Kinetics of Blue Dye with Hypochlorite Bleach

How does bleach keep your whites white?

Introduction

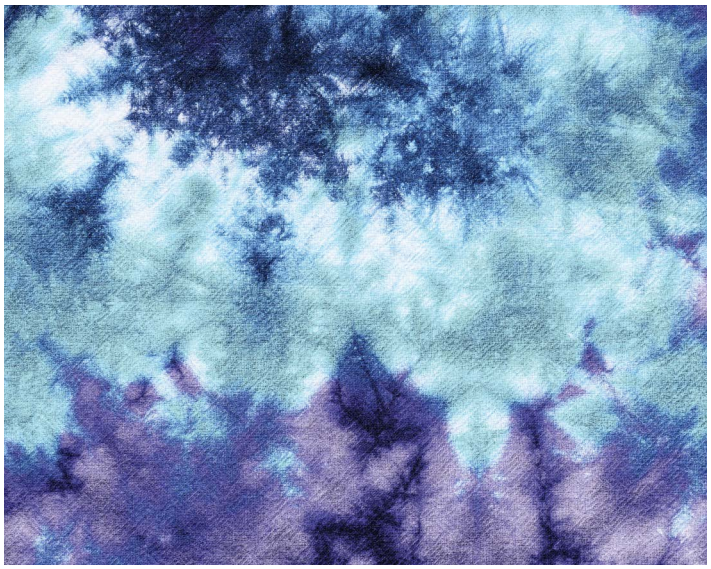
Blue No. 1 dye consists of a single molecule with a strong absorbance band whose wavelength of maximum absorbance (λ_{max}) is at 632 nm. The dye molecule is colored because it has an electronic structure called a chromophore that corresponds to an electron occupying a filled orbital that is separated from an empty orbital by an energy gap. If a photon of the correct energy hits the molecule, the photon is absorbed and that excited electron jumps up into the empty orbital.

If the electronic or physical structure of the dye molecule is altered, it can affect the size of the energy gap between the filled and empty orbitals. While small changes in the energy gap might make the molecule appear to be a different color, larger changes, such as oxidizing a portion of the molecule, can inactivate the chromophore completely and cause the color to go away.

A common product that is used to oxidize molecules is liquid bleach. Bleach is a dilute solution of sodium hypochlorite (NaOCl) that reacts with colored compounds to turn them into colorless ones. An example of this would be how bleach is utilized to remove stains in clothing.

In this experiment, you will study the reaction between blue food dye and hypochlorite bleach:

dye + bleach → colorless products *Equation 1*



With this reaction we can write the rate law as:

$$\textbf{Rate} = k[\text{dye}]^m[\text{bleach}]^n \qquad \textit{Equation 2}$$

Beer's Law tells us that concentration is proportional to absorbance, so the concentration of the dye ([dye]) can be monitored during the reaction by monitoring the absorbance at 632 nm.

In **Part A**, you will determine the order of reaction with respect to [dye]. The experiment is set up so that the concentration of bleach ([bleach]) is much larger than [dye] that it effectively remains constant throughout the reaction. This has the effect of simplifying *Equation 2* to:

Rate = k'[dye]^m *Equation 3*

where $k' = k$[bleach]^n k' is called a *pseudo rate constant*

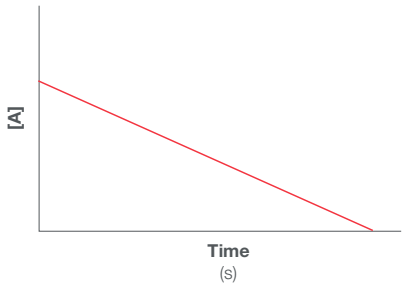
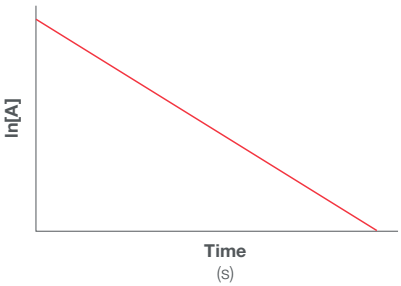
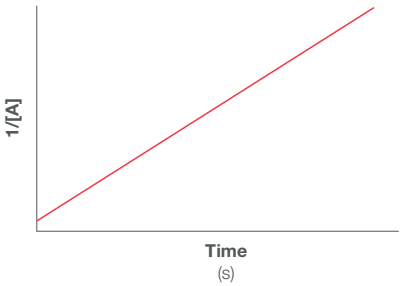
Recording the absorbance as a function of time after mixing the reactants allows the creation of integrated rate plots using the reactant concentration versus time data. The complexity of kinetics that define the order of reaction can be assigned using the integrated rate laws for zero, first, and second order reactions based on the best linear fit according to Table 1 below.

The order of [dye] in the reaction can be determined by which of the following graphs gives the best straight line:

- For zero order: Plot absorbance (Abs) or concentration of dye ([dye]) vs. time; the reaction is zero order in [dye] (***m*** in *Equation 3* = 0)
- For first order: Plot the natural logarithm of absorbance ((ln(Abs)) or concentration of dye (ln[dye]) vs. time; the reaction is first order in [dye] (***m*** = 1)
- For second order: Plot the inverse of absorbance (1/Abs) or concentration of dye (1/[dye]) vs. time; the reaction is second order in [dye] (***m*** = 2)

In **Part B**, you will monitor a second reaction where the [bleach] is doubled (while keeping the [dye] the same as in Part A) and the rate of reaction is measured again by computing an *instantaneous initial rate* close to the start of the reaction. This rate can be calculated by dividing the change in concentration over a short period of time by the number of seconds. Comparing the instantaneous initial rates at the same point in time to those in Part A will enable the observation of what effect doubling [bleach] has on the rate of reaction. If ***n***, the order with respect to [bleach], is zero, *Equation 2* tells indicates that doubling the [bleach] will have no effect on the measured rate, because any number to power zero equals 1. Similarly, if ***n***=1, the rate should double when we double [bleach] ($2^1 = 2$) and if ***n***=2 the rate should quadruple ($2^2 = 4$).

Table 1

Reaction Order	Zero	First	Second
Description	The rate is independent of the reactant concentrations.	Rate is proportional to the concentration of one reactant.	Rate is proportional to the square of the concentration of a single reactant.
Rate Law	Rate = k	Rate = k [A]	Rate = k [A]^2
Integrated Rate Law*	$[A] = -kt + [A]_0$	$\ln[A] = -kt + \ln[A]_0$	$\frac{1}{[A]} = kt + \frac{1}{[A]_0}$
Half-Life	$t_{1/2} = \frac{[A]_0}{2k}$	$t_{1/2} = \frac{\ln 2}{k}$	$t_{1/2} = \frac{1}{k[A]_0}$
Linear Plot*	[A] vs t	ln[A] vs t	$\frac{1}{[A]}$ vs t
Y intercept*	$[A]_0$	ln $[A]_0$	$\frac{1}{[A]_0}$
Slope*	$-k$	$-k$	k
Example plot*			

* The integrated rate laws for zero, first, and second reaction orders can be fit to the equation for a straight line, y = mx + b, where m is the slope and b is the Y intercept. $[A_0]$ is the initial concentration and [A] is the concentration at another time point.

You will have experimental data for the measured instantaneous initial rate for both [dye] and [bleach] at the time you measured the rate. Since you will now know ***m*** and ***n*** in *Equation 2*, you can plug in all the known quantities and solve for the rate constant *k*.

In **Part C**, you will repeat the experiment from Part A at two slightly different temperatures. The rate law does not change as you change temperature, but the rate constant *k* does. You will calculate the rate constants at these two additional temperatures, then make a plot of ln(*k*) (y-axis) versus 1/T (x-axis, temperature in Kelvin).

This plot comes from the Arrhenius Equation:

$$\ln(k) = -\frac{E_a}{R}\left(\frac{1}{T}\right) + \ln[A] \qquad \textit{Equation 4}$$

The slope of the line is the negative of E_a (the activation energy for the reaction) divided by R (the gas constant = 8.314 $J \cdot mol^{-1} \cdot K^{-1}$).

Kinetics is a complicated topic, however by understanding it and designing experiments carefully, we can determine all the rate parameters for a reaction is a straightforward way.

Purpose

This experiment consists of three different parts which can be completed in order or in separate sessions:

1. Part A: Determination of the order of reaction with respect to the concentration of [dye]
2. Part B: Determination of the order of reaction with respect to the concentration of [bleach]
3. Part C: Determination of the activation energy for the reaction E_a

Experimental

Reagents

- McCormick® Blue No. 1 dye solution
  - Approximately a 10.0 x 10^{-6} M stock solution can be prepared by diluting 18 drops of dye to 1 L of water.
  - The actual concentration of the dye solution can be calculated using the molar absorptivity of the dye where ε = 130,000 $L \cdot cm^{-1} \cdot mol^{-1}$.
- Clorox® brand sodium hypochlorite bleach
  - The concentration of the bleach solution can be estimated as 1.00 M.
  - The exact concentration of bleach in the bottle can be calculated using the concentration of sodium hypochlorite by weight and the density.

Part A. Determine the order of reaction in [dye]

1. Obtain four well-matched cuvettes for measuring in the spectrophotometer and a cuvette rack for cuvette storage. Ensure that the optical faces are free of scratches and that the cuvettes are clean and not stained from use in previous experiments.

    a. Fill one cuvette with distilled water to serve as your blank. Store it in position 1 of your cuvette rack.

2. Place 25 mL of the stock blue dye solution in a beaker, add 2 mL of water, and mix. Fill the second cuvette with this solution and set it aside. This will serve as your “Standard of comparison”. Place it in position 2 of your cuvette rack.

3. Place 25 mL of the stock solution and 1 mL of water in a second beaker. Measure and record the temperature of this solution. Obtain 1 mL of bleach and prepare to perform the following steps quickly.

    a. Select the Kinetics method and enter 632 nm as the measured wavelength. Set the Experiment time to 800 seconds, the Data interval to 5 seconds and the Integration time to 0.5 seconds (Figure 1).

    b. Wipe the optical faces of the blank cuvette from Step 1 with a lint-free laboratory tissue and place it in the sample stage. Ensure that the optical faces are in the beam. Close the lid and select Continue and then Blank to zero the instrument. Once the blank measurement is complete, remove the cuvette and return it to position 1 of your cuvette rack.

    c. Add 1 mL of bleach to the solution in the beaker from Step 3. Mix thoroughly with a stirring rod.

    d. Quickly fill cuvettes 3 and 4 with the solution from step 3c.

    e. Place cuvette 3 in position 3 of your cuvette rack for you to observe the reaction progress.

    f. Wipe the optical faces of the cuvette 4 with a lint-free laboratory tissue, place it in the sample stage in the spectrophotometer and close the lid.

    g. Select Measure to record the absorbance until cuvette 3, which you've observed throughout the reaction, appears colorless. You can select Stop to end the data collection early (Figure 2). Remember that cuvette 4 in the spectrophotometer contains a duplicate of the reaction and looks exactly like the contents of cuvette 3. If the experiment time needs to be extended, more time can be added by selecting the clock on the GENESYS touch screen. Record your observations of what happens to the intensity of the color in cuvette 3 (Figure 3).

4. Retain cuvettes 1 and 2 and their contents in the cuvette rack, discard the solutions in cuvettes 3 and 4, and then rinse the cuvettes 3 and 4 with distilled water.

5. Export your data and use a spreadsheet program to generate the plots and complete the calculations

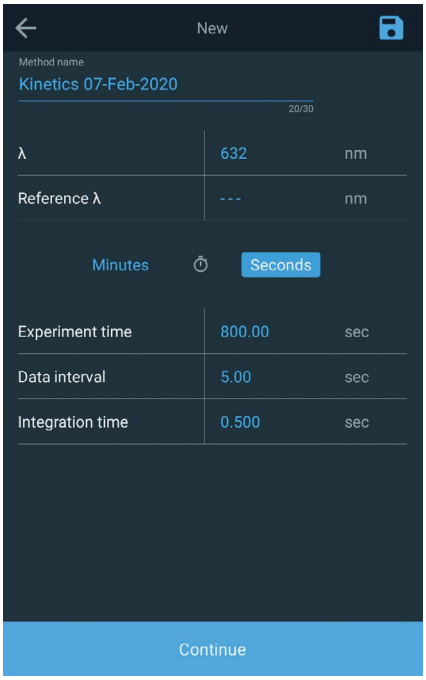


Figure 1: Kinetics method setting

Figure 2: Stop function in Kinetics method

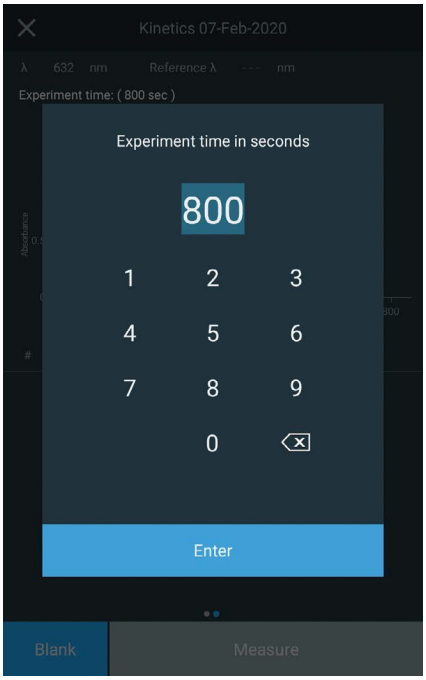


Figure 3: Add more time to experiment

Part B. Determine the order of reaction in [bleach]

1. Place 25 mL of the dye stock solution in a third beaker. Obtain 2 mL of bleach and prepare to perform the following steps quickly.
    a. Set up your spectrophotometer and measure the blank cuvette as outlined in Part A (steps 3a and 3b) if you have not already done so.
    b. Add 2 mL of bleach to the solution and mix.
    c. Quickly fill cuvettes 3 and 4 with this solution.
    d. Place cuvette 3 in position 3 of your cuvette rack for you to observe.
    e. Insert cuvette 4 into the spectrophotometer.
    f. Select Measure to record the absorbance until cuvette 3 appears colorless. Observe cuvette 3 as the reaction progresses. Extend the reaction time if needed.
2. Retain cuvettes 1 and 2 and their contents in the cuvette rack, discard the solutions in cuvettes 3 and 4, and then rinse cuvettes 3 and 4 with distilled water.
3. Export your data and use a spreadsheet program to generate the plots and complete the calculations necessary to answer the questions on the Lab Report.

Part C. Determine the activation energy of the reaction

1. Place 25 mL of the stock solution and 1 mL of water in a fourth beaker. Obtain 1 mL of bleach and prepare to perform the following steps quickly.
    a. Set up your spectrophotometer and measure the blank cuvette as outlined in Part A (steps 3a and 3b) if you have not already done so.
    b. Prepare a hot water bath by heating approx. 150 mL of water in a 250 mL beaker on top of a hotplate.
    c. Warm the beaker containing the 25 mL of dye solution in a warm water bath prepared
    d. Warm the solution to 5°C above (± 1°C) room temperature. Record the room temperature and the temperature of the heated solution.
    e. Add 1 mL of bleach to the solution, mix and quickly fill cuvettes 3 and 4 with this solution.
    f. Place cuvette 3 in position 3 of your cuvette rack for you to observe.
    g. Insert cuvette 4 into the spectrophotometer.
    h. Record the absorbance until cuvette 3 appears colorless. You can select Stop to end the data collection early. Observe cuvette 3 as the reaction progresses.
2. Repeat the same procedure from Part C step 1 (a–h) with a solution that was warmed to 10°C above (± 1°C) room temperature. Make sure to record the exact temperature.
3. Export your data and use a spreadsheet program to generate the plots and complete the calculations necessary to answer the questions on the Lab Report.
4. Discard all solutions then clean and return cuvettes and all laboratory glassware.

Lab Report

Kinetics of Blue Dye with Hypochlorite Bleach

Name: _____

Date: _____

Section No. or Lab Period: _____

Part A. Determine the order of reaction in [dye]

Questions

1. Enter your time and absorbance data for the entire reaction into a spreadsheet program to compute columns C, D, and E. Use the value of the molar absorptivity ε = 130,000 $L \cdot cm^{-1} \cdot mol^{-1}$ to compute the concentration of column C.

Spreadsheet example

	A	B	C	D	E
1	Time (seconds)	Absorbance	[dye] (M)	ln[dye]	1/[dye] (M^{-1})
2	0				
3	5				
4	10				

2. Use the spreadsheet program to make zero, first, and second order rate plots. Put a line of best fit, with the corresponding rate equation and R^2 values, on the graph with the best straight line of the three.

3. Staple printouts of your integrated rate law graphs to this page when you submit this report.

4. Report the temperature of your dye solution at the start of the experiment: _____

5. How long did the reaction take to reach completion (no more color visible in cuvette 3)?

Remember:

- Staple hand-drawn or printed graphs to your lab report
- Staple the four sheets of the lab report together before you hand them in

6. Based on your integrated rate plots, what is the order of reaction with respect to [dye]?

☐ Zero ☐ First ☐ Second

7. What is the value of the rate constant k' from the integrated rate plot?

8. Look at either your absorbance (Abs) or [dye] vs. time data. Determine the half-life of the reaction across three different absorbance intervals by the time it takes for a chosen absorbance or concentration value to decrease by half.

Data Table 1

From (Abs) or [dye]	To (Abs) or [dye]	Half-Life (seconds)

a. Are the values approximately the same, or radically different?

b. If the half-lives are similar, calculate the mean of the three values.

Name _____

9. Calculate the value of the rate constant k' from the half-life that you measured in question 8 on the previous page. Use the appropriate equation based upon the order of reaction that you determined in question 6 on the previous page.

10. Calculate the percent error between the value of k' obtained from the plot (question 7 on the previous page) and the half-life equation (question 9 above).

Part B. Determine the order of reaction in [bleach]

1. Use a spreadsheet program to make:

   a. A plot of [dye] vs. time

   b. The appropriate integrated rate plot for the order of reaction that you determined in Part A. Put a line of best fit, with the corresponding rate equation and R^2 values, on the second plot.

2. Staple printouts of your plots to this page when you submit this report.

3. For the reactions in both Part A and Part B, calculate the *instantaneous initial rate* at the same time point close to the start of both runs that corresponds to the change in [dye] over a period of time. For example, you might choose the time interval between 30 and 35 seconds.

   a. To calculate this use the [dye] vs. time data in your spreadsheet for the reactions with 1 mL (Part A) or 2 mL of bleach (Part B):

$$\textit{Instantaneous initial rate} = \frac{\Delta[\text{dye}]}{\Delta\text{time}}$$

4. Report the instantaneous rates that you calculated. Include the correct units.

Data Table 2

Part	Instantaneous initial rate	Units
A		
B		

5. What happened to the instantaneous initial rate of the reaction when you doubled the concentration of bleach?

6. Use this data to calculate the order of reaction with respect to [bleach]. Write the full rate law in the form of *Equation 2* with the values of *m* and *n* filled in.

Name _____

7. Into your full rate law from question 6 on the previous page, solve for the value of the rate constant *k*. Remember to include the correct units for the rate constant. Use the following values to insert into the equation:

   a. The instantaneous initial rate from the data in Part A or Part B that you used in question 3 on the previous page.

   b. The [dye] (from column C in the spreadsheet) at the point where you calculated the instantaneous rate.

   c. The [bleach] (calculated from the concentration of the stock solution and the dilution that occurred when you added it the dye solution in Part B (step 1b) of the Experimental procedure).

8. In Part B we added twice the amount of bleach to the reaction compared to Part A to achieve a concentration of bleach that was double what we used in Part A. With that difference in mind, explain the purpose of the 1 mL of water that was added in Part A, but not in Part B?

Part C. Determine the activation energy for the reaction

1. For each data set, use a spreadsheet program to make the appropriate integrated rate plot for the order of reaction that you determined in Part A. Put a line of best fit, with the corresponding rate equation and R^2 values, on each plot.

2. Staple printouts of your plots to this lab report when you turn it in.

3. Use the slope of the best fit line to calculate *k´* and divide this value by [bleach] to get the value of *k*. Do this for the data obtained in Part A and in Part C. You will have three values of *k*.

Data Table 3

Plot	Slope	*k´*	[bleach]	*k*
1				
2				
3				

4. Make an Arrhenius plot (see Equation 4) with ln(*k*) on the y-axis and 1/T (in Kelvin) on the x-axis.

Data Table 4

Plot	Temperature		1/T	*k*	ln(*k*)
	(°C)	(K)			
1					
2					
3					

5. The slope of this plot is equal to

$$-\frac{E_a}{R}$$

Record the slope of the plot: _____

thermo scientific

Name _____

6. Calculate the value of E_a, which is the activation energy of the reaction.

7. The Arrhenius Equation can be rewritten for data at two temperatures as:

$$\ln\left(\frac{k_2}{k_1}\right) = \frac{E_a}{R}\left(\frac{1}{T_1} - \frac{1}{T_2}\right)$$

   a. Use your data at room temperature as T_1 and at room temperature +10°C as T_2 to determine E_a using this equation.

8. Calculate the percent error between the values of E_a determined in question 6 and Question 7a.

   a. Which of the two values would you have more confidence in? Explain why.