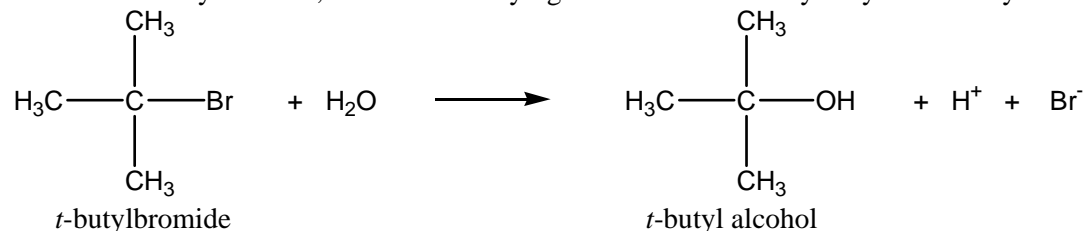


Determination of the Order, Rate Constant, Half-Life, and Activation Energy for the Hydrolysis of *t*-Butyl Bromide

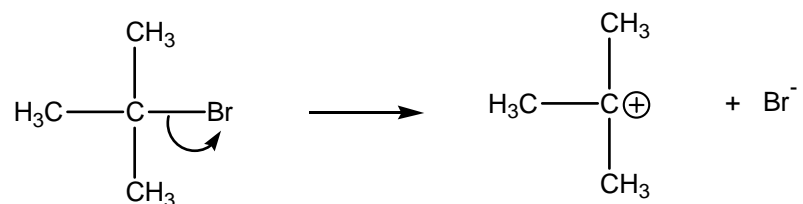
INTRODUCTION

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

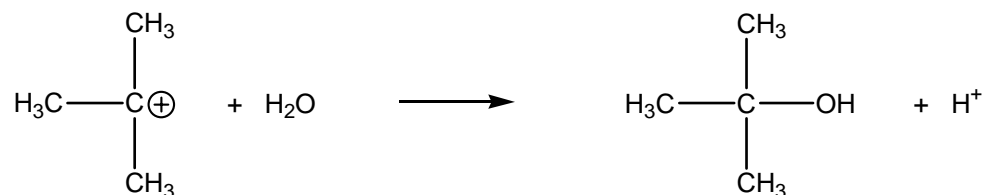


The above equation provides information about the overall stoichiometry of the reaction, but does not provide any information about the pathway or mechanism of the reaction. However, similar reactions have been shown to proceed in two steps:

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:

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

Because we will study this reaction in aqueous solution, our reaction of study is "zero order" with respect to [HOH]. The amount of water produced or consumed is generally so small in comparison to the total amount of water available that small changes in the water concentration have virtually no effect upon the reaction rate even though water appears as a reactant. Therefore, the rate expression may be simplified to:

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

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 termed the energy of activation, E_{act} 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_{act} . By determining the rate constant of a reaction at two different temperatures, it is possible to calculate the value of E_{act} for a reaction from the Arrhenius equation (see below).

Our experiment will involve several determinations. You will first determine the order of the reaction with respect to [BuBr] by measuring the concentration of t-BuBr remaining at various times in the reaction at room temperature. After determining whether the reaction is zero, first, or second order, you will determine the rate law constant, k , and the half-life of the reaction, $t_{1/2}$, for the reaction from the integrated rate equations. In addition, by varying the temperature of the reaction, we can determine the k at low temperature and calculate the activation energy.

Part 1: Determination of the order of the reaction for [t-BuBr]

We will determine the order of the reaction for t-butyl bromide by monitoring the percent of the original t-BuBr concentration remaining at various times in the reaction. As the hydrolysis reaction proceeds, the amount of remaining t-BuBr will constantly diminish. As there is less reactant, the reaction will slow. Eventually, the reaction will stop when all the t-BuBr has been consumed.

We will plot the concentration of t-BuBr remaining as a function of time. If the plot of the unreacted [t-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-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-BuBr concentration ($1/[t\text{-BuBr}]$) vs. time. If that yields a straight line, we determine the reaction to be second order in t-butyl bromide.

Because the data we will get in the lab is not as “perfect” as we find in our textbooks, we should make 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 highly 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-BuBr at various time intervals is difficult. However, we can measure the concentration of H^+ ions produced at various time intervals. In the reaction, one H^+ ion is produced for each t-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 directly proportional to the amount of t-BuBr which has undergone reaction. If we know the amount of t-BuBr which has reacted, we can subtract that amount from the initial amount and calculate the amount of t-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.

Experimental overview of part 1:

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-BuBr is added. The reaction solution will be pink. Then, a precise volume of t-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 9 data points with which to work.

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. We will call this value the "Infinity Titration Value." By finding the ratio of the total amount of NaOH added at any time interval to this infinity 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.

For example, if 81.7-mL of NaOH is required to completely titrate all the H⁺ ions produced by the hydrolysis of all the t-BuBr in the flask, then at the time when 4-mL of the NaOH was sufficient, only 4.9% of the total NaOH required would have been present. If 4.9% of the total NaOH necessary had been used, then 4.9 % of the t-BuBr had reacted, and 95.1% of the initial [t-BuBr] remained in the flask.

Part 2: Determination of rate constant, k.

In part one 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.

Part 3: What is the half-life, t_{1/2} of the t-butyl bromide?

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.

Part 4: Determine 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 T_1 and T_2 respectively. R is the constant $8.3145 \text{ J/K}\cdot\text{mol}$ and E_a is the activation energy.

EXPERIMENTAL PROCEDURE

Obtain ~ 400 mL of a 50:50 isopropyl alcohol:water solvent mixture.

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 ~ 16 pellets of solid NaOH into a clean, flask and add ~ 200 mL of the 50:50 isopropyl alcohol:water solvent mixture. 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), several 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 a total of nine aliquots of NaOH. However, for the third-ninth aliquot of NaOH, add only ~ 2.0 mL of NaOH solution. 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 ten minutes. All the remaining t-BuBr will be hydrolyzed with time, but heating will significantly increase the rate of the process. Within 10 minutes at the higher temperature, 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: Titration and time data

Initial burette reading: 1.22 mL

Burette Reading (mL)	Total volume of NaOH added (mL)	Volume of NaOH aliquot (mL)	Elapsed time to color change (s)	% NaOH added	% tBuBr remaining
1.22 (initial)	0.0	0.00	0	0	100
3.22	2.00	2.00	14	5.2	94.8
5.16	3.94	1.94	38	10.3	89.7
7.18	5.96	2.02	(1min :12s) 72	15.6	84.4

(+ *additional intervals*)

Infinity titration

Final burette reading: 39.42 mL
Total volume NaOH added: 38.20 mL

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. Average the k values of the two trials.
3. Calculate $t_{1/2}$ for the reaction. Average the values of the half-life for the two trials.

D. Rate measurements at low temperature.

Prepare an ice-water bath. 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. If the time intervals are too long, smaller aliquots of NaOH may be added. You may want 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 six or more data points, perform the infinity titration.

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.

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

Data, Results, & Graphs:

Data analysis and graphing may (should) be done using Excel. Each individual must make his or her own tables and graphs to turn in.

DISCUSSION

Please answer the following questions as part of your discussion:

1. Explain how the NaOH serves as a measure of the extent of reaction that has occurred.
2. Based on the mechanism proposed in the background information for the experiment, what would you predict the order of the reaction to be? Explain.
3. Write the rate law for t-BuBr in the differential and in the integrated forms.
4. Do your graphs support the proposed mechanism? Explain.
5. Discuss errors in your data or deviations from expected results. Propose reasonable sources of error in the experiment.

CONCLUSIONS:

Be sure to address all elements of the purpose for this experiment.