Kinetics of the Bleaching of Dyes

Thermodynamics allows us to predict whether a reaction is favorable, but it does not tell us if the reaction will occur in a reasonable amount of time. To know something about the conditions that favor a timely reaction we must study the reaction's kinetics. The relationship between a reaction's rate and the concentrations of species that affect the rate is given by a rate law, which takes the general form

$$R = k[\mathrm{A}]^a[\mathrm{B}]^b \cdots [\mathrm{E}]^e$$

where k is the rate constant and A, B, and E are species whose concentration might affect the reaction's rate. The superscripts associated with the concentration terms are called reaction orders and may be positive or negative integers; they may even be zero or fractional.

In this two-week, open-ended experiment you will investigate the kinetics of the reaction responsible for the effectiveness of bleach. Commercial bleaches are solutions that contain one or more oxidizing agents. One of the most common oxidizing agents in bleach is the hypochlorite ion, OCl^-, which usually is added in the form of its sodium salt, NaOCl, typically at a concentration of 5–6 % w/v.

Bleaches work by oxidizing stains, converting the compound responsible for the stain to a colorless product. Most stains are just colored organic dyes; thus, we will use blue food coloring as a model stain compound. The overall reaction, then, simplifies to

$$\mathrm{dye}(aq) + \mathrm{OCl}^- \rightarrow \text{colorless product}$$

and the rate law for the reaction can, as a first estimate, is

$$R = k[\mathrm{dye}]^\alpha[\mathrm{OCl}^-]^\beta$$

The goal of this study is to characterize the factors that affect the reaction's rate; more specifically, you will

- determine the rate law for the reaction, including the reaction orders and the rate constant
- study the effect of pH on the rate law

Preparing for Lab

Planning for this lab is critical to your success. Be sure to complete the relevant sections of your notebook before each week's lab session. As you develop strategies for determining the reaction's rate law keep the following in mind:

- As the reaction proceeds the solution will fade from its initial blue color to a colorless solution. You can follow the reaction's kinetics, therefore, by monitoring the solution's absorbance as a function of time. To use absorbance in place of concentration, however, you must establish that Beer's law applies to your solution of dye. You may wish to review your work from earlier labs to see how you have accomplished this. In addition, to obtain smooth kinetic data you need to minimize the noise in your absorbance spectra.
- To study a reaction's kinetics you must ensure that the concentration of only one reactant is changing; that is, you will study the reaction under pseudo-order conditions in which the initial concentration of dye is significantly smaller than the initial concentration of OCl^-. Be sure to review how pseudo-order kinetics work and verify that the rate law under these conditions is $R = k_{obs}[\mathrm{dye}]^\alpha$ with an observed rate constant, k_{obs}, that is equal to $k[\mathrm{OCl}^-]$.
- You need to verify that the initial concentrations of dye and OCl^- are suitable for a pseudo-order kinetic study. The dye's molar absorptivity is 1.38×10^5 M^{-1} cm^{-1} at a wavelength of 630 nm. To determine the concentration of OCl^- in bleach you may adapt the following general redox titrimetric approach: Pipet 1 mL of bleach into a suitable flask and add approximately 50 mL of deionized water and 2 g

of KI. Swirl the solution to dissolve the KI and then add approximately 3 mL of 3 M H_2SO_4. The resulting solution will be brown due to the formation of I_2, as shown by the following reaction

$$OCl^-(aq) + 2I^-(aq) + 2H_3O^+ \rightarrow I_2(aq) + Cl^-(aq) + 3H_2O(l)$$

Determine the amount of I_2 produced by titrating with a solution of $Na_2S_2O_3$ of known concentration using the procedure described in lab. The titration reaction is

$$I_2(aq) + 2S_2O_3^{2-}(aq) \rightarrow S_4O_6^{2-}(aq) + 2I^-(aq)$$

- You need to determine how kinetic data consisting of absorbance as a function of time can be used to determine the reaction order for the dye and the reaction's observed rate constant.
- You need to think about how kinetic runs using different initial concentrations of OCl^- can be used to extract information about its reaction order and the reaction's true rate constant, k. Consider, as well, how you might prepare solutions of OCl^- with different concentrations.
- Because OCl^- is a weak base it is reasonable to expect that pH might affect the reaction's rate. Give some thought to reasonable pH levels to investigate and how you might set up a suitable kinetic experiment. Note: the reported pK_a values for blue food coloring are 5.63 and 6.85.

Procedure

To prepare your dye solution, try adding 18 drops of dye to a liter of deionized water and then adjust the concentration so that the solution's maximum absorbance is between 0.8 and 1.0. All kinetic runs should consist of 25 mL of a dye solution and 1 mL of a bleach solution. Be sure to begin data acquisition the moment you add the bleach and then transfer a portion of the solution to the spectrometer as soon as possible. Collect data until the absorbance reaches zero or a steady-state value.

Cautions

There are no serious cautions for this lab other than the normal respect for chemicals.

Waste Disposal

All solutions can be disposed of down the drain, flushing with copious amounts of water.

Lab Report

As a group, you will prepare a report for this lab in the form of a scientific poster. Instructions and a template are available from the course's archive page. Your group's poster is due by the last day of final exams.