

Chemistry 213

A KINETIC STUDY: REACTION OF CRYSTAL VIOLET WITH NaOH

LEARNING OBJECTIVES

The objectives of this experiment are to . . .

- study the reaction rate of crystal violet with NaOH using a Spectronic 20 spectrometer.
- observe that reactant concentration affects reaction rate
- determine the reaction order with respect to each of the reactants.
- calculate the room temperature rate constant for the reaction.

BACKGROUND

Reaction Chemistry

Chemical kinetics is the study of reaction rates. In this experiment, the kinetics of the reaction between crystal violet and NaOH will be studied. A Spec-20 spectrophotometer which will be used to monitor the crystal violet concentration as a function of time. The reactant and product structures and the reaction stoichiometry are shown in Figure 1 on the next page.

All of the reactants and products shown in Figure 1 are colorless except for crystal violet which has an intense violet color. Thus, during the course of the reaction, the reaction mixture color becomes less and less intense, ultimately becoming colorless when all of the crystal violet has been consumed.

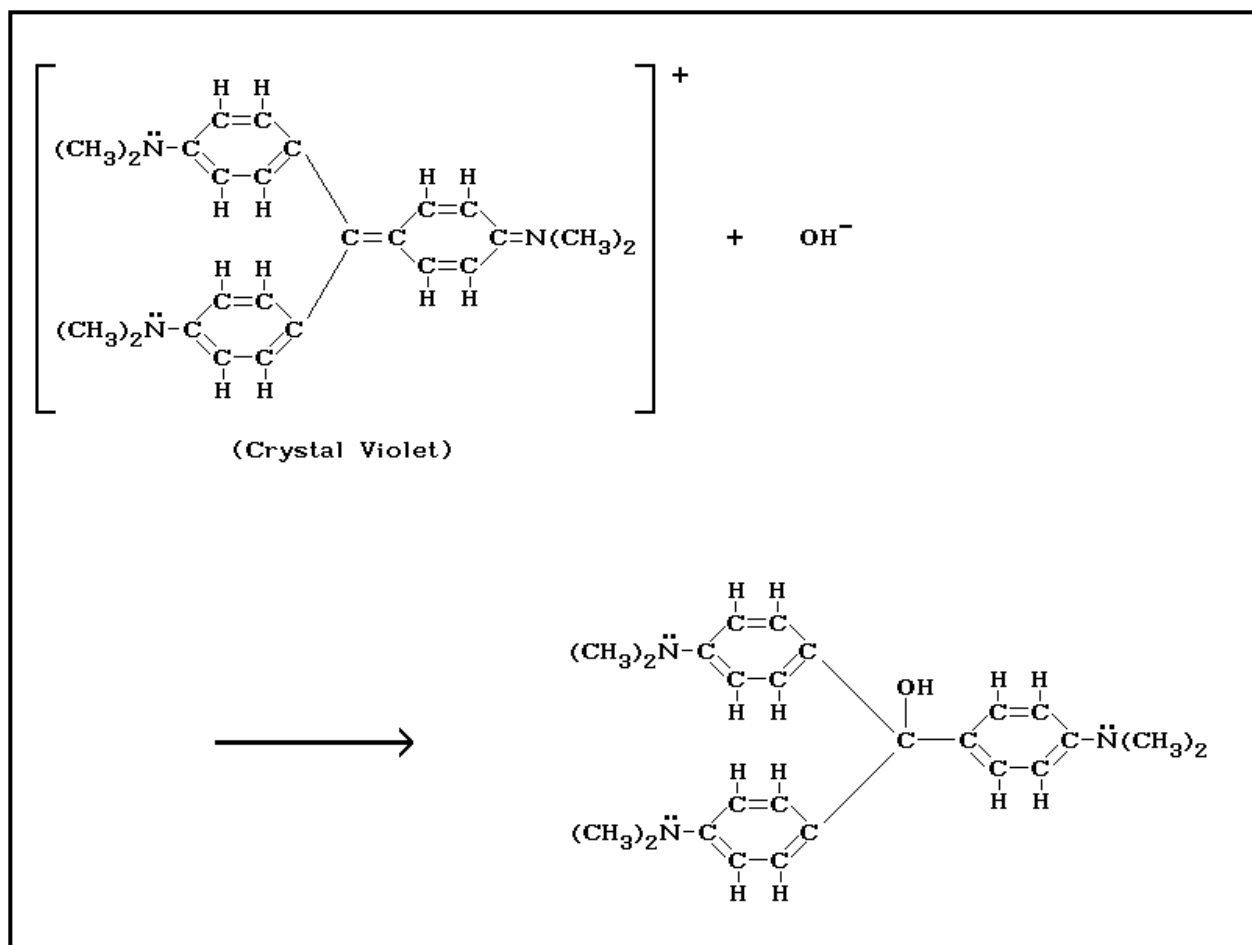


Figure 1. Stoichiometry of the Reaction between Crystal Violet and NaOH.

The crystal violet color 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 crystal violet structure and note that in the reaction product, the three rings are no longer in conjugation with one another, and hence, the material is colorless.

Kinetic Rate Laws

The rate of the crystal violet/NaOH reaction is given by the following generalized rate law.

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

In equation 1, **k** is the rate constant for the reaction, **CV** is an abbreviation for crystal violet, $\text{C}_{25}\text{H}_{30}\text{N}_3^+$, **x** is the reaction order with respect to OH^- , and **y** is the reaction order with respect to CV. The values of **x** and **y** will be determined experimentally. Possible **x** values are 1 or 2 (first order or second order). Possible **y** values are also 1 or 2.

In this experiment, the initial $[\text{OH}^-]$ is made much greater than the initial $[\text{CV}]$. Thus, the $[\text{OH}^-]$ change, during the time that the CV is consumed, is negligible. For this reason, $[\text{OH}^-]^x$ can be treated as a constant and Equation 1 can be written as follows,

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

where $k' = k [\text{OH}^-]^x$. k' is termed a *pseudo* rate constant.

The integrated form of the pseudo rate law (2) depends on the reaction order with respect to CV. The integrated rate laws for $y = 1$ and 2 are given in Equations 3 and 4. Compare each with the general form of a linear equation, $y = mx + b$.

$$(3) \quad \ln [\text{CV}]_t = -k' t + \ln [\text{CV}]_0$$

$$(4) \quad \frac{1}{[\text{CV}]_t} = k' t + \frac{1}{[\text{CV}]_0}$$

In Equations 3 and 4, $[\text{CV}]_0$ is the concentration of crystal violet in the reaction mixture at time zero, before any reaction has occurred; $[\text{CV}]_t$ is the concentration at any time t during the course of the reaction. If a plot of $\ln [\text{CV}]_t$ versus time is linear, $y = 1$ and the reaction is first order in CV. Similarly, a linear plot of $1/[\text{CV}]_t$ versus time indicates a second order reaction in CV. Only one of these plots will be linear. For the one that is linear, the resulting straight line slope (its absolute value) equals the pseudo rate constant, k' .

In order to do the graphing just described, we need to have data showing how the CV concentration changes with time. This data will be obtained using a Spectronic 20 spectrometer.

Crystal violet solutions obey Beer's law. Thus, the relationship between percent transmittance and the CV concentration is given by:

$$(5) \quad A_t = -\log\left(\frac{\%T}{100}\right) = \epsilon bc$$

In Equation 5, A_t is the reaction solution absorbance at any time t ; ϵ is the CV molar absorptivity, $5.0 \times 10^4 \text{ L}/(\text{cm mol})$; b is the cell path length (1.00 cm); and c is the CV molar concentration at time t , $[\text{CV}]_t$. Thus, Beer's law can be used to calculate $[\text{CV}]_t$ from each percent transmittance reading during the kinetic run.

SAFETY PRECAUTIONS

Crystal violet solutions may cause skin and eye irritation. Sodium hydroxide solutions are caustic and will cause skin burns. Any skin contact with either chemical should be immediately washed. Safety goggles must be worn in the lab at all times. Wash hands with soap and water before leaving the lab.

EXPERIMENTAL PROCEDURE

Measurements

1. Set the spectrometer wavelength to 590 nm.
2. Before beginning the kinetic measurements, a 0 % and 100 % transmittance calibration needs to be performed according to the instructions on the Spectronic 20 spectrometer. Use distilled water as the blank. Remember to wipe off any fingerprints on the outside of the cuvet. When completed, empty the cuvet and shake dry.
3. Using the buret provided, dispense 9.00 mL of $1.5 \times 10^{-5} M$ crystal violet solution into a clean, *dry* 50 mL beaker. Using a pipet, add 1.00 mL of 0.050 M NaOH to the CV solution as rapidly as possible without splashing.
4. Thoroughly mix the CV/NaOH solution in the beaker and then fill the cuvet $\frac{3}{4}$ full. Place the cuvet in the spectrometer and read and record the %T. Do this rapidly, but accurately to insure that the first measurement will be made as close to the reaction start as possible. Read and record the %T every 30 seconds for half an hour. Enter the data directly into the Excel spreadsheet.
5. Repeat the experiment with the 0.100 M NaOH.

Data Analysis

1. Enter the spreadsheet and retrieve your data file. In column C compute Absorbance (Eq. 5). Then, in the next column, compute $[CV]_t$ for each data point using Beer's law. Format the data in this column to be in scientific notation. Be sure to properly label all columns. In columns E and F compute $1/[CV]$ and $\ln[CV]$.
2. Plot $1/[CV]_t$ (y-axis) *versus* time in seconds (x-axis). If the reaction between crystal violet and NaOH is second order in crystal violet, this plot will be linear. If it is not second order, this plot will be curved. Test for linearity with a first order (or linear regression) curve fit. Look at the actual data points. If they clearly follow a curved departure from the regression line it should be concluded that the reaction is not second order in crystal violet and need not be printed.
3. Repeat step (2), substituting $\ln [CV]_t$ for $1/[CV]_t$. A linear graph in this instance would indicate a first order dependence on crystal violet. Closely examine your data as done in step 2 above.

4. Prepare and print a carefully labeled graph for the plot which exhibited the best linear relationship. Include the first order (or linear regression) curve fit line. With this plot you have identified y , the reaction order with respect to $[CV]$. Record the value of y on the report sheet. The absolute value of the slope for the straight line (shown in the regression equation at the top) is the best value of k' . Record this value with proper units and to the correct number of significant figures. Include this graph with your report.
5. Repeat for second experiment data.

Data Analysis (continued)

1. From the ratio of the two k' values, determine the reaction order with respect to OH^- (the value of x). Clearly show your calculation of x . You will need to use the NaOH concentrations after dilution with CV. Note: The value of x should be an integer. If your value is not an integer, it is because of experimental error (probably in measuring and adding the NaOH solutions). If necessary, round your x value to the nearest integer.
2. Calculate the true rate constant (k) value from each of the k' values. Be sure to use OH^- concentrations that have been adjusted for dilution. Finally, average the two k values obtained. Again, be sure to watch significant figures and use proper units.

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Experiment Part A.

1. Work through the data analysis section of the procedure with sample data provided below (your laboratory instructor will guide you through this process).
2. Turn in the “Sample Data Sheet” and the graphs generated from the sample data. Make sure graphs are properly labeled and the equation for the trendline is clearly displayed with sufficient significant figures.

SAMPLE DATA for parts 1 and 2: use to calculate the theoretical rate constant.

CV + 0.050 M NaOH		CV + 0.10 M NaOH	
<u>Time</u> (s)	<u>% T</u>	<u>Time</u> (s)	<u>% T</u>
53.46	19.93716	44.94	19.17344
293.52	26.83577	284.94	31.534
533.52	34.08174	525	44.79991
773.58	40.62858	765	57.61866
1013.6	47.32374	1005.1	68.18245
1253.6	53.91303	1245.1	76.71005
1493.6	60.12763	1485.1	83.60497
1853.6	68.38302	1845.1	90.65389

Kinetics Experiment Part A

Name _____

Attach graph to this document.

REACTION OF CRYSTAL VIOLET WITH NaOH: A KINETIC STUDY

Data Sheet (Sample Data)

CV Reaction Order (y)

Key equation: $\text{rate} = k' [\text{CV}]^y$ ($y = 1$ or 2)

Part 1 (using 0.050 M NaOH) y _____ k' (give units) _____

Part 2 (using 0.10 M NaOH) y _____ k' (give units) _____

Hydroxide Reaction Order (x)

Key equation: $k' = k [\text{OH}^-]^x$ ($x = 1$ or 2)

$\frac{k' (\text{part 2})}{k' (\text{part 1})} = \frac{k[\text{OH}^- (\text{part 2, after dilution})]^x}{k[\text{OH}^- (\text{part 1, after dilution})]^x}$ x _____ rounded x _____

Show one of the above dilution calculations and the calculation of x .

Rate Constant (k)

Key equation: $k' = k [\text{OH}^-]^x$ (use rounded x)

Part 1

[OH⁻], after dilution _____

k' (part 1) _____

k _____

Part 2

[OH⁻], after dilution _____

k' (part 2) _____

k _____

Average k (with units) _____

Summary

Final rate law _____

Rate constant (k) with units _____

Did you get the same rate constant for both experiments? Discuss your results.

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REACTION OF CRYSTAL VIOLET WITH NaOH: A KINETIC STUDY

Data Sheet (Experimental Data)

CV Reaction Order (y)

Key equation: $\text{rate} = k' [\text{CV}]^y$ (y = 1 or 2)

Part 1 (using 0.050 M NaOH) y _____ k' (give units) _____

Part 2 (using 0.10 M NaOH) y _____ k' (give units) _____

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Part 1

[OH⁻], after dilution _____

k' (part 1) _____

k _____

Part 2

[OH⁻], after dilution _____

k' (part 2) _____

k _____

Average k (with units) _____

Summary

Final rate law _____

Rate constant (k) with units _____

1. Did the concentration of the crystal violet decrease over time? Explain.
2. In determining the rate constant, did both experiments yield the same value? If not, why?
3. If the rate constant determined from the sample data is the theoretical value for the rate constant, calculate the percent difference and discuss the accuracy of the results for the experimental portion.