Experiment 13I

12/18/2018

THE REACTION OF RED FOOD COLOR WITH BLEACH[1]

MATERIALS: 100 mL volumetric flask, 50 mL beaker (2), 5 mL pipet (1), 13 x 100 mm test tubes, Spec-20 (1), plastic droppers.

PURPOSE: To determine the rate law for the chemical reaction between FD&C Red Dye #3 and sodium hypochlorite.

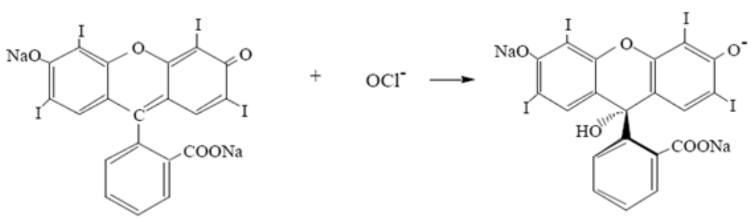
LEARNING OBJECTIVES: By the end of this experiment, the students should be able to demonstrate the following proficiencies.

1. Relate absorbance measurements to concentrations, using the Beer-Lambert Law.
2. Apply the method of comparing initial reaction rates to determine the order of reaction with respect to one reactant.
3. Apply the graphical (integrated rate law) method to determine the order of reaction with respect to one reactant.

PRE-LAB: Complete the pre-lab questions on OWL **PRIOR** to coming to lab. A similar exercise is available on page E13I-9.

DISCUSSION:

Most people are familiar with the action of bleach on fabrics. If one has done much laundering of clothes, one will recall the warning on the side of a Clorox® bottle against its use on brightly colored clothes. This "bleaching" is a chemical reaction whose kinetics can be easily studied.



Red Dye #3 (red dye) | **Hypochlorite Ion** (bleach or OCl^-) | **Colorless Product**

The rate of the bleaching reaction is dependent on the concentration of red dye and on the concentration of bleach. This is expressed in the rate law for the reaction:

$$\textbf{rate} = \textbf{k}\,[\textbf{red dye}]^{a}\,[\textbf{OCl}^-]^{b} \quad (1)$$

Experimental data will allow the values of the orders with respect to each reactant, **a** and **b**, to be determined, as well as the rate constant, k.

Beer-Lambert Law. Because reaction (1) involves a colored substance, the reaction can be studied using spectrophotometry, an analytical technique used to measure the amount of light absorbed by a substance (or substances) in solution. This is illustrated in Figure 1. I_o and I_t are the incident and transmitted intensity of light, respectively, through a solution of path length ℓ. The amount of light transmitted through a solution can be expressed as the percent transmittance, %T, which is simply (I_t/I_o) x 100. Note that %T has no units because the units of intensity cancel. Absorbance, A, is defined as

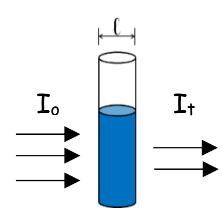


Figure 1. Transmittance of light through a solution in a cuvette. ℓ = 1.00 cm in this experiment.

$$A = -\log\frac{\%T}{100} \quad (2)$$

[1] Adapted from Henary, M.M., Russell, A.A. *J. Chem. Educ.*, **2007**, 84, 480-482.

Depending on the spectrophotometer used, you will measure %T and/or A. The latter is needed to determine the molar concentration of the absorbing species, c, through the Beer-Lambert law:

$$A = \varepsilon \ell c \tag{3}$$

where ε is the molar absorptivity. Note that it is the absorbance that is directly proportional to the concentration, not the percent transmittance. The molar absorptivity, ε, is unique for an absorbing species at a particular wavelength. In other words, if a substance does not absorb light at a certain wavelength, ε (for that substance) will be zero at that wavelength. If the substance is strongly absorbing at that wavelength, ε will be large. The units of ε are determined from only ℓ and c because absorbance has no units (because of %T). Additional information on the Beer-Lambert law and spectrophotometry is given in Appendix I (Spectrophotometry) on the Plebe Chemistry Website.

Determination of a: ***Pseudo Rate Law Method (graphical).***

One method for determining reaction orders outlined in general chemistry textbooks involves determining whether a reaction follows certain graphical profiles. However, this method can only be applied if the rate law for the reaction involves only one reactant. This may appear rather limiting, since most chemical reactions involve at least two reactants. As shown below, however, there is a way, in principle, to cause a reaction involving multiple reactants to appear to include the change in only one reactant. This method is known as the Pseudo Rate Law Method. By running the bleaching reaction with a large excess of bleach, OCl^- , the change in concentration of bleach, $\Delta[OCl^-]$, will be approximately equal to zero. We therefore set $k[OCl^-]^b$ equal to a constant, k':

$$\mathbf{k' = k\,[OCl^-]^b} \tag{4}$$

The rate law: **rate = k [red dye]^a [OCl^-]^b** (equation 1) now simplifies to

$$\mathbf{rate = k'[red\ dye]^a} \tag{5}$$

and the rate of reaction leads directly to the order with respect to red dye, **a**.

Instead of quantitatively determining the rates (Δ[conc]/Δt) directly, we will monitor [red dye] over time and use plots to determine the order, a. In other words, we will utilize integrated rate laws. Applicable integrated rate laws for this experiment are

$$zero\ order: \quad \underbrace{[\text{red dye}]}_{y} = \underbrace{-\text{k}'\text{t}}_{m\,x} + \underbrace{[\text{red dye}]_0}_{b} \tag{6}$$

$$1st\ order: \quad \underbrace{\ln[red\ dye]}_{y} = \underbrace{-\text{k}'\text{t}}_{m\,x} + \underbrace{\ln[red\ dye]_0}_{b} \tag{7}$$

$$2nd\ order: \quad \underbrace{1/[\text{red dye}]}_{y} = \underbrace{\text{k}'\text{t}}_{m\,x} + \underbrace{1/[\text{red dye}]_0}_{b} \tag{8}$$

By constructing the three plots: (i) [red dye] vs time, (ii) ln[red dye] vs time, and (iii) 1/[red dye] vs time, one can determine the reaction order with respect to [red dye], **a**, from the plot that is most linear. For example, if *[red dye] vs time* is most linear, this means that the reaction order with respect to [red dye], **a**, is zero.

Determination of b: ***Method of Initial Rates.***

The Method of Initial Rates for determining orders of reaction is illustrated in Example 14.3 (pp. 518-519) of the Kotz textbook. This method involves a comparison of two different trials, the only difference between the trials being the concentration of one of the reactant species. Since k′ = k[OCl^-], measurements of k′ at two different [OCl^-] allows the order to be determined. Note that in our experiment, we will be comparing k' (and not rate) to [OCl^-]. But k' is proportional to rate (equation 5) at constant [dye], so the end result is the same.

PROCEDURE:

SAFETY: ALWAYS wear safety goggles and an apron, and handle the intensely colored dye carefully to avoid stains on clothing. Sodium hypochlorite, household bleach, is a bronchial irritant. Keep solutions in the hood, and avoid breathing the vapors. Handle the bleach solutions with care to avoid bleach spots on clothing. Immediately wipe-up any spills of the red dye or bleach.

Part A. Prepare a diluted red dye solution from the initial stock solution & determine the absorbance

1. On the data sheet, record the concentration of the red dye stock solution using the correct number of significant figures.

2. Obtain about 10 mL of the red dye stock solution in a 50 mL beaker.

3. Rinse the inside walls of a 5.00 mL pipet with a small amount of the red dye stock solution, then transfer 5.00 mL of this red dye stock solution into the 100 mL volumetric flask. Carefully fill the flask up to the 100.0 mL mark with distilled water. Cap the flask and invert the solution several times to mix well.
   <u>It is THIS DILUTED RED DYE SOLUTION that will be used in all reaction mixtures described in Part B.</u>

4. Set the Spec-20 wavelength to 530 nm and calibrate it using distilled water as the blank. Measure and record the absorbance of the diluted red dye solution from Step A(3).
   <u>Note</u>: From this you will be able to calculate the molar absorptivity, ε, of the red dye solution.

Part B. Absorbance measurements of reaction mixtures

Amounts of the components in the mixtures are given in the table below. The density of the solution is 1.00 g/mL, so mL or grams can be used. <u>Follow these directions precisely</u> to prepare the mixtures.

1. Obtain about 15 mL of the bleach solution in a 50 mL beaker. Record the mass percent of sodium hypochlorite in the bleach solution on the data sheet.

2. Use the dye solution from Step A(3) to perform the first kinetic run (**reaction #1**).

3. Using the top loading balancing, transfer 4.00 ± 0.02 g of your <u>diluted red dye solution from Step A(3)</u> into a clean, dry test tube. (**<u>Note</u>**: Put an empty beaker on the balance to support the clean, dry test tube. Zero the balance and then add the red dye solution.)

4. **READ THIS ENTIRE SECTION BEFORE BEGINNING.** Transfer 2.00 ± 0.02 g of bleach solution *into a clean, dry test tube*. Use a clean, dry plastic pipet to withdraw all of the bleach solution from the test tube. To initiate the reaction, squirt the bleach solution into the <u>test tube containing the diluted red dye solution from Step B(3)</u>. Suction and squirt the mixture once with the plastic pipet to mix. Insert the test tube into the Spec-20. Start recording time and absorbance readings every 30 seconds for 15 minutes or until the absorbance drops to 0.05, whichever comes first. Record the time and absorbance measurements on the data sheet.

5. For **reaction #2**, the same procedure will be used. First, transfer to a test tube the <u>appropriate amounts of dye solution and water</u>, as indicated in the table below. Next, transfer 1.00 ± 0.02 g of bleach solution *into a second clean, dry test tube*. Use a clean, dry plastic pipet to withdraw all of the bleach solution from the test tube. To initiate the reaction, squirt the bleach solution into the <u>test tube containing the dye-water mixture</u>. Suction and squirt the mixture once with the plastic pipet to mix. Insert the test tube into the Spec-20. Record the absorbance every 60 seconds for 20 minutes or until the absorbance drops to 0.05, whichever comes first.

Reaction #	diluted red dye solution (mL or grams)	deionized water (mL or grams)	bleach solution (mL or grams)
1	**4.00**	**0.00**	**2.00**
2	**4.00**	**1.00**	**1.00**
Note: The density = 1.00 g/mL for both water and the solutions.			

Clean up:

Be sure to remove the sample from the Spec-20. Discard all solutions in the sink. Wash and rinse glassware thoroughly to remove red dye and bleach residue. Shut down the Spec-20 as instructed.

Name ____________________________ Section ____________________

Date _____________________

DATA SECTION
Experiment 13I

Part A. Concentration and Absorbance of red dye solutions & mass percent of bleach
Note: Use proper significant figures and units.

1. Initial concentration of red dye stock solution (in g/L): ________________ g/L

2. Calculate the initial molar concentration of red dye (molar mass = 879.9 g/mol) in the stock solution.

________________ mol/L

3. Record the Absorbance of the diluted red dye solution prepared in Step A(3): ______________ (no units)

Part B. Absorbance data for each reaction mixture

1. Mass percent of sodium hypochlorite in the bleach: ______________ (by mass)
2. Time & absorbance measurements:

Time (sec)	Absorbance Reaction #1

Time (sec)	Absorbance Reaction #2

CALCULATIONS & DATA TREATMENT
Experiment 13I

Part A. Determining concentrations & molar absorptivity

Note: Use proper significant figures and units.

A1. Using $M_{(conc)}V_{(conc)} = M_{(dilute)}V_{(dilute)}$ and the initial concentration of the stock solution recorded in Part A, calculate the **<u>molar concentration of the diluted red dye solution you made in Step A(3)</u>**.

[red dye], Step A(3) ________________

A2. Use Beer's Law and the absorbance recorded in Data Section Part A(3) to calculate the molar absorptivity, ε, of the red dye solution. *Remember to include units*. See equation 3.

Molar absorptivity ________________

A3. Mass percent of sodium hypochlorite in the bleach (from Data Section, Part B): _____________________

A4. Assuming that the density of the bleach solution is 1.00 g/mL, calculate the molarity of the sodium hypochlorite in the bleach solution provided.

A5. Using $M_{(conc)}V_{(conc)} = M_{(dilute)}V_{(dilute)}$, calculate the initial molarity of the sodium hypochlorite in reaction mixture #1.

[bleach] Reaction #1 _______________

A6. Using $M_{(conc)}V_{(conc)} = M_{(dilute)}V_{(dilute)}$, calculate the initial molarity of the sodium hypochlorite in reaction mixture #2.

[bleach] Reaction #2 _______________

Part B: Data analysis

Reaction #1

B1. Enter your time and absorbance data for **Reaction #1** into an Excel spreadsheet.

B2. Create new columns for [red dye], ln[red dye], and 1/[red dye]. Do not use your calculator - ENTER FUNCTIONS into the spreadsheet to perform each calculation! Recall that [red dye] can be calculated using equation 3, where the concentration c is [red dye].

B3. Construct three separate plots using your data from Reaction #1: [red dye] vs. time, ln[red dye] vs. time, and 1/[red dye] vs. time.
- (Note that they are in the form y vs x, where [red dye], ln[red dye], and 1/[red dye] are on the y-axes.) The plot that visually appears the most "linear" tells you the order of the reaction with respect to [red dye], **a**.
- Perform a trendline analysis on each plot, and display the equation and R^2. Three significant figures should be shown in the equation. If not, change the trendline format to scientific with at least three significant figures. The plot with the R^2 value closest to 1.0 is the most linear.

B4. Which plot has an R^2 value closest to 1.0: ____

B5. What is the reaction order with respect to [red dye], **a**: ___________________________________

B6. Slope of the trendline for reaction #1, with units: ___________________________________

B7. Consulting equations 6, 7, and 8, what is the slope equal to in the applicable equation? ___________

B8. What is the OCl^- molar concentration for reaction #1? ________________________ mol/L
(This was just calculated in A5.)

Reaction #2

B9. Repeat steps B.1 through B.3 data for **Reaction #2**.

B10. Which plot has an R^2 value closest to 1.0: ____
(Consult your instructor if reactions 1 & 2 do not have the same plot with R^2 values closest to 1.0.)

B11. What is the reaction order with respect to [red dye], **a** (should be identical to B5 above): ______________

B12. Slope of the trendline for reaction #2, with units: ___________________________________

B13. Consulting equations 6, 7, and 8, what is the slope equal to in the applicable equation? _____________

B14. What is the OCl^- molar concentration for reaction #2? ________________________ mol/L
(This was just calculated in A6.)

Determination of b and the rate law

B15. Now that you know k' for both reactions, along with the corresponding OCl^- molar concentrations, equation 4 can now be used in a ratio form to determine the reaction order with respect to $[OCl^-]$, **b**:

$$\frac{k'_{rxn\ \#1}}{k'_{rxn\ \#2}} = \frac{k[OCl^-]^b_{rxn\ 1}}{k[OCl^-]^b_{rxn\ 2}}$$

Determine the value of **b**. Show all work.

B16. Write the experimental rate law (using appropriate integer values) based on the order of the red dye and the order of the OCl^- that you obtained in your analysis. (See equation 1 for the general form.)

B17. Calculate the rate constant, k, for this reaction using information from reaction #1 (remember to include proper units and show all work). *hint: equation 4*

B18. Calculate the rate constant, k, for this reaction using information from reaction #2 (remember to include proper units and show all work).

B19. Calculate the average value of the rate constant, k (remember to include proper units and show all work).

QUESTIONS
Experiment 13I

1. For Reaction #1, determine the initial number of moles of red dye in the test tube.

2. For Reaction #1, determine the initial number of moles of sodium hypochlorite in the test tube.

3. In the pseudo rate law method used to determine the order in red dye, it is important that the concentration of the hypochlorite ion remain constant.

   a. Using your values from questions 1 and 2, calculate the final moles of hypochlorite ion.
   Hint: Consider what is the limiting reactant.

   b. Did the hypochlorite ion concentration remain constant?

Name ___________________________________ Section ______________________

Date _________________________

PRE-LAB EXERCISES
Experiment 13I

BRING YOUR LAPTOP TO LAB

1. Calculate how many grams of sodium hypochlorite, NaOCl, were dissolved in distilled water to make 1.00 L of a 0.806 M stock solution.

2. Calculate the molarity of a solution of red dye #3 (MW 879.9 g/mol) if a 3.0104 g sample is diluted with distilled water to 10.00 L.

3. Calculate the dye concentration of a solution made by adding 5.00 mL of the solution from question #2 above into a 100.00 mL volumetric flask and diluting with distilled water to the 100.00 mL mark.

4. Calculate the [dye] and [OCl^-] (both in moles/L) when 2.00 mL of the bleach solution from question #1 is added to 4.00 mL of the dye solution in question #3.

5. The absorbance of a red dye was measured in a cuvette with a path length of 1.00 cm. The concentration of the red dye was expressed in units of mol/L. Using the equation **$A = \varepsilon \ell c$** to calculate the molar absorptivity, ε, what would be the units of ε?

   a. cm
   b. 1/cm
   c. mol/L
   d. L/mol
   e. L/mol • cm
   f. mol/L • cm
   g. cm • mol/L
   h. no units

6. A plot of ln[red dye] vs time (in minutes) was constructed and was found to be linear. A trendline analysis was then performed. What would be the units of the slope? *Hint: See equation 7.*

   a. minute
   b. 1/minute
   c. mol/L
   d. L/mol
   e. minute • mol/L
   f. mol/L • minute
   g. L/mol • minute
   h. no units