Experiment 13I

THE REACTION OF RED FOOD COLOR WITH BLEACH

| PROBLEM: | 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. Properly make aqueous solutions, given target volumes and molarities.
2. Relate absorbance measurements to concentrations, using the Beer-Lambert Law.
3. Apply the method of comparing initial reaction rates to determine the order of reaction with respect to reactants.
4. Apply the graphical (integrated rate law) method to determine the order of reaction with respect to one reactant.
5. Control experimental conditions, as needed, to assure proper comparison of rate information.

PRE-LAB: Review Appendix I (Spectrophotometry) for a discussion of spectroscopy and application of Beer’s Law: http://www.chemistry.usna.edu/manual/ApdxI.pdf

Complete the pre-lab questions on page E13I-8 prior to coming to lab.

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.

\[
\text{Red Dye #3} \quad \text{Hypochlorite Ion} \quad \text{Colorless Product} \\
\text{(red dye)} \quad \text{(bleach or } \text{OCl}^- \text{)} \quad \\
\text{COONa} \quad \text{COONa} \\
\]

\[
\text{NaO} \quad \text{O} \quad \text{I} \quad \text{I} \quad \text{I} \quad \text{I} \\
\text{I} \quad \text{C} \quad \text{C} \quad \text{C} \quad \text{C} \\
\text{I} \quad \text{O} \quad \text{COONa} \\
\]

\[
\text{NaO} \quad \text{O} \quad \text{I} \quad \text{I} \\
\text{I} \quad \text{C} \quad \text{C} \quad \text{C} \\
\text{I} \quad \text{O} \quad \text{H} \quad \text{COONa} \\
\]

\[
+ \text{OC}^\text{I-} \quad \rightarrow \\
\]

\[
\text{Red Dye #3} \quad \text{Hypochlorite Ion} \quad \text{Colorless Product} \\
\text{(red dye)} \quad \text{(bleach or } \text{OCl}^- \text{)} \quad \\
\text{COONa} \quad \text{COONa} \\
\]

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

rate = k [red dye]^a[OCl]^b

(1)

Experimental data will allow the values of the orders with respect to each reactant, \(a\) and \(b\), to be determined.

**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 \(\Delta[OCl^-]\) will be approximately equal to zero, therefore, \(k' = k[OCl^-]\) and the rate law simplifies to: rate = \(k'[\text{red dye}]^a\) and the rate of reaction leads directly to the order with respect to red dye, \(a\).

**Determination of \(b\): Method of Initial Rates.**

The Method of Initial Rates for determining orders of reaction is illustrated in Example 13.3 (pp. 575-576) of the Chang textbook. This method simply involves a comparison of two different trials, the only difference between the trials being the concentration of one of the reactant species. The value of \(b\) in this experiment will be found by this method through holding the concentration of red dye constant and changing the concentration of \(OCl^-\).

Since all of the reactions studied in this experiment involve a species (red dye) that will absorb visible light a Spectrophotometer (Spec 20) will be used to collect absorbance (A) data which can then be related to concentration (c) data using Beer’s Law:

\[ \Lambda = \varepsilon l c \]

(2)

where \(l = \) pathlength of the cuvette (1.00 cm in this experiment) and \(\varepsilon = \) molar absorptivity for red dye.

**MATERIALS:** 100 mL volumetric flask, 50 mL beaker (2), 5 mL pipet (1), 2 mL pipet (3), 1 mL pipet (2), Spec-20 (1), cuvette (2), rubber stopper for cuvette (1), plastic droppers (2).

**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. 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 stock solution to four decimal places
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 the red dye 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. It is THIS SOLUTION that will be used in all reaction mixtures described in Part B.
4. Set the wavelength of the Spec-20 to 530 nm. Set the instrument to %T mode. Adjust the zero with no sample in the instrument. Next, fill a cuvette ~2/3 full with deionized water, wipe the outside of the cuvette with a lab tissue, insert into the instrument and set 100% transmittance.

5. Switch the Spec-20 to Absorbance mode.

6. Transfer 4.00 mL of your dilute solution from Part A (3.) into a clean, dry cuvette. The easiest way to transfer 4.00 mL to a cuvette is by using a plastic pipet to transfer 4.00±0.02 g of the dye solution into a tared test tube placed in a small beaker. **USE THE TOP LOADING BALANCE.** Insert the cuvette with the dye into the sample compartment and record the absorbance on data sheet.  
   Note: From this you will be able to calculate the molar absorptivity, ε, of the red dye solution.

Part B. Absorbance measurements of reaction mixtures

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

2. Use the solution from Part A(6.) to perform the first kinetic run.

3. Transfer 2.00 mL of bleach solution into a clean, dry test tube. Use a clean, dry plastic pipet to withdraw all of the hypochlorite solution into the plastic pipet. To initiate the reaction, squirt the bleach solution into the cuvette containing the dye-water mixture. Stopper the cuvette, invert once to mix, then wipe the cuvette with a lab tissue and insert into the Spec-20. Wait until the absorbance drops to 0.60 and then start recording time and absorbance readings. Record the absorbance at t = 0 (approximately 0.60) and then remove the cuvette. Take a second absorbance measurement 30 seconds later and then record the absorbance every 30 seconds for 10 minutes or until the absorbance drops to 0.05, whichever comes first. **To maintain constant temperature, REMOVE the cuvette from the sample compartment between readings.** Record time vs. absorbance on the data sheet.

4. For reaction #2, the same procedure will be used. First, fill a cuvette with appropriate amounts of dye solution and water. Next, transfer 1.00 mL of bleach solution into a second clean, dry test tube. Use a clean, dry plastic pipet to withdraw all of the hypochlorite solution into the plastic pipet. To initiate the reaction, squirt the bleach solution into the cuvette containing the dye-water mixture. Stopper, mix and record the absorbance once the absorbance drops to 0.60. Take a second absorbance 60 seconds later, and then record the absorbance every 60 seconds thereafter for 20 minutes or until the absorbance drops to 0.05, whichever comes first. Remember to remove the cuvette between readings.

<table>
<thead>
<tr>
<th>Reaction #</th>
<th>dye solution (mL)</th>
<th>deionized water (mL)</th>
<th>bleach solution (mL)</th>
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</thead>
<tbody>
<tr>
<td>1</td>
<td>4.00</td>
<td>0.00</td>
<td>2.00</td>
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<tr>
<td>2</td>
<td>4.00</td>
<td>1.00</td>
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Clean up:

1. 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.
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. Initial concentration of red dye (MW = 879.9 g/mol) stock solution (in mol/L):

   __________________ mol/L

3. Record the Absorbance of the solution prepared in Part A (6.): ________(no units)

4. Mass percent of sodium hypochlorite in the bleach: ______________

Part B. Absorbance data for each reaction mixture

<table>
<thead>
<tr>
<th>Time (sec)</th>
<th>Absorbance Reaction #1</th>
<th>Time (sec)</th>
<th>Absorbance Reaction #2</th>
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CALCULATIONS & DATA TREATMENT
Experiment 13I

Part A. Determining concentrations & molar absorptivity

Note: Use proper significant figures and units.

(A.1) Using $M_{\text{conc}}V_{\text{conc}} = M_{\text{dilute}}V_{\text{dilute}}$ and the initial concentration of the stock solution recorded in Part A, calculate the concentration of the red dye solution you made in Part A (3).

[red dye] Part A(1) __________________________ [red dye] Part A(3) __________________________

(A.2) Use Beer’s Law and the absorbance recorded in Part A (6) to calculate the molar absorptivity of the red dye solution.

Molar absorptivity ________________

(A.3) Mass percent of sodium hypochlorite in the bleach: ______________

(A.4) Assuming that the density of bleach solution is 1.00 g/mL, calculate the molarity of the sodium hypochlorite in the stock bleach solution provided.

(A.5) Using $M_{\text{conc}}V_{\text{conc}} = M_{\text{dilute}}V_{\text{dilute}}$, calculate the molarity of the sodium hypochlorite in reaction mixtures #1 and #2:

[bleach] Reaction #1 ________________

[bleach] Reaction #2 ________________
Part B: Data analysis

For a refresher on using Excel to perform calculations and graph data, check out the tutorials on the Chemistry Department website: http://www.chemistry.usna.edu/plebeChem/excel_tutor/index.htm

(B.1) Enter your time and absorbance data for Reaction #1 into an Excel spreadsheet.

(B.2) 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:

\[ [\text{red dye}] = \epsilon \times \ell \]  

(B.3) Prepare three plots using your data from Reaction #1: [red dye] vs. time, ln[red dye] vs. time, and 1/[red dye] vs. time. The plot that visually appears the most “linear” tells you the order of the reaction, with respect to [red dye]. Perform linear regressions on each plot. The plot with the R^2 value closest to 1.0 is the most linear.

Note: Record which plot has an R^2 value closest to 1.0: ____________________________

Record the order with respect to [red dye], a: ________________________

(B.4) Enter time and absorbance data for Reaction #2 in the same Excel worksheet. Refer to your record of which plot was most linear (B.3) and construct this same plot for Reaction #2. Perform a linear regression on the plot, making sure to include the equation of the trend-line and R^2 value for the graph.

Note: Use the slope of each trend-line to solve for the order in bleach

Slope (= -k’_{\text{EXP#1}} if 0 or 1st order, = k’_{\text{EXP#1}} if 2nd order) of trend-line Rxn #1: ____________________________

Slope (= -k’_{\text{EXP#2}} if 0 or 1st order, = k’_{\text{EXP#2}} if 2nd order) of trend-line Rxn #2: ____________________________

(B.5) By comparing the slopes of the trend-lines for Reactions #1 and #2 and the initial bleach concentrations calculated in (A.5), determine b, the order of the reaction with respect to bleach (i.e. OCl^-). Remember, the slopes of your graphs equal –k’ if the reaction is 0 or 1st order and equals k’ if the reaction is 2nd order, and k is numerically the same for both reactions.

\[
\frac{k'_{\text{EXP#1}}}{k'_{\text{EXP#2}}} = \frac{k [OCl^-]_{\text{EXP#1}}^b}{k [OCl^-]_{\text{EXP#2}}^b}
\]

(B.6) Write the experimental rate law based on the order of the red dye and the order of the OCl^- that you obtained in your analysis

(B.7) Calculate the rate constant, k, for this reaction (remember to include proper units)
1. For Reaction #1, determine the initial (time = 0 minutes) and final (time ≈ 10 minutes) concentrations of the hypochlorite ion. Does this justify the assumption that the rate law depends only on the red dye concentration for this reaction? Explain.

2. Shown below are six proposed mechanisms for the reaction of red dye with bleach. Which of the following mechanisms is consistent with the rate law you determined in this experiment? In the mechanisms below, D represents the red dye molecule and DO represents the colorless product.

<table>
<thead>
<tr>
<th>Mechanism #1</th>
<th>Mechanism #2</th>
</tr>
</thead>
<tbody>
<tr>
<td>2 D(aq) → D₂(aq)</td>
<td>(Slow) D(aq) + OCl⁻(aq) → DOCl⁻(aq)</td>
</tr>
<tr>
<td>D₂(aq) + OCl⁻(aq) → DO(aq) + D(aq) + Cl⁻(aq)</td>
<td>(Fast) DOCl⁻(aq) → DO(aq) + Cl⁻(aq)</td>
</tr>
<tr>
<td>Mechanism #3</td>
<td>Mechanism #4</td>
</tr>
<tr>
<td>2 D(aq) + OCl⁻(aq) → DO(aq) + DCl⁻(aq)</td>
<td>(Slow) OCl⁻(aq) → O(aq) + Cl⁻(aq)</td>
</tr>
<tr>
<td>DCl⁻(aq) + D(aq) → 2 D(aq) + Cl⁻(aq)</td>
<td>(Fast) O(aq) + D(aq) → DO(aq)</td>
</tr>
<tr>
<td>Mechanism #5</td>
<td>Mechanism #6</td>
</tr>
<tr>
<td>D(aq) + 2 OCl⁻(aq) → DO(aq) + OCl₅²⁻(aq)</td>
<td>(Slow) 2 OCl⁻(aq) → O₂(aq) + 2 Cl⁻(aq)</td>
</tr>
<tr>
<td>OCl₅²⁻(aq) + OCl⁻(aq) → 2 OCl⁻(aq) + Cl⁻(aq)</td>
<td>(Fast) O₂(aq) + 2 D(aq) → 2 DO(aq)</td>
</tr>
</tbody>
</table>
PRE-LAB EXERCISES
Experiment 13I

BRING YOUR NETBOOKS TO LAB

1. Calculate how many grams of sodium hypochlorite (NaOCl) solution were dissolved in 1.00 L of distilled water to give a 0.81 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.