Experiment 25: The Kinetics of the Reaction between Hypochlorite and Food Dyes

Introduction The hypochlorite ion (OCl^-) reacts with various food dyes to form colorless products:

$$OCl^- + \text{dye} \rightarrow \text{colorless products} \qquad \text{Equation 1}$$

The rate law for this reaction is expected to be of the form:

$$\text{Rate} = k[OCl^-]^x[\text{dye}]^y \qquad \text{Equation 2}$$

Where Rate is the rate of the reaction, k is the rate constant for the reaction, x is the order of the reaction with respect to OCl^- and y is the order of the reaction with respect to the dye. The rate constant, k, as well as x and y are parameters that can be determined by experiment. If the reaction between OCl^- and a particular food dye is carried out at identical dye concentrations but two different OCl^- concentrations, two different rates will result:

$$Rate_1 = k[OCl^-]_1^x[dye]^y \qquad \text{Equation 3a}$$
$$Rate_2 = k[OCl^-]_2^x[dye]^y \qquad \text{Equation 3b}$$

The difference in the rates of the two reactions will be a consequence of the different [OCl^-] concentrations in the two experiments. This difference in concentration is indicated by the subscript on [OCl^-] in equations 3. If we divide equation 3a by Equation 3b, the following results:

$$\frac{Rate_1}{Rate_2} = \frac{k[OCl^-]_1^x[dye]^y}{k[OCl^-]_2^x[dye]^y} = \frac{[OCl^-]_1^x}{[OCl^-]_2^x} \qquad \text{Equation 4}$$

Where we note that k and $[\text{dye}]^y$ cancel, given that these are identical between the two experiments. Taking the natural logarithm of both sides of Equation 4:

$$\ln\left(\frac{Rate_1}{Rate_2}\right) = \ln\left(\frac{[OCl^-]_1^x}{[OCl^-]_2^x}\right) = x\ln\left(\frac{[OCl^-]_1}{[OCl^-]_2}\right) \qquad \text{Equation 5}$$

In the experiments conducted in this laboratory, we will ensure that the second trial will always contain twice the [OCl^-] of the first trial. Therefore, we can write Equation 5 as:

$$\ln\left(\frac{Rate_1}{Rate_2}\right) = x\ln\left(\frac{1}{2}\right) = -0.693x \qquad \text{Equation 6}$$

Solving for x, we have:

$$x = -1.44\ln\left(\frac{Rate_1}{Rate_2}\right) \qquad \text{Equation 7}$$

Equation 7 therefore gives us a convenient way of determining x, the order of the reaction with respect to hypochlorite ion.

Once the value of x is determined, the values of k and y need to be found in order to determine the entire rate law. To see how we find these values, let's first revisit equation 2:

$$\text{Rate} = k[OCl^-]^x[\text{dye}]^y \qquad \text{Equation 2}$$

In the experiments conducted in this laboratory, the concentration of OCl^- remains much, much higher than the concentration of dye. As a result, the $[OCl^-]$ remains essentially constant throughout each trial. Because of this, we can define an approximate constant called k':

$$k' = k[OCl^-]^x \qquad \text{Equation 8}$$

Substitution of Equation 8 into Equation 2 yields:

$$\text{Rate} = k'[\text{dye}]^y \qquad \text{Equation 9}$$

It is known from kinetic studies that certain plots versus time yield linear results when the order of a reaction with respect to a reactant is zeroth, first or second order (Table 1).

Table 1: Plots for the determination of reaction order with respect to a particular reactant

Order of Reaction	**Plot**	**Slope of line is equal to**
0	[dye] versus time	-k'
1	ln[dye] versus time	-k'
2	1/[dye] versus time	k'

Because the dye is colored, we can monitor the dye concentration by measuring its absorbance at a particular wavelength throughout the reaction. Recall that the absorbance of a dye is related to its concentration through the relationship:

$$A = \varepsilon b[dye] \qquad \text{Equation 10}$$

Where A is absorbance, ε is the molar absorptivity of the dye (see Table 2) and b is the path length (the small, medium and large MicroLab vials are 1.445 cm, 1.665 cm, and 2.245 cm, respectively).

Table 2: Molar absorptivity of various food dyes

Dye	**Wavelength**	**Molar absorptivity M^{-1} cm^{-1}**
Blue #1	635 nm	2×10^5
Yellow #5	580 nm	3.6×10^4
Red #3	530 nm	8×10^4

Rearranging, Equation 10 can be written as:

$$[dye] = \frac{A}{\varepsilon b} \qquad \text{Equation 11}$$

Thus, measured absorbance values can be converted into dye concentrations, using Equation 11.

Now to find the value of y, we measure the time dependent absorbance of the dye in its reaction with OCl^-. These absorbance values are converted into dye concentrations, using Equation 11. Next, the various plots indicated in Table 1 are constructed, and we identify which plot is linear. If [dye] versus time is linear, the value of y is 0. If ln[dye] versus time is linear, the value of y is 1. If 1/[dye] is linear, the value of y is 2.

Once the values of x and y are both found, we can determine the value of the rate constant, k for each reaction. To do so, we first need to determine the rate of each reaction. Reaction rates are often determined using the method of initial rates; we will use this method in this lab. A plot of [dye] versus time is made (Fig 1)

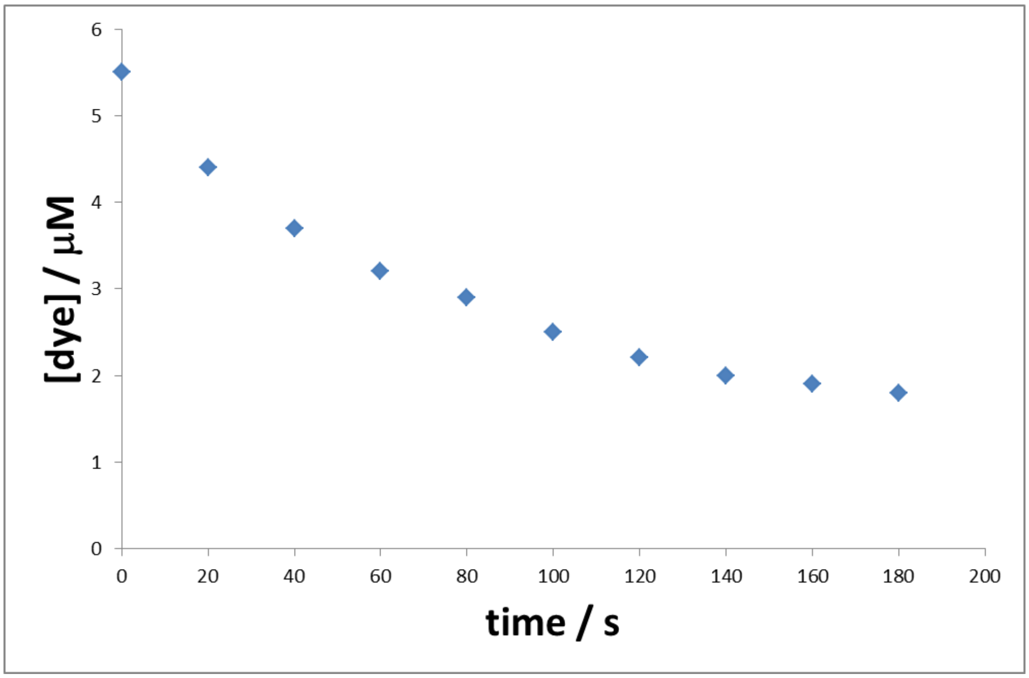


Figure 1: Determination of reaction rate by the method of initial rates. The [dye] is 5.5 µM at t = 0 s and 4.4 µM at t = 20 seconds.

We choose two data points very close to t = 0, and find the average rate of the reaction between these two points:

$$Rate = \frac{\Delta[dye]}{\Delta t} = \frac{[dye]_f - [dye]_i}{t_f - t_i}$$

Equation 12

For example, using t_i = 0 s (where [dye] = 5.5 mM) and t_f = 20 seconds (where [dye] = 4.4 mM), we calculate a value of 0.055 µM s^{-1} for the rate of a reaction. Once this rate is found, we can use Equation 2:

$$Rate = k[OCl^-]^x[dye]^y$$

In the following form:

$$k = \frac{Rate}{[OCl^-]^x[dye]^y} \qquad \text{Equation 13}$$

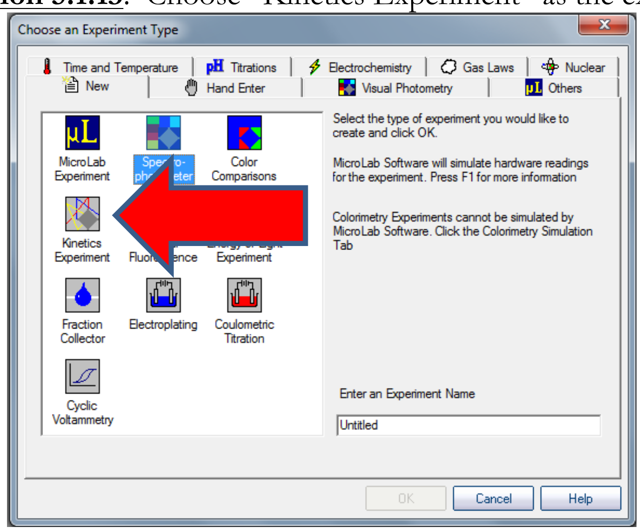
To find the value of k.

Materials: MicroLab FS522, blue dye #1 (about 10 drops per L), yellow dye #5 (about 10 drops per L), red dye #3 (about 10 drops per L), household bleach.

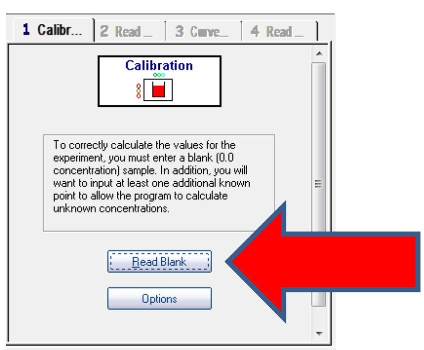
Procedure

Set up of the experiment. **NOTE: USE MICROLAB VERSION 5.1.13!!! If your computer does not run this version of MicroLab, you can download it quickly from the MicroLab website at www.microlabinfo.com**

1. Pipette exactly 10.0 mL of the dye of your choice into two separate, large MicroLab vials.
2. Place 10 mL of DI water in a large MicroLab vial.
3. Open MicroLab **version 5.1.13**. Choose "Kinetics Experiment" as the experiment type.

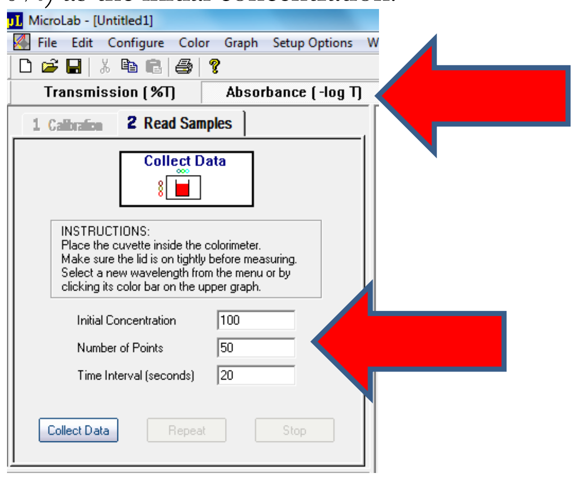


4. Place the DI water (blank) in the spectrophotometer, cover with the film canister, then Choose "Read Blank":



Running the reaction to determine the rate law

1. Click the "Absorbance (-log T)" tab, enter the total number of points as 50, and the time interval as 20 seconds. Just choose 100 (100%) as the initial concentration.



2. Read this step through in entirety before starting: Click on the start button, add 5 drops of bleach (this experiment will have $[OCl^-]$ = 0.015 M) to the 10 mL of food dye, cap, mix well, place the vial into the spectrophotometer, and place the film canister on top. Keep in mind you have only 20 seconds to complete this entire process!!
3. Allow the reaction to run until the sample displays less than 30% of the absorbance at time t = 0.
4. Click stop, and save the absorbance data in Excel.
5. Open the data in Microsoft Excel. Plot the absorbance data at the appropriate wavelength (635 nm for blue dye, 502 or 525 nm for red dye) versus time.
6. Convert the absorbance data to dye concentration, using Equation 11, b = 1.445 cm (small vial), b = 1.665 cm (medium vial) or 2.245 cm (large vial) and the value of ε appropriate for the dye.
7. Plot dye concentration versus time.
8. Determine the initial rate of the reaction, using the plot constructed in step 7, Equation 12 and two points very close to t = 0.
9. Repeat steps 2 – 8, but this time add 10 drops of dye (this experiment will have $[OCl^-]$ = 0.030 M).

<u>Data Analysis:</u>

1. Note that dye concentration is identical in experiments 1 and 2. Also note that $[OCl^-]$ in trial 1 is twice that $[OCl^-]$ in trial 2. Therefore, we use Equation 7 to find the value of x, the order of the reaction with respect to $[OCl^-]$.
2. Prepare plots of ln[dye] versus time and 1/[blue dye] versus time for all trials.
3. From these plots, determine y, the order of the reaction with respect to the dye.
4. Determine the initial concentration of the dye used in your experiments using Equation 11.
5. Using Equation 13, determine k, the value of the rate constant. Recall that $[OCl^-]$ = 0.015 M for the runs with 5 drops of bleach added and $[OCl^-]$ = 0.030 M for the runs with 10 drops of bleach added. You will need to use the initial concentration of the dye calculated in step 4 of this analysis.

<u>Questions</u>: Fill in the chart below. Be sure to include the appropriate units for k.

Reaction	k (rate constant)	x	y
Blue dye + OCl^-			
Red dye + OCl^-			

<u>References:</u>

Henary, M. M. and Russell, A. A. **2007** *Journal of Chemical Education 84*, 480 – 482.

Arce, J.; Betancourt, R.; Rivera, Y. **1998** *Journal of Chemical Education 75*, 1142 – 1144.