Introduction

Bleaching is a process by which a chemical reaction occurs that causes a colored compound to become colorless. Most common bleaching reactions involve an oxidant oxidizing a colored dye. In the reaction, the dye becomes colorless.

oxidant + dye → reduced oxidant + colorless product

In the case of laundry bleaching, there are two kinds of bleaches, chlorine and "color safe." Chlorine bleach uses the hypochlorite ion, OCl^-, as the oxidant. The OCl^- oxidizes stain molecules to render them colorless.

$OCl^-(aq)$ + dye → $Cl^-(aq)$ + dye-O

The oxidized dye, dye-O, does not necessarily leave the cloth being bleached. That is, the stain is not necessarily removed, but simply becomes invisible because it no longer absorbs visible light.

In this experiment we will determine the rate law of the chlorine bleaching process as well as the activation energy of the reaction. We use the reaction between hypochlorite ion and blue food dye.

The bleaching reaction is:

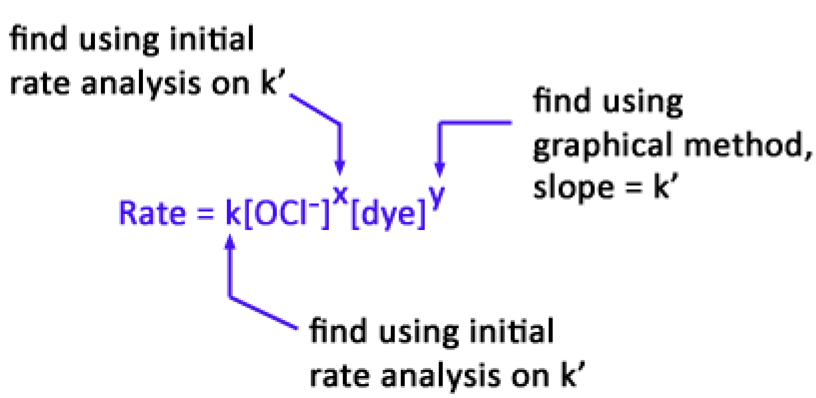
$OCl^-(aq)$ + dye(aq) → dye-O(aq) + $Cl^-(aq)$

PART 1. Determining the Rate Law

The general rate law is,

$$\text{rate} = k[OCl^-]^x[\text{dye}]^y$$

To determine the rate law, we must determine the orders for the reaction, x and y, and the rate constant, k. The reaction is followed by observing the absorbance due to the blue dye disappear over time.



Part 1. Procedure

You will record the absorbance due to blue food dye using the MeasureNet Colorimeter provided (directions on separate sheet). The reaction is performed with three different concentration of hypochlorite ion and data should be recorded for each.

$[OCl^-]$ solutions are actually based on NaOCl solutions. Bleach in the bottle is 6%. The most concentrated solution used here is diluted 1:10. The other two are diluted 1:1 each from that. So, the concentrations are 0.60%, 0.30%, and 0.15%. Use that information to calculate the molarity of NaOCl in each of the three solutions.

The most concentrated NaOCl solution leads to the fastest reaction, for which data should be recorded every 10 seconds. For the slower reactions, data can be recorded less frequently. The absorbance will start out near 1.0 and should be recorded until reaching approximately 0.20.

To perform each experiment, add 5 mL of one of the bleach solutions to a small, dry beaker. Add 5 mL of the dye solution to a different dry beaker. Then mix the two together quickly and add enough to a cuvette to make the absorption measurements. Place the cuvette in the spectrometer quickly and start taking readings right away. When the absorbance decreases to below 0.2, the experiment is done.

Repeat the experiment for each of the three different bleach solutions. Perform the experiment for *the least concentrated bleach solution first*, then move to the middle one, and do the most concentrated bleach solution last.

Part 1. Calculations

You now have three sets of data showing how absorbance decreases over time for each of the three reactions you performed. You will use the graphical method to determine the rate law.

During these reactions, the bleach concentration is much greater than that of the blue food dye. Therefore, a very small fraction of the OCl^- reacts and the concentration of OCl^- can be considered essentially constant. Recall, however, that when you mix the bleach and dye solutions, the concentration of the bleach is cut in half.

$$[OCl^-] >> [dye]; \quad [OCl^-] \sim \text{constant}$$

The rate law can be rewritten,

$$\text{rate} = k'[dye]^y$$

$$k' = k[OCl^-]^x$$

Since this new rate law contains only a single changing species, the graphical method can be used to determine both the numerical value of k' as well as the value of y, the order of the reaction for dye. To do this, we make the (well tested) assumption that the absorbance we measured is proportional to [dye]. This is a safe assumption.

<u>Finding x, the order for [dye]</u>

For each of your three reaction trials, prepare three plots:

zero order:	absorbance vs. time
first order:	ln(absorbance) vs. time
second order:	1/absorbance vs. time

Only one of these types of plots will lead to a straight line for the three trials. Which one is linear tells you the value of y.

<u>Finding y, the order for [OCl^-]</u>

The absolute value of the slope of each linear plot tells you the value of k' for that trial. By comparing the three values of k' with the concentrations of OCl^- for each trial, the order of the reaction for OCl^- can be found.

$k' = k[OCl^-]^x$

Notice what happens to k' when [OCl^-] doubles:

if k' does not change, the reaction is zero-order in OCl^- (x = 0)
if k' doubles, the reaction is first-order in OCl^- (x = 1)
if k' quadruples, the reaction is second-order in OCl^- (x = 2)

<u>Finding k</u>

Once you know the value of x, you can solve for the value of k for each of the three trials by substituting in the known value of [OCl-]. *Remember that the stock solution was diluted in half when mixed with the dye solution.* Determine k for each and report the average.

Report the overall rate law as a single equation.

PART 2. Determining the Activation Energy

To determine the activation energy, the rate constant, k, must be measured at different temperatures. We will do so at three temperatures:

- 0^{o} C
- room temperature
- about 40 ^{o}C

Part 2. Procedure

0 ^{o}C
Place test tubes of the dye and the 0.034 M bleach solution in an ice bath. Wait till the temperature equilibrates. Repeat the experiment in Part 1 by mixing these two together and measuring absorbance over time. Because the solutions will warm as the reaction proceeds, only record this trial for 5 minutes. It will not go nearly to completion, but that's not bad.

Room Temperature
No additional experiment need be done here. You can use your trial from Part 1 here. Just record the temperature of the solutions that you used.

About 40 ^{o}C
Place test tubes of the dye and the middle-concentration bleach solution in a warm water bath at about 40 ^{o}C. It does not need to be exactly 40 ^{o}C, but you need to know (and record) the exact temperature. Repeat the experiment. This reaction will go fast, so record data at a short interval.

Part 2. Calculations
Determine the rate constant, k, for each of these three trials. (You already did for the room temperature experiment, so just do so for the other two). NOTE: because the temperature changes as the reaction proceeds, use only the first minute or so of your data when determining the rate constants for the cold and warm reactions.

Prepare an Arrhenius plot of ln k vs. 1/T. The slope of this plot is used to determine the activation energy using the Arrhenius equation.

$$\ln k = \ln A - \frac{Ea}{R}$$

So, the slope of the Arrhenius plot is equal to $-E_a/R$.   R = 8.314 J/K·mol.