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 by monitoring concentration using a Spectronic 20 colorimeter,
• observe that reactant concentration affects reaction rate,
• determine the reaction order with respect to each of the reactants, and
• 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 colorimeter 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 below.

![Chemical Reaction Diagram]

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

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.

\[
\text{Rate} = k [\text{OH}^-]^x [\text{CV}]^y
\]  

In equation 1, \(k\) is the rate constant for the reaction. \(\text{CV}\) is an abbreviation for crystal violet, \(C_{25}H_{18}N_{3}\), \(x\) is the reaction order with respect to \(\text{OH}^-\), and \(y\) is the reaction order with respect to \(\text{CV}\). 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 \(\text{CV}\) is consumed, is negligible. For this reason, \([\text{OH}^-]^x\) can be treated as a constant and Equation 1 can be written as follows,

\[
\text{Rate} = k' [\text{CV}]^y
\]

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 \(\text{CV}\). The integrated rate laws for \(y = 1\) (1st order) and 2 (2nd order) are given in Equations 3 and 4. Compare each with the general form of a linear equation, \(y = mx + b\).

\[
\ln[\text{CV}] = -k't + \ln[\text{CV}]_0
\]

\[
\frac{1}{[\text{CV}]} = -k't + \frac{1}{[\text{CV}]}_0
\]

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

In order to complete the graphing just described, the data showing how the \(\text{CV}\) concentration changes with time are needed. These data will be obtained using a Spectronic 20 colorimeter through absorbance readings
which are based on the amount of light absorbed by the sample. Higher concentrations of colored solutions are more intensely colored and absorb more light. The concentration of CV and color intensity decrease as the CV/NaOH reaction proceeds and the absorbance will also decrease.

Crystal violet solutions obey Beer's law. The relationship between absorbance and the CV concentration is given by:

\[ A = \varepsilon l c \]  

(5)

In Equation 5, \( A \) is the reaction solution’s absorbance value at any time \( t \); \( \varepsilon \) is molar absorptivity value and for crystal violet, \( \varepsilon = 5.0 \times 10^4 \text{ M}^{-1} \text{ cm}^{-1} \); \( l \) is the cell path length (1.00 cm); and \( c \) is the CV molar concentration at time \( t \), \([CV]_t\). Thus, Beer’s law can be used to calculate \([CV]_t\) from each absorbance 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 (Part 1)

1. Set the colorimeter 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 colorimeter [0%T with no cuvet (left knob) and 100%T with distilled water blank (right knob)]. Remember to wipe off any fingerprints on the outside of the cuvet. When completed, empty the cuvet and shake dry.
3. Set the colorimeter to read absorbance.
4. Set up an Excel spreadsheet with the following columns:
   A. Time (min) - enter 0.0 to 35.0 in 0.5 min increments.
   B. Absorbance (A) - to be read during the experiment.
   C. \([CV]_t\) (M) - enter equation: =B2/5E4
   D. \(1/[CV]_t\) - enter equation: =1/C2
   E. \(\ln[CV]_t\) - enter equation: =ln(C2)

!!! The following steps should be completed as quickly as possible. This will insure that the first measurement will be made as close to the reaction start as possible!!!

4. Using the buret provided, dispense 9.00 mL of 1.5 x 10^{-5} \text{ M} crystal violet solution into a clean, dry 50-mL beaker.
5. Using a 1-mL volumetric pipet, add 1.00 mL of \(~0.050 \text{ M} \) NaOH to the CV solution as rapidly as possible without splashing. Record the exact concentration of the NaOH.
6. Thoroughly mix the CV/NaOH solution in the beaker and then fill the cuvet ¾ full. Place the cuvet in the colorimeter.
7. Immediately, record the initial absorbance, \( t = 0.0 \text{ min} \). Continue recording absorbance readings every 30 seconds for at least 30 minutes.
8. Remove cuvet from colorimeter and discard the solution. Rinse with distilled water and shake dry.
Data Analysis
1. Plot $1/[\text{CV}]$ (y-axis) versus time in minutes (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.

2. Repeat step (1), substituting $\ln [\text{CV}]$ for $1/[\text{CV}]$. A linear graph in this instance would indicate a first order dependence on crystal violet. Closely examine your data as done in step 1 above.

3. Prepare and print carefully a labeled graph for the plot which exhibits the best linear relationship. Include the first order curve fit line (linear trendline), the trendline equation, and the $R^2$ value. With this plot you have identified y, the reaction order with respect to [CV]. Clearly report the value of y. The slope (or its absolute value) of the trendline is the value of $k'$. Record this value with proper units and to the correct number of significant figures. Include this graph with your report.

Recall that the $k'$ value just obtained is a pseudo rate constant, whose value depends upon the OH$^-$ concentration, i.e. $k' = k[\text{OH}^-]^x$. In the next part of the experiment, the value of x and the value of the true rate constant, $k$, will be determined.

In part 1 of the experimental procedure, 9.00 mL of $1.50 \times 10^{-5}$ 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 NaOH concentration will be doubled to ~0.10 M.

Experimental Procedure (Part 2)
Repeat experimental steps 4-8 above using 1.0 mL of ~0.10 M NaOH in place of ~0.050 M NaOH.

Data Analysis
1. Repeat the data analysis steps as listed above and again determine and record the $k'$ value. There is no need to plot a second order graph if you determined the reaction in part 1 to be first order.

2. 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 calculate and use the NaOH concentrations after dilution with CV. (Remember $M_1V_1 = M_2V_2$.) Note: The value of x should be an integer. If your value is not an integer, it is due to experimental error, probably in measuring and adding the NaOH solutions. Round your x value to the nearest integer.

3. Calculate the true rate constant ($k$) value from each of the experimental $k'$ values. Use OH$^-$ concentrations that have been adjusted for dilution. Finally, report the two $k$ values calculated and average them to obtain an experimental rate constant value. As always, watch significant figures and use proper units.

4. Obtain the average rate constant values from other groups. Calculate a class average with standard deviation. Compare your team’s results to the class results.