# Kinetics of the Bleaching of Dyes

Thermodynamics allows us to predict whether a reaction is favorable, but it does not inform us of the likelihood that the reaction will occur in a reasonable amount of time. To know something about the conditions favoring a timely reaction we must study the reaction's kinetics.

The relationship between a reaction's rate and the concentrations of species affecting the rate is given by a rate law, which takes the general form

rate = 
$$k[A]^a[B]^b \cdots [E]^e$$

where k is the rate constant and A, B, and E are species whose concentration might affect the reaction's rate. The superscript associated with each concentration term (e.g. a, b, and e) 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 containing one or more oxidizing agents. One of the most common oxidizing agents in bleach is the hypochlorite ion, OCl<sup>-</sup>, which usually is added in the form of its sodium salt, NaOCl, typically at a concentration between 5 and 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 compounds; thus, we will use an aqueous organic dye (blue food coloring) as a model stain compound. The overall reaction, then, simplifies to

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

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

$$rate = k[dye]^a[OCl^-]^b$$

The goal of this study is to characterize the factors affecting the rate of this reaction. More specifically, you will

- determine the rate law for the reaction, including the reaction orders a and b, and the value of the rate constant, k
- 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. Review how you accomplished this in an earlier lab.
- 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 what is called a pseudo-order condition in which the initial concentration of dye is significantly smaller than the initial concentration of

OCl<sup>-</sup>. You should do some preliminary reading in your textbook to familiarize yourself with how pseudo-order kinetics work and verify that the rate law under these conditions is

rate = 
$$k_{\text{obs}}[\text{dye}]^a$$

with an observed rate constant,  $k_{obs}$ , of

$$k_{\text{obs}} = k[\text{OCl-}]^b$$

• You need to verify that the initial concentrations of dye and OCl<sup>-</sup> are suitable for a pseudo-order kinetic study. The dye's molar absorptivity is 1.38×10<sup>5</sup> M<sup>-1</sup> cm<sup>-1</sup> at a wavelength of 630 nm. To determine the concentration of OCl<sup>-</sup> 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<sub>2</sub>SO<sub>4</sub>. The resulting solution will be brown due to the formation of I<sub>2</sub>, as shown by the following reaction

$$OCl^{-}(aq) + 2I^{-}(aq) + 2H_{3}O^{+}(aq) \rightarrow I_{2}(aq) + Cl^{-}(aq) + 3H_{2}O(l)$$

Determine the amount of I<sub>2</sub> produced by titrating with a solution of Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> of known concentration using the ORP probe to monitor redox potential as a function of the volume of titrant. Redox titration curves are analyzed in the same manner as acid-base titration curves; review the tutorial on "Titrimetry" and your earlier standardizations of NaOH and HCl for further details. 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, a, for the dye and the reaction's observed rate constant, k<sub>obs</sub>.
- You need to think about how kinetic runs using different initial concentrations of OCl<sup>-</sup> can be used to extract information about the reaction order, *b*, for OCl<sup>-</sup> and the reaction's true rate constant, *k*. Consider, as well, how you might prepare solutions of OCl<sup>-</sup> with different concentrations.
- Because OCl<sup>-</sup> 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.

When asked, you should be prepared to discuss your thoughts on these points during lab.

#### **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 the bleach is added 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

Details on this group report will be distributed separately.