

Experiment 446.7**KINETICS OF THE REDUCTION OF METHYLENE BLUE BY ASCORBIC ACID****Theory**

Understanding a chemical reaction requires one to determine the mechanism of reaction, predict it by some plausible set of elementary steps, determine the rate constants involved, and predict the magnitudes of the various parameters, if possible. Mechanisms can be quite involved, as for example in the catalyzed decomposition of ozone or the formation of HCl from H_2 and Cl_2 , even though the overall reaction may appear simple.

Consider the simplest single-step mechanisms. For example, one is the transformation of a reactant A to product, which is of first order at all times:



For such a first-order reaction, the rate equation is:

$$v = -\frac{dC_A}{dt} = k_1 C_A, \quad (7.2)$$

where C_A is the reactant concentration and k_1 is the **first-order rate constant**. The solution of this equation gives the manner in which the concentration of reactant changes with time:

$$\ln\left(\frac{C_A(t)}{C_A(0)}\right) = -k_1 t. \quad (7.3)$$

This is the **linearized form** of the rate equation. A plot of the logarithm of the concentration versus t is a straight line, with a slope of $-k_1$. From the slope of such a plot, one extracts the rate constant.

Some reactions do not go to completion as assumed in the previous paragraph. In the following two-step mechanism, A is converted to B , and B is converted to A , both by first-order processes.



The equation for the disappearance of A by this mechanism is:

$$-\frac{dC_A}{dt} = k_1 C_A - k_{-1} C_B \quad (7.5)$$

The equation for the rate of appearance of B is identical in form. The solution of this equation is:

$$\ln\left(\frac{C_A(t) - C_A(\infty)}{C_A(0) - C_A(\infty)}\right) = -(k_1 + k_{-1})t, \quad (7.6)$$

where the concentration at any time t is given by $C_A(t)$. In particular, after a very long time (indicated by ∞), the reaction may produce a state in which both A and B are present.

For this mechanism, the linearized form of the equation is also logarithmic, however the argument of the logarithm is a difference of concentrations, so one has to form a function of concentrations to determine the rate constants, but these are available from the measured concentrations of A . The situation is shown in Figure 7.1.

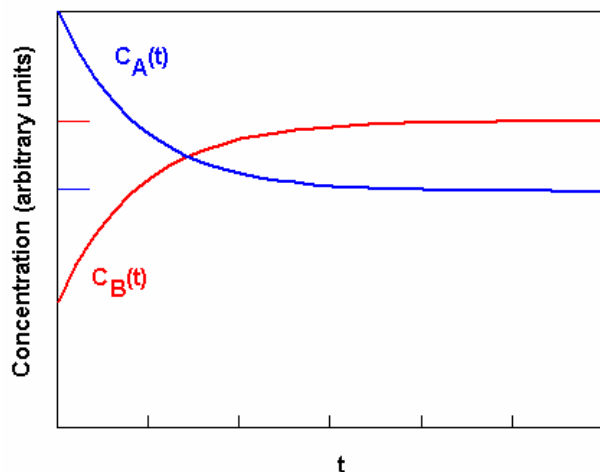


Figure 7-1. First-order approach to equilibrium. The lines on the left indicate the equilibrium values of the concentration of the two components.

This mechanism illustrates the approach to dynamic equilibrium. It appears from equation (7.6) that the only information from such a graph is the sum of the rate constants. However, at dynamic equilibrium (i.e. at very long times), the rates of these two processes are equal, which allows one to determine the ratio of the rate constants.

$$\frac{C_B(\infty)}{C_A(\infty)} = \frac{k_1}{k_{-1}}. \quad (7.7)$$

From this equation and the slope of an appropriate logarithmic graph, one has two equations in two unknowns, which allows an independent evaluation of both k_1 and k_{-1} .

Dynamic equilibrium is very important. Consider, for example, a reaction sequence in which the forward step is of first order in A and the reverse step is of second order in B . While the mathematics of the

solution of the equation at any time may be difficult, at equilibrium the two rates must be equal, which gives a relationship between the two rates constants and the equilibrium concentrations:

$$\frac{C_B^2(\infty)}{C_A(\infty)} = \frac{k_1}{k_2}, \quad (7.8)$$

in which the rate constant of the reverse step, since it is of second order, is labeled k_2 .

Second-order reactions form an important class in kinetics. There are two kinds of second-order reaction steps, those that are of second order in a single species, and those that are of second order by virtue of being first-order in each of two distinguishable species.

Consider the simplest second-order mechanism that this just a single step of the former type. The reaction is:



and the velocity equation is:¹

$$v = -\frac{1}{2} \frac{dC_A}{dt} = k_2 C_A. \quad (7.10)$$

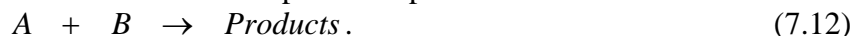
The solution of this equation gives the time course of the reactant:

¹ In this equation, I define the velocity according to the proper convention. In many texts, one sees equations that do not include the factor for the stoichiometric coefficient, 1/2. Those equations give a “rate constant” for the disappearance of A , not the rate constant for the reaction.

$$\frac{1}{C_A(t)} = \frac{1}{C_A(0)} + 2k_2t. \quad (7.11)$$

This is the linearized form of the equation, so a plot of the inverse of the concentration of a reactant versus time should give a straight line, the slope of which is $2k_2$.

The second form occurs for reaction of two distinguishable species (each having a unique starting concentration) that react in a one-to-one step to form products:



The rate equation derivable for this process is:

$$v = -\frac{dC_A}{dt} = -\frac{dC_B}{dt} = k_2 C_A C_B. \quad (7.13)$$

This differential equation may be solved, subject to known initial concentrations, to give the following complex equation:

$$\ln\left(\frac{C_B(t)}{C_A(t)}\right) = \ln\left(\frac{C_B(0)}{C_A(0)}\right) + (C_B(0) - C_A(0))k_2t. \quad (7.14)$$

The function that one must plot to obtain a linearized form of the rate law requires one to measure **simultaneously** and **independently** the concentrations of both reactants. If that can be done, a plot of the logarithm of the ratios of the concentrations gives a straight line with a slope of $(C_B(0) - C_A(0))k_2$, from which one may extract the rate constant.

The form of equation (7.14) becomes indeterminate for the condition that the initial concentrations of the two species are equal. One may show that, under these conditions, one need only follow the concentration of one species (since the other must always be of identical concentration). The equation for its change is similar to that of the identical-species second-order result:

$$\frac{1}{C_A(t)} = \frac{1}{C_A(0)} + k_2t, \quad (7.15)$$

except that the slope is the rate constant for the reaction. This is obviously mathematically simpler to analyze than equation (7.14), but the difficulty of ensuring that the initial concentrations of the two reactants are identical provides a practical barrier to using this technique.

Limiting Reagents

Consider the situation in which a reaction of the type in equation (7.12) is carried out under conditions that one reagent is present at concentrations many hundreds or thousands of times lower than the concentration of any other. Under these conditions, even though the concentration of the reagent in excess is changing, the changes are so slight that it may be considered, practically, constant over the course of the experiment. Then, to a very good order of approximation, the rate equation for a process that obeys equation (7.12) is:

$$-\frac{dC_A}{dt} = k_{eff} C_A, \quad (7.16)$$

where

$$k_{eff} = k_2 C_B(0), \quad (7.17)$$

if A is the material present in limited amounts. Equation (7.16) is of the same form as equation (7.2). The solution is of the same form:

$$\ln\left(\frac{C_A(t)}{C_A(0)}\right) = -k_{eff}t. \quad (7.18)$$

Under these conditions in which A is a limiting reagent, one may follow the concentration of the limiting reagent to determine the effective rate constant.

The idea of limiting reagents is much more general than just first-order reaction steps. For example, consider the reaction:



which is not necessarily an elementary reaction, but denotes the relative stoichiometry. Then one may write a general rate equation for the loss of A .

$$-\frac{dC_A}{dt} = k C_A^m C_B^n, \quad (7.20)$$

where m and n are the orders with respect to A and B , respectively. Under the condition that B is present in large excess, this equation simplifies to:

$$-\frac{dC_A}{dt} = k_{eff} C_A^m, \quad (7.21)$$

where

$$k_{eff} = k C_B^n(0). \quad (7.22)$$

For example, $m = 1$ gives equation (7.18), but if $m = 2$, this technique gives a second-order dependence of C_A on time, and so forth. The use of limiting reagents gives a means to determine the effective rate constant from a plot, provided one can measure the concentration of the limiting reagent as a function of time.

Equation (7.22) also indicates another feature of the use of a limiting reagent. A series of studies of the effective rate constant for a reaction in which the excess reagent's concentration is changed (but still remains in excess) gives a means of determining the order with respect to that reagent as well. Equation (7.22) may be rewritten in the form:

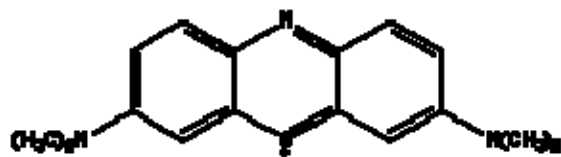
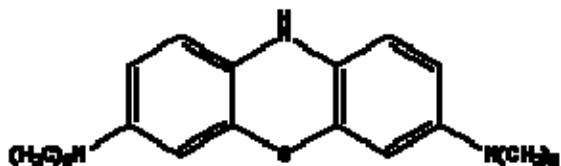
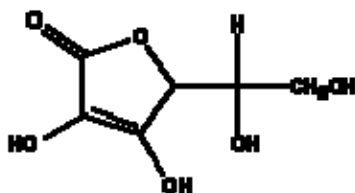
$$\ln k_{eff} = \ln k + n \ln C_B(0). \quad (7.23)$$

A plot of the logarithm of the effective rate constant versus the logarithm of the concentration of the excess reagent is a straight line with a slope that gives the order and an intercept that is the logarithm of the rate constant.

Measuring Concentrations; Actinometry

The biggest practical problem in chemical kinetics is relating what is measured to what needs to be measured. All equations derived above require that one measure the concentration of a single reactant or the concentrations of several reactants independently as functions of time. In cases in which there is a simple relation to the concentration of a product, one may measure the time dependence of the product's concentration to obtain the same information.

Reaction rates are monitored through measurement of a wide variety of variables. For gas-phase reactions, the measurement of total pressure as a function of time is relatively easy to do, however, one often has to determine the concentration of reactant from this total pressure by a calculation of the partial pressure. For reactions in solution that change hydrogen-ion concentration, monitoring the pH of the solution as a function of time is a convenient means to determine the extent of reaction. In some cases, the reaction produces a change in volume of the solution, in which case the reaction may be followed by **dilatometry**. Ionic reactions may be followed electrochemically. Of particular interest in this experiment is **actinometry**, the

**METHYLENE BLUE****LEUCOMETHYLENE BLUE****ASCORBIC ACID****Figure 7-2. Structures of components in the reaction to be studied.**

determination of concentration by intensity of a colored solution. Any quality of a solution that is proportional to the concentration of a reactant may be used as a monitor of the concentration.

A consideration in choosing a measurement parameter is the measuring technique's response time. It must be sufficiently short that the time dependence of the concentration can be adequately determined. For example, if a reaction reaches equilibrium in a time of the order of 0.5 second, a measuring device that requires 2 seconds to make a single measurement is not a useful probe of the course of the reaction. The response time must be fast enough that the concentration be determined a large number of times during the course of reaction. With the desire to observe and characterize ever-faster reactions, this limitation comes into play in many of experiments.

Protonation of Methylene Blue

In this experiment, you investigate the spectroscopy of a dye and subsequently use the spectroscopy to monitor a reaction involving the dye. The reactant is methylene blue, the dye shown at the top of figure 7.2. It has a vivid blue color. Leucomethylene blue, which is produced from it, gives a colorless solution. In the experiment, you use actinometry to measure the concentration of methylene blue as the reaction

proceeds.

The absorption of light by a solution is measured by the **absorbance**:

$$A = abc, \quad (7.24)$$

where c is the concentration of the absorbing species, b is the cell length, and a is a fundamental property called the **absorptivity**. In a spectroscopic cell of constant path length, the absorbance is directly proportional to the concentration of the absorbing material. The absorbance is related to an intensity ratio:

$$A = \log_{10} \left(\frac{I_0}{I} \right), \quad (7.25)$$

where I_0 is the incident intensity of the radiation field and I is the intensity of the radiation field transmitted by the solution in the cell.

The absorbance depends on frequency, ν , or equivalently the wavelength, λ , of the radiation. Some molecules absorb only in selected regions, which gives rise to the observed color. In a mixture such as one has in a reaction, it is possible that more than one component may absorb at a particular wavelength. In that case, the absorbance at a particular frequency may not represent the concentration of a single component. It is important to check the spectroscopy of all possible materials to ensure that the conditions one chooses to make the measurement

allows a representative determination of the limiting reagent's concentration. If there are interferences from other materials, it may be possible to measure concentration by extracting from the measured spectrum the absorbance due to the limiting reagent, which can be used to monitor the concentration changes during reaction. To be as sensitive as possible, one should choose to measure the absorbance in some region in which the reagent strongly absorbs.

Safety

The reagents for this experiment are methylene blue, a relatively safe material, and ascorbic acid (vitamin C). In addition, you are using hydrochloric-acid solutions. Thus, in addition to the usual safety precautions, you should ensure that you do not spill these materials on yourself or others in handling them, as you may get acid burns. To ensure your safety, take precautions to protect yourself against splashes of the acid.

General Remarks about Solutions for Kinetics Experiments and Experimental Technique

In this experiment, you carry out kinetics runs to determine the protonation of methylene blue by ascorbic acid.² It is important to determine, as closely as possible, the start time of the experiment. Therefore, the way you make the reaction mixture is important for obtaining good results. **Always add the solution of methylene blue to the other material last** and mix several times before you immediately put it in the cuvette and then the cuvette in the spectrometer for analysis. Detection should start as quickly as possible, so it is approximately at the time that mixing has occurred. Be certain that you add sufficient amounts to fill the cuvette.

You need several solutions. Make a stock solution of 50 mL of methylene blue in distilled water at an approximate concentration of 4×10^{-4} mol/dm³ and approximately 50 mL of an ascorbic acid in distilled water at approximately 0.100 mol/dm³.³ There should be a stock solution of HCl available in the laboratory. From these, you make a series of solutions, so it is important that you make the solutions carefully and know the concentrations precisely. There are three sets of experiments you must run.

There is a wash bottle with deionized water near the experiment that should be helpful in adding water to solutions. Refill it from the deionizer.

In the first set of kinetics experiments (called the A set), you hold the HCl concentration in the solution constant at some value near 0.06 mol/dm³ (usually a concentration near that of the stock solution) and the ascorbic acid concentration constant at some value near 0.025 mol/dm³. (**In advance**, you must calculate how much of the stock solutions to add to ensure that the final concentration is an appropriate value.) Make up these solutions using 10-mL volumetric flasks, always adding the methylene blue last, mixing, and quickly add the material to the cuvette. In this set of experiments, the concentration of methylene blue should be varied over several concentrations that span the range from about 5×10^{-6} to about 4×10^{-5} mol/dm³. (Important: add the methylene blue component immediately before you are ready to begin the experiment, and add water to volume.)

In the second set of kinetics experiments (called the B set), you should fix the concentrations of HCl (at some concentration around 0.06 mol/dm³) and the methylene blue (at

² S. Mowry and P. J. Ogren, *J. Chem. Ed.*, 76, 970-974 (1999).

³ Methylene blue can be very messy and stain clothing and counters. Handle it very carefully and clean all utensils thoroughly immediately after using them.

some concentration near 1.5×10^{-5} mol/dm³), and vary the ascorbic-acid concentration (from 0 up to about 0.04 mol/dm³). Again, add the methylene blue last immediately before running the kinetics run.

In the third set of kinetics experiments (called the C set), fix the ascorbic acid concentration at some value near 0.04 mol/dm³ and the methylene blue concentration at the concentration of 1.5×10^{-5} mol/dm³ of the previous runs. In this set, vary the HCl concentration from 0.01 to about 0.06 mol/dm³.

The easiest way to create solutions is to determine how much of the stock solutions of HCl, ascorbic acid, and methylene blue must be added to the 10-mL volumetric flask for each solution. Add the HCl and ascorbic acid. When you are ready to start a run, quickly add the proper volume of methylene blue solution, mix and pipette to the cuvette, turn the cuvette once or twice to mix the materials, insert in the Agilent 8453 spectrophotometer and immediately begin taking data with the kinetics program. To do this, you must have determined beforehand how much of each of the stock solutions you are to add to the cuvette to produce the appropriate concentrations and have the spectrophotometer ready to go.

It is extremely important that you clean the cuvettes and glassware thoroughly between runs and before starting the experiments. Rinse all glassware including cuvettes with 0.1 mol/dm³ HCl and then rinse them with copious amount of deionized water several times before use. If you do this, you should get very good, reproducible data.

Procedure

The Visible Spectra of Methylene Blue and Leucomethylene Blue

Before you determine kinetics, you should determine the spectra of methylene blue and final product mixture. This is done in the *Standard* mode of the Agilent 8453 spectrophotometer. For the spectrum of methylene blue, use a solution of methylene blue in water that is approximately 4×10^{-5} mol/dm³. Scan from 200 to 800 nm. Run a blank first, then the sample.

Save your data as a *.CSV file, which allows you to view the file with Excel. To do this, click on the spectrum you have obtained, then in the *File* menu, select *Export Selected Spectrum . . . CSV Format*. Save it with the name SMQP.CSV, where Q is the section number and P is your group number on your flash drive. Thus, group 1 of section 10 would save the spectrum as SM1001.CSV.

You also should determine the spectrum of the product mixture over the same range. Create a solution that is approximately 0.06 mol/dm³ in HCl, 0.025 mol/dm³ in ascorbic acid, and 1.5×10^{-5} mol/dm³ in methylene blue. Let this sit on the desk for 5 minutes to allow reaction to happen. Place the cuvette in the spectrometer and determine the spectrum of the final product mixture over the same region as you did above. Save this file as SLQP.CSV, where Q and P are the section and group number respectively.

Kinetics Experiments

Be sure you know and record the temperature in the room. Rather than take the whole spectrum every time, decide where the **maximum signal** of the **methylene blue** solution is from the spectroscopy experiment, making sure it is a region where **ONLY** methylene blue absorbs, and not also leucomethylene blue. This is the point at which the spectrometer should be set to determine the methylene blue absorbance as a function of time in the kinetics runs. This setting

is done in the *Kinetics* mode of the Agilent 8453 spectrophotometer program. In *Time & Calculation*, set the wavelength in the *Use Wavelength WLI* field and choose *None* in the *Background Correction* field. Then the *y-Scaling* in the *Trace Monitor* option can be modified from 0 to 0.5 or a lower value, depending on the initial concentration of the reactant being monitored.

Another parameter to set is the total time to determine kinetics. This is set in the *Timing, Run Time* field. The value depends on how fast the reaction proceeds. In set A, try a total time of 120 seconds; this should be sufficient to watch the reaction go to completion. In set B, in which the ascorbic acid concentration is varied, the reaction proceeds more slowly at concentrations below about 0.01 mol/dm^3 , so you need to use a longer time, say 10 minutes, with no ascorbic acid present. With slightly higher concentrations of the ascorbic acid, you may be able to shorten this time to 6 minutes. The important thing is that you must be able to see that the absorbance has leveled off at the end of each run. If not, repeat the experiment with a longer time. You must also set the *Start Time* at 0 s and the *Cycle Time* at 1 s. You may want to set this last one shorter for reactions that happen quickly, but a 1-s cycle time seems to work fairly well.

You need to indicate where to save the data after it is taken. This is done in the *Method Option & Info* menu by checking the *Autosave spectra to file...* option. Use the following name structure for your file: KQPAn.KD, where Q is the section number, P is the group number, A is either A, B or C, depending on the set, and n is a number representing the experiment number. This number should be recorded in your notebook with the pertinent information on the concentrations of the various constituents.

Introduce your blank first and click the *Blank* button. When you are ready to do the kinetic measurement, click on *Time Measurements* and answer *OK*. Introduce the cuvette and click *Start* to record. The spectrophotometer should then begin recording the absorbance as a function of time for the time you specified.

To export data to your diskette for later use, click on the graph. In the *File* menu, select *Export Selected Data as CSV Format...* and follow the name structure given above.

Calculations

1. Plot the spectra of methylene blue solution and the solution of final products from 200 to 800 nm. The most convenient means to do this is with a program such as EXCEL. After bringing the data into EXCEL, you will have a set of x and y data.
2. Analyze each set of kinetic data with a program like EXCEL.⁴ As in calculation 1, you have to generate x data. Before analysis, be sure to find the long-time absorption and subtract this from each point, so that you are looking at only the time-varying part of the absorption. For part A, analyze each kinetics run as first order or second order in methylene blue. After this part, you should decide whether this reaction is most appropriately considered a first-order or a second-order reaction in methylene blue. In subsequent analyses, use this information and only analyze the data in the manner you decide the data are changing.
3. For the data in part B, extract the effective rate constant for each of the runs from an appropriate plot. This rate constant depends on the ascorbic concentration. Since methylene

⁴ If there is a residual signal after reaction is complete, remember that you will need to subtract this from the data at all times to give a signal that is proportional to the reactant concentration. If there is no (or a small) residual signal, then this is not necessary. You decide!

blue is a limiting reagent, one may use equation (7.23) to determine the order with respect to ascorbic acid from a plot of the effective rate constant versus ascorbic acid concentration.

4. For the data of part C, do a similar analysis as in calculation 3 to determine the order with respect to hydrochloric acid.

Discussion Questions

1. Describe the spectroscopy of methylene blue in terms of the molecule's quantum structure. Ascribe any unique bands to transitions between quantum states. Be as specific as possible.
2. Based on these analyses, is the order with respect to methylene blue first or second? What evidence do you have for this finding?
3. What are the orders with respect to ascorbic acid and hydrochloric acid?
4. Write the rate law for this reaction as you know it from your experiments.
5. Write a balanced equation for the reaction of methylene blue with ascorbic acid. Include full structures of all reactants and products, not abbreviations, in your equations. Think carefully about the chemistry involved in this reaction; are there other materials than those found in Figure 7.2 that are components of the reaction?
6. Propose a mechanism that is consistent with the observed experimental results. Explain the mechanism and how it gives the rate law you derived above. Show that this mechanism gives the rate law you propose. What assumptions about various steps in your mechanism are necessary to achieve agreement with your experimental rate law?
7. In solution, much is made about diffusion control. Estimate the effect of diffusion control on this reaction by estimating the diffusion-controlled rate constant from reasonable estimates of the diffusion coefficients and sizes of the reactants.