

Kinetic Study of a Bleaching Reaction*

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(Revised 4/04, 10/08)

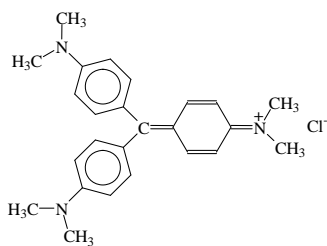
Purpose of this exercise: To study the factors which affect the rate of bleaching of a dye by reaction with base. To compare the reactivity of two closely related dyes.

Background Information

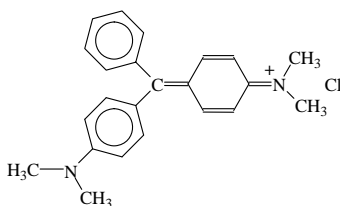
We have studied the properties of dyes more than once in this laboratory sequence. Last semester we studied their absorption of visible light, plotting their spectra and establishing the relationship between concentration and absorbance (Beer's Law). We used paper chromatography to separate and identify the dyes present in food colorings.

Dyes, like other material things, don't last forever. A brightly colored new garment, after exposure to air, sunlight, sweat, detergents, and bleaches, loses much of its initial brightness and becomes faded. This is because dyes are unsaturated organic substances which can be attacked by reactive chemical species and converted to colorless (or unattractively colored) products. Bleaches are strong oxidizing agents specifically intended to destroy colored organic molecules by oxidizing their double bonds.

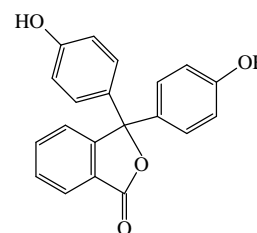
In this exercise, we will study a chemical reaction of a dye called Malachite Green (MG^+). This dye has a structural relationship to a green dye, Crystal Violet (CV^+) and to phenolphthalein, the indicator we have frequently used in acid-base titrations. Shown below are structures for each of these three dyes:



CRYSTAL VIOLET



MALACHITE GREEN



PHENOLPHTHALEIN

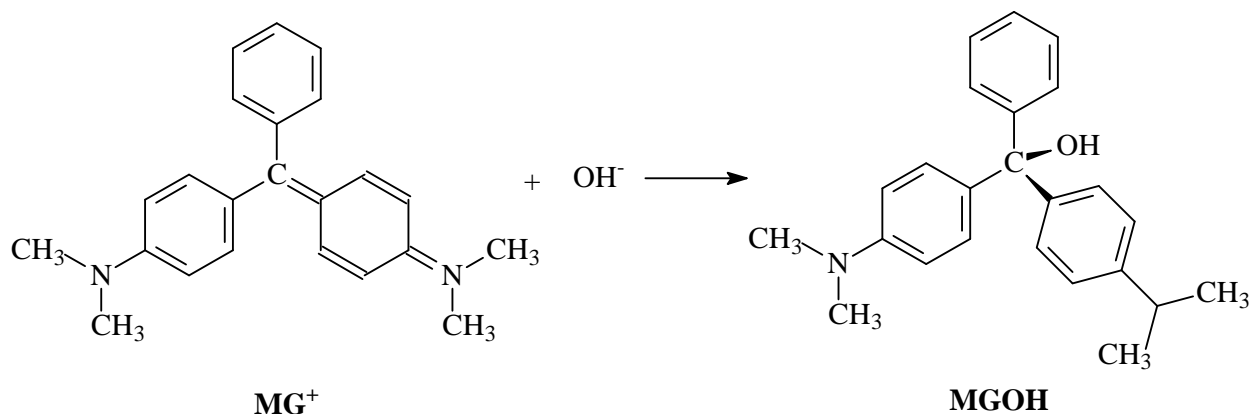
In both MG^+ and CV^+ , the coloring material is present as a cation (positively charged ion). These cations can be attacked by hydroxide ion, when the latter is at sufficiently high concentration, to form colorless products. This is therefore an example of a bleaching reaction.

In this exercise, we will study how rapidly this reaction occurs, and how the rate is affected by the concentrations of the reacting species; this constitutes a kinetic study of the reaction. Chemical kinetics is the study of reaction rates and how they are affected by reaction conditions, especially concentration. The kinetics of a reaction provides important evidence concerning the *mechanism* of the reaction, i.e. the detailed, step-by-step process by which it occurs. For a general reaction $\text{A} + \text{B} \rightarrow \text{C}$, the kinetic behavior may be described by an equation, called a rate law, which has the form:

$$\text{Rate of reaction} = -d[A] / dt = +d[C] / dt = k[A]^m [B]^n.$$

In this equation, **k** is called a rate constant (the specific rate), but it is constant only at a given temperature, pressure, etc. As always, [A] means "the concentration of species A in moles per liter." The exponents **m** and **n** show the dependence of the rate on the concentration of the species A and B, respectively. The sum of **m + n** is the *kinetic order* of the reaction. Thus, if **m** and **n** are each one, the reaction is said to be second order. The superscripts **m** and **n** cannot be predicted in general from the reaction stoichiometry; rather, they must be determined experimentally in a study of the kinetics of the reaction. That is what we will do for the reaction of Malachite Green with hydroxide ion.

The overall reaction is:



Since one *reactant* is brightly colored and the *product* is not, the obvious way to follow the progress of the reaction is to monitor the *disappearance* of the color. We already know that the absorbance at a given wavelength is directly proportional to the concentration of the absorbing species (Beer's Law). So we can use our colorimeter to measure the absorbance A at the analytical wavelength of Malachite Green (617 nm) over a period of time as the dye is consumed in reaction.

The rate law for this reaction may be expressed as:

$$\text{rate} = -d[\text{MG}^+]/dt = k[\text{MG}^+]^m [\text{OH}^-]^n \quad (1)$$

In order to get the reaction to occur at a convenient rate, we will carry out the reaction using a large excess of sodium hydroxide. The concentration of MG^+ will be about $1 \times 10^{-5} \text{ M}$, which allows easy measurement of its absorbance, but the concentrations of hydroxide ion will be in the range of $4\text{-}8 \times 10^{-3} \text{ M}$. Under these conditions, the concentration of hydroxide ion changes by only a fraction of a percent when all of the CV^+ is used up, and can be considered a constant. Therefore, the apparent rate law will be

$$\text{rate} = -d[\text{MG}^+]/dt = q[\text{MG}^+]^m, \quad \text{where } q = k[\text{OH}^-]^n. \quad (2)$$

This equation tells us how the rate will be affected as reaction occurs and the MG^+ gets used up. If $\mathbf{m} = 1$, this would be described as a *pseudo-first order reaction*; if \mathbf{m} is 2, this would be described as *pseudo-second order*. We say pseudo (fake) because we have washed out the effect of hydroxide concentration by using a large excess. After we have determined the values of \mathbf{q} and \mathbf{m} in this manner, we can do further runs using different concentrations of hydroxide ion, $[\text{OH}^-]$, to determine \mathbf{n} , thereby getting a more complete picture of the overall kinetics.

The rate law equations above have described how the *rate* ($-\text{d}[\text{MG}^+]/\text{dt}$) should vary with *concentration*. But what we really measure is the **absorbance** which, because of Beer's Law, is proportional to the concentration of A, and therefore we measure *concentration* versus time. To get an equation which directly relates the concentration or absorbance to time, it is necessary to *integrate* the rate equation. This requires some assumption about possible values of \mathbf{m} . If we assume that $\mathbf{m} = 1$, then integration of equation (2) can be shown to give us the relation

$$\ln ([\text{MG}^+]_0 / [\text{MG}^+]_t) = \ln (A_0 / A_t) = qt, \quad (3)$$

where the subscripts 0 and t refer to values at the beginning of the reaction and after elapse of t minutes, respectively. The quantity q is the same quantity shown in equation (2). Note that the Beer's law constant is cancelled out by taking the ratio, so we do not need to determine it in this case. Rearranging the equation into a more convenient form gives

$$\ln (A_t) = \ln (A_0) - qt. \quad \text{Where } A_0 \text{ is the absorbance at } t = 0 \quad (4)$$

Therefore if the reaction is pseudo-first order (i.e., $\mathbf{m} = 1$), then a plot of $\ln (A_t)$ versus t should be linear, with a slope equal to $-\mathbf{q}$ and an intercept equal to $\ln (A_0)$. Finding such a linear plot would validate the assumption that the reaction is pseudo-first order. Alternatively, we can plot $-\ln (A_t)$ versus t to give a straight line with a positive slope, \mathbf{q} .

If, on the other hand, the reaction is pseudo-second order (i.e., $\mathbf{m} = 2$), then integration of equation (2) gives the relationship

$$1 / [\text{MG}^+]_t = 1 / [\text{MG}^+]_0 + qt, \quad (5)$$

and a plot of the reciprocal of the concentration of MG^+ vs. time should be linear, with a slope of \mathbf{q} . As before, finding such a linear plot would validate the assumption of a pseudo-second order reaction. We will prepare both plots to determine which kinetic behavior is followed.

Then, having determined \mathbf{q}_1 (the value of q in an initial run) and \mathbf{m} , we can make a second kinetic run using different concentrations of hydroxide ion in order to determine the effect of a changed value of $[\text{OH}^-]$ on the rate, and thus \mathbf{n} and \mathbf{k} . We will also make a comparison of the rate of reaction of Crystal Violet with the rate of reaction of Malachite Green assuming both dyes follow the same rate law.

Procedures

CAUTION Sodium hydroxide is very caustic and can cause painful burns. In case of contact with the skin, flush the area with large amounts of water for several minutes. Crystal Violet and Malachite Green may stain garments and skin.

1. You will do this exercise in pairs, the teams being assigned by your TA. One partner should prepare a solution by diluting 10.0 mL of stock Malachite Green solution (measured by Dewick pipet) to 50.0 mL in a 100 mL graduated cylinder. The other partner will simultaneously prepare a base solution by diluting 4.0 mL of stock NaOH solution (approximately 0.1 M: record the actual value) to 50 mL. 150 mL beakers are recommended for these solutions.

2. These individual solutions should be equilibrated at room temperature by placing them in a plastic basin containing room-temperature water from a carboy in the hood. Do **not** use tap water, which is colder than room temperature, for this purpose. Swirl the solutions frequently in the water bath for several minutes. You may wish to measure the temperatures of the water bath and the solutions to insure that they are all at the same temperature.

3. While the solutions are coming to room temperature, you should do two things:

a.) set the wavelength of your Spectronic 20 spectrophotometer to 617 nm, and set the 0% and 100% transmittance points. 0% corresponds to no sample and 100% to a blank consisting of distilled water in the cuvette. If your spectrophotometer includes a filter that must be engaged or disengaged at 600 nm, be sure the filter is in the correct position;

b.) Measure the absorbance of the stock solution of the 10 fold **diluted** Malachite Green provided in the laboratory and record it in your notebook. You should verify that this corresponds to the initial concentration of the dye in the kinetic runs that follow. We use this single measurement to determine the Beer's Law constant for the dye in case it becomes necessary to use that value in the subsequent analysis.

4. To begin the run (at $t = 0$), one partner **pours the two solutions together** at the same time that the other **starts the timer**. Mix the solutions thoroughly by pouring back and forth between the two beakers, and as soon as possible, use a **small** portion to rinse the cuvette, fill the cuvette with the well-mixed solution, clean off the outside if necessary, and insert the cuvette into the Spectronic 20. Take an absorbance reading and simultaneously a time reading, and then discard the solution. **Leave the timer running**. Leave the remaining solution in the water bath to keep its temperature constant.

5. After the appropriate number of seconds (see the Table at the end of this section), place a fresh sample in the cuvette, and make another reading of absorbance and total elapsed time. Discard the sample after making the measurement. **Leave the timer running at all times**. Repeat at the appropriate time intervals until at least eight readings have been obtained.

6. After the first run, enter the time (in **seconds**) and absorbance data in the laboratory computer. The computer will produce graphs of $-\ln A_t$ (y-axis) vs. t (x-axis) and $1/A_t$ vs. t . In addition, it will produce the equation of the best straight line through the derived data points and the measure of goodness of fit, R^2 , for each line. The line with the largest value of R^2 is the one

which your data support as the best fit of your data. On that basis, record **m**, the order of the reaction with respect to MG^+ . The slope of the selected line is **q₁**, the pseudo specific rate for the reaction. Make sure your value of the slope has the appropriate number of significant figures. What are the units of **q₁** for the line that produced the best fit?

7. Make an additional kinetic run using identical dye solutions as prepared in step 1, but using 2.0 mL of $\sim 0.1\text{ M}$ NaOH diluted to 50 mL in the second run. The reaction will presumably proceed less rapidly in this case (Why?), so the time intervals between absorbance measurements should be adjusted correspondingly (See Table below). Enter the time and absorbance data in the laboratory computer. Again, two graphs are produced along with the equations of the best straight lines and the goodness of fit of each. From the graph of the *same quantity that gave the best fit in the first run*, determine the slope, **q₂**, of the line for the second run.

How does varying the concentration of hydroxide ion affect **q**? What is **n**, the order of the reaction with respect to $[\text{OH}^-]$? What is the specific rate of the reaction, **k**?

Note that the relationship between **q** and the specific rate involves the Beer's Law constant in the case of second order kinetics. (Problem 3 of the pre-laboratory exercise addresses this issue.

8. In order to compare the relative reactivity of two different dyes to base, prepare solutions as in step 1 but diluting 10 mL of stock solution of Crystal Violet rather than Malachite Green, and using 8.0 mL of base. Measure the absorbance of a separate solution of the appropriate concentration of Crystal Violet to obtain the absorbance at $t=0$. Using the Spectronic 20, follow the decrease of absorbance at 590 nm (remember to reset the zero and 100% transmittance settings, and the filter if your Spectronic 20 has one) for Crystal Violet, just as you did in steps 4-5 for Malachite Green. You should adjust the time interval used, taking measurements as shown in the Table below. Assuming the same kinetic order (that is, **m** and **n** the same as you found for Malachite Green), determine **k** for Crystal Violet by plotting the absorbance as a function of time for the conditions in the table below. Which is more reactive (i.e., which has the larger specific rate)?

Dye	mL of NaOH Stock Solution	Time interval (seconds)
Malachite Green	4.0	60
Malachite Green	2.0	120
Crystal Violet	8.0	180

Attach the computer generated graphs to your data sheets (one set per pair of students).

Beer's Law:

You are asked to review Beer's Law which was explored in an earlier exercise in the laboratory course. Beer's Law states that:

$$A = \epsilon b c$$

where:

A = Absorbance

e = absorptivity of the absorbing species

b = path length through the absorbing sample

c = concentration of the absorbing species

It may be necessary or appropriate to measure percent transmittance (%T) instead of absorbance. These two quantities are related by:

$$A = \log (100 / \%T) = 2 - \log (\%T) \quad (\text{The number 2 is exact})$$

In this exercise, the exact relationship between absorbance and concentration can be required (if the reaction is found to be second order in the dye). If the same cuvette is used throughout the exercise, the relationship between absorbance and concentration simplifies to:

$$A = k_B c$$

where k_B is the Beer's Law slope. This quantity is determined by a single measurement of the absorbance of a dilute solution of the dye.

SUSB-023 Data Sheet

Notebook Grade: _____

Safety Grade: _____

Name _____ Section _____ Date _____

Partner's Name _____

Conc. of NaOH stock solution _____ M Temp. of water bath _____

First Run: Malachite Green – 60 sec intervals – 617 nm

Volume of NaOH stock solution used _____4.00_____ mL

Volume of diluted MG⁺ solution _____ mL

Initial Volume of Reaction mixture _____ mL

Concentration of NaOH in reaction mixture _____ M

Beers Law Constant for MG⁺ _____ mL/mmol

Time (sec.)	Absorbance, A _t	Time (sec.)	Absorbance, A _t

Which plot is most nearly linear, log (Abs) or 1/Abs? _____

What is the kinetic order with respect to MG⁺? _____

Best value of q (from linear plot): _____

Units of q (from linear plot): _____

Second Run: Malachite Green – 120 sec intervals – 617 nm

Volume of NaOH stock solution used _____2.00_____ mL

Volume of diluted MG⁺ solution _____ mL

Initial Volume of Reaction mixture _____ mL

Concentration of NaOH in reaction mixture _____ M

SUSB-023 Pre-Laboratory Assignment

Name

Section

Date

1. Assuming the NaOH stock solution is 0.097 M, what are the initial concentrations of crystal violet and hydroxide ion in a solution made up of 4.0 mL of the NaOH stock solution diluted to 50 mL **plus** 50 mL of 1.00×10^{-5} M Crystal Violet solution?

2. The reaction of a dye called "O'Hara Scarlet" with 2.00×10^{-3} M sodium hydroxide solution is found to occur with a pseudo rate constant q_1 of 0.84. With 4.00×10^{-3} M sodium hydroxide, q_2 is 3.36. Assuming the reaction is first order with respect to the dye, what are n and k for this reaction? (If you cannot do this pre-laboratory exercise, you will also not be able to analyze the experimental data in this exercise!)

3. In the plot of $-\ln(\text{Abs})$ vs t (first order), we have noted that the slope of the plot is independent of the Beer's law constant for the dye. How does the slope, q , obtained from plotting $1 / \text{Abs}$ vs t depend on the Beer's law constant for the dye?

4. A plot of the reciprocal of absorbance of a dye called "Brick Yellow" versus time when it reacts with 2.00×10^{-3} M sodium hydroxide solution is found to have a slope q_1 of 1×10^{-3} . With 4.00×10^{-3} M sodium hydroxide, q_2 is 4×10^{-3} . Assuming the reaction is second order with respect to the dye, what are n and k for this reaction? Assume the Beers Law constant for Brick Yellow is 1.0 X 10

