Experiment 8 —

Kinetics of S_N1 Solvolysis

Pre-lab preparation (1) Textbook Ch 8 covers the S_N2 and S_N1 mechanisms. Read/review as necessary. (2) Write balanced rxns (a) for S_N1 solvolysis with EtOH as the nucleophile, (b) with water as the nucleophile, and (c) for the E1 reaction with either EtOH or water (pick one) as the base. (3) Write the complete mechanism for S_N1 reaction of *t*Bu–Cl with EtOH. (4) After reading the experimental procedure, explain why S_N2 and E2 don't compete with the ionization mechanisms in this experiment. (5) Draw the blue form of the bromthymol blue indicator (just follow the e^--pushing instructions below). (6) Calculate the total quantity of 0.01 M aq NaOH needed to neutralize the HCl produced by complete solvolysis of the *t*BuCl in 0.5 ml of 0.2 M *t*BuCl in acetone.

Reaction rates can be determined by monitoring the decrease in concentration of reactant(s) or the increase in concentration of product(s) as a function of time. Concentrations of reactants, the nature of the solvent, and the temperature can all affect rates. Measurements of reaction rates as a function of temperature provides information on the activation energy for the reaction.

In this lab we will be measuring the rate of solvolysis of *tert*-butyl chloride as a function of temperature, solvent polarity, and concentration of reactant.

The solvolysis will be done in aqueous ethanol (i.e. a mixture of EtOH and H_2O). After the rate-determining ionization of the *t*Bu–Cl, the *tert*-butyl cation can rapidly undergo three parallel reactions: (1) nucleophilic attack by ethanol, (2) nucleophilic attack by water, and (3) loss of a proton. As your balanced equations show, each of these pathways produces one molecule of (solvated) HCl. Since the rate of ionization determines the overall rate of the reaction, the rate of HCl production is exactly the same as the rate of ionization of the *tert*-butyl chloride reactant.

The rate of this 1st-order reaction can be expressed as the decrease in concentration of reactant per unit time (or the increase in the [HCl] per unit time),

$$\frac{-\,d[t\text{BuCl}]}{dt} = k[t\text{BuCl}]$$

Rearranging to

$$\frac{d[t\text{BuCl}]}{[t\text{BuCl}]} = -\,k\,dt$$

and then integrating from the initial alkyl chloride concentration, $[t\text{BuCl}]_0$ at t = 0 to $[t\text{BuCl}]$ at time t,

$$\ln[t\text{BuCl}] = \ln[t\text{BuCl}]_0 - kt \qquad (1)$$

Thus, plotting $\ln[t\text{BuCl}]$ vs time gives a line with a negative slope of k and an intercept that corresponds to $\ln[t\text{BuCl}]_0$. (Zumdahl, *Chemical Principles*, 5th ed, section 15.4 has a more detailed discussion of kinetic expressions.)

For first-order reactions, the half-life, $t_{½}$, i.e. the amount of time that it takes for the concentration of reactant to decrease to half of its initial value, is

$$t_{1/2} = \ln 2/k$$

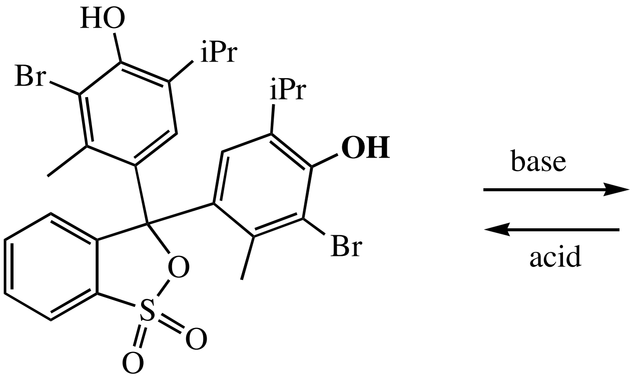
or

$$k = \ln 2/t_{1/2} \qquad (2)$$

We will measure the rate of HCl (actually $EtOH_2^+\ Cl^-$) production by titration with aqueous NaOH. From this we will be able to determine the amount of *tert*-butyl chloride that has reacted as a function of time.

Procedure. Add the stock 0.01 M NaOH solution to your burette. Prepare 500 ml of EtOH/H_2O mixture by combining 225 ml of 95% aq ethanol and 275 ml of water. (this will give a mixture that is 43% ethanol and 57% water by volume). Mix and store this in an Erlenmeyer flask, not a beaker.

Add 100 ml of this mixture to a suitable Erlenmeyer flask, followed by 3 or 4 drops of bromthymol blue indicator (structure below). In acidic solution this indicator is in the form shown below and is yellow; in basic solution it is blue. The blue form is created when base deprotonates one of the phenolic OH groups. See if you can push electrons from the negative O of the conjugate base through the aromatic ring, and onto the O of the sulfonate "leaving group", breaking that C–O bond in the process. The extensive conjugation created by this process is the feature that gives this form its blue color. Under acidic conditions, the process is reversed.



Add a magnetic stir bar and set the flask on a magnetic stirrer. If the surface of the stirrer is dirty you may want to place a piece of white paper under the flask so that the indicator color is easier to see. Stir the solution gently. Stirring too vigorously will churn atmospheric CO_2 into the solution, where it reacts with water ("carbonation") to form H_2CO_3. This lowers the pH. Typically the initial solution will be slightly acidic because of dissolved CO_2, so you'll need to start by "pre-titrating" with a few drops of aq NaOH until the indicator *just barely* changes from acidic *yellow* to basic *blue*. Try not to breathe into the flask. If the pH drifts back to the acidic side the time you're ready to start the experiment, don't worry about it — close to neutrality is good enough.

Instead of the "standard" procedure of stopping the solvolysis at different times and titrating the acid produced, we're going to "overshoot" by adding a specific quantity of base, then record the time required for the reaction to generate enough HCl to neutralize it and change the indicator from basic blue to acidic yellow. Your kinetics will be based on the times required for the solvolysis reaction to neutralize the specific amounts of base that you've added.

You'll need to add the aq NaOH solution in 0.5-ml increments and record the *time* required for the reaction to neutralize it, so set up a table that lists total volume of NaOH added in one column and time in the other. Fetch a timer and get ready...

Once you have everything set up, do some stretching exercises, take a few deep breaths, and get yourself pumped up by grunting or making other suitable noises. Please avoid banging heads (ouch) with your partner or others in the lab until after the experiment is completed.

Start by adding the first 0.50 ml portion of aq NaOH. Now add **0.5 ml of the 0.2 M stock solution of *tert*-butyl chloride** in acetone — this is your time = 0 point. Record the time required for the reaction to neutralize the first 0.5-ml portion of base. Immediately add the next 0.5 ml of base, record the time it takes the reaction to neutralize it, etc. Remember that the *t*Bu–Cl will continue to react whether the solution is basic or acidic, so you must add each 0.5 ml aliquot of base immediately after the solution changes from basic blue to acidic yellow. Continue to add aliquots of base and measure times until you have 7 - 10 data points.

Once you have recorded your final time point, don't add more base. Drive the reaction to completion by heating it on a steam bath for 5 - 10 min. The indicator doesn't work properly at too high a temperature, so cool the solution to room temp (time is valuable, so use ice, don't sit and stare at it), then titrate the acid produced. This time you're looking for the exact point at which the indicator just turns to blue, so don't overshoot! This will give you the total amount of base required to react with the HCl produced by solvolysis of *all* the *t*Bu–Cl. From this you can determine the exact quantity of *t*Bu–Cl you started with.

Do one or two trial experiments to gain confidence in your technique. Make a plot of your data on semi-log paper — this should give a line with negative slope. Now there are two ways that we can get the rate constant — (1) we can use the titration data to figure out exactly how much *t*BuCl we started with and how much was present at each point along the way, but that's a lot of calculatin'. Or (2), we can recognize that the total volume of base needed (after driving the reaction to completion) minus the volume used at any time point is *proportional to* the amount of *t*BuCl present. That is, the final quantity of base is proportional to the amount of *t*BuCl we had to begin with, and the volume needed to neutralize the acid produced at a particular time is proportional to the amount of *t*BuCl that reacted by that time.

If we plot ln(total vol NaOH used – vol NaOH used by time t) vs time, we should get a line (whose slope is not *k*, but is proportional to *k*). Now here's a clever trick to get the actual rate constant. If we use "semi-log paper" — this is graph paper with a logarithmic scale on the y-axis — we can just plot **total vol NaOH used – vol NaOH used by time t** vs **time**, and we'll get a nice line. Unfortunately, we can't extract the *k* from the slope, but we can very easily extract the reaction half-life, $\mathbf{t_{½}}$. Then, using eqn 2, we can convert the half-life to ***k***. Quick 'n' dirty, no need for fancy plots and linear regression analysis, out pops the answer with a minimum of time and effort. This procedure is explained in more detail, with pictures, on the handout you will get in lab.

Do trial runs with 0.5 ml of *t*Bu–Cl solution at room temp (standard conditions) until you get at least two sets of data that give nice lines and reasonably consistent *k* values.

Get together with two other groups. Each of the three groups should now do *one* of the following experiments below (each examines variation of one parameter and consists of two separate runs) and determine the half-life and 1st-order rate constant.

(1) Single runs with different concentrations of starting material at room temperature. Use 0.75 ml of *t*Bu–Cl solution for one, and 0.25 ml for the other.

(2) Single runs with different solvent compositions at room temperature. Use a water/95% aq. ethanol ratio of 65/35 for one and 45/55 for the other (remember, your initial trials used a 55/45 ratio.)

(3) Single runs at temperatures above and below room temperature. Shoot for temps of about 40°C and 10°C. This will allow a determination of the activation energy for the reaction. To maintain as constant a temperature as possible, immerse the flask in a large volume of warm or cool water in a plastic wash tub. Give the solution a chance to thermally equilibrate with the bath before starting. Now in this case you're going to some function of *k* vs some function of T, so you're going to need an **accurate temperature** for each value of *k*. How do you think this is best measured? (a) thermometer *in the reaction flask*, (b) thermometer in the bath and assume

it's the same as the temp inside the flask, or (c) thermometer in someone else's bath because you forgot to measure your own (wrong)?

The detailed experimental design is left up to you. If the reactions are too fast or too slow, perhaps you can vary the quantity of base used in each aliquot, or even the quantity of *t*BuCl you start with.

When you're finished, please rinse your burette with distilled water and clamp it upside down with the stopcock open. Be sure you extract the necessary data from your partner groups before you leave.

Your report will be due at the beginning of your next lab period. This one is worth 25 points. Be sure to include all your primary data and plots that you used to determine the $t_{½}$ and the k values. You should also include the primary data and plots for the one experiment (1, 2, or 3 above) that your group performed. Report just the $t_{½}$ and the k values (and other relevant data like solvent composition, initial quantities of *t*BuCl, *temperatures*, etc) obtained by your partner groups. Be sure to state the source of the data. You do not need to present their primary data or plots, only the $t_{½}$ and the k values derived from them.

Discuss the variation in rate constant (if any) with the change in initial concentration of *t*BuCl. Would you expect such a variation? Explain. Were the actual results consistent with your expectations?

Discuss the variation in rate constant (if any) with solvent composition. In this part of the experiment, mixtures of water and 95% aqueous ethanol were used. (What was the ratio of water to ethanol in each mixture?) Were the results consistent with your expectations? Explain.

Now let's extract an activation energy from the k vs T data. The dependence of reaction rate constant on temperature and activation energy is given by the Arrhenius equation,

$$\boldsymbol{k = Ae^{-Ea/RT}}$$

where E_a is the activation energy in cal/mol (n.b., that's calories, not kilocalories), T is the temperature in Kelvin, R is the gas constant, most conveniently expressed as 1.987 cal/molK, and A is the "Arrhenius pre-exponential factor", which is related to the probability that a molecule with enough energy to cross over the barrier will actually do it. Take the natural log of both sides of that equation, and rearrange it so that's in the form of a line — you need an "x" that contains the temp, T, and a "y" that contains the *k*. It should be clear what you need to plot and how to extract the desired parameters from the slope and intercept. So plot away.

How does your E_a compare with E_as that you've encountered in class? For example, you'll recall that rotation around a single bond has an E_a of about 3 - 4 kcal/mol, inversion of NH_3 has an E_a of about 5 kcal/mol — these are both super-fast (ps timescale at room temp) processes. A cyclohexane chair-to-chair ring-flip has $E_a \approx 11$ kcal/mol — that happens on the microsecond timescale at room temp. Rotation around a π-bond has an E_a of about 65 kcal/mol, so that doesn't happen at all below about 700°C. Is your E_a reasonable in comparison? If not, did you have an accident with the units? Ooooops. That's embarrassing...

Assuming that the A value is independent of solvent composition, how much did the E_a change when the solvent composition was varied? Which solvent mixture lowered the E_a, and which raised it? Is that consistent with your previous predictions?

If we tried to do this experiment with other organo-halides under the same conditions that we used for *t*Bu–Cl, some would react much faster, and others would react much slower. For halides that react faster or slower, how might we vary the conditions so that we could comfortably measure the rxn rates at room temperature?