Alkyl Halide, Hydrolysis Reaction Part I
(prepared by Jyotsna Pradhan Ph.D. updated Oct 1998)

Note: This is a modified procedure. You need to read your textbook for the background and the final calculations. (See experiment 22.)

This experiment consists of measuring the concentration of a substrate that has reacted in a hydrolysis reaction, with respect to time elapsed from the start of the reaction. The hydrolysis reaction of either tertiary butyl bromide or α-phenylethyl bromide in at least two solvents of differing polarities will be studied. The solvent systems to be used are given below.

- **t-Butyl bromide in:**
  - A) 35% acetone solution in water
  - B) 20% acetone solution in water

- **α-Phenylethyl bromide in:**
  - A) 60% ethanol solution in water
  - B) 45% ethanol solution in water

The data obtained will be handled graphically to obtain a rate constant and calculate the half-life of the reaction for each solvent system. Comparison of the values in the two solvents should give insight into the effect of solvent polarity on the mechanism and the rate of the reaction of the hydrolysis reaction.

Because the alkyl halides hydrolyze rapidly under conditions used in this experiment, students must perform the kinetic studies working in pairs. One student will measure the time while the other one does the addition of base and records the data. These roles may be reversed for the study of the second solvent system so that each student has a feel for different aspects of the experiment. Each student pair will be assigned one of the alkyl halides listed above to study. Data for the other halide’s kinetic study may be obtained from another group.

**Material Prep** (I will assign two students to prepare these)

Prepare a stock solution of **ONE** of the alkyl bromides, which will be assigned to you by your instructor, according to the following instructions:

- **t-Butyl bromide:** dissolve about 0.3 g t-Butyl bromide in 50 mL of dry, reagent-grade acetone.
- **α-Phenylethyl bromide:** dissolve about 0.6 g α-Phenylethyl bromide in 50 mL of dry, reagent-grade acetone.

Store these solutions in a stoppered 125 mL Erlenmeyer flask to protect them from moisture.

Prepare four 125 mL Erlenmeyer flasks as needed to carry out the experiment. Label the flasks as **A_{run}, A_{inf}, B_{run}, and B_{inf}**. Each flask should contain 50 mL of the appropriate solvent (A or B), and 2-3 drops of bromothymol blue indicator. Flasks “A_{inf}” and “A_{run}” will contain solvent ‘A’ and “B_{inf}” and “B_{run}” will contain solvent ‘B’. The indicator, Bromothymol blue, has a yellow color in acid solution and a blue color in alkaline solution.

Fill a 50 mL burette with approximately 0.01 N sodium hydroxide solution that will be provided. Using the burette, accurately add approximately 3.00 mL of NaOH solution to flask **A_{inf}** containing solvent one, repeat this for the second flask **B_{inf}** containing solvent two. Using a volumetric pipet add 1.00 mL of the stock solution containing the alkyl halide (this is the prepared solution **NOT** the pure alkyl halide) to each of these two flasks. Make sure there is a label on the flasks with reference to the solvent contained, write the time of day on the flask and stopper them.
Put these aside till the end of the period (they should be heated for at least an hour). Both these flasks will provide one set of infinity readings for the two solvents. It may be necessary to place these flasks on a steam bath to force the reaction to completion in the limited time allowed for the experiment. If this is the case it will not be possible to stopper the flasks. Check with your instructor for the specific procedure regarding the infinity flasks.

**Kinetic Titrations**

Kinetic measurements will be done in the remaining two flasks i.e. flasks $A_{\text{run}}$ and $B_{\text{run}}$, each containing a different solvent. From the burette accurately add approximately 1.00 mL of sodium hydroxide solution to the $A_{\text{run}}$ flask as you start the experiment. Record this volume. Refill the burette if necessary. When you are ready take the flask $A_{\text{run}}$ and, using a volumetric pipette, transfer 1.00 mL of the stock alkyl halide and start timing when the pipette is half emptied into the erlenmeyer flask. Once started, the clock does *NOT* stop. The color change of the reaction mixture from blue to yellow or blue to green indicates that the time should be recorded for the previously added volume. Some of the mixtures exhibit an abrupt change from blue to yellow whereas other mixtures involve slower reactions and produce gradual changes of blue to green.

(If the color changes while you are still adding the alkyl bromide, i.e. the reaction occurs too rapidly, then quickly add enough sodium hydroxide to change the color back to blue, (do check with the instructor, if possible). Add this volume to the previous volume already recorded. This will give you a little more time to note the color change.)

When the solution turns yellow/green record the time, meanwhile your lab partner quickly adds enough sodium hydroxide to the flask to change the color back to blue and records the volume. Repeat this change of color and addition of more NaOH drill at least three more times for a total of at least four points. After the last addition of sodium hydroxide has changed color, label and stopper the flask and put it aside for the reaction to go to completion until you are ready to measure the infinity reading. Ideally this flask should sit for an hour before the titration for the infinity reading is performed. It may be necessary to place these flasks on a steam bath for at least 30 minutes to force the reaction to completion in the limited time allowed for the experiment. If this is the case it will not be possible to stopper flasks. Check with your instructor for the specific procedure for driving these *run* reactions to completion.

The above procedure is repeated with the other flask ($B_{\text{run}}$) that contains the second solvent for your assigned halide. Ideally, this flask should also stand for at least 45 minutes or be placed on a steam bath for 30 minutes after the kinetic measurements have been made to obtain the infinity value. The rate of reaction is not of concern now we only need to know how much starting material was present when the reaction was begun. By measuring the total amount of acid produced when no more reaction occurs, we can deduce the amount of starting material that was present.

Once the data for both the solvent systems have been obtained, return to the original flasks $A_{\text{inf}}$ and $B_{\text{inf}}$ that were put aside for infinity values. Titrate both of these to obtain a set of infinity readings for each of the solvents used. After the appropriate time has elapsed, titrate the reaction flasks $A_{\text{run}}$ and $B_{\text{run}}$, which had been put away after the kinetic runs. The infinity readings obtained by the two procedures should be similar (i.e. $A_{\text{inf}}$ similar to $A_{\text{run}}$, and $B_{\text{inf}}$ similar to $B_{\text{run}}$).

Fill in the tables, as indicated below, using the average $V_{\text{inf}}$ values for each solvent studied.
Kinetics Part I

Halide Used: __________________________

Flask $A_{\text{run}}$

<table>
<thead>
<tr>
<th>Addition Number</th>
<th>Elapsed Time (sec)</th>
<th>Burette Reading (mL)</th>
<th>Cumulative NaOH Volume Consumed (mL)</th>
<th>$V_\infty - V_t$</th>
<th>$\frac{V_\infty}{V_\infty - V_t}$</th>
<th>$\ln \left( \frac{V_\infty}{V_\infty - V_t} \right)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Initial</td>
<td>From #1 below</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Each Cumulative volume in the table above is calculated by adding the difference in two successive burette readings to the previous cumulative NaOH volume.

Example: A

Addition #3  Burette Reading = 3.28 mL  Cumulative Volume = 4.27 mL
Addition #4  Burette Reading = 4.19 mL  cumulative Volume = (4.19 – 3.28) + 4.27 = 5.18 mL

1) Initial volume of NaOH added before adding the halide: _______________

2) Infinity Titration for $A_{\text{run}}$
   A) Initial burette reading: _______________
   B) Final burette reading: _______________
   C) NaOH $\Delta V$: _______________

3) Total NaOH volume, $V_\infty$, added [Run total (addition #4) + $\Delta V$]: _______________

Flask $A_{\text{inf}}$

4) Initial volume of NaOH added before the reaction: _______________

5) Infinity Titration for $A_{\infty}$
   A) Initial burette reading: _______________
   B) Final burette reading: _______________
   C) NaOH $\Delta V$: _______________

6) Total NaOH Volume, $V_\infty$, added (Initial Volume + $\Delta V$): _______________

The two values for $V_\infty$ should agree to within an established error limit determined by your instructor to be useful. Ask your instructor if they don’t.
**Data Table**

**Halide Used:** ______________________

<table>
<thead>
<tr>
<th>Flask B&lt;sub&gt;run&lt;/sub&gt;</th>
<th></th>
<th></th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Addition Number</td>
<td>Elapsed Time (sec)</td>
<td>Burette Reading (mL)</td>
<td>Cumulative NaOH Volume Consumed (mL)</td>
<td>$V_{\infty} - V_t$</td>
<td>$\ln \left( \frac{V_{\infty}}{V_{\infty} - V_t} \right)$</td>
</tr>
<tr>
<td>1</td>
<td>Initial From #1 below</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1) Initial volume of NaOH added before adding the halide: _______________

2) Infinity Titration for B<sub>run</sub>
   A) Initial burette reading: __________________
   B) Final burette reading: __________________
   C) NaOH $\Delta V$: __________________

3) Total NaOH volume, $V_{\infty}$, added [Run total (addition #4) + $\Delta V$]: _______________

**Flask B<sub>inf</sub>**

4) Initial volume of NaOH added before the reaction: _______________

5) Infinity Titration for B<sub>inf</sub>
   A) Initial burette reading: __________________
   B) Final burette reading: __________________
   C) NaOH $\Delta V$: __________________

6) Total NaOH Volume, $V_{\infty}$, added (Initial Volume + $\Delta V$): _______________

The two values for $V_{\infty}$ should agree to within an established error limit determined by your instructor to be useful. Ask your instructor if they don’t.
# Kinetics Part I
## Shared Data Sheet

**Halide Used:** ____________________

<table>
<thead>
<tr>
<th>Flask A&lt;sub&gt;run&lt;/sub&gt;</th>
<th>Addition Number</th>
<th>Elapsed Time (sec)</th>
<th>Burette Reading (mL)</th>
<th>Cumulative NaOH Volume Consumed (mL)</th>
<th>( V_\infty - V_t )</th>
<th>( \frac{V_\infty}{V_\infty - V_t} )</th>
<th>( \ln \left( \frac{V_\infty}{V_\infty - V_t} \right) )</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Initial</td>
<td>From #1 below</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Each cumulative volume in the table above is calculated by adding the difference in two successive burette readings to the previous cumulative NaOH volume.

**Example:** A

 Addition #3 Burette Reading = 3.28 mL Cumulative Volume = 4.27 mL  
 Addition #4 Burette Reading = 4.19 mL cumulative Volume = (4.19 – 3.28) + 4.27 = 5.18 mL

1) Initial volume of NaOH added before adding the halide: ________________

2) Infinity Titration for A<sub>run</sub>
   
   A) Initial burette reading:  
   
   B) Final burette reading:  
   
   C) NaOH \( \Delta V \):  

3) Total NaOH volume, \( V_\infty \), added [Run total (addition #4) + \( \Delta V \)]: ________________

**Flask A<sub>inf</sub>**

4) Initial volume of NaOH added before the reaction: ________________

5) Infinity Titration for A<sub>inf</sub>
   
   A) Initial burette reading:  
   
   B) Final burette reading:  
   
   C) NaOH \( \Delta V \):  

6) Total NaOH Volume, \( V_\infty \), added (Initial Volume + \( \Delta V \)): ________________

The two values for \( V_\infty \) should agree to within an established error limit determined by your instructor to be useful. Ask your instructor if they don’t.
## Data Table
### Shared Data Sheet

### Halide Used: _______________________

#### Flask $B_{run}$

<table>
<thead>
<tr>
<th>Addition Number</th>
<th>Elapsed Time (sec)</th>
<th>Burette Reading (mL)</th>
<th>Cumulative NaOH Volume Consumed (mL)</th>
<th>$V_\infty - V_1$</th>
<th>$\frac{V_\infty}{V_\infty - V_1}$</th>
<th>$\ln \left( \frac{V_\infty}{V_\infty - V_1} \right)$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Initial</td>
<td>From #1 below</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>2</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>3</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>4</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

1) Initial volume of NaOH added before adding the halide: _______________

2) Infinity Titration for $B_{run}$
   
   A) Initial burette reading: _______________
   
   B) Final burette reading: _______________
   
   C) NaOH $\Delta V$: _______________

3) Total NaOH volume, $V_\infty$, added [Run total (addition #4) + $\Delta V$]: _______________

#### Flask $B_{inf}$

4) Initial volume of NaOH added before the reaction: _______________

5) Infinity Titration for $B_{inf}$
   
   A) Initial burette reading: _______________
   
   B) Final burette reading: _______________
   
   C) NaOH $\Delta V$: _______________

6) Total NaOH Volume, $V_\infty$, added (Initial Volume + $\Delta V$): _______________

The two values for $V_\infty$ should agree to within an established error limit determined by your instructor to be useful. Ask your instructor if they don’t.