

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?

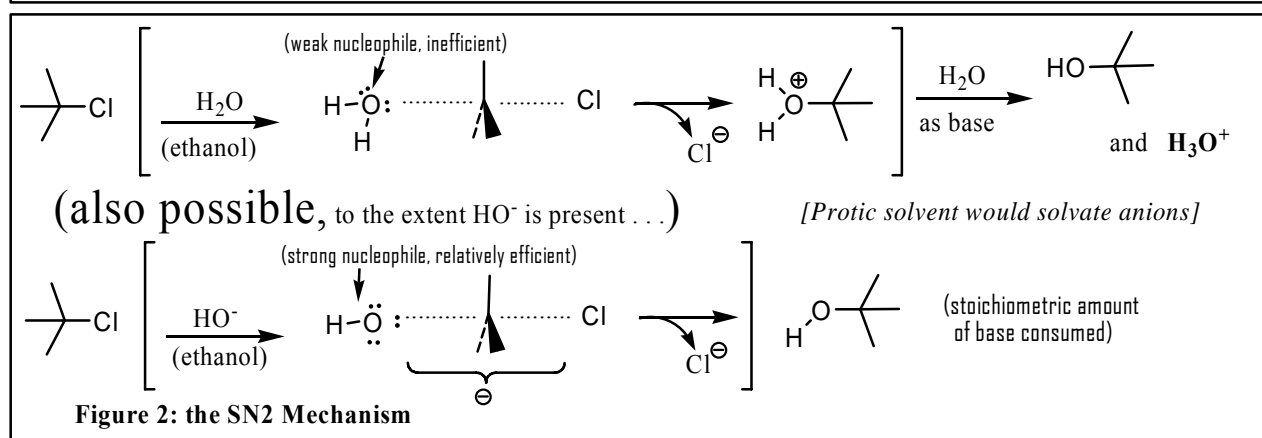
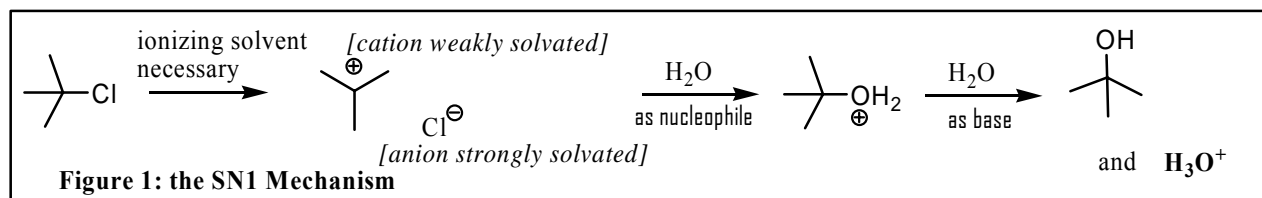
Yes: the mechanism is consistent with the evidence (it may be correct, but is not proven to be so).

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 replacing the Cl with a different nucleophile – a water oxygen (which eventually becomes an –OH group). Two mechanisms can be imagined (S_N1 and S_N2 , both shown below).

Annotate these mechanisms with δ^+ , δ^- , and curved arrows, and **identify rate-limiting step in each**, before reading further.



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 a single solvent, and will also analyze results gathered by another pair using a different solvent.*

This experiment is designed to show how kinetics behavior can be used to probe the validity of proposed mechanisms. It has three required objectives plus one optional objective:

1. (a) For each mechanism in turn, predict the effect on reaction rate that would result from changing the concentration of *tert*-butyl chloride. To do this you need to identify all the participants in the slow step of each mechanism. *Should the rate law be first-order in [*tert*-butyl chloride], or some other order, for the S_N1 model? For*

the S_N2 model?) **(b)** Compare each mechanism's predictions (using the pertinent integrated rate law for each) to experimental behavior of rate vs. concentration.

2. Determine the quality of fit of experimental data to predicted behavior. 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.

3. **(a)** For each mechanism in turn, predict the effect on reaction rate that would result from changing the solvent 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 accelerate, to slow, or to have no effect on the rate-limiting step of the S_N1 model? Of the S_N2 model?*) Note that in the S_N2 model, you must consider how solvent interacts with both the nucleophile and the leaving group.

(b) Compare these predictions to experimental behavior.

4. (optional for extra credit) If neither mechanism can be rejected, outline additional experimentation that *would* permit you to reject one of them. In the outline, use pertinent theory to explain how and why the experiment would settle the issue.

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 *t*-butyl chloride molecule that reacts. The procedure is described in the next paragraph.

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. 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.

The paragraph above is a clue to writing a proper Experimental Section. Do not copy, but emulate its style when you write yours. Note in particular the lack of tedious numeric data about sample preparation. However, values for starting concentration of t-bu-Cl (after all ingredients have been mixed!), as well as solvent composition, must be included.

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.

Tips on titration:

- Do the titration over a white surface to aid in detecting the end point.
- Titration should always be done with magnetic stirring. Show the instructor your setup in case she has suggestions for improvement.
- Ethanol plus indicator probably will be blue, but will turn yellow when you add the sample. It stays yellow during most of the titration. As the end point nears the color will shift gradually to chartreuse, then turn forest green, then turn blue. **Continue titrating if there is any yellow left in the green. The drop just before it turns blue marks the end point. You have gone too far if it turns blue.** Recommended: titrate a couple of mL of dilute HCl to practice before you start the real thing. 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 chartreuse because the hydrolysis continues slowly. Don't add more base or you will get base volumes that are too high.

- To read the buret, hold a small piece of white paper with a sharp dark line behind it to help you read the volume. Look straight at the meniscus to avoid parallax, and read the bottom of the meniscus.

Half of the class will do the reaction in 60:40 water:95% ethanol; the other half will use 50:50 water:95% ethanol. Every reaction mixture contains the same volume of 0.1 M *t*-butyl chloride in 95% ethanol – *note that this is NOT pure t-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 *t*-butyl chloride after all additions have been made and write it in your notebook.

EXPERIMENTAL SECTION

Before starting the experiment, take time to understand why each operation is necessary and why speed is essential. Things happen fast once you start, and you won't have time to scratch your head and figure it out. Refer back to the sequence of events in the Arial-font paragraph on the previous page. 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 ethanol mixture, depending on your timing method.

Necessary equipment:	1	50 mL buret, ring stand and buret clamp
	1	small funnel to help fill buret
	1	5 mL micropipetter + 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

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 5×10^{-3} M NaOH. Finally, fill it completely with the NaOH. *Force all the air bubbles out of the valve/tip – ask instructor to check.*

Preparation for sampling: Gather 125 mL flasks, with stoppers to fit, as shown in the table below. Use a graduated cylinder to add about 20 mL of water to each of the three "∞" flasks. Add about 10 mL of 95% ethanol to each "timed sample" flask (purpose: to quench, or stop, the reaction). Add enough bromophenol blue indicator to all flasks to make each distinctly colored after mixing.

	<u>50:50 solvent</u>	<u>60:40 solvent</u>
reaction mixture	1	1
infinite time samples ("∞")	3	3
timed samples:	1 (will titrate immediately)	8 (will titrate after all are taken)
Total flasks needed:	5	12

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

Preparation of reaction mixture and initiation of hydrolysis:

Mix volumes as shown for the solvent you are using. Use bottles equipped with dispensettes for the *tert*-butyl chloride in ethanol and the ethanol. Add water LAST from a graduated cylinder and begin timing as you pour it in. Mix WELL by swirling!

	<u>50:50 solvent</u>	<u>60:40 solvent</u>
<i>t</i> -bu-Cl stock (0.1 M in 95% EtOH)	10.0 mL	10.0 mL
95% EtOH	15.0 mL	10.0 mL
Water (from graduated cylinder)	25.0 mL	30.0 mL

Sampling and titrating technique: After mixing, immediately withdraw a 4.0 mL aliquot from the reaction flask and drain it into the first of your sample flasks (the ethanol in this flask stops the reaction in the aliquot). Record the time at which about half of the aliquot has run into the flask. Mix the contents well. As soon as possible, remove three additional 4.0 mL aliquots from the reaction flask and add them to the three "∞" flasks. **Mix these well** by

swirling, then stopper all three and set them aside until the end of the experiment. Their purpose is to foster complete hydrolysis of all the t-butyl chloride.

50:50 solvent: Sample about every 6 minutes. Each can be titrated as soon as it is taken since there is enough time before the next sample is due. **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. If you are using a single sample flask, discard its titrated contents down a sink drain, shake the flask free of liquid, add about 10 mL of 95% ethanol (graduated cylinder or dispensette) plus indicator, and repeat the process above.

60:40 solvent: Sample every 2 minutes. This is too short an interval to permit immediate titration, so collect all aliquots first. **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. Discard titrated samples down the drain.

You may titrate timed aliquots whenever convenient. Early samples are the most valuable. Be careful: the first sample may not require much base since it did not have much time to react! For each successive sample you can rapidly run in as much base as the previous titration required (assuming you didn't overshoot), but then slow down.

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 or 60:40). 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 solvent that you did NOT use. **Record the names of the group that generated the data you copy.**

DATA ANALYSIS

Let RCl = *tert*-butyl chloride. The rate of solvolysis is defined as the change in [RCl] per unit time. The predictions from the S_N1 and S_N2 mechanisms of the rate law for solvolysis of RCl (expressed in differential form) are:

$$\begin{array}{ll} \text{If SN1 is followed (1}^{\text{st}}\text{-order rxn)} & \text{If SN2 is followed (2}^{\text{nd}}\text{-order overall)} \\ -d[\text{RCl}]/dt = k_1 \cdot [\text{RCl}] & -d[\text{RCl}]/dt = [\text{RCl}] \cdot (k_2 \cdot [\text{H}_2\text{O}] + k_3 \cdot [\text{HO}^-]) \end{array}$$

where k_1 is a first-order rate constant, and k_2 and k_3 are second-order rate constants.

If the S_N2 mechanism were followed, the reaction rate technically would depend on [RCl], [H₂O] and [HO⁻]. But because [H₂O] is so large, its concentration changes very little during the solvolysis, and so is a constant. The [HO⁻] is very low due to the acidic pH and thus would not contribute measurably to the rate. Given these facts, what rate law will such a reaction appear to follow? (*Address this question in your lab report.*)

If first-order behavior is followed, the reaction rate will depend only on [RCl]. In this case, kinetics data plotted as the logarithm of [RCl] vs. time should fit a straight line.

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

$$-d[\text{RCl}]/[\text{RCl}] = k_1 \cdot dt$$

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

$$-\ln[\text{RCl}]_t + \ln[\text{RCl}]_0 = k_1 t \quad \text{which rearranges to}$$

$$\ln[\text{RCl}]_t = -k_1 t + \ln[\text{RCl}]_0 \quad (\text{a linear equation whose slope} = -k_1)$$

Thus, **IF the reaction obeyed first-order kinetics**, rate data plotted as $\ln[\text{RCl}]_t$ 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.)

Further explanation: $[\text{RCl}]_t$ remaining at any time is equal to the original concentration minus the loss to hydrolysis. This difference is directly related to $(V_\infty - V_t)$, where V_∞ represents the volume of base needed to titrate all the protons that would be produced by complete hydrolysis. V_∞ is proportional to $[\text{RCl}]_0$, since one proton is produced by hydrolysis of one RCl, and you insured 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 $[\text{RCl}]$ lost to hydrolysis up to that time.

To see if the data fit the above relationship, construct a spreadsheet table of **volume of base used** 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_∞ . (If V_∞ is lower than your largest timed sample, treat the largest value of V_t as if it were V_∞ and ignore your V_∞ titrations.) *This table is NOT to be included in your report since you will instead be showing plots made from the table data.*

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_∞ 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 value (made positive) is the value of 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.** Comparison of rate constants for reactions run in the two solvents shows whether solvent polarity affects the rate of hydrolysis, and if so how.

REPORT: Since this experiment is data-intensive, it makes sense to have separate Results and Discussion sections. Pay careful attention to the following:

- **Introduction:** Show both mechanisms using the actual reagents.
 - a. Explain from theory how changing the concentrations of RCl and possibly HO^- should affect the rate of attaining the transition state in each mechanism ($\text{S}_{\text{N}}1$ AND $\text{S}_{\text{N}}2$).
 - b. Show the rate law expected for each mechanism.
 - c. Explain from theory how changing the solvent polarity is expected to affect the rate of attaining the transition state in each mechanism ($\text{S}_{\text{N}}1$ **and, separately,** $\text{S}_{\text{N}}2$).
 - d. Explain how the progress of the reaction will be followed.
 - e. Explain (mathematically, using the appropriate integrated rate law) how you plan to plot rate data and why you chose this method.
- **Results section:** Before you start writing, review the objectives of the experiment, and plan how to present the two major results from each solvent clearly, concisely and convincingly to satisfy the objectives.

No Tables of data should be included, since the plot (a figure) summarizes this sort of information most clearly. *Follow format rules for figures – ignoring them costs credit! Hint: the legend for the figure that presents your results must include information about both solvent compositions. It should also identify the students who generated the second set of data.*

Prepare your reader for what to expect in the figure before you present it. Do this by means of one or more declarative sentences. A figure may be placed anywhere in the report AFTER its introductory sentence, as long as it is in proper numerical order with other figures. This makes it easy to avoid splitting a figure across two pages. *As soon as possible after you introduce a figure, the results contained in it must be summarized for the reader.* This summary may be presented preceding or following the figure itself.

- **Discussion section:** Each objective of the experiment should be the topic of one paragraph. Open each paragraph with a review of theoretical background relevant to that objective (e.g., identify the rate-limiting step in each mechanism, predict the effect of changing [RCl] and solvent polarity on rate of reaction for each mechanism, etc.).

Objective 1: Why S_N1 & S_N2 are not distinguishable using [RCl] effect on rate? Why was a log plot chosen to represent the data? For the S_N1 model, do your kinetics data fit the theoretical prediction of a straight line well? Do these data fit the prediction of the S_N2 model given your experimental conditions? Can you reject either model based solely on the effect of concentration on kinetics (excluding the polarity evidence)?

Objective 2: What is the effect of solvent in S_N1 and S_N2 ? What effect, if any, does water play in deciding if S_N1 or S_N2 is the appropriate mech. for this exp.? How reliable are your results? In other words, how good is the fit of experimental data to each trendline? Use the correlation coefficients to answer this question for each set of results.

Objective 3: Explicit conclusion that states whether or not both S_N1 and S_N2 mechanisms are consistent with results in this experiment. Compare values of the rate constants for reactions run in the two solvents. Does the observed difference match the prediction of the S_N1 model? Of the S_N2 model? Can you reject either model on the basis of the solvent polarity effect on rate?

Objective 4: (For extra credit) If you cannot reject either mechanism, can you suggest additional experimentation that should permit you to reject one of them? (Explain exactly what you would do and how the results would decide the issue.)

Enrichment Questions (attach answers to the end of your report)

Change #1: (Only a qualitative answer is possible for this question.) Maintain constant concentration of *tert*-butyl chloride but increase temperature by 25° C. What would change (*rate*, *rate constant*, or *both*)? **Why?**

Change #2: Maintain constant temperature but triple the concentration of *tert*-butyl chloride. How would this change the *rate of reaction*? (Give a numeric answer **using the rate law**.) Would the *rate constant* change? Explain **why** for each answer.