

## Lab 6: CHEMICAL KINETICS TO DYE FOR

### Laboratory Goals

In this week's lab you will:

- Determine concentrations via spectroscopy using Beer's Law
- Determine the rate law for the reaction between bleach and two dyes
- Determine the rate constant for the same reaction.

### Introduction

In this lab, you will be determining how quickly household bleach reacts with a couple of different dyes. In order to be able to understand this, we have to first visit the world of kinetics.

### Kinetics

Chemical Kinetics is the branch of chemistry which is concerned with the study of the rate of chemical reactions. The rate of a reaction is a measure of how quickly reactants are turned into products. This area of study directly complements the study of thermodynamics which focuses exclusively upon the energetic favorability of reactions. Consider the hypothetical reaction



The rate of formation of C is:

$$Rate_c = \frac{[C]_f - [C]_i}{t_f - t_i} = \frac{\Delta[C]}{\Delta t} \quad (2)$$

where  $[C]_f$  and  $[C]_i$  are the concentrations of C at times  $t_f$  and  $t_i$ , respectively. The symbol  $\Delta$  stands for "change." The rate of formation of C is the change in the concentration of C over the time interval  $\Delta t$  ( $t_f - t_i$ ). Similarly, the rate of formation of D is

$$Rate_D = \frac{\Delta[D]}{\Delta t} \quad (3)$$

The rates of consumption of A and B are

$$Rate_A = -\frac{\Delta[A]}{\Delta t} \quad (4)$$

$$Rate_B = -\frac{\Delta[B]}{\Delta t} \quad (5)$$

The negative signs in equations (4) and (5) arise from the fact that although the rates are positive numbers, the concentrations of the reactants decrease with time so their changes are negative. From the stoichiometry of reaction (1) we see that the consumption of 1 mole of A results in the consumption of 2 moles of B and the formation of 2 moles of C and 1 mole of D. B is consumed twice as fast as A, and C is produced twice as fast as D. Thus, the relationships between the rate expressions in equations (2)-(5) is

$$\frac{\Delta[D]}{\Delta t} = \frac{1}{2} \frac{\Delta[C]}{\Delta t} = -\frac{\Delta[A]}{\Delta t} = -\frac{1}{2} \frac{\Delta[B]}{\Delta t} \quad (6)$$

The rate of the reaction,  $\text{Rate}_{\text{RXN}}$ , can be expressed either in terms of the rate of disappearance of reactants or the rate of appearance of products:

$$\text{Rate}_{\text{RXN}} = \frac{\Delta[D]}{\Delta t} = \frac{1}{2} \frac{\Delta[C]}{\Delta t} = -\frac{\Delta[A]}{\Delta t} = -\frac{1}{2} \frac{\Delta[B]}{\Delta t} \quad (7)$$

In general, the rate of a reaction depends on the concentration of the reactant as follows:

$$\text{Rate}_{\text{RXN}} = k[A]^x[B]^y \quad (8)$$

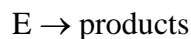
Equation (8) is the rate law for the reaction. In the generic rate law the concentration of each of the reactants raised to a power to give the overall rate law. This makes intuitive sense because one would anticipate that as the reactant concentration was increased that the rate of the reaction would also increase due to a greater number of molecular collisions between the reactants. In this case it shows that the rate is proportional to the product of the concentrations of the reactants raised to some power,  $x$  or  $y$ . The proportionality constant,  $k$ , is the rate constant and depends only on temperature. The exponents  $x$  and  $y$  are the reaction order with respect to A and B, respectively. These exponents are usually the integers 0, 1, 2, or 3, but in some reactions are found to be fractions or even negative! The sum of the exponents is the overall order of the reaction.

*For example*, if  $x = 1$ , and  $y = 2$ , then the reaction is said to be first order in A, second order in B, and third order overall.

*The values of the exponents in the rate law MUST be determined by experiment and CAN NOT be determined from the stoichiometry of the reaction.*

### **Rate Laws involving only one reactant:**

For the reaction



the rate law is:

$$\text{Rate}_{\text{RXN}} = -\frac{\Delta[E]}{\Delta t} = k[E]^x$$

If  $x = 1$  then the reaction is first order and

$$-\frac{\Delta[E]}{\Delta t} = k[E]^x$$

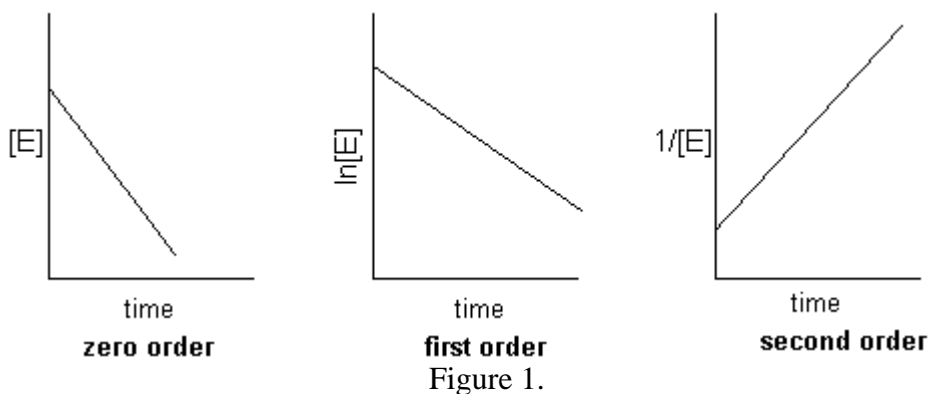
Using calculus and integrating this equation give equation 9 which is known as the integrated rate law (yes, this is creative naming here.)

$$\ln[E] = -kt + \ln[E]_0 \quad (9)$$

In equation 9,  $[E]_0$  is the initial concentration of E, and  $[E]$  is its concentration at time  $t$ . The integrated rate law gives the concentration of reactant as a function of time. Integrated rate laws for zero, second and third order reactions are given below.

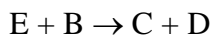
| Order  | Rate Law                              | Integrated Rate Law                         |      |
|--------|---------------------------------------|---|------|
| Zero   | $-\frac{\Delta E}{\Delta T} = k$      | $[E] = [E]_0 - kt$                          | (10) |
| First  | $-\frac{\Delta E}{\Delta T} = k[E]$   | $\ln[E] = -kt + \ln[E]_0$                   | (9)  |
| Second | $-\frac{\Delta E}{\Delta T} = k[E]^2$ | $\frac{1}{[E]} = kt + \frac{1}{[E]_0}$      | (11) |
| Third  | $-\frac{\Delta E}{\Delta T} = k[E]^3$ | $\frac{1}{[E]^2} = 2kt + \frac{1}{[E]_0^2}$ | (12) |

The integrated rate laws can be used to determine the order of a reaction. For example, if a reaction is first order, equation (9) predicts that a plot of  $\ln[E]$  vs. time is linear with a slope of  $-k$ . If the reaction is zero order then a plot of  $[E]$  vs. time is linear with a slope of  $-k$ . If the reaction is 2<sup>nd</sup> or 3<sup>rd</sup> order, then graphs of either  $1/[E]$  or  $1/[E]^2$  vs. time will be linear respectively and the slope will again relate to  $k$ . Some examples are shown in Figure 1.



### Pseudo rate orders

The above rate laws can not directly be used for reactions with more than one reactant (and most reactions fit into this category) since changes in both reactant concentrations are occurring simultaneously (and potentially with different reaction order.) Any reaction that has more than one reactant usually falls into this category, including the ones you will do. In such situations, chemists often will instead find the *pseudo rate law* for the reaction. In this method, one of the reactants is present in large excess relative to the other. For example, consider the reaction



Suppose that the initial concentrations of E and B are  $1.000 \times 10^{-4}$  M and 0.2000 M, respectively. We see that  $[B] \gg [E]$ . If the reaction goes to completion, all of E is consumed as it is the limiting reactant, and the concentrations of both reactants will have decreased by  $1.00 \times 10^{-4}$  M. The final concentration of B at the end of the reaction is  $0.2000 - 1.000 \times 10^{-4}$  M = 0.1999 M, a decrease of only 0.05 %. Therefore the concentration of B remains essentially constant during the reaction, and equation (8) becomes:

$$\text{Rate}_{\text{RXN}} = k_{\text{obs}} [\text{E}]^x \quad (13)$$

where  $k_{\text{obs}}$  is the observed  $k$  and

$$k_{\text{obs}} = k[\text{B}]^y = \text{a constant} \quad (14)$$

The only variable in equation (13) is the concentration of E, and just like before the order with respect to E can be determined by plotting each of the quantities: [E], ln([E]), 1/[E] and 1/[E]<sup>2</sup> vs time to determine which plot is linear. As indicated above,  $k_{\text{obs}}$  can be determined directly from the graphs. The order with respect to B can be determined by using different excess concentrations and observing the effect this has on  $k_{\text{obs}}$ . For example, if doubling [B] doubles  $k_{\text{obs}}$  then  $y = 1$  in equation 14. On the other hand if doubling [B] causing  $k_{\text{obs}}$  to increase by a factor of 4, then  $y = 2$ . Mathematically this can be represented as:

$$\frac{k_{\text{obs}1}}{k_{\text{obs}2}} = \frac{[\text{B}_{\text{run}1}]^y}{[\text{B}_{\text{run}2}]^y}$$

If the  $[\text{B}_{\text{run}2}] = 2[\text{B}_{\text{run}1}]$  (doubled the concentration) and this results in  $k_{\text{obs}2} = 2 \times k_{\text{obs}1}$ , then the above equation can be simplified to:

$$\frac{k_{\text{obs}1}}{2k_{\text{obs}1}} = \frac{[\text{B}_{\text{run}1}]^y}{(2[\text{B}_{\text{run}1}])^y} \quad \text{or} \quad \frac{1}{2} = \left(\frac{1}{2}\right)^y \frac{[\text{B}_{\text{run}1}]^y}{[\text{B}_{\text{run}1}]^y} = \left(\frac{1}{2}\right)^y$$

For this example  $y = 1$ . Alternatively, in some reaction it is feasible to switch which reaction is in excess. Note that when you need to do this, you need to be very careful to be sure that you are using the right values of  $k$  and using the concentrations of the reactant in excess.

### The Importance of Rate Laws

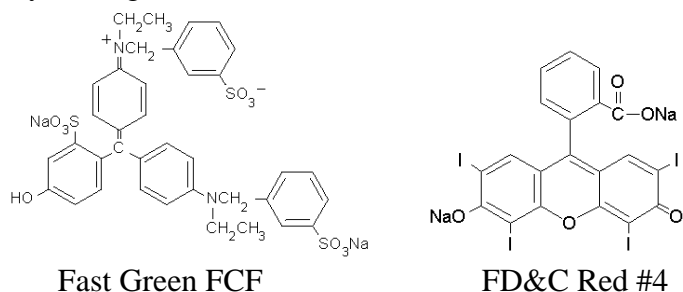
Not only do the rate laws allow us to mathematically predict the rate and manner in which products will disappear and that reactants will form, but the rate law also give us insight into how the reaction may be occurring at the molecular level. Reactions occur through a series of individual steps which comprise the reaction mechanism. The rate law for a mechanism can be easily determined. If this determined rate law does not equal the observed rate law then we know that the mechanism is incorrect. Keep in mind that just because a mechanism that fits the experimentally determined rate law, it does not mean that you have the correct mechanism for the reaction. Mechanisms can only ever be disproven, never proven. We will take a more in depth look at mechanisms in lab next week.

### Bleach and Dyes

Today you will be studying the kinetics of the reaction between sodium hypochlorite, NaOCl, and the food dyes Fast Green FCF (C<sub>37</sub>H<sub>34</sub>N<sub>2</sub>Na<sub>2</sub>O<sub>10</sub>S<sub>3</sub>) and FD&C Red #4 (C<sub>20</sub>H<sub>6</sub>I<sub>4</sub>Na<sub>2</sub>O<sub>5</sub>). (You can also bring in other materials as well to test. For example if you bring in Mountain Dew, you can actually find the order of the reaction of bleach with FD&C Yellow #5. If you opt to bring in another sample, be sure that it can be dissolved (or already is dissolved) in water and that it is clear. If there is more than one colored compound, you will just have to determine if you can detect each independently on the spectrophotometer.) Sodium hypochlorite is the active ingredient in commercial bleaches such as *Chlorx* and *Purex*. The reactions are



The structures for the two dyes are given below:



The rate law for reaction 15 and 16 are

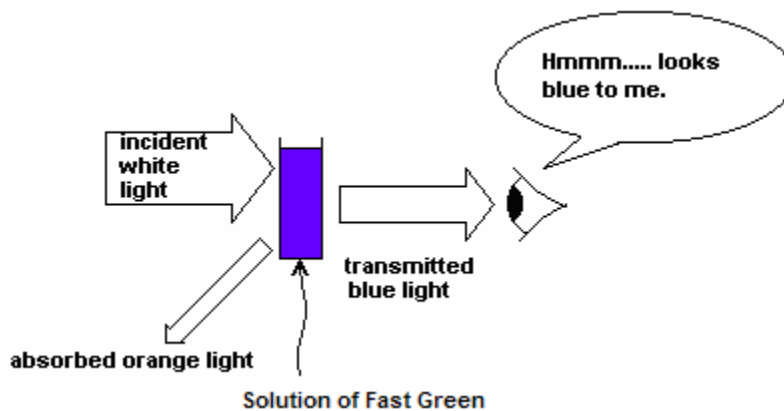
$$\text{Rate} = k[\text{NaOCl}]^x[\text{Green}]^y \quad (17)$$

$$\text{Rate} = k[\text{NaOCl}]^u[\text{Red\#4}]^v \quad (18)$$

The purpose of the experiment is to determine the order with respect to each reactant for each of the two dyes (i.e. find values for x, y, u and v in equations 17 and 18.) You will need to use pseudo order in order to determine the rate law with the NaOCl being in excess. If NaOCl is present in large excess, its concentration is essentially constant, and we define a new constant,  $k_{\text{obs}}$ , where  $k_{\text{obs}} = k[\text{NaOCl}]^x$ , and equation (17) then becomes

$$\text{Rate} = k_o[\text{Green}]^y \quad (19)$$

All of the reactants and products are colorless except Fast Green FCF (the same is true when using the red#4). The blue color of a solution of Fast Green FCF is due to the fact that the dye molecules absorb a portion of the visible spectrum. That part of the spectrum which is not absorbed is transmitted and gives the solution its blue color. As shown in Figure 2, The dye molecules absorb orange light (wavelength of about 615 nm).



The concentration of the dye can be determined by measuring the amount of light absorbed by the reaction mixture as a function of time similar to your work to determine the phosphate concentration in Lab 6 last semester. The measurement of light absorption will be done with the Ocean Optics. You should hopefully have a good sense of how light absorption works to give color by now. If not, look back at your labs from last semester.

Using the absorbance data, you can then determine the concentrations of your dye at each of the different time points using Beer's Law.

## Procedure

You will work in groups of three this week. Each group will have their own spectrometer with which to work.

### *Beer's Law*

For this lab you will have to first test your dye to ensure that it follows Beer's Law at the concentrations with which we are concerned. (Refer back to LBS 171 Lab 5 for a review of how to do this.) You should use a  $\lambda$  for which your dye absorbs intensely (610 nm works well for green and 525 works well for red. You will be able to check that these wavelengths are accurate while making your Beer's Law plots. Once you have determined that your dyes do indeed follow Beer's Law, then you can progress on with determining the order. If you find that your dyes do not follow Beer's Law, then you will have to determine the concentrations at which they do follow Beer's Law. If it turns out that these concentrations are too low to be detected, then it is possible that this will not constitute a suitable dye to be measured in this manner. At this point consult your LA for ideas of how to proceed.

### *Testing the rates*

As described above, since there are two reactants in this reaction, we will need to have one in a significant excess in order to be able to apply the pseudo rate law concepts. Since we are hoping to follow the extent of reaction by the color, then it must be the dye that is the limiting reagent and the bleach in excess (otherwise the color wouldn't change appreciably.) In order to prevent the reaction from occurring too quickly, it will be necessary to dilute the initial bleach concentration. For your initial attempts, you will likely find 20% and 10% bleach concentrations to be effective. If you find that the reaction is either going too slow or too fast, you can subsequently adjust the concentration of bleach. You will probably need to make about 80 mL of each solution (and it is best to only make them once to minimize possible error.) For the 20% solution this will require 16 mL of bleach diluted to 80 mL of total volume.

The concentrations of the green and red dyes will be provided on the bottle.

In order to measure the absorbance of the solution, you will need to:

- Zero the spectrometer using a blank (you should use your bleach diluted with an equal volume of water to make the blank. This will approximate the residual materials left in your cuvette after the reaction has completed. If you change bleach concentrations you will need to repeat this step.
- Prepare the spectrometer for running a timed sample. Your LA will be able to instruct you on how to do this.
- Mix 10 mL of bleach solution and 10 mL of your dye solution in a 100 mL beaker. Quickly swirl this to mix the solutions, then transfer a portion of the liquid to your cuvette.
- Begin collecting data.
- Save the data.
- Repeat 2 more times with the same concentrations of reagents.

You will then need to perform the same reaction using a different concentration of bleach. Remember that you will need to re-zero your spectrometer with a new “blank” solution made from the new concentration of bleach.

Repeat with a second dye, though you only need to determine the order of this reaction with respect to the dye. If you wish to additionally determine the order with respect to the bleach you are welcome to do so, though it is not necessary.

### **Results (Graphs, calculations and tables)**

This lab (and subsequent lab report) will rely heavily upon the data that you have generated. Converting this information to the understandable and helpful graphs and tables will be critical. You should be sure to include graphs for time vs. the different forms of concentration to demonstrate how you determined which order was correct. You should be sure to include the ones that were not straight as a reference as well (and please try to conserve paper here. You can probably put the graphs testing for orders of 0,1,2 and 3 all on one piece of paper.) Remember that you should only use that data which falls in the absorbance range where you demonstrated that Beer’s Law held true. All tables and graphs should be computer produced (Excel or other spreadsheet programs work well). Doing this will also allow you to quickly get the appropriate trendline from the computer. Remember that the slope of the straight line that you get in your graph to determine the correct order is related back to the value of  $k_{obs}$ .

In terms of the calculations, it will be necessary to know that commercial bleach is 5% NaOCl (by weight). You will have to use this to first determine the concentration present in the bleach and follow all of the different dilutions that you did to determine the concentration in your actual reaction. This will be necessary to determine the actual value for the rate constant.

### **Lab Report**

This will be a lab report written with your partner(s). You should include a title page, abstract, procedure, results, discussion, data, calculations and conclusions.

Be sure to address the concentrations of dye and 20% NaClO in the reaction mixture **before** reaction occurs. Explain if your assumption is justified or not.

### Chemicals

Bleach solution (5% NaOCl), red dye, green dye (caution: all these may leave permanent marks on clothes)

### Equipment

UV/Vis spectrometers, volumetric flasks

### Chemical Disposal

All chemicals and solution may be disposed of down the drain.

### References

1. Mike Perona, “Chemical Kinetics to Dye For”. CSU Stanislaus Chemistry Department. Accessed online at: <http://wwwchem.csustan.edu/chem1112/DyeKinetics.htm>