**Determination of a Rate Law by Visible Spectroscopy**

**Introduction.** There are several ways by which a rate law for a given reaction may be determined. For example, reactant concentration can be systematically varied and reaction rates measured in order to determine the reaction order of each species. This is referred to as the method of initial rates. Alternatively, the concentration of the species of interest can be measured as a function of time in order to determine if it follows first or second order kinetic pathways. This method is particularly attractive if the compound of interest absorbs light since it allows the use of spectroscopic methods to measure the concentration. This second method is the focus of today’s lab.

As you are probably well aware, many dyes and colorings are sensitive to strong oxidizing agents. For example, many fabric dyes fade quickly when treated with common household bleach. In today’s lab, you will determine the rate law a similar reaction, the oxidation of blue food coloring (FD&C Blue #1; see structure below) by sodium hypochlorite, NaClO, the active component in laundry bleach.

![FD&C Blue #1 structure](image)

The rate law will have the form, \( rate = k [\text{dye}]^m [\text{ClO}^-]^n \) and you will experimentally determine the values of \( m \) and \( n \). The reaction yields colorless products so the extent of the reaction can be easily followed by monitoring the absorbance due to the dye as a function of time. By plotting the resulting data as \( \ln [\text{dye}] \) vs. time on one graph, and \( 1/[\text{dye}] \) vs. time on a separate graph, you will be able to determine the order of the reaction with respect to the dye, that is, the value of \( m \) in the above rate law.

But how do we determine the reaction order of hypochlorite ion? This is not a colored species so we cannot measure its concentration directly – another method must be used. This is not an uncommon problem and the solution is to perform the reaction under what is called **pseudo-first order conditions**. (!?!) This simply means to perform the reaction with a large excess of one of the reactants such that its concentration stays roughly constant over the course of the reaction. For example, assume the following hypothetical reaction is first order in A and B, that is, it has the rate law, \( rate = k [A][B] \).

\[
A + B \rightarrow C
\]
If the concentration of both A and B are equal at the beginning of the reaction, they will remain equal over the course of the entire reaction and classical second order kinetics will be observed, i.e., a plot of 1/[A] vs. time will be linear. If, on the other hand, a large excess of B is present at the beginning, a different result is seen – the decomposition of A will follow first order kinetics and a plot of ln [A] vs. t will be linear. Why? The explanation lies in what happens to the relative concentrations of A and B over the course of the reaction.

If \([A]_{\text{init}} = 0.001 \text{ M} \) and \([B]_{\text{init}} = 0.100 \text{ M} \), when A is completely consumed, [B] will equal 0.099 M, a value very close to its initial concentration. In other words, [B] is essentially constant in the reaction. As such, it acts like a constant in the rate law. So, if [B] is a constant, we can define a new constant as follows,

\[
k_{\text{obs}} = k \ [B]
\]

where \(k_{\text{obs}} \) is referred to as the observed rate constant. This substitutes into the rate law as follows,

\[
\text{rate} = k_{\text{obs}} \ [A]
\]

which has the form of a first order process. But how do you determine the order of the reaction in B? Simple. Perform the reaction at several concentrations of \([B]_{\text{init}} \) (all in large excess of \([A]_{\text{init}} \)), and observe the effect on the value of \(k_{\text{obs}} \). If there is no effect, then [B] has no effect on the reaction rate and the reaction is zero order in B. If the observed rate constant is directly proportional to [B], the reaction is first order in B. *(What would happen to \(k_{\text{obs}} \) if the reaction was second order in B?)*

In this lab, you will perform several trials of the reaction, each under pseudo-first order conditions at different hypochlorite concentrations. You will then calculate the value of \(k_{\text{obs}} \) for each run and plot these against the [OCl\(^-\)] to determine the order of the reaction in hypochlorite.

**Procedure.** Prepare 150 mL of a solution of FD&C Blue #1 dye such that the absorbance in a 1 cm cell is between 1.7 and 2.0. (This will require only about 2 drops of a solution of commercial food coloring). Use a volumetric pipet to deliver 25 mL of this solution to a 125 mL Erlenmeyer flask. Set up the spectrometer software in time acquisition mode to monitor the absorbance at 630 nm at least every second. Set up a filename and be ready to begin collecting data before you mix your solution.

When you are ready to begin collecting kinetic data, use a buret to deliver 2.0 mL of the 3.0 % sodium hypochlorite solution, swirl quickly to mix well, and deliver the solution to a cuvette to immediately begin collecting absorbance data. Fill a 1 cm cell with the solution and begin the time acquisition experiment on the spectrometer. Collect data (at 630 nm and 700 nm) until the absorbance at 630 nm is nearly equal to that of the baseline nearby. Stop the time acquisition and save the data to the hard drive or a flash drive. Repeat the procedure with three other volumes of hypochlorite solution. Your range of hypochlorite volume used should be at least a factor of ten.
Import the data into Excel or another spreadsheet and adjust the raw absorbance values by subtracting the absorbance measure at 700 nm from each of the points at 630 nm (this compensates for drift in detector response and related non-random errors in the data acquisition). Make a plot of the adjusted absorbance as a function of time. Your plot should look something like:

![Absorbance vs. Time](image)

Now, calculate the concentration of the dye at each point using Beer's Law ($\varepsilon = 125,000 \text{ M}^{-1} \text{ cm}^{-1}$). At this point you can make a first order plot ($\ln[A]$ vs. $t$) and a second order plot ($1/[A]$ vs. $t$) of the data. From whichever plot yields a straight line, use the slope to calculate $k_{\text{obs}}$. Repeat for each of your trials and then make a plot of $k_{\text{obs}}$ vs $[\text{OCI}^-]$. In your conclusion, describe the rate law that your results yield. Also calculate the value of the actual rate constant, $k$ and discuss any peculiarities in your results.