The concentration of sodium hydroxide that we use is not that important, provided we use the same solution for all trials, because we will be measuring all concentrations as a percentage of the total.

Place ~ _____ g of solid NaOH (~ _____ pellets) into a clean, flask and add ~ 200 mL of the 50:50 isopropyl alcohol:water solvent mixture into a clean 500 mL Erlenmeyer flask. Dissolve the pellets and mix thoroughly. Stopper the flask to prevent dissolving of CO₂ from the air, thereby causing the concentration of the solution to change over time.

Carefully wash a burette, first with water, then swish the inside with about 5-mL of the NaOH solution. Drain the NaOH through the tip into the sink. Temporarily cover the top of the burette to prevent unnecessary contact with CO₂ from the atmosphere.

B. Rate Measurements at room temperature:

Set up a reaction flask on a magnetic stirrer. Add 75-mL of the solvent mixture (the stock 50:50 isopropyl alcohol:water – no NaOH), 4-5 drops of phenolphthalein and a stir-bar to a dry 250-mL Erlenmeyer flask fitted with a rubber stopper. Immerse the reaction flask in a water bath at room temperature. Use an appropriate clamp to hold the Erlenmeyer flask in place. Allow the flask to sit in the water bath for about 15-min to insure that the temperature of the contents in the flask is equal to that of the water bath. Record the initial volume of NaOH in the burette and then add ~ 3.00-mL of the NaOH solution to the flask, recording the precise volume on the burette. Mix the solution well and **record the temperature**. Turn on the magnetic stirrer and have your instructor add 0.75-mL of *t*-butyl bromide to your reaction flask. Note, to the second, the time at which the *t*-BuBr is added to the reaction flask.

Make note, to the second, of the time when the pink color suddenly fades to colorless – this may not take long! Immediately add another ~ 3.0-mL of NaOH solution, record the precise volume from the burette, and wait until the pink color fades to clear, record the time again. Repeat this procedure for six more aliquots of NaOH. At the end of this process, do NOT discard the reaction mixture!

We must now determine the total amount of NaOH required to neutralize all of the H⁺ produced by the hydrolysis of *t*-BuBr. To accomplish this, place the reaction flask in a warm water bath (about 40°C) for at least ten minutes. Heating will increase the reaction rate, and all of the remaining *t*-BuBr will be hydrolyzed – in other words, the reaction will have gone to completion. At that point, titrate the mixture to an endpoint – a faint pink color. This will be the point at which just enough NaOH has been added to react with all of the H⁺ produced by the complete reaction. Be careful not to overrun the endpoint. The volume of NaOH required will be referred to as the “infinity titration”. By dividing the additive volumes of NaOH by the infinity titration value, you can calculate the % of total NaOH used at each time interval. From this, you can then calculate the % *t*-BuBr remaining at each time interval. See the example data above.

Data Notes:

- At $t = 0$, none of the NaOH has reacted. The first 3.00-mL aliquot has reacted at the first pink \rightarrow colorless transition.
- Each time there is a pink \rightarrow colorless transition, press the “lap” button on the stopwatch to read the time, while the timer actually continues to measure time. We must do this because we need to know the total elapsed time for each data point, not the time between data points.
- For each data point, sum the total amount of NaOH solution that has been added since the beginning of the experiment. *Consider the following sample data:*

Table 1: Titration & Time Data and Percent Concentration Values

Reaction Mixture Temperature: _____

Burette Reading (mL)	Volume of NaOH reacted at the elapsed time (mL)	Reference only: Volume of NaOH aliquot (mL)	Elapsed time to color change (s)	% NaOH added	% <i>t</i> -BuBr remaining	ln (% <i>t</i> -BuBr)	$\frac{1}{(\% \text{ } t\text{-BuBr})}$
1.22 (initial)	0.0	0.00	0	0	100	4.6052	0.01000
4.22	3.00	3.00	14	7.85	92.15	4.5234	0.01085
7.16	5.94	2.94	38				
9.18			(1min :12s) 72				
(+ additional intervals)							
Final buret reading (after heating): 39.42	Total NaOH volume added: 38.20	N/A	N/A	100	0	N/A	N/A

C. Data analysis

1. Determination of the order of the reaction.
 - Using MS Excel, or other data analysis software, prepare plots of:
 - % *t*-BuBr vs. time
 - ln (% *t*-BuBr) vs. time
 - 1 / (% *t*-BuBr) vs. time
 - Based on which graph yields a straight line, determine the order of the reaction.
 - **Write both the differential and integrated rate law forms for this reaction.**
2. From the slope of the graph yielding a straight line and the integrated rate law equation, calculate *k*, including units.
3. Calculate $t_{1/2}$ for the reaction.

D. Rate measurements at low temperature.

Prepare a slushy ice-water bath in a 600-mL beaker. Place the reaction flask in this cold bath on a magnetic stirrer and repeat the previous procedure. The rate at the lower temperature will be MUCH slower and the color changes will take longer to appear. It is recommended to use 1.0 mL aliquots. Make a written note of the temperature *within* the reaction flask. Measure the temperature in the Erlenmeyer flask, not the temperature of the ice-water bath. When you have measured the time for *six* or more aliquots reacted, perform heat the reaction mixture to drive to completion, and titrate to get the full quantity of NaOH required for the reaction.

E. Data analysis (continued)

4. Plot the same graphs and perform the same calculations for the cold temperature trial, as were done for the room temperature trials. If the low temperature trials are inconclusive for the order determination, or differ from the room temperature determination, defer to the order determined from room temperature data, and base all of you calculations on that order. Thje room temperature data is more reliable, as we will be observing a more significant portion of the reaction.

Using the Arrhenius equation with your two values of *k* and T, calculate the value for E_{act} of this reaction.

Note on Data, Results, & Graphs:

Data analysis and graphing should be done using MS Excel or other appropriate graphing or spreadsheet software. Each individual student must make his or her own tables and graphs to turn in, even if working with a partner.

Determination of the Order, Rate Constant, Half-Life, and Activation Energy for the Hydrolysis of *t*-Butyl Bromide

PRE-LAB QUESTIONS

Name: _____

1. A student collected the following data for the determination of the order of *t*-BuBr. Complete the table below:

Burette Reading (mL)	Total volume of NaOH added (mL)	Aliquot volume (mL)	Elapsed time to color change (s)	% NaOH added	% <i>t</i> -BuBr remaining	ln (% <i>t</i> -BuBr)	$\frac{1}{\% \text{ } t\text{-BuBr}}$
2.55	0	0	0	0	100		
4.57			34				
6.55			64				
8.54			89				
9.56			127				
11.59			165				
13.55			223				
15.52			294				
17.56			398				
Final buret reading (after heating): 21.76	Total NaOH volume added:	N/A	N/A	100	0	N/A	N/A

Sample calculation (show work for one interval calculation):

- Using the student data given, plot the three necessary graphs and determine the order of the reaction with respect to $[t\text{-BuBr}]$. ***These graphs may be done on graph paper or using excel.*** State the differential and integrated rate equations based on the order determination.
- Using any reasonable method, determine k (including units) for the reaction, based on the student's data.
- Calculate $t_{1/2}$ for the reaction, based on the student's data.

Determination of the Order, Rate Constant, Half-Life, and Activation Energy for the Hydrolysis of *t*-Butyl Bromide

Assignment & Report Guidelines

READING Experiment – Lab Handout Download

Chemistry, 5th or 6th ed. by Silberberg: Sections 16.1-16.3

PRE-LAB Begin the prelab on a new page of your laboratory notebook. **ALL elements of the pre-lab MUST be completed before an experiment is started.** The COPY page from your notebook will be collected as you enter the lab. The original pages must stay in your notebook.

Heading

- Title of experiment and number, your name, the dates of the experiment.

Purpose & Balanced Equation

- Briefly, but specifically explain the purpose(s) of the experiment with respect to the reaction studied and provide the balanced equation for the overall reaction in the context of the purpose.

Procedure Overview/Strategy

- In no more than one page, provide a brief overview that clearly explains how the experiment and procedure will result in finding the desired information as stated in the Purpose.

Data Table

- On a NEW page, prepare a table recording each quantity you will measure in the lab. (Do **not** turn in with the prelab. It will be checked off in your notebook at the start of lab.)

Answers to Pre-Lab Questions

- Answer the questions directly on the handout pages. For the graphs, use appropriate graphing software. Create your graphs individually. Turn in a hardcopy of the graphs with your prelab assignment.

LAB REPORT

*Begin the lab report section on a new page of the lab notebook. **The discussion and conclusion sections should be word-processed.** Other parts of the report - calculations, etc. may be typed or written in the lab notebook.*

Heading

- Title of experiment and number, your name, your lab partner's name(s) if applicable, the dates of the experiment.

Data / Observations / Results

- ORIGINAL QUALITATIVE & QUANTITATIVE DATA (signed data pages from your lab notebook).
- **Reminder:** Record ALL data directly in your lab notebook.

Calculations / Results

Show complete calculations for the following quantities. Use proper format for labeling and showing calculations in a formal report. Organize your results.

- Full calculations for the % NaOH and % *t*-BuBr for one trial in the experiment.
- Additional trial calculations may be carried out using Microsoft Excel or other spreadsheet software if you choose (highly recommended). Data and results of the calculations, as well as values needed for graphing, should be presented in an appropriate table either prepared with a spreadsheet or word processor, or neatly written in the lab notebook.
- Additional calculations, graphs, and presentation of results as outlined in the **Data Analysis** sections of the procedure.

Discussion – Theory / Results / Error Analysis

Briefly summarize and explain the experiment, as well as evaluate your results. Your discussion should include all of the following points, but should not be limited to them:

- Explain the concepts underlying the experimental process and the analysis of the results.
- Explain how the NaOH serves as a measure of the extent of reaction that has occurred.
- Based on the mechanism proposed in the background information for the experiment, what would you predict the order of the reaction to be? Explain.
- Does your order determination support the proposed mechanism? Explain.
- Evaluate the effect of changing the temperature on the rate constant and the order of the reaction.
- Discuss errors in your data or deviations from expected results. Propose reasonable sources of error in the experiment.

Conclusions

Provide appropriate conclusions.

Answers to Post-Lab Questions – None assigned.