Experiment 3: Chemical Kinetics[1]

Purpose: Determine the rate law for the reaction of the dye crystal violet with hydroxide.
Reading: Olmstead and Williams, *Chemistry*, sections 13.3 and 13.4.

Introduction

The reaction of crystal violet with hydroxide is:

This reaction can be represented as:

$$CV^+ + OH^- \rightarrow CVOH$$
$$\text{purple} \qquad\qquad \text{colorless}$$

The kinetics of this reaction can be monitored spectrophotometrically by observing the decrease in absorbance of crystal violet, CV, with time. The rate law in general form is:

$$\text{rate of disappearance of CV} = k\,[CV]^x\,[OH^-]^y \qquad\qquad (1)$$

where x and y are the reaction order with res
oxide is determined in this experiment. Next week the order with respect to CV is determined.

   The rate of the reaction is equal to the negative of the change in concentration of crystal violet divided by the time interval, where $\Delta[CV]$ is the change in CV concentration and Δt is the time between measurements. Using finite differences is an approximation to the rate because the rate changes over the time interval. However, in this experiment the *initial rate* of the reaction is determined. Initial rate experiments are performed so that the concentration of reactants remains within 1% of their starting values:

$$\text{rate}_o = \frac{-\Delta[CV]}{\Delta\text{time}} = k\,[CV]_o^x\,[OH^-]_o^y \qquad\qquad (2)$$

The initial rate, rate_o, is determined by the negative of the slope of the concentration versus time curve at the beginning of the reaction. Beer's Law allows calculation of the concentration of crystal violet using the experimentally determined value of ε_{max} at the wavelength of maximum absorption, λ_{max}:

$$[CV] = \frac{A}{(1\text{ cm})\varepsilon_{max}} \qquad\qquad (3)$$

The first step in this analysis will be to determine the wavelength of maximum absorbance for crystal violet and the corresponding molar absorption coefficient at that wavelength. This wavelength will be used to monitor the disappearance of crystal violet throughout the course of the experiment.

In an initial rate study, the concentration of one reactant is varied while leaving the concentration of the other reactant constant. In this experiment the concentration of hydroxide, $[OH^-]$, is varied allowing determination of y in equation 2. Because this reaction has two reactants and is likely to follow a complicated mechanism, the reaction orders may not be simple whole numbers. Initial rate studies work well with non-integer order. Taking the logarithm of both sides of the equation 2 gives:

$$\log (rate_o) = \log (k) + x \log [CV]_o + y \log [OH^-]_o \qquad (4)$$

In this experiment, the term $x \log [CV]_o$ is constant because $[CV]_o$ is held constant. The term $\log (k)$ is also constant since the rate constant, k, is characteristic of each reaction and therefore constant. A plot of $\log (rate_o)$ vs. $\log [OH^-]_o$ gives a straight line with a slope of y, which is the order with respect to OH^-. Alternatively natural logarithms, $\ln x$, can be used.

Example Analysis

Using the kinetic data provided below for the reaction, $A + B \rightarrow C + D$, determine the order of the reaction with respect to A, determine the order of the reaction with respect to B, write the rate expression for the reaction, and calculate the rate constant.

Experiment	[A] (M)	[B] (M)	Rate (M/s)
1	0.100	0.100	0.0101
2	0.100	0.200	0.0206
3	0.100	0.400	0.0403
4	0.200	0.500	0.203
5	0.300	0.500	0.452
6	0.400	0.500	0.841

Answer: (1). With Rate $= k [A]^x [B]^y$, to determine "x", the data from experiments 4-6 are used, because [A] varies while [B] remains constant in these experiments. A plot of log(rate) vs. log [A] for experiments 4-6 gives a slope of about 2, Figure 1. The uncertainties in the concentrations and rates are around 2%. Therefore x = 2, within experimental uncertainty.
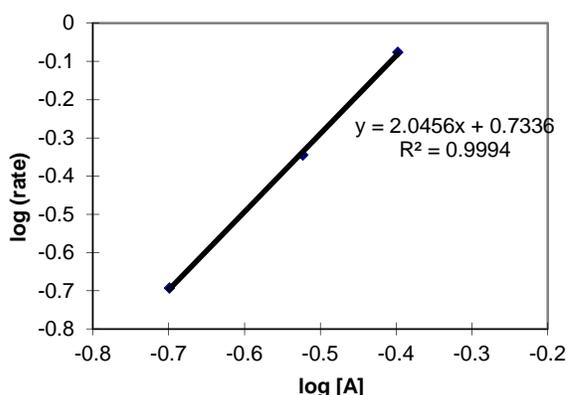

Figure 1: Initial rate determination of the order with respect to A. The plot is the log (rate) versus log [A].

(2). The value of "y" can be determined by plotting log (rate) vs. log [B] for experiments 1-3. This yields a slope of about 1, Figure 2. Therefore y = 1, within experimental uncertainty.
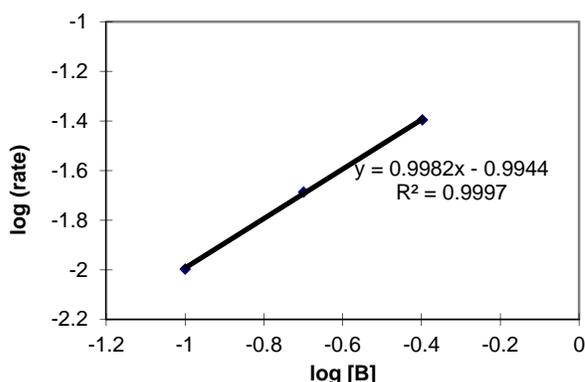
Figure 2: Initial rate determination of the order with respect to B. The plot is the log (rate) versus log [B].

(3). The rate law is correspondingly given as: Rate = k $[A]^2$ [B].

(4). The rate constant can be determined from any single experiment. For example, using the data in experiment 3:   0.0403 M/sec= k $(0.100 M)^2$ (0.400 M), or k = 10.1 $M^{-2} s^{-1}$.

Procedure

   The first step in experiment is to determine the wavelength of maximum absorbance, λ_{max}, of CV and the corresponding molar absorption coefficient, ϵ_{max}. Please consult the "SpectroVis Plus Spectrophotometers with Vernier Data Acquisition Software Instructions" Sections I-IV, which will be available in the laboratory, for detailed instructions on the use of the instrument.
   You will use automatic micropipettors for the precise and accurate delivery of small volumes. There are two sizes of Finnpipettes® in the lab: 40-200 µL (yellow), and 200-1000 µL (blue). The numerical labels on the micropipettors refer to the maximum volume **in microliters** (µL) that can be delivered; e.g., the yellow ones can dispense a maximum of 200 microliters. Never dial a pipettor past the maximum volume. The 200-1000 µL pipettors take blue tips; the 40-200 µL take yellow tips. To draw the sample into the pipette tip, push the button down to the first notch, immerse the tip in the sample, and slowly release the button. Check the tip to make sure no air bubbles have been captured. To dispense the sample, push the button all the way down.

A. Preliminary Experiment to Determine λ_{max} and ϵ_{max}

1. Calibrate the spectrophotometer using water as the reference.

2. Keeping your total solution volume 3.00 mL in all cases, take the absorbance of a solution of CV in water. A stock solution of 1.00 x 10^{-4} M CV will be available. Prepare a dilution with the maximum absorbance value below 1.5. Several dilutions may be necessary to obtain a good spectrum that is on-scale, but you can collaborate with another student to determine an appropriate concentration. Be as accurate as possible when making up the solution, as you will use this concentration to calculate the molar absorption coefficient.

2. Once you find an appropriate dilution, make sure that you record both λ_{max} and the absorbance at that wavelength on your own spectrophotometer. Wavelengths and absorbances may differ from spectrophotometer to spectrophotometer.

3. Use Beer's Law to calculate the value of ε_{max} for CV based on the measured absorbance and the concentration (the path length is 1 cm). Rather than a multipoint standard curve, one data point is used to determine the molar absorption coefficient to save time.

B. Kinetics Experiments with Crystal Violet Constant, Variable Hydroxide

In this set of experiments the volume of sodium hydroxide, NaOH, is varied while keeping the volume of crystal violet constant.

1. Set up an absorbance vs. time run on the spectrophotometer at the experimentally-determined λ_{max}, and collect data every 4 seconds for 90 seconds using the provided Vernier instructions. Reaction rates usually depend on temperature, as a result record the room temperature. Again, the total volume of each trial should be 3.00 mL. Your first kinetics trial should contain a volume of CV that gives an absorbance of about 1.0-1.5 (based on your findings from **Part A**). Plan to add the same volume of 0.100 M NaOH as you have of CV, but don't add the NaOH yet! Add the crystal violet to your cuvette, then the appropriate volume of water that will make your final volume 3.00 mL (be sure to account for the NaOH that you will add). Finally, add the NaOH, mix quickly with the pipette tip, and immediately start collecting kinetic data with the spectrophotometer. The absorbance should drop as the CV decolorizes in the presence of base. When data collection is complete, save the data using Save As… from the File menu as described in the SpectroVis Plus Instructions. Determine the initial rate as described in Part C. Data Analysis, below.

2. Set up another 3.00 mL reaction with less hydroxide than in the first trial (make sure that you record the exact amount). Again, add the same volume of crystal violet as last time (this amount will remain constant in this whole series of trials), water (make sure that you increase the volume of water to make up for the decrease in the amount of hydroxide). Add the 0.100 NaOH, and collect kinetics data again and save this data.

3. Repeat until you have five kinetics trials, each with a total volume of 3.00 mL, a constant volume of crystal violet, and a known, varying amount of hydroxide.

C. Initial Rate Study Data Analysis
1. Observe the data table in the Vernier software. The first column should be time in seconds; the second column, the absorbance.

2. Using the following instructions, insert a new column for the CV concentration, using the absorbance data and your molar absorption coefficient calculated in **Part A** to determine these values ($c = A/\varepsilon$; path length is 1 cm). Choose New Calculated Column from the Data menu. Enter "[CV]" as the Name, "[CV]" as the Short Name, and set the unit to "M." Enter the correct formula for the column into the Expression edit box: to do this, select "Absorbance at…" from the Variables (columns) list. (You may need to repeat this step.) Then type in "/" and your absorption coefficient. In the Equation edit box, you should now see displayed something like: "A"/1.234e4. Click ⬚ Done ⬚. Click on the y-axis label in the plot window. Choose [CV] and uncheck any other boxes. The crystal violet concentration should now be plotted as a function of time. You may need to increase the displayed number of decimal places in the concentrations. To

change the number of displayed decimal places, right click on the heading of the concentration column in the spreadsheet. Choose Column Options then [CV]. In the Calculated Options window, that then appears, change Displayed Precision to 9. Click Done.

3. Autoscale the y-axis by clicking on ![A icon]. Highlight the initial portion of the time-course curve using the mouse. To do the linear curve fit, click the Linear Fit button, ![Fit icon]. The slope of the best-fit line gives the initial rate of the reaction. Report **four digits** in the slope to avoid round-off error.

4. Repeat your initial rate determinations for each of the five kinetics trials that you perform in lab today. You now have a set of data that contains a rate for each initial hydroxide concentration.

5. Plot log(rate) vs. log [OH⁻]$_{initial}$ in Excel. You can also use natural logarithms, ln(rate) vs. ln [OH⁻]. The slope of the best-fit line is the reaction order for OH⁻ ["y" in the rate law equation (2) above]. Print copies of the Excel spreadsheet for inclusion in the lab notebooks of each partner. Print copies of the plot for your lab reports.

Literature Cited:
Adapted from <u>Chemistry The Central Science, Laboratory Experiments</u>, 6th Edition, by J.H. Nelson and K.C. Kemp and <u>Laboratory Inquiry in Chemistry</u>, by R. C. Bauer, J. P. Birk, and D. J. Sawyer.

LABORATORY REPORT: Use the Report form for this experiment.

Use complete sentences, the proper number of significant figures, and include units. Equations, reactions, tables, and diagrams can be written by hand. The sections of your report are:

Introduction (2-sentence maximum): State the scientific purpose of the experiment. Describe the method you will use, in a general sense. Do not discuss the experimental procedure details or data analysis steps. Don't include pedagogical goals (e.g to teach us how to use…..).

Procedure: A one-sentence description of the method that you used to determine the order of the reaction with respect to hydroxide is:

   "The order of the reaction with respect to hydroxide was determined spectrophotometrically by an initial rate study with varying hydroxide concentration.[1]"

The reference is to the lab write-up on the CH142 On-line Laboratory Manual. List any changes. Give the cell material and path length and the manufacturer and model of the spectrophotometer.

Results: Give the temperature of the kinetics determinations. Report the CV concentration and absorbance for the solution you used to obtain the molar absorption coefficient. Report the molar absorbance coefficient. Use the table of uncertainties in the "Error Analysis Example" handout to determine the proper number of significant figures for the molar absorbance coefficient. Give your results in tabular form for the concentrations and initial rates for the determination of the order with respect to hydroxide. Include the logarithms of the hydroxide concentration and the initial rate in the table. Report the slope and intercept and associated uncertainties of the curve fit for the order determination. Attach the plot used for the initial rate study. Make sure the axes are

labeled (which can be handwritten). Mention any student errors that may have caused problems in the determinations. All tables and plots should have a table or figure number and a caption. Refer to this Table or Figure with an explicit reference (e.g. see Figure 3) in the text of this section.

Discussion:
(a). Purpose accomplished: Restate the purpose of the experiment, but as completed goal.
(b). Write the reaction that you are studying (you can use the acronyms CV^+ and CVOH).
(c). Give the final results for the order with respect to hydroxide including the uncertainty.
(d). Consider the effect of random and systematic errors on the order of the reaction.
   (i). The standard deviations of the slope and intercept are the expression of the observed precision of the order of the reaction. Discuss if the order is sufficiently close to an integer value or a simple rational fraction (e.g. ½, ¾, etc.), within experimental error. Name the predominant random error in the measurements (see the table in the "Error Analysis Example" handout that is posted on the lab Web site).
   (ii). Suggest a source of systematic error. Remember that student mistakes are neither random nor systematic errors; student mistakes are just student mistakes. Systematic error always causes an error in the same direction, which is always low or always high. What effect does the source of systematic error have on the final results? (For example, does the systematic error cause curvature in the plots or increase or decrease the value determined for the reaction order?)
(e). To summarize the experiment answer the following questions:
   (i). In the kinetics studies, you always brought the total volume in the cuvette to 3.00 mL. Why is constant volume necessary?
   (ii). Is the order of the reaction with respect to hydroxide the same as the stoichiometry? Is the order of the reaction necessarily the same as the stoichiometry?
   (iii). What is the change in the rate of the reaction if the concentration of hydroxide is increased by a factor of two.

Literature Cited: Give all literature cited, numbered according to the references in the body of your report. See the previous lab reports for the format of the reference to the on-line General Chemistry lab manual. Include last accessed dates for on-line resources.

Attach the plot used for the initial rate study.