Experiment

REACTION OF CRYSTAL VIOLET WITH NaOH A KINETICS STUDY with Activation Energy Calculation

The CCLI Initiative

Computers in Chemistry Laboratory Instruction

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LEARNING OBJECTIVES

The objectives of this experiment are to . . .

- study the rate of reaction of crystal violet with NaOH using the ***MicroLAB*** interface colorimeter.
- determine the order of reaction with respect to both reactants.
- calculate the rate constant for the reaction at room temperature.
- Determine the activation energy, E_a, for the reaction from supplied data. (Students will not take this data since most general chemistry labs do not have the necessary equipment for doing these experiments.)

BACKGROUND

Reaction chemistry

Chemical kinetics is the study of reaction rates. In this experiment, the kinetics of the reaction of crystal violet with NaOH will be studied using the ***MicroLAB*** interface colorimeter to monitor concentrations as a function of time. The stoichiometry of the reaction is shown in Figure 1 on the next page.

All of the reactants and products in Figure 1 are colorless except for crystal violet which has ϵ_{max} at 590 nm and is an intense purple color. Thus, during the course of the reaction, the color of the reaction mixture becomes less and less intense, ultimately becoming colorless when all of the crystal violet has been consumed.

The color of crystal violet is due to the extensive system of alternating single and double bonds which extends over all three benzene rings and the central carbon atom. This alternation of double and single bonding is termed *conjugation*, and molecules which have extensive conjugation are usually highly colored. Trace the conjugation in the structure of crystal violet and note that in the reaction product, the three rings are no longer in conjugation with one another, and hence, the material is colorless.

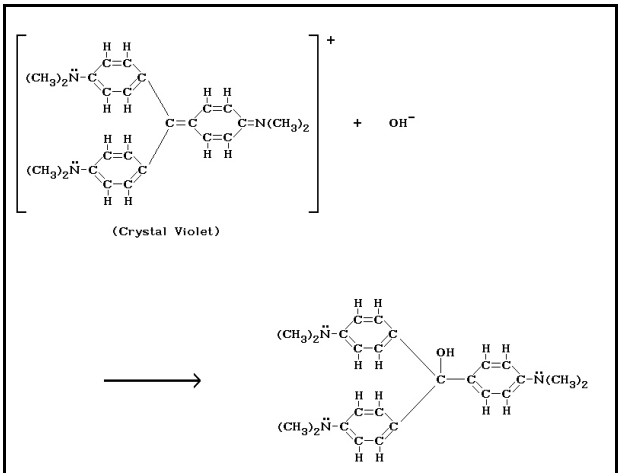


Figure 1. Stoichiometry of the Crystal Violet reaction.

Kinetic rate laws

The rate of the reaction of crystal violet with NaOH is given by the generalized rate expression

$$\text{Rate} = k[OH^-]^x [CV]^y \qquad (1)$$

In Equation (1), **k** is the rate constant for the reaction, **CV** is an abbreviation for crystal violet, $C_{25}H_{30}N_3+$, **x** is the order of reaction with respect to OH^- , and **y** is the order of reaction with respect to CV. The values of x and y will be determined experimentally. Possible values are 0, 1, or 2 (zero order, first order or second order).

In the experiment you will perform, the $[OH^-]$ will always be much greater than [CV]. Thus the *change* in $[OH^-]$ has a negligible effect on the initial $[OH^-]$. For this reason, $[OH^-]^x$ can be treated as a constant and Equation (1) can be rewritten

$$\text{Rate} = k'[CV]^y \qquad (2)$$

where $k' = k[OH]^x$, k' is termed a *pseudo* rate constant.

The integrated form of the rate law depends on the order of reaction with respect to the concentration of CV. The integrated rate laws for y = 0, 1, and 2 are given in Equations 3 through 5.

$$[CV]_t = -k't + [CV]_o \quad \text{(zero order)} \qquad (3)$$

$$\ln[CV]_t = -k't + \ln[CV]_o \quad \text{(first order)} \qquad (4)$$

$$\frac{1}{[CV]_t} = +k't + \frac{1}{[CV]_o} \quad \text{(second order)} \qquad (5)$$

In Equations 3 - 5, $[CV]_o$ is the concentration of crystal violet in the reaction mixture at time zero before any reaction occurs; $[CV]_t$ is the concentration at any time during the course of the reaction. Equations 3, 4 and 5 are each an equation of a straight line. If a plot of $[CV]_t$ *versus* time is linear, y = 0 and the reaction is zero order in CV. Similarly, a linear plot of $\ln[CV]_t$ *versus* time indicates a first order reaction in CV, and a linear plot of $1 / [CV]_t$ *versus* time indicates second order behavior. In every case, the slope of the resulting straight line would be the pseudo rate constant, k'. All three of these plots will be made to determine the actual value of y and the value of k'.

In order to do the graphing just described, we will need to have data showing how the concentration of CV changes with time. This data will be obtained using the ***MicroLAB*** interface colorimeter, using the **Kinetics** program at 590 nm wavelength. The light from the LED will pass through the solution containing CV and NaOH and then fall on the system photocell. The photocell circuit will then produce a current in microamps (I) which is proportional to the light intensity striking the photocell surface. This current is divided by the current obtained with the blank (I_o), and is termed **Transmittance.**

Solutions of crystal violet obey Beer's Law. Thus, the relationship between the observed current and the concentration of CV is given by

$$A_t = -\text{Log}(I_t/I_o) = \epsilon bc \qquad (6)$$

In Equation (6), $\mathbf{A}_t$ is the reaction solution absorbance at any time t; I_o is the photocell current observed for pure water; $\mathbf{I}_t$ is the current observed for the CV reaction mixture at time t, ϵ is the molar absorbtivity of crystal violet; **b** is the cell path length (2.54 cm for the ***MicroLAB*** colorimeter); and **c** is the molar concentration of CV at time t, $\mathbf{[CV]}_t$. Since ϵ and b are constants, it should be clear that the absorbance, $\mathbf{A}_t$, is directly proportional to the concentration of CV at any time during the reaction and can be used in place of $[CV]_t$ in preparing the graphs described above.

SAFETY PRECAUTIONS

Crystal violet solutions may cause skin and eye irritation. Sodium hydroxide solutions are caustic and will cause skin burns if not immediately washed with copious amounts of water. Safety goggles must be worn at all times. As usual, wash hands with soap and water before leaving the laboratory.

BEFORE PERFORMING THIS EXPERIMENT . . .

...you will need a ***MicroLAB*** **Kinetics** program which will measure Transmittance and convert it to Absorbance.

EXPERIMENTAL PROCEDURE - PART I

Measurements

Open the ***MicroLAB*** **Colorimeter Experiment** program by selecting it, then clicking **OK**. Enter the experiment filename when requested. Data will come from the interface. Be sure the ***MicroLAB*** interface is connected to the computer and turned on. From that point follow the procedures listed below.

1. Before beginning kinetic measurements, the current reading for pure H_2O, I_o , will be obtained. Fill a clean, rinsed colorimeter vial about ¾ full with distilled H_2O, dry the outside of the cell thoroughly with a KimWipe being careful to remove any finger prints, insert the cell into the colorimeter and place the cap. *Note carefully and mark the positioning of the cell for future reference.*

2. Click on the **Blank** button. The program will now measure I_o for each of the 10 wavelengths, divide each by itself and multiply by 100 to get the 100% transmittance value.

3. Empty the vial and dry it thoroughly inside and out.

4. Set the **Time Interval** to 5 seconds, and the **Number of Points** to 300.

5. Using the buret provided, dispense exactly 9.00 ml of 1.50×10^{-5} *M* crystal violet solution into a clean, *dry* colorimeter vial

6. Using the calibrated plastic dropper provided, add 1.0 ml of 0.050 *M* NaOH to the CV solution as rapidly as possible without splashing. Cap the vial, rotate it twice to mix the CV/NaOH , place the cell in the colorimeter in *exactly* the same manner as was used for the blank and cap the colorimeter. All of the operations in this step should be completed as quickly as possible in order that the first measurement will be made as close to the beginning of the reaction as possible.

7. As soon as the vial is in place and capped, press the **Start** button, the program will take readings at 5 second intervals for a period of 60 minutes and then automatically stop. If there is a need to stop data collection prior to the end of 60 minutes, click on the **Stop** button and the program will terminate. It 300 points are insufficient, increase the number of points.

8. When the reaction is completed, save the file with the name *CV.kin.XM.DH*, where CV.kin defines the type of data, XM indicates the NaOH concentration (0.10 or 0.05, etc.), and DH is the student's initials.

EXPERIMENTAL PROCEDURE - PART II

Measurements

Recall that the k' just obtained is a pseudo rate constant, whose value depends upon the concentration of OH^- , i.e., $k' = k[OH^-]^x$. In this part of the experiment, the value of *x* will be determined as well as the value of the true rate constant, k.

In Part I of the experiment, 9.00 ml of 1.50×10^{-5} *M* crystal violet and 1.0 ml of 0.050 *M* NaOH were combined to form the reaction mixture. A second kinetic run will now be made in exactly the same way *except* that the concentration of NaOH will be doubled to 0.10 *M*.

Repeat each of the six experimental steps four through eight using 1.0 ml of 0.10 *M* NaOH in place of 0.050 *M* NaOH.

CALCULATION OF Ea, PART III

Attached hereto as part of the Appendix is the data for the crystal violet experiment carried out in triplicate at 25, 35, 45 and 55 °C. You are to do the following:

1. Determine the mean (average) "k" value and the associated standard deviation for the triplicate results for each temperature.

2. Plot ln(k) vs. 1/T (in Kelvin)

3. Calculate the activation energy (Ea) for the hydrolysis reaction of crystal violet.

DATA ANALYSIS: PART I

1. Retrieve your ***MicroLAB*** data file under the name you saved it.

2. Click on the **Linear - Zero Order** tab at the bottom of the graph. If the reaction you just did was zero order on the concentration of crystal violet, this will show a horizontal straight line. Print this screen as follows:
   a. Press **Ctrl-Print Screen** to capture the screen image.
   b. Open Wordpad by clicking **Start > Programs > Accessories > Wordpad**.
   c. Press **Ctrl-V** to paste the screen image into Wordpad.
   d. Press **Ctrl-P** to print the item.

3. Repeat step (2), clicking on the **Logarithmic - First Order** tab. A linear graph in this instance would indicate first order dependence on the concentration of crystal violet. Print this screen also.

4. Finally, click on the **Inverse - Second Order** tab to determine if the reaction is second order in crystal violet. Also print this screen

5. With the linear plot you have identified the value of y, i.e., the order of the reaction with respect to CV. Record the value of y in your lab book. The slope of the straight line at the top of the linear regression plot is the best value of k'. Record this value with proper units and to the correct number of significant figures in your lab book. Attach a copy of your printout to your lab book.

DATA ANALYSIS, PART II

1. Repeat data treatment steps 1 through 6 above, and again record the value of k' in your Lab Book.
2. From the ratio of the two k' values to one another, determine the order of reaction with respect to OH^- (the value of x). Clearly indicate your reasoning in evaluating x.

   Note: The value of x should be an integer. If your value is not an integer, it is probably due to experimental error (probably in measuring and adding the NaOH solutions). If necessary, round your value to the nearest integer.

3. Calculate the value of the true rate constant k using each of the k' values. In the calculations, the concentrations of OH will have to be adjusted to account for the dilutions which occurred when the NaOH and crystal violet solutions were mixed. Finally, average the two k values obtained. Again, be sure to watch significant figures and use proper units.

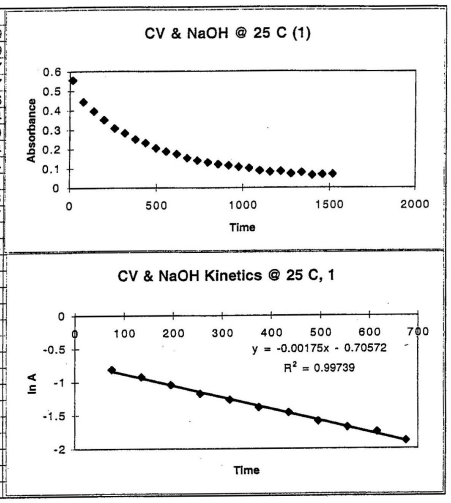
4. Using the linear plot from your first kinetics experiment, calculate the value of the molar absorptivity, ~, for crystal violet under these experimental conditions. Include units in your answer. The colorimeter vial is 2.54 cm thick. (**Hint:** The intercept of your linear plot is important.)

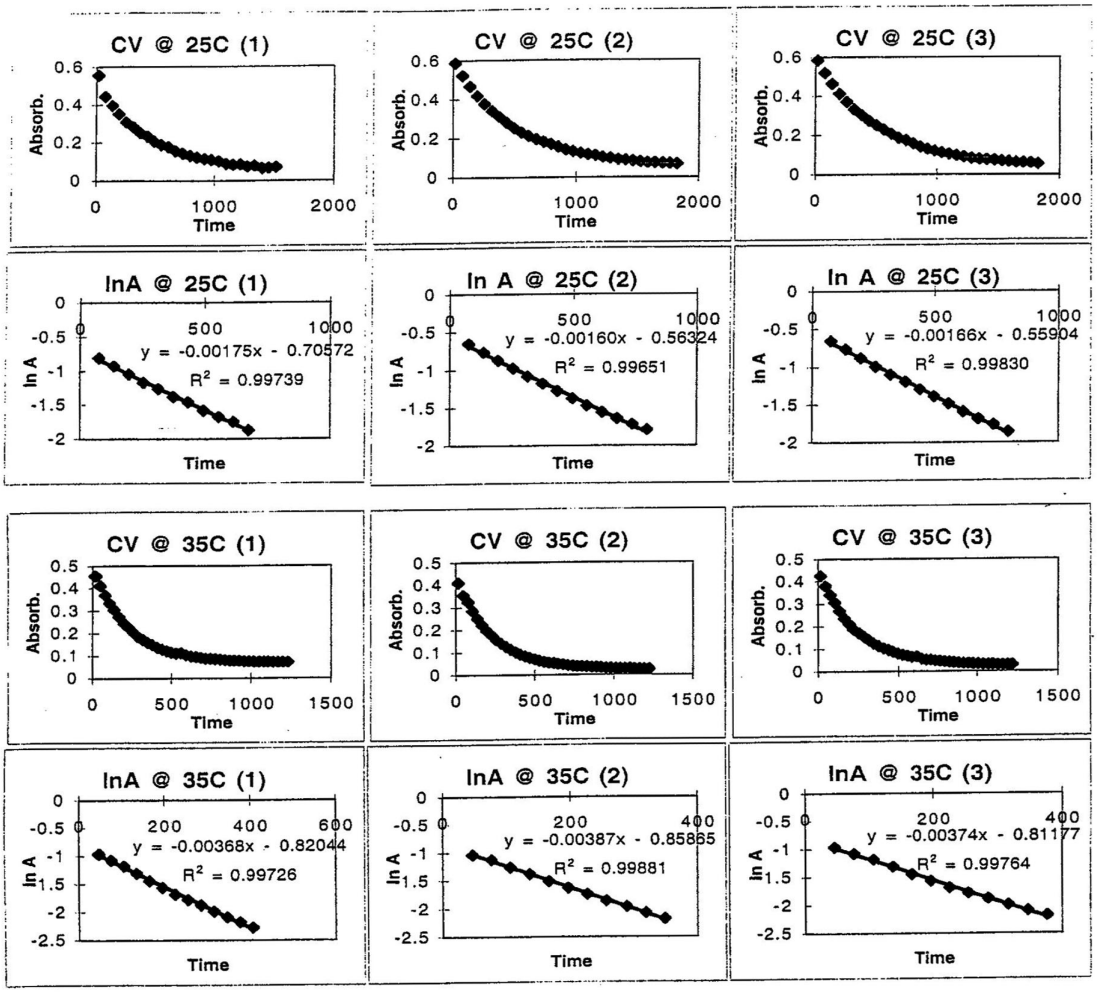
APPENDIX DATA FOR E_a CALCULATIONS

The following data was taken by two chemistry students using a special spectrophotometer set up which could control the temperature and monitor the Absorbance at the appropriate wave length. The rate was then measured in triplicate at 25, 35, 45 and 55 °C, and the raw data was plotted on a graph of Absorbance versus time. The natural logarithm of the Absorbance was taken, and this was also plotted against time in order to determine the rate constant. An example spreadsheet with graphs is attached to illustrate this, as well as two pages of the graphs for each temperature run. The three rate constants for each of the temperatures are given in the table below, as given on the two pages of graphs. Your task is to find the average and standard deviation of the triplicate measurements for each temperature, then to determine the activation energy of the reaction of the crystal violet with the sodium hydroxide.

Run / Temp.	25 °C	35 °C	45 °C	55 °C
Run 1	-0.00175	-0.00368	-0.00431	-0.00537
Run 2	-0.00160	-0.00387	-0.00437	-0.00727
Run 3	-0.00166	-0.00374	-0.00438	-0.00961
Mean value				
Standard dev.				

Time (sec)	Absorbance	ln(b)
15.058	0.555	-0.58879
75.2	0.443	-0.81419
135.257	0.395	-0.92887
195.415	0.351	-1.04697
255.527	0.308	-1.17766
315.583	0.281	-1.2694
375.624	0.250	-1.38629
435.686	0.231	-1.46534
495.724	0.204	-1.58964
555.925	0.186	-1.68201
616.117	0.173	-1.75446
676.265	0.152	-1.88387
736.393	0.140	-1.96611
796.565	0.129	-2.04794
856.657	0.120	-2.12026
916.719	0.113	-2.18037
976.719	0.106	-2.24432
1036.776	0.100	-2.30259
1096.973	0.086	-2.45341
1157.034	0.080	-2.52573
1217.219	0.083	-2.48891
1277.401	0.071	-2.64508
1337.61	0.077	-2.56395
1397.672	0.063	-2.76462
1457.721	0.065	-2.73337
1517.752	0.068	-2.68825





CRYSTAL VIOLET KINETICS WITH NaOH @ 25, 35, 45 and 55 C