# The Kinetics of a Homogeneous Reaction in Solution

## Background

There are a couple of points that need to be clarified in the background theory given in the manual. First, this reaction is not what you would traditionally consider an SN2 reaction because it proceeds through a different mechanism. The presence of the benzene ring precludes backside attack on the chlorine-bearing carbon, and thus there can be no inversion at that point. Instead, the lone-pair of the nucleophile (piperidine) attacks the electron-deficient π-system of the benzene ring to form an intermediate “Meisenheimer complex” in the first step, as shown in the manual. In the next step, a second piperidine molecule abstracts a proton from the first piperidine AND the chlorine from the DNCB. This is not clearly depicted in the figure for Step II in the manual, but likely occurs in a concerted fashion to form the Pip:HCl salt, as shown below.



Figure . Step II

Overall, however, the reaction is not a concerted mechanism as in SN2, but the rate equation is still bimolecular because formation of the intermediate is the rate determining step.

## Procedure

We will only be doing the “Real Time” procedure and data analysis, and not the “Frozen Time” analysis. The general outline for the 3 weeks of this lab is as follows:

* Week 1: Mixed 2nd Order Kinetics and Simple 2nd Order Kinetics
* Week 2: Pseudo-1st Order Kinetics and DNPP calibration curve
* Week 3: Repeat Runs (if necessary) and begin data analysis (important)

### DNPP Calibration

The extinction coefficient (**ε**) of the product (2,4-dinitrophenylpiperidine or DNPP) can vary slightly due to the instrumental setup, so it is best to do a calibration curve to determine the value for yourself, rather than taking the number from the manual (p. 356). This is also a good concept for you to understand, and helps you familiarize yourself with the UV-Vis spectrometer. During the data analysis, you should determine the rate constant using both the experimentally determined **ε** value and the value given in the book, and then compare them to see which fits the data better. If you make a mistake or have a problem with the calibration curve, you can always resort to using the value from the book.

The procedure for the calibration curve is as follows.

1. **Prepare 4 solutions of DNPP at different concentrations.** By diluting the stock solution given, make solutions with concentrations of **0.001 M**, **0.003 M**, **0.005 M**, and **0.007 M**, and put them in 4 separate disposable cuvettes. If you use the narrow cuvettes, you only need 1.5 mL of each solution, otherwise you’ll need about 3.0 mL of each. It is not important that you use these exact numbers, but it is important that you be precise in your measurements so you can calculate the true concentrations of each solution. Graduated cylinders seem to work ok, but volumetric syringes are better as long as they are used properly and you don’t leave air bubbles inside. Avoid using the pump-action Eppendorf type pipettes, as they are calibrated to give the volume based on the density of water, not ethanol. Also, the **concentrations should not go above ~0.0075 M**, as the measured absorbance will begin to deviate from the Beer-Lambert law in that region.
2. **Prepare the blank.** Fill a 5th cuvette with ethanol about ⅔ of the way.
3. **Setup the spectrometer.** Make sure all the instrument settings are correct and it is set to scan some region around 472 nm, generally from 480 nm to 460 nm.
4. **Scan the samples.** Run the ethanol blank first, as directed by the instrument, then each of the 4 samples.
5. **Export the data.** You can export it in csv, tsv, or xml format, but make sure you choose to save it as a “Spectrum” file, and not a “Report” type.
6. **Process the data.** Open the files in your preferred spreadsheet program. Make a table of x-y pairs with the calculated concentrations of each solution as the x-values in one column, and the absorbance at 472 nm as the y-value in another column. If the instrument did not automatically do the blank subtraction, make sure you subtract the absorbance of the blank at 472 nm from the absorbances of each of the other solutions.
7. **Plot the calibration curve.** Create a scatter plot of concentration in M (x-value) vs. absorbance at 472 nm (y-value). Add a trend-line and find the equation for it. Force the trend-line to pass through the origin by setting the y-intercept to 0. According to the Beer-Lambert law, Eq. ( 1 ), **the slope of this line is equal to the extinction coefficient multiplied by the pathlength**. If you used 1 cm pathlength cuvettes, the slope is numerically equal to the extinction coefficient.

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|  |  | ( 1 ) |

### Kinetic Runs

The procedure for this part is essentially the same as given on p. 356. The only difference between the 3 cases is the volumes of DNCB, Pip, and ethanol used, and the amount of time scanned. The general outline for all 3 cases is given below, and the exact numbers for volumes and time after.

1. Set the spectrometer to do a “Rate” measurement and specify the monitoring wavelength as 472 nm. Set it to acquire data points every 5 seconds, for the total time specified below.
2. Ignore the point about the “reference cell”. We are using single-beam spectrometers.
3. Combine the specified volumes of ethanol and DNCB solution in a disposable plastic cuvette.
4. Place the ethanol/DNCB solution (**without** the Pip) in the spectrometer. Start the instrument scan so that it asks for the blank, and run this solution as the blank.
5. When the blank is finished, remove the cuvette from the spectrometer and add the specified volume of Pip. Working quickly, mix the solution thoroughly, return the cuvette to the spectrometer, close the cover, and continue the run. The spectrometer will scan the specified wavelength every 5 seconds for the amount of time given.
6. When the scan completes, export your data as a “Spectrum” file in either csv, tsv, or xml format. When you open this file in your spreadsheet program, it will have a column of time values (in seconds) and a column of absorbances for each of those times.

### Mixed 2nd Order Kinetics

Use **1.050 mL ethanol** and **0.300 mL of DNCB** solution. Add **0.200 mL Pip**, and scan for **3600 seconds** (1 hour). Make sure you are using the 0.0104 M DNCB and 0.620 M Pip stock solutions to prepare these.

### Simple 2nd Order Kinetics

Use **1.500 mL of DNCB** solution (**no ethanol is needed**). Add **0.050 mL Pip**, and scan for **2700 seconds** (45 min). Make sure you are using the 0.0104 M DNCB and 0.620 M Pip stock solutions to prepare these.

### Pseudo-1st Order Kinetics

Use **0.750 mL ethanol** and **0.300 mL of DNCB** solution. Add **0.500 mL Pip**, and scan for **1800 seconds** (30 min). Make sure you are using the 0.0104 M DNCB and 0.620 M Pip stock solutions to prepare these.

## Data Analysis

There are several issues with the data analysis in the manual, due to the derivations of the integrated rate laws for the three conditions. The integrations used to arrive at Equations 10b, 12b, and 14b are done properly under the assumption that the reaction begins with [DNPP]0 = 0 at time t = 0. However, because it takes some finite amount of time to mix the piperidine in the solution, return the solution to the spectrometer, and continue the run, the reaction will already have begun and there will be some non-negligible amount of [DNPP]0 at time t = 0.

On page 357 of the manual, it says that this can be accounted for by simply adding a term for a non-zero [DNPP]0, calculated from the initial absorbance recorded and the extinction coefficient of DNPP, but this is incorrect. To see why, consider the equation given on p. 357:

In the limit of large times, the term in parentheses approaches 1, and the equation becomes:

However, this must be incorrect because it implies that the final concentration of [DNPP] will be greater than the initial concentration of [DNCB], which is clearly impossible. Since this equation artificially introduces some arbitrary initial amount of DNPP, it does not properly model the reaction. Instead, the differential equations 10, 12a, and 14a all need to be explicitly integrated with the correct initial conditions. Doing so yields the following three equations:

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| *Mixed*  *2nd*  *Order* |  | (10c) |

|  |  |  |
| --- | --- | --- |
| *Simple*  *2nd*  *Order* |  | (12c) |

|  |  |  |
| --- | --- | --- |
| *Pseudo*  *1st*  *Order* |  | (14c) |

The object of this lab is to model the experimental absorbance data for the three reaction conditions using these three equations. This requires the use of regression analysis, as described in “Nonlinear Least-Squares Curve Fitting with Microsoft Excel Solver” by Daniel C. Harris (*J. Chem. Ed.* **1998**, *75*, 119-121). The Solver add-on for Microsoft Excel is usually included in Windows versions and later Mac versions. See the following links for further help in obtaining or activating Solver:

<http://www.solver.com/excel-solver-how-load-or-start-solver>

<http://www.solver.com/welcome-mac-users-solver-now-included-excel-2011>

You are expected to read that article and understand the concept in order to implement the curve fitting procedure for your data. An outline is given here, which must be repeated for each of the three conditions:

1. Open your data file from the spectrometer in Excel and ensure that it is in the correct format with times in the first column (Column A) and measured absorbances in the second column (Column B). If you use a program other than Excel to analyze your data, you will need to figure out how to do the curve fitting on your own, and I may or may not be able to help you.
2. You will need about 5 or 6 columns for data processing. Apart from these, set aside an area in the spreadsheet to hold values for the parameters that you will need to reference in your formulas. These parameters are: **ε**, [DNCB]0, [Pip]0, and k. Enter the value for **ε** that you calculated from your calibration curve, and the initial reactant concentrations ([DNCB]0 and [Pip]0) calculated from the solution volumes and concentrations that you used to prepare them. You can make an initial guess for the value of k using the expressions at the bottom of p. 357 in your manual.
3. Next to the time and absorbance columns, make a third column (Column C) containing the experimental DNPP concentrations. This column should be calculated in Excel by entering a formula for the Beer-Lambert law that references the measured absorbance and the cell containing the value for **ε**. Give this column a heading name such as “Experimental [DNPP]”.
4. Make a fourth column (Column D) using the appropriate model equation (10c, 12c, or 14c, above) and referencing the cells containing values for t, [DNCB]0, [Pip]0, and k. This equation will thus give you a theoretical result for the DNPP concentration at time t based on your guess for the rate constant, k. Give this column a heading name such as “Theoretical [DNPP]”.
5. In the fifth column (Column E), enter a formula to calculate the square of the difference between Columns C and D. For example, the formula entered into cell E2 would be “=(C2-D2)^2”. These values are thus the squares of the errors between the experimental concentration and the theoretical concentration (based on the k value guessed). If all of the data points aligned perfectly with the curve given by the model equation, all of these errors would be zero. The further the data is from the curve, the more positive the squares of the errors are. Give this column a heading name such as “Squared Errors”.
6. In a nearby cell, enter a formula to calculate the sum of all of the squared errors in Column E. This will give a non-negative result that measures the overall deviation of the data from the model equation. Changing k will change the theoretical concentrations calculated in Column D, and thus this sum.
7. Plot both the experimental DNPP concentration (Column C) and the theoretical concentration (Column D) as a function of time (Column A) *on the same graph*. Give the curves different styles or colors to distinguish them and see how well they overlap. Since you have only estimated a value for k, they will probably be very different.
8. Invoke the Solver add-on (usually found on the *Data* tab in Excel) as described in the *J. Chem. Ed.* article and use it to minimize the sum of the squares of the errors by varying the parameter k. In the Solver window, in the field for “Set Objective” you will enter the cell containing the sum of the squared errors, choose the “Min” radio button, and enter the cell containing the value of k in the field that says “By Changing Variable Cells”. When you click ok, the program will run for a few seconds and then a window will open up. ***Make sure you read this information window, as it will tell you if Solver was able to find a solution or not****.* If it works, you can click “OK” and it will replace the value of k in your spreadsheet with the new, optimal value it has calculated. If you just close the window, it will throw the solution away and you’ll only see your original guess again. Try a few different initial guesses for k and make sure that Solver converges to this same result (or very, very close) every time. Make a note of the value for k found, and look at how well the two curves you made in the previous step now overlap.
9. If you used your experimental value for **ε**, replace that value in the cell with the value from the manual, and re-run Solver to find a new k. Compare this new k to the first k you found. Which result gives a better overlap of the two curves in the graph?
10. Repeat this procedure for each of the three reaction conditions using the relevant model equation.

## Lab Report

Your lab report should consist of the following parts:

* **Title, Author and Date**
* **Introduction and Objective** – A paragraph describing what we hope to find in this experiment, and how.
* **Experimental Procedure** – This should be a very brief general outline of the procedure, written out as a paragraph or two. Give the make and model for any major instruments you used, as well as any important settings.
* **Results & Discussion** – This should include the following:
  + Graph of your calibration curve (if applicable) with the equation and the value of **ε**.
  + Calculate the initial concentrations of the reactants for each of the reaction conditions.
  + 3 graphs for the three different reaction conditions. Each of these three graphs should show the experimental data curve and the curve corresponding to the relevant model equation, both clearly marked in a legend. All of your graphs should also have properly labelled axes and a caption briefly describing what they show.
  + Determine which is the limiting reactant in each case, and use that to find the expected final concentration of DNPP as . Indicate whether that value agrees with your graph.
  + Show that equation **10c** (above) has the proper limiting behavior as . In other words, what is the final concentration of DNPP according to equation **10c**, and does that make sense in terms of the stoichiometry?
  + Include a couple of paragraphs describing your results, giving the calculated value of **ε** and the values of k for each reaction *with proper units*. For this discussion, comment on whether the rate constants for all three cases are the same, and how that does or doesn’t meet your 4 expectations. Also comment on how well the theoretical and experimental concentration curves match up for each case, and what that says about the accuracy of your value of k.
  + If you repeated the analysis using another extinction coefficient (**ε**) then give those graphs as well, and comment on which set is better and why you think that might be.
  + For the calibration curve (if done) give a quantitative estimate for the uncertainty in the measured absorbances, the solution concentrations, and the value of **ε** obtained.
  + For the kinetic runs, give quantitative estimates of the initial solution concentrations, the measure absorbances, and the concentration calculated from those using Beer’s law (*i.e.* the error in Column C). In other words, how do the errors in the initial concentrations and in **ε** propagate through to the error in the experimental concentrations as a function of t?
  + What is the most significant source of error? Estimate the error in the values of k you obtained.
  + There are two important factors to consider in choosing a nucleophile (or base) for a reaction like this – steric bulkiness and electron donating ability. Considering the specific mechanism here (and the RDS), discuss how these two factors will affect the rate of reaction. Give some ideas for reaction conditions (different nucleophiles, solvents, etc.) that could decrease the rate. Give some ideas for conditions that could speed it up.
* **Conclusion**
* **References**
* **Appendix** – At the very end of your report, include examples of any calculations that you did by hand. Provide digital copies of the Excel (or other) files that you used to generate your graphs.