SOLVOLYSIS OF tert-BUTYL CHLORIDE: TESTING A MECHANISM

Organic chemists are keenly interested in how and why chemical reactions occur. They propose a plausible mechanism for a given reaction, then do experiments designed to test its validity. It is never possible to prove that a mechanism is correct, but it is possible to prove it incorrect. Experiments are designed to test chemical and/or physical behaviors predicted by the proposed mechanism. Then one asks: did the behavior predicted by the mechanism actually occur in the experiment?

Yes: the mechanism is consistent with the evidence (it may be correct, but is not proven to be so).
No: the mechanism is definitely wrong because it does not predict actual behavior accurately.

Kinetics is the study of how changes in experimental conditions affect the rate of a chosen reaction. Reaction kinetics can be used to probe the validity of a proposed mechanism. For each proposed mechanism, factors that should influence the rate of attaining the transition state, and thus the rate of the reaction, are identified. This leads to a rate law that the kinetics should obey if the reaction proceeds via the proposed mechanism. The mathematical form of the rate law, in turn, suggests a suitable graphical way to present the rate data to see if they obey the law. Selected factors are manipulated, and the measured effect on reaction kinetics is compared to the effect predicted by the mechanism.

A simple nucleophilic substitution reaction, solvolysis of tert-butyl chloride, is used to illustrate the technique. Solvolysis means “splitting by solvent”. The substrate, tert-butyl chloride, has an electronegative chlorine attached to a 3° carbon. This causes significant polarity in the molecule. Other polar molecules, like water, will be electrostatically attracted to the positive and negative surfaces of tert-butyl chloride molecules. This sets up the possibility of pulling the Cl off (as Cl⁻) and replacing it with a water oxygen (which eventually becomes an –OH group). It is generally accepted that this reaction follows an S_N1 path.

Annotate the mechanism with Δ+, Δ−, and curved arrows, and identify its rate-limiting step, before reading further.

![Figure 1: the SN1 Mechanism](image)

Recall that experiment conditions, such as polarity of the solvent, can be adjusted to favor the S_N1 pathway over others (what reaction conditions generally favor S_N1 pathways?). In this experiment the rate of consumption of tert-butyl chloride in two solvents of different polarity will be measured as a function of time by pairs of students. Each pair will run the solvolysis in one solvent composition, and will also analyze results gathered by another pair that used a different solvent composition.

This experiment is designed to show how kinetics behavior can be used to probe the validity of a proposed mechanism. If experimental behavior does not fit the predictions of a model, the model must be rejected. The main objective of this experiment is to answer the following question:

Do the experimentally measured rates of solvolysis support or contradict the rate behavior predicted by the S_N1 model?

Part of this is evaluation of the quality of fit of experimental data to predicted behavior. See page 5 for one way to do this. Are points scattered and thus not very reliable, or do they fit the model’s prediction well? This latter assessment is important because it determines the level of confidence that you can place in the claims you make.

The other part of this is comparing rates of solvolysis in solvents of different polarity. The more polar a solvent, the more effective it is at solvating anions, whether they are reactant or product. Would you expect tight caging of anions to help the reacting molecule reach the transition state or not? In other words, would the properties of the solvent accelerate, slow, or have no effect on the rate-limiting step of the S_N1 model?
Experimental Rationale
The course of solvolysis of tert-butyl chloride could be followed by monitoring the concentration of any of the chemicals involved. In practice, it is easiest to monitor the production of H\(^+\), which can be done by titrating samples of the reacting solution with base. One proton is produced for every tert-butyl chloride molecule that reacts.

In this experiment, the basic steps will proceed as follows: tert-Butyl chloride is allowed to hydrolyze in a solvent at room temperature. Aliquots of the reacting mixture are removed at suitable intervals after initiation of reaction and quenched in ethanol to stop the reaction. (Ethanol, though polar and protic, is far less effective than water at solvating ions.) Each is titrated with dilute NaOH to a bromophenol blue endpoint to find the amount of H\(^+\) present. Additional aliquots ("infinite time" samples) are permitted to react completely with nearly pure water as a way to estimate the exact starting concentration of tert-butyl chloride.

There are two types of samples to be made.
**Infinity samples (lasting the longest):** A sample of the reaction mixture is mixed with water and allowed to react to completion – that is, that all tert-butyl chloride transferred to that flask is used up.
**Timed samples (at regular time intervals as the reaction proceeds):** A sample of the reaction mixture is quenched with ethanol to stop the reaction at that point in time—that is, that whether or not the tert-butyl chloride transferred to that flask is used up, the reaction is stopped mid-progress to analyze what’s there (a “snapshot” of what’s going on in the main reaction flask).

Temperature control is crucial to the success of any kinetics experiment. Ideally, the experiment should be done in a constant temperature bath, but for our purposes it works well enough as long as everything stays at room temperature. Be sure ALL of your solutions are at room temperature!

The NaOH has been made up in fresh deionized water to be sure that it is free of carbon dioxide, which consumes NaOH. Please keep the cap on the stock bottle. Don’t take any more than you need at a given time. If you let it sit around in an open beaker it will absorb carbon dioxide. It is good practice to keep the top of your buret covered with a small inverted beaker or vial to minimize air circulation and dust entry.

Half of the class will do the reaction in 60:40 water:95% ethanol; the other half will do it in 50:50 water:95% ethanol. Every reaction mixture contains the same volume of 0.1 M tert-butyl chloride in 95% ethanol – note that this is NOT pure tert-butyl chloride, but rather a dilute solution of it in 95% ethanol. To this are added different proportions of additional 95% ethanol and water as described in the Experimental Section. Compute the FINAL concentration of tert-butyl chloride after all additions have been made (it’s not 0.1 M) and write it in your notebook.

Before starting the experiment, be sure you understand why each operation is necessary and why speed is essential. Things happen fast once you start, and you won’t have time to figure it out. Refer back to the sequence of events described at the top of this page, and see the last page for an example of how each partner can be involved. Samples must be taken at short intervals during the early part of the reaction. Intervals can be longer later in the reaction. In this section, the phrase "record the time" means either time of day or elapsed time since addition of water to the mixture of ethanol and tert-butyl chloride, depending on your timing method.

**EXPERIMENTAL SECTION**

**Equipment & Setup**

1. Necessary equipment:  
   - 1 50 mL buret, ring stand and buret clamp  
   - 1 small funnel to help fill buret  
   - 1 5 mL micropipette + tip OR 4 mL volumetric pipet & pipet bulb  
   - 1 10 mL graduated cylinder if no dispensettes on reagent bottles  
   - 1 wash bottle with room temperature DI water  
   - several 125 mL Erlenmeyer flasks (see below for more details)

2. Rinse the buret with water and verify that it drains cleanly. If it doesn't, scrub it with a buret brush and Alconox. When it drains cleanly, rinse it thoroughly with water, then three times with about 10 mL of 5 x 10\(^{-3}\) M NaOH.
Finally, set the buret up on a ring stand with a buret clamp and fill it to about 0 mL with fresh $5 \times 10^{-3}$ NaOH. Force all the air bubbles out of the valve/tip – ask instructor to check. Cover the opening with a small beaker.

3. Practice titrating twice.* To prepare yourself, titrate a couple of mL of $5 \times 10^{-3}$ HCl with the $5 \times 10^{-3}$ NaOH. (you can add water to the HCl for more volume to see better – the moles of HCl won’t change by doing that).
  - Near the end point, add NaOH one drop at a time, noting color carefully.
  - Deliberately overshoot the end point (make it definitely blue) so that you can contrast the colors prior to the end point, at the end point, and one drop past the end point. In the actual experiment, the end point will gradually fade back to green because the hydrolysis continues slowly. Don’t add more base or you will get base volumes that are too high.

*Tips on titration:
- Have the same partner titrate every time for consistency.
- Titrate over a white surface to help you detect the end point.
- Use a piece of white paper with a sharp dark line to help you read the buret volume. Look straight at the meniscus to avoid parallax, and read the volume at the bottom of the meniscus.
- Use a magnetic stir bar during any titration so you have your hands free. Show the instructor your setup.
- The bromophenol blue endpoint is forest green.
  - Ethanol plus indicator may be blue, but will turn yellow when you add the aliquot later.
  - Look for: Yellow (when acidic, most of titration) $\rightarrow$ Chartreuse (gradual) $\rightarrow$ Forest green $\rightarrow$ Blue
  - Continue adding NaOH if there is any yellow left in the green. The last drop of NaOH just before the solution turns blue marks the end point. Blue means you overshot the end point.

4. Gather 125 mL Erlenmeyer flasks with stoppers. The purpose of each flask is itemized below:

<table>
<thead>
<tr>
<th></th>
<th>50:50 solvent</th>
<th>60:40 solvent</th>
</tr>
</thead>
<tbody>
<tr>
<td>reaction mixture</td>
<td>1</td>
<td>1</td>
</tr>
<tr>
<td>infinite time samples</td>
<td>3</td>
<td>3</td>
</tr>
<tr>
<td>(“∞”)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>timed samples:</td>
<td>1 (will titrate immediately since there is more time between)</td>
<td>9 (will titrate after all are taken since there is less time between)</td>
</tr>
</tbody>
</table>

**Total flasks needed:** 5 13

5. Decide how you will time the reaction: stopwatch or wall clock.

6. Set up an area where one partner will pipette the reaction mixture into sample flasks, and another area down the bench where the other partner will titrate the sample flasks once they have samples added to them.

<table>
<thead>
<tr>
<th>Partner A (pipetting station)</th>
<th>Partner B (titration station)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Need proximity to:</td>
<td>Needs:</td>
</tr>
<tr>
<td>reaction mixture flask</td>
<td>Needs proximity to a timer and your lab notebook.</td>
</tr>
<tr>
<td>either the micropipetter set to 4 mL OR 4 mL volumetric pipet &amp; pipet bulb</td>
<td>Accessibility to extra NaOH as you run low.</td>
</tr>
<tr>
<td>a timer and your lab notebook</td>
<td>See tips on titrating above, and practice titrating twice before starting the reaction.</td>
</tr>
<tr>
<td>timed sample and ∞ sample flasks</td>
<td>Refill the buret to close to 0 and record the starting volume in your notebook</td>
</tr>
<tr>
<td>Note where t-bu-Cl dispensette is located</td>
<td></td>
</tr>
</tbody>
</table>
Sample Preparation. (50:50 Solvent Composition)

6. Label, arrange, and prepare flasks. Mix volumes as shown for the solvent you are using. Use bottles equipped with dispensettes for the tert-butyl chloride stock (0.1M in 95% ethanol) and the 95% ethanol. Use a graduated cylinder for water.

<table>
<thead>
<tr>
<th>50:50 Solvent</th>
<th>Timed Sample</th>
<th>∞ Sample</th>
<th>Reaction Mixture (make last)</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Label as:</td>
<td>Timed Sample</td>
<td>∞ 1, ∞ 2, ∞ 3</td>
<td>Reaction Mixture</td>
<td></td>
</tr>
<tr>
<td>Number of flasks</td>
<td>1 (repeat in same flask every time)</td>
<td>3 (triplicate analysis)</td>
<td>15 mL 95% EtOH 10 mL t-bu Cl stock</td>
<td>5</td>
</tr>
<tr>
<td>Add:</td>
<td>10 mL 95% EtOH 4-5 drops indicator*</td>
<td>20 mL water 4-5 drops indicator*</td>
<td>25 mL water (set aside, add last)</td>
<td></td>
</tr>
</tbody>
</table>

* Add enough bromophenol blue indicator to all flasks to make each distinctly colored after mixing, but be consistent in # of drops.

7. For each solvent, calculate & record the actual starting concentration of t-bu-Cl given its volume in the mixture.

Sampling and Titrating: (50:50 Solvent Composition)

<table>
<thead>
<tr>
<th>Partner A (pipetting station)</th>
<th>Partner B (titration station)</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>When you are ready</strong> to start the reaction:</td>
<td><strong>When you are ready</strong> to start the reaction:</td>
</tr>
<tr>
<td>• Add water to the reaction mixture last from a graduated cylinder and begin timing as you pour it in (or have your partner start timing). Mix WELL by swirling! As SOON as possible after adding water (i.e. the start of the reaction):</td>
<td>• Start the timer when your partner adds the water to the reaction flask and mixes it.</td>
</tr>
<tr>
<td><strong>Take Time 0 Sample &amp; Infinity Samples (immediately following start of reaction):</strong></td>
<td><strong>Take Time 0 Sample &amp; Infinity Samples (immediately following start of reaction):</strong></td>
</tr>
<tr>
<td>• Immediately withdraw a 4.0 mL aliquot from the reaction flask and transfer it into the timed sample flask to quench it in the ethanol. (<em>Use proper pipette technique above.</em>)</td>
<td>• For the Time 0 Sample, stopper &amp; mix the contents of the flask by swirling, and record the time at which you quenched the aliquot.</td>
</tr>
<tr>
<td>• As soon as possible, transfer three additional 4.0 mL aliquots of this reaction mixture to the infinity flasks.</td>
<td>• For Time 0 Sample, titrate &amp; record volume of NaOH added (final buret reading – initial buret reading) to get to the endpoint. Be careful! The first sample didn’t have much time to produce H⁺ so you won’t need much base to reach the endpoint.</td>
</tr>
<tr>
<td>• Stopper &amp; mix Infinity Samples 1, 2, 3, and set aside until the end of the experiment. Make sure they are mixed well! Don’t titrate these until the end.</td>
<td>• After titrating Time 0 Sample, discard the contents of the Timed Sample flask, shake it out, and get a fresh 10 mL ethanol + indicator in it for the next sample coming up.</td>
</tr>
<tr>
<td><strong>Take Time 1 Sample (6 minutes after start of reaction):</strong></td>
<td><strong>Take Time 1 Sample (6 minutes after start of reaction):</strong></td>
</tr>
<tr>
<td>• (Continue proper pipetting practice) Transfer a 4 mL aliquot from the reaction mixture to the Time 1 Sample flask.</td>
<td>• Stopper &amp; mix Time 1 Sample, then titrate &amp; record volume of NaOH added.</td>
</tr>
<tr>
<td>• Record the time elapsed since adding water to the flask.</td>
<td><strong>Take Time 2 Sample (12 minutes after start of reaction):</strong> Continue as before.</td>
</tr>
</tbody>
</table>

Repeat these steps with all the time samples until you run out of reaction mixture (or the reaction appears to be over). Lengthen the sampling interval by a minute or two if the amount of base required doesn’t increase much from one sample to the next.

Once you have titrated all your timed samples, show your data to the instructor. If the reaction looks as though it is substantially over, you can add 10 mL of 95% ethanol to the "infinite time" samples you saved and titrate them. Otherwise you may need to wait a while to assure complete reaction. All three of the ∞ samples should require the same volume of base, and it should be the largest volume required by any sample.

Compute the volume ratio of water to 95% ethanol for the solvent you used and verify the result with an instructor before you leave the lab (it should be 50:50). Put this and your titration results on the black-board. Identify your data with your names (both members of the group). Copy what you think is a set of good data for a run in the 60:40 solvent that you did NOT use. Record the names of the group whose data you copy.
Sample Preparation. (60:40 Solvent Composition)

6. Label, arrange, and prepare flasks. Mix volumes as shown for the solvent you are using. Use bottles equipped with dispensettes for the tert-butyl chloride stock (0.1M in 95% ethanol) and the 95% ethanol. Use a graduated cylinder for water.

<table>
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<tr>
<th>60:40 Solvent</th>
<th>Timed Sample</th>
<th>∞ Sample</th>
<th>Reaction Mixture (make last)</th>
<th>Total</th>
</tr>
</thead>
<tbody>
<tr>
<td>Label as:</td>
<td>Timed Sample 1, 2, 3, 4, 5, 6, 7, 8, 9</td>
<td>∞ 1, ∞ 2, ∞ 3</td>
<td>Reaction Mixture</td>
<td></td>
</tr>
<tr>
<td>Number of flasks</td>
<td>9 (a new flask for each sample)</td>
<td>3 (triplicate analysis)</td>
<td>1</td>
<td>13</td>
</tr>
<tr>
<td>Add:</td>
<td>10 mL 95% EtOH 4-5 drops indicator*</td>
<td>20 mL water 4-5 drops indicator*</td>
<td>10 mL 95% EtOH 10 mL tert-butyl Cl stock 30 mL water (set aside, add last)</td>
<td></td>
</tr>
</tbody>
</table>

* Add enough bromophenol blue indicator to all flasks to make each distinctly colored after mixing, but be consistent in # of drops.

7. For each solvent, calculate & record the actual starting concentration of tert-butyl chloride given its volume in the mixture.

Sampling and Titrating: (60:40 Solvent Composition)

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<td>Start the timer when your partner adds the water to the reaction flask and mixes it.</td>
</tr>
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</tr>
<tr>
<td>• Stopper &amp; mix Infinity Samples 1, 2, 3, and set aside until the end of the experiment. Make sure they are mixed well! Don’t titrate these until the end.</td>
<td>• Set aside the finished Time 0 Sample flask and get ready for the next sample.</td>
</tr>
<tr>
<td>• Get the next flask ready for Time 1 Sample.</td>
<td></td>
</tr>
<tr>
<td><strong>Time 1 Sample</strong> (2 minutes after start of reaction):</td>
<td><strong>Time 2 Sample</strong> (4 minutes after start of reaction): Continue as before. Discard titrated samples down the drain.</td>
</tr>
<tr>
<td>• (Continue proper pipetting practice) Transfer a 4 mL aliquot from the reaction mixture to the Time 1 Sample flask.</td>
<td></td>
</tr>
<tr>
<td>• Record the time elapsed since adding water to the flask.</td>
<td>• Stopper &amp; mix Time 1 Sample, then titrate &amp; record volume of NaOH added.</td>
</tr>
<tr>
<td></td>
<td>• Set aside the finished sample and move onto the next one.</td>
</tr>
</tbody>
</table>

Repeat these steps with all the time samples until you run out of reaction mixture (or the reaction appears to be over). Lengthen the sampling interval by a minute or two if the amount of base required doesn’t increase much from one sample to the next.

Once you have titrated all your timed samples, show your data to the instructor. If the reaction looks as though it is substantially over, you can add 10 mL of 95% ethanol to the “infinite time” samples you saved and titrate them. Otherwise you may need to wait a while to assure complete reaction. All three of the “∞” samples should require the same volume of base, and it should be the largest volume required by any sample.

Compute the **volume ratio of water to 95% ethanol** for the solvent you used and verify the result with an instructor before you leave the lab (it should be 50:50). Put this and your titration results on the black-board. Identify your data with your names (both members of the group). Copy what you think is a set of good data for a run in the 60:40 solvent that you did NOT use. **Record the names of the group whose data you copy.**
DATA ANALYSIS (For a review on rate laws, click here.)

Let RCl = tert-butyl chloride. The rate of solvolysis is defined as the change in [RCl] per unit time (represented as \(-\frac{d[RCl]}{dt}\); remember that fun calculus stuff?). If first-order behavior is followed, the reaction rate will depend only on [RCl]. The prediction from the S_N1 mechanism of the rate law for solvolysis of RCl (expressed in differential form) is:

\[-\frac{d[RCl]}{dt} = k \cdot [RCl]\]

where \(k\) is a first-order rate constant.

The rate law equation for a first-order reaction is not a linear equation. However, it can be linearized as follows. Separate the variables:

\[\frac{-d[RCl]}{[RCl]} = k \cdot dt\]

Integration of the left side between the limits of \([RCl]_0\) and \([RCl]_t\) (these represent \([RCl]\) at time zero and at the time of measurement, respectively), and the right side between times of 0 and \(t\), gives:

\[-\ln[RCl]_t + \ln[RCl]_0 = kt\]

which rearranges to

\[\ln[RCl]_t = -kt + \ln[RCl]_0\]

(a linear equation \([y=mx+b]\) whose slope = \(-k\))

Thus, **IF the reaction obeyed first-order kinetics**, rate data plotted as \(\ln[RCl]_t\) vs. time should fit a straight line. (If the reaction did not follow first-order kinetics, the data will not fit the straight line demanded by this model.)

Recall the solvolysis reaction:

Further explanation: As t-butyl chloride (designated as RCl) is solvated, the amount of RCl (reactant) in the reaction mixture decreases and, proportionally, the amount of product in the mixture increases. For every mole of reactant that is used up, one mole of each product (t-butanol and H3O+) is produced. Thus, as H3O+ is formed during your reaction, the assumption is that t-butyl chloride disappearing at a proportional rate.

**How can we represent this change with data?** \([RCl]_t\) remaining at any time is equal to the original concentration \([RCl]_0\) minus the loss of \([RCl]\) to hydrolysis as it reacts, \([RCl]_t\). This difference \(([RCl]_0 - [RCl]_t)\) is directly related to \((V_\infty - V_t)\), where \(V_\infty\) represents the volume of base needed to titrate all the protons that would be produced by complete hydrolysis (tested in the infinity flasks). \(V_\infty\) is proportional to \([RCl]_0\), since (a) one proton is produced by hydrolysis of one RCl, (b) one mole of proton produced is neutralized by one mole of base, and (c) you ensured that all RCl was hydrolyzed in the three “infinite time” samples. Further, the volume of base needed to titrate any of the timed samples (call these values \(V_t\)) is proportional to the number of protons released up to that time. Thus, \(V_t\) is proportional to \([RCl]\) lost to hydrolysis up to that time. \(V_t\) is a value we will use to graph the data.

To see if the data fit the above relationship, construct a spreadsheet table of volume of base used, \(V_t\), for each timed aliquot vs. elapsed time (in seconds). Compute the average volume of base used to titrate the "infinite time" samples and call it \(V_\infty\). (If \(V_\infty\) is lower than your largest timed sample, treat the largest value of \(V_t\) as if it were \(V_\infty\) and ignore your \(V_\infty\) titrations.)

**What information do we want to obtain from the data?** Recall the experiment objective: Do the experimentally measured rates of solvolysis support or contradict the rate behavior predicted by the S_N1 model? We tested two different solvent environments to see if there would be a difference in the rates of solvolysis between them. So, we want the data we gather to tell us what those reaction rates were for each. We also want to see how well the data fit the
proposed trend (we call this “validity”). If you look at a graph of a first order reaction that shows the concentration of the reactant over time, you’ll see that it decreases on a curved path, like so:

This representation of the data doesn’t lend itself easily to generating a value for reaction rate, or one for data validity. So, we rearrange the data in a way that can be graphed linearly, so we can generate a linear trendline with measures for reaction rate and validity both: the natural log function, shown above. In the above example, we take the natural log of both sides to eventually linearize our data. This can be done because you’re interested in the relationship between your variables, not the exact raw values themselves. You’re interested in the trend rather than the absolute values.

Use the spreadsheet to prepare on a single chart plots of \( \ln(V_\infty - V_t) \) vs. time for solvolyses run in both solvents (\( V_\infty \) cannot be plotted). Do NOT connect data points. DO impose a linear trendline on each data set. Decide whether or not to exclude certain points (are they obvious outliers?). Make the program give you the “correlation coefficient” for each line (after excluding obviously bad points). This value is a measure of how closely the data points fit the line. Interpretation: 0.999 = excellent fit; 0.99 = good; 0.90 = fair. This plot tests whether the reaction in each solvent followed the first-order model. If it did, the data points for the reaction in that solvent will fit a straight line, whose slope (absolute value) is the rate constant for the reaction in that solvent. Make sure that the spreadsheet gives you the proper number of significant figures for the slopes. Ask for help if you do not know how to do this.

LABORATORY REPORT (different format this week!): There is not a lab “report” this week, as you are used to. You will turn in your pre-lab notebook pages, and the answers to the following questions. Please copy the entire set of questions, paste it into a new document, delete the sample graph and data tables, and add your answers below each question. Note that you will be generating figures (charts & table) for Part II: Analysis. You must turn in your own, original work and give credit to students you work with. In this format of assignment, it is especially easy to notice plagiarism issues, so please steer clear.
Questions for “Testing a Reaction Mechanism”:

Part I – The chemistry concept behind the experiment

1. To answer Questions 1a through 1d, refer to the figures below and Section 6.10 (pg 255) of your textbook:

![Figure 1: the SN1 Mechanism]

**Figure 1: the SN1 Mechanism**

![Figure 2: Reaction coordinate diagram for an SN1 reaction](http://www.chemconnections.org/organic/chem226/Presentations/Ch10-Sn1.pdf)

**Figure 2: Reaction coordinate diagram for an SN1 reaction**

   a. In Figure 2 above, identify the reaction events that take place at points A, B, and C (the relative free energy maxima). Identify the most difficult step to complete assuming that it follows the SN1 pathway. Why did you choose this step?

   b. How does the most difficult step you identified in Question 1a relate to the major transition state for the reaction? Idenfity the location of the major SN1 transition state on the diagram in Figure 2.

   c. Explain how the rate of the most difficult step is related to the overall rate of the solvolysis reaction.

   d. For this experiment specifically, identify all species in solution during the major transition state you identified in Question 1b. Which of these species are directly involved in the SN1 reaction, and which species in solution serve(s) to stabilize those that are directly involved?

2. Use your answers to Question 1 to compose a complete but concise statement discussing why, chemistry-wise, one would expect consumption of t-buCl over time to obey a first-order rate law. (Consider the meaning of “first order” and also what is meant by the phrase “consumption of t-buCl”.)

Part II – Analysis, interpretation, and presentation of experimental data to support the chemistry concept

3. Present your experimental results as a data table and two figures (3&4) as illustrated below. *Follow format rules for tables and figures (the samples below are not complete):*

   http://www.linfield.edu/assets/files/chem/Courses/CHEM%20321/Tables_Guidelines.pdf

   http://www.linfield.edu/assets/files/chem/Courses/CHEM%20321/Figures_Guidelines.pdf

   a. Table 1 – Display raw and modified data with properly labeled column headings and a title that indicates what the data represents.

   b. Figure A – Display a scatter plot of raw data for both solvent compositions, properly labeled axes, and a proper caption that indicates what the figure shows and what the two data series are.

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1 “Unimolecular Nucleophilic Substitution (SN1).” Chemconnections.

c. Figure B – Display a scatter plot of modified data for both solvent compositions with trendlines and \( R^2 \) values, properly labeled axes, and a proper caption that indicates what the figure shows, in what solvent each depicted reaction was run, and the students who generated data for the second series. The reader should be able to look at the figures and captions without having read a whole report about the experiment and still be able to understand what was done to generate the data.

<table>
<thead>
<tr>
<th>60:40 Data</th>
<th>50:50 Data</th>
</tr>
</thead>
<tbody>
<tr>
<td>time(sec)</td>
<td>V(t ml base)</td>
</tr>
<tr>
<td>60</td>
<td>3.15</td>
</tr>
<tr>
<td>223</td>
<td>7.2</td>
</tr>
<tr>
<td>304</td>
<td>8.05</td>
</tr>
<tr>
<td>450</td>
<td>8.65</td>
</tr>
<tr>
<td>593</td>
<td>10.35</td>
</tr>
<tr>
<td>720</td>
<td>10.55</td>
</tr>
<tr>
<td>841</td>
<td>10.9</td>
</tr>
<tr>
<td>965</td>
<td>10.9</td>
</tr>
<tr>
<td>( V_{inf(ave)} ml )</td>
<td>11.63</td>
</tr>
</tbody>
</table>

**To add trendline in excel,** right-click on any point in a given series
* click "Add Trendline…"
* Choose "linear" and click boxes at bottom to add equation and R-squared value
* click OK, right-click in box that appears; click "Format trendline label…”
* choose "number", "scientific" and 2 decimals
* Position box as desired

4. What is the significance of \([V_{inf} - V_t]\)? What is the benefit of plotting first-order kinetics data as \( \ln(V_{inf} - V_t) \) vs time as opposed to \([V_{inf} - V_t]\) vs time?

5. What are the rate constants (with proper units) for each data set? Where did you find these values and their units?

6. What does the \( R^2 \) value tell you? Use this value for each of your data series in Figure B to determine how confident you are in the quality of each. What value of R-squared is considered “strong”?

7. Recall the expected rate order for this reaction and the benefit of logarithmically plotting the data gathered. In Figure B, how are the data series similar to one another? How do they differ? How can these trends be related to rate behavior of the 60:40 solvent compared with the 50:50 solvent?
Part III – Putting it all together

8. Recall the experimental conditions that favor a unimolecular reaction pathway. What effect did solvent polarity have on the rate of the solvolysis of t-buCl for YOUR DATA? Your answer should:
   a. Identify which solvent is more polar and why;
   b. Include a ratio of rate constants for reaction in 60:40 solvent / reaction in 50:50 solvent;
   c. Provide directional effect (i.e. “As solvent polarity increased/decreased, the rate of solvolysis of t-buCl increased/decreased, made evident by____”)’
   d. Identify what the proposed/expected trend is; and
   e. Identify whether the observed trend matches the proposed/expected trend.

9. Does this solvent effect (i.e. relative ionizing capabilities) support or contradict the prediction of the S_N_1 model? Explain, focusing on the interactions between solvent and the participants in the transition state.

10. Do the overall results of this experiment support the validity of the S_N_1 model proposed for this reaction? Provide 2 reasons in support of your conclusion.

11. Do the overall results prove that S_N_1 is the model that is followed in this reaction?

Part IV Feedback

12. How did conducting this experiment support you in learning about the SN1 reaction mechanism?

13. What was confusing about this experiment?

14. How did answering these questions help you tie the experimental data and analysis into the concept of the SN1 mechanism? Do you have any suggestions for improving clarity of the assignment?

Recommended courses of action for each partner in the pair: 60:40 solvent composition

- Set up an area where one partner will pipette the reaction mixture into sample flasks, and another area down the bench where the other partner will titrate the sample flasks once they have samples added to them.

| Partner A (pipetting station) | Partner B (titration station) |
### Needs:
- Proximity to the reaction mixture flask
- Proximity to either the micropipette set to 4 mL or 4 mL volumetric pipet & pipet bulb
- Proximity to a timer and lab notebook
- Other flasks should be near you
- Note where t-bu-Cl dispensette is located
- Volume of water set aside in graduated cylinder, separately
- *Each time you pipette from the reaction flask, first draw the mixture into the pipette tip to prime it, expel the solution back into the flask to flush the tip, and then draw up the sample of reaction mixture to be transferred

### When you are ready to start the reaction:
Add the t-bu-Cl to the reaction flask from the dispensette, then add the water to it from the graduated cylinder, have partner start the timer, and mix well. As SOON as possible after adding water (i.e. the start of the reaction):

#### Take Time 0 Sample (immediately following start of reaction):
- (*With proper pipetting practice, noted above*) Transfer 4 mL aliquots of this reaction mixture to each of the infinity sample flasks you have prepared.
- AND transfer a 4 mL aliquot to the Time 0 Sample flask.
- Record the time elapsed since adding water to the flask.

#### Stopper & mix Infinity Samples 1, 2, 3, and set aside until the end of the experiment. Don’t titrate these until then.

#### Stopper & mix Time 0 Sample, then titrate & record volume of NaOH added (final buret reading – initial buret reading) to get to the endpoint.

#### Leave the Time 0 Sample flask (stoppered and mixed) aside and get ready for the next sample with the Time 1 Sample flask you already have prepared. (This way you don’t have to worry about being done with a titration in under 2 minutes.)

#### Take Time 1 Sample (2 minutes after reaction has started):
- (Continue proper pipetting practice) Transfer a 4 mL aliquot from the reaction mixture to the Time 1 Sample flask.
- Record the time elapsed since adding water to the flask.

#### Stopper & mix Time 1 Sample, then titrate & record volume of NaOH added.

#### Take Time 2 Sample (4 minutes after reaction has started):
- Continue as before.

Repeat these steps with all the time samples until you run out of reaction mixture. Lengthen the sampling interval by a minute or two if the amount of base required doesn’t increase much from one sample to the next. Then quench all infinity sample flasks with 10 mL 95% EtOH and titrate each.

### Recommended courses of action for each partner in the pair: 50:50 solvent composition
- Flasks can be prepared by both of you. For all timed sample flasks and infinity sample flasks, label and add the appropriate solvent and indicator to each (use the same bottle of indicator, and the amount of indicator for each flask, for consistency). For the reaction mixture flask, label and add the needed amount of ethanol (you do not need indicator in the reaction flask). Be sure each stopper has a fitting stopper. **Arrange flasks** so that the reaction mixture flask is by itself, the infinity flasks are grouped together, and the timed sample flasks are grouped together (or by itself if you have just one).
- Set up an area where one partner will pipette the reaction mixture into sample flasks, and another area down the bench where the other partner will titrate the sample flasks once they have samples added to them.

<table>
<thead>
<tr>
<th>Partner A (pipetting station)</th>
<th>Partner B (titration station)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
</tr>
</tbody>
</table>

**Partner A (pipetting station):**
- Pipette reaction mixture into sample flasks.

**Partner B (titration station):**
- Titrate sample flasks.
### Needs:
- Proximity to the reaction mixture flask
- Proximity to either the micropipetter set to 4 mL OR 4 mL volumetric pipet & pipet bulb
- Proximity to a timer and lab notebook
- Other flasks should be near you
- Note where t-bu-Cl dispensette is located
- Volume of water set aside in graduated cylinder, separately
- *Each time you pipette from the reaction flask, first draw the mixture into the pipette tip to prime it, expel the solution back into the flask to flush the tip, and then draw up the sample of reaction mixture to be transferred*

### When you are ready to start the reaction:
Add the t-bu-Cl to the reaction flask from the dispensette, then add the water to it from the graduated cylinder, have partner start the timer, and mix well. As SOON as possible after adding water (i.e. the start of the reaction):

**Take Time 0 Sample** (immediately following start of reaction):
- (*With proper pipetting practice, noted above*) Transfer 4 mL aliquots of this reaction mixture to each of the infinity sample flasks you have prepared.
- AND transfer a 4 mL aliquot to the Time 0 Sample flask.
- Record the time elapsed since adding water to the flask.

**Take Time 1 Sample** (6 minutes after start of reaction):
- (Continue proper pipetting practice) Transfer a 4 mL aliquot from the reaction mixture to the Time 1 Sample flask.
- Record the time elapsed since adding water to the flask.

**Take Time 2 Sample** (12 minutes after start of reaction):
- Continue as before.

Repeat these steps with all the time samples until you run out of reaction mixture. Lengthen the sampling interval by a minute or two if the amount of base required doesn’t increase much from one sample to the next.

Then quench all infinity sample flasks with 10 mL 95% EtOH and titrate each.

### Needs:
- Proximity to 50 mL buret (first rinsed with 5 x 10^-3 M NaOH and verified that it works), filled with NaOH, and top opening covered with a small beaker, set up on a ring stand with a buret clamp (green)
- Proximity to a timer and lab notebook
- A piece of white paper to place under the flask to be titrated
- A paper with a straight black line on it to help read buret volumes
- See tips on titrating above, and practice titrating twice before starting the reaction.
- Refill the buret to close to 0 and record the starting volume in your notebook