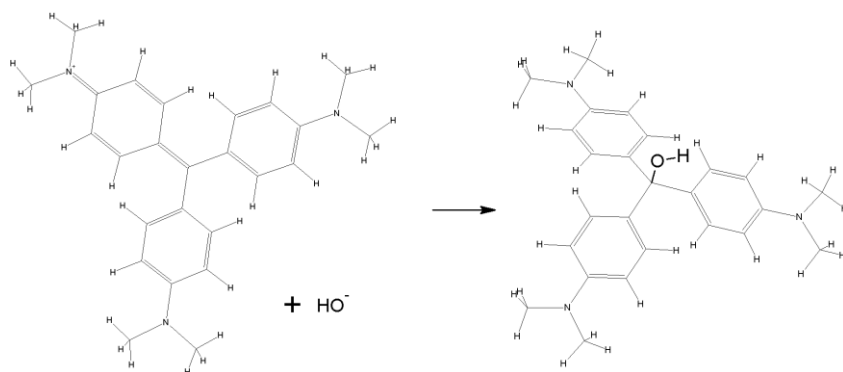


Kinetics of the reaction of crystal violet with sodium hydroxide

Introduction

The rates of chemical reactions are a function of the concentrations of the reactants and of the temperature at which the reaction occurs.¹ In this experiment you will study the reaction of the cation of a dye called crystal violet with hydroxide ion at room temperature, then again at a higher temperature to gain some insight into the activation energy for the reaction. The reaction is depicted in scheme 1, and is depicted for simplicity as



Scheme 1. The reaction of crystal violet cation with hydroxide anion occurs at the central carbon. This reaction localizes π -electrons to only one aromatic ring, which means that the product is colorless, even though the reactant is deep purple.

The cation has a delocalized charge which leads to the intensely purple color.² When the VOH bond is formed, the charge is neutralized, and, because of the change in the structure from planar to non-planar, the electrons become localized and the color disappears. The reaction of crystal violet with hydroxide ion can be followed colorimetrically with a spectrometer. As the color decreases, the absorbance associated with that color decreases. A linear Beer's Law plot of known concentrations versus measured absorbance can be used to convert the spectroscopic absorbance data to

concentrations as a function of time, which can be used to calculate kinetic information on the reaction. The slope of the concentration gives the rate at any time, and the rate can be expressed as a function of the concentrations of reactants in a rate law. The rate of disappearance of a reactant or appearance of the product in a reaction is given by the differential rate law:²

$$Rate (mol \cdot L^{-1} s^{-1}) = k[V^+]^p [OH^-]^q \quad (2)$$

where the rate constant is k . In this experiment you will first determine the values of the orders, p and q , and the rate constant, k . In order to determine p , you will follow the disappearance of the crystal violet as a function of time in the presence of a large excess of hydroxide ion. Under these conditions, the concentration of hydroxide is effectively constant for the entire course of the reaction (not much is consumed relative to the amount present, thus $k[OH^-]^q$ is also effectively a constant, which is labeled k' . The rate law then becomes:

$$Rate (mol \cdot L^{-1} s^{-1}) = k'[V^+]^p \quad (3)$$

where $k' = k[OH^-]^q$. The constant k' is called a *pseudo*-rate constant.¹ This equation can be integrated to give the integrated rate equations which can be used for graphical (linear) analysis. The integrated rate equations are shown in Table 1 for zero, first, and second order reactions in a single reactant.¹ Note that all three integrated rate equations have the form of a straight line for a given reaction to follow that order. Since a reaction will be zero or first or second order, only one linear form will actually “work”. Thus, if you plot your concentration data in all three forms as a function of time, only one graph will be linear and, thus, determine the order, p , of the reaction. The slope of the line will provide the value of the pseudo-rate constant, k' . The process of determining q , the order with respect to hydroxide, is different.

To determine q , you must first find k' (or the slope of the line of the linear form) at two different (specially selected) concentrations of hydroxide: $[OH^-]_1$ and $[OH^-]_2$, where $[OH^-]_2 = 2[OH^-]_1$. In other words, the second hydroxide concentration is exactly twice the value of the first. Since $k' = k[OH^-]^q$, for $[OH^-]_1$, we know that $k'_1 = k[OH^-]_1^q$. Here, we have used the subscript on k' to indicate that this is the value of k' that we get in the experiment with the first

concentration of OH⁻. Defining k_2' similarly for [OH]₂, and noting that [OH]₂ = 2[OH]₁, we can solve for k_2' in terms of the first concentration of OH⁻ and k , the actual rate constant for the reaction:

$$k_2' = k[\text{OH}^-]_2^q = k(2[\text{OH}^-]_1)^q = 2^q \cdot k[\text{OH}^-]_1^q \quad (4).$$

This allows us to determine q using the ratio of the pseudo-rate constants at different concentrations:²

$$\frac{k_2'}{k_1'} = \frac{(2^q \cdot k[\text{OH}^-]_1^q)}{k[\text{OH}^-]_1^q} = 2^q \quad (5).$$

Since q must be 0, 1, or 2, then (as in the initial rates method), by inspection of the value of the calculated ratio, you should be able to determine q . In this laboratory, you will determine the overall rate law for the reaction of crystal violet cation with sodium hydroxide.

Table 1. Integrated rate laws for zero, first, and second order reactions in a single reactant. The final column lists the variables which yield a straight line of formula $y = mx + b$. Plots of [V⁺], ln[V⁺], and 1/[V⁺] can thus be used to determine the reaction order, as only one plot will yield a straight line.

| | | | |
|----------------------|---|--------------------------------------|------------------------------------|
| Zero order (p = 0) | $[V^+]_t = -k't + [V^+]_0$ | $y = [V^+]_t$ $m = -k'$ | $x = t$ $b = [V^+]_0$ |
| First order (p = 1) | $\ln[V^+]_t = -k't + \ln[V^+]_0$ | $y = \ln[V^+]_t$ $m = -k'$ | $x = t$ $b = \ln[V^+]_0$ |
| Second order (p = 2) | $\frac{1}{[V^+]_t} = k't + \frac{1}{[V^+]_0}$ | $y = \frac{1}{[V^+]_t}$ $m = -k'$ | $x = t$ $b = \frac{1}{[V^+]_0}$ |

Nearly every chemical reaction is temperature dependent. The Arrhenius rate constant, $k(T)$, has an exponential temperature dependence related to the activation energy (E_a) of the reaction,

$$k(T) = Ae^{-\frac{E_a}{RT}} \quad (6),$$

where A is the pre-exponential factor accounting for non-energy dynamics and R is the ideal gas law constant. Measuring k at two different temperatures allows the determination of A and E_a by fitting

$$\ln k = \ln A - \frac{E_a}{R} \frac{1}{T} \quad (7)$$

to a straight line.

Experimental Procedures

Six crystal violet (cation) aqueous solutions are prepared for you in advance. One is the reaction standard solution that will be used for all of the reaction kinetics runs. The crystal violet concentration for the reaction standard is 1.5×10^{-5} M. The other five calibration standard solutions are for the preparation of a Beer's Law Calibration Curve. They are 0.75×10^{-5} M, 0.325×10^{-5} M, 0.162×10^{-5} M, 0.081×10^{-5} M, and 0.0405×10^{-5} M. In addition, your blank will be deionized water. Two standardized NaOH solutions (with one exactly twice the concentration of the other) have been prepared within a concentration range of $0.2\text{M} \sim 0.4\text{M}$.

1. Measure the spectrum of the highest concentration calibration standard as a function of wavelength to determine the peak at which you should monitor the reaction.
2. Measure and record the absorbance of each of the calibration standards, starting from the least concentrated and moving to the highest concentration. Rinse the cuvette thoroughly before moving on to the kinetics runs.
3. Using the appropriate labeled graduated cylinder, measure out 25 mL of the reaction standard solution into a beaker. In the appropriate labeled graduated cylinder, measure out 25 mL of the first hydroxide solution. Do not mix the solutions until you are ready to begin your kinetics run. At the moment you pour the hydroxide solution into the beaker with the reaction standard solution, the reaction begins. This is $t = 0$ seconds. You must mix the two solutions together with a stirring rod (quickly but carefully), rinse the cuvette once, fill and wipe the outside of the cuvette, and place the cuvette carefully into the spectrometer and immediately begin taking data in kinetics mode. This will all take at least 25 seconds, time in which your reaction is already proceeding. Measure transmittance and time simultaneously. Collect data until your transmittance is below 0.05 AU. Repeat the run with the same hydroxide concentration in order to have duplicate values for k' . This will also allow you to evaluate the precision and accuracy of your k' .
4. Perform two kinetics runs with the second concentration of hydroxide.
5. On the temperature controlled spectrometer, you will perform two runs, but will not need to recalibrate because you are only interested in the ratio of the two different rate constants. Using the OH^- concentration of your choosing, perform two runs each at 25°C and 50°C .

Pre-Lab

Before you can begin work on the lab, outline the procedure completely, concisely, and clearly. Answer the following questions, and refresh your memory on Beer's Law and the use of the Spec-20.

1. Aside from the Beer's Law plot, what other data will be collected (i.e., what observable will be measured as a function of what parameter)? How many times, and for under what conditions?
2. Look for literature values for the rate constant. Where can you find such values?

Data Analysis and Lab Reports

Introduction: You can summarize kinetics using a table similar to Table 1. Remember, you just need the major equations that the reader needs to understand your work. The experimental section should be written so that another CHEM 451 student with experience using the spectrometers will know what to do.

Data: First, prepare the Beer's Law calibration plot (plot absorbance as a function of concentration). Determine the best fit line through the calibration data. For each of your four kinetics runs, convert each absorbance measurement to concentration of crystal violet ion using the Beer's Law calibration plot.

Next, plot one of your kinetics runs as each of the following:

1. zero order ($[\text{V}^+]$ versus time)
2. first order ($\ln([\text{V}^+])$ versus time)
3. second order ($1/[\text{V}^+]$ versus time).
4. The graph that is most linear indicates the order. For whatever order you select, plot your other kinetics runs in the same manner. For each, determine the slope of the line and, thus, k' . At this point, you should have a total of seven plots: a Beer's Law calibration plot, three different plots for the first run (as indicated in the bullet list above), and one for each of the other experimental runs. For each linear plot, indicate the best fit line on the graph. Be certain that all plots are legible, have units, and that it is clear why each one is where it

is. There is absolutely no need for plots to consume more than 1/6 of a page each. You can wrap text around them, and you can combine several plots as one figure with a single caption. This is appropriate when they logically go together, as for the three different plots of the first kinetic run.

5. Do the same with your temperature-dependent data, then plot $\ln(k(T))$ as a function of $1/T$ to determine the activation energy and A pre-factor.

Finally, write a few brief sentences of narrative description in addition to the figure captions for each figure. The narrative should connect all the graphical data together, explaining the purpose of each plot and what information it conveys.

Discussion: Here, you will connect your spectroscopic data to the kinetics you want to study. Ultimately, you want to be able to give a complete rate law for the reaction. Follow these steps to do that.

1. You have two data sets for each concentration of hydroxide. For each set of two runs, average your k' value and discuss the reproducibility and possible experimental errors of your data.
2. For each concentration of hydroxide, you should have now a k' value. From this determine the order (q) with respect to hydroxide. You should round to an integer value of q (0, 1, or 2).
3. Having determined q , you should be able to calculate k , since $k' = k[\text{OH-}]^q$ and $k = k'/[\text{OH-}]^q$.
4. State the full rate law for the crystal violet ion/hydroxide ion reaction and the units of the rate constant, k . Indicate the activation energy, and predict the rate at 75 °C. Be sure to include error bars on all numbers, properly explained.

Answer the following questions in addition to the information above.

1. Is your measured spectrum consistent with the color of the solution? Explain why or why not.
2. What is the experimental uncertainty in your measurement? What other sources of error could be present in your data that are not instrumental uncertainty? Can you give a ballpark estimate of the error in your value of k ? Give percent errors for k relative to literature values (cite those!).

Conclusions: How general is this approach for measuring kinetics? For what systems is it possible, and what might make it not useful? What range of reaction times is possible with this approach?

Safety/References: Usual items should be included – need safety information on reagents, and references for background, literature data, and safety.

References

1. Engel, T; Reid, P. *Physical Chemistry*, 4th Ed.; Pearson Education: Glenview, IL, 2019; pp. 455-479.
2. Corsaro, G. "Colorimetric chemical kinetics experiment", *J. Chem. Educ.* **41**, 48 (1964).