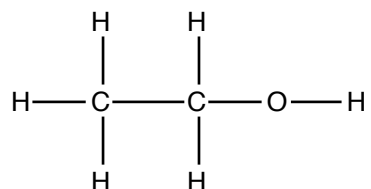


Experiment 14: A Kinetic Study of the "Breathalyzer" Reaction

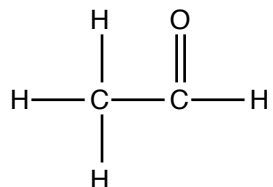
Objective: In this experiment, you will study the kinetics of the reaction of ethanol and acidic potassium dichromate to determine whether the reaction is zero, first or second order with respect to dichromate concentration and to determine the rate constant of the reaction.

Introduction

In the 1960's, as concern over the increasing number of injuries and fatalities caused by drunken drivers began to rise, chemists looked toward the development of simple screening tests that could be used by police officers to determine the level of alcohol in the blood of a car operator. Drinking alcohol, referred to by chemists as **ethanol**, has the following chemical structure:

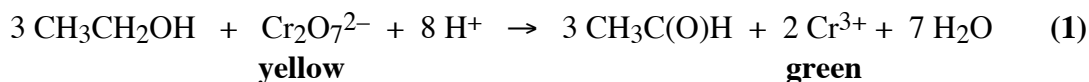


It can react with a variety of oxidizing agents to produce the compound **acetaldehyde**, which has the structure shown:



One oxidizing agent that will accomplish this transformation is potassium dichromate, $\text{K}_2\text{Cr}_2\text{O}_7$. (See Tro, pp 1004-1008, for further discussion regarding alcohols and aldehydes.)

Potassium dichromate produces a yellow solution when dissolved in acid. As an acidic solution of dichromate reacts with ethanol, the Cr(VI) species is reduced to a Cr(III) species, which is green in aqueous solution. The overall reaction is as follows:



Because the reaction is accompanied by this dramatic color change, it is possible to monitor it spectrophotometrically.

In a "Breathalyzer", a portable instrument used by the police to test alcohol levels in the blood, the breath is passed through an ampoule that contains an aqueous solution of $\text{K}_2\text{Cr}_2\text{O}_7$ and sulfuric acid. Alcohol contained in the breath is then oxidized to acetaldehyde while the chromium in the ampoule is reduced to the Cr(III) species. Light

of the appropriate wavelength (440 nm) is passed through the ampoule and compared to a reference solution that contains only acidic potassium dichromate. The absorbance difference between the two solutions is then interpreted to give the percent of ethanol contained in the breath.

The color change associated with the oxidation of ethanol also provides a convenient means for studying the *kinetics*, or rate, of the reaction (see Tro, Chapter 14, especially pp 624-641). The complete rate equation for reaction (1) has the form:

Eq. 1

$$-\frac{d[\text{Cr}_2\text{O}_7^{2-}]}{dt} = k[\text{Cr}_2\text{O}_7^{2-}]^x[\text{CH}_3\text{CH}_2\text{OH}]^y[\text{H}^+]^z$$

where k is the **rate constant**, t is the time, the quantities in brackets indicate concentration of the reactants, and the values for x , y and z must be determined experimentally. However, under conditions where the concentrations of ethanol and acid are large (and therefore remain approximately constant throughout the reaction), the rate equation reduces to:

$$-\frac{d[\text{Cr}_2\text{O}_7^{2-}]}{dt} = k[\text{Cr}_2\text{O}_7^{2-}]^x$$

Eq. 2

The objective of this experiment is to determine whether $x = 0$, 1 or 2; that is, whether the rate law is zero, first or second order with respect to dichromate.

Let us examine each case individually. If we let the initial concentration of dichromate ion equal a , and the concentration of dichromate which will have reacted at time t equal c , then the concentration of dichromate that remains at t is equal to $(a - c)$. The rate equation becomes:

$$+\frac{dc}{dt} = k(a - c)^x$$

Eq. 3

For a zero order reaction, $x = 0$ and the rate equation reduces to:

$$+\frac{dc}{dt} = k$$

Eq. 4

Integrating, we obtain:

$$c = kt$$

Eq. 5

In this case, a plot of concentration, c , versus time, t , will produce a straight line with the slope equal to the rate constant, k .

For a first order reaction, $x = 1$ and the rate equation is:

$$+\frac{dc}{dt} = k(a - c)$$

Eq. 6

Integrating, we obtain:

$$\ln [a / (a - c)] = kt \quad \text{Eq. 7}$$

Thus, a plot of $\ln [a / (a - c)]$ versus t will produce a straight line with a slope of k .

Finally, for a second order reaction, $x = 2$ and the rate equation is:

$$+\frac{dc}{dt} = k(a - c)^2 \quad \text{Eq. 8}$$

Integrating, we obtain:

$$1/(a - c) = kt + 1/a \quad \text{Eq. 9}$$

In this case, a plot of $1/(a - c)$ versus t will give a straight line with a slope of k and a y-intercept of $1/a$.

In order to determine the quantities a and c , we must convert the absorbance of the solution at a wavelength of 440 nm to the concentration of dichromate ion in solution. Recall Beer's Law (see Experiment 6):

$$A_0 = \epsilon a \ell \quad \text{Eq. 10}$$

where A_0 = initial absorbance of the solution, a = initial concentration of dichromate ion, ℓ = path length of the cell and ϵ = the molar absorptivity constant. Rearranging equation 10:

$$a = A_0/\epsilon \ell \quad \text{Eq. 11}$$

At time t , the equation becomes:

$$a - c = A_t/\epsilon \ell \quad \text{Eq. 12}$$

where A_t is absorbance of the solution at time t . Substituting equation 11 and rearranging:

$$c = (1/\epsilon \ell)(A_0 - A_t) \quad \text{Eq. 13}$$

For the zero order reaction equation, making the appropriate substitution for c into equation 5 results in the following equation:

$$A_t = A_0 - k(\epsilon \ell)t \quad \text{Eq. 14}$$

A plot of A_t versus t will produce a straight line for a zero order reaction with the slope equal to $-k(\epsilon \ell)$ and a y-intercept equal to A_0 .

To obtain the quantity $a / (a - c)$ in terms of absorbance values for a first order reaction (equation 7), we must divide:

$$a / (a - c) = (A_0/\epsilon \ell)(\epsilon \ell / A_t) = A_0/A_t$$

$$\ln (A_0/A_t) = kt \quad \text{or}$$

$$\ln A_t = \ln A_0 - kt \quad \text{Eq. 15}$$

Thus, a plot of $\ln(A_t)$ versus t will produce a line with a slope equal to $-k$ and a y-intercept equal to $\ln(A_0)$ for a first order reaction.

Lastly, substituting absorbance values into equation 9 gives:

$$1/A_t = (k/\epsilon\ell)t + 1/A_0 \quad \text{Eq. 16}$$

where a plot of $1/A_t$ versus t gives a straight line with a slope equal to $k/\epsilon\ell$ and a y-intercept of $1/A_0$ for a second order reaction.

A correction must be introduced at this point. When the reaction reaches completion, at $t = \infty$, there will remain some absorbance of light at a wavelength of 440 nm. This residual absorbance, A_∞ , must be subtracted from each absorbance term in equations 14, 15 and 16:

$$(A_t - A_\infty) = (A_0 - A_\infty) - k\epsilon\ell t \quad \text{Eq. 17}$$

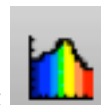
$$\ln \left[\frac{(A_0 - A_\infty)}{(A_t - A_\infty)} \right] = kt \quad \text{Eq. 18}$$

$$\frac{1}{(A_t - A_\infty)} = \left(\frac{k}{\epsilon\ell} \right) t + \frac{1}{(A_0 - A_\infty)} \quad \text{Eq. 19}$$

Procedure (outline the steps of this section for your pre-lab assignment)

Two students will be assigned to work together to prepare one reaction solution. Each pair will be assigned to a specific computer and SpectroVis Plus, which they must use to acquire all their measurements throughout the course of the experiment.

In the Applications folder, click on the button labeled **Logger Pro** to open the Logger Pro software. From the **Experiment** menu, choose **Data Collection**. From the drop-down menu next to **Mode**, choose **Time Based**. Change the **Length** of the experiment to **420 seconds**, and change the sample rate to **0.1 samples/second**, which is **10 seconds/sample**. Click on **Done**.



Click on the **Configure Spectrometer** button in the toolbar:

In the dialog box that appears, click in the circle next to **Absorbance vs. Time**. Scroll through the listing in the center of the box to find the number closest to **440 nm**. Click in the appropriate box to place a \checkmark next to this wavelength. Choose **Single 10 nm Band** from the drop-down menu on the left. Click on **OK**.

From the **Experiment** menu, choose **Calibrate** followed by **Spectrometer: 1**. Wait 90 seconds for the lamp to warm up. Fill a clean, dry cuvet with deionized water and place it in the SpectroVis Plus. Be sure the inverted triangle on the cuvet is next to the white triangle that is painted on the box. When the warm-up is completed, click on **Finish Calibration**. When the calibration is completed, click on **OK**. In the lower left corner of the screen, the box should display: Absorbance at 440 nm is 0.000.

CAUTION: Compounds that contain chromium (VI) are toxic and suspected carcinogens. Wear gloves. Wash your hands thoroughly with soap and water after handling solutions that contain Cr(VI). Do not pour any solution containing chromium down the sink!

Using a volumetric pipet, transfer 5 mL of 0.0196 M potassium dichromate, $K_2Cr_2O_7$, solution into a clean, dry 125 mL Erlenmeyer flask. Add 50 mL of 3.9 M sulfuric acid, H_2SO_4 , to the flask using a graduated cylinder, and swirl the flask well to thoroughly mix the solution.

Fill a new clean, dry cuvet with this acidic dichromate solution. Wipe off the outside of the cuvet with a Kimwipe so that is clean and dry, and place it in the SpectroVis Plus. Record the absorbance of the acidic dichromate solution (lower left corner of the screen) in your notebook (this is the initial absorbance, at $t = 0$).

Remove the cuvet from the instrument and pour the contents back into the Erlenmeyer flask. Your instructor will add 0.13 mL of ethanol to the solution via syringe. **Click on the green Collect button at the precise time that the ethanol is added.** Quickly and carefully swirl the solution, then rinse and fill the cuvet and return it to the SpectroVis Plus. The computer will record the absorbance of the solution along with the time. Try to place the cuvet in the SpectroVis Plus within 60 seconds after the addition of ethanol.

Allow the computer to take readings of the absorbance and the corresponding time for a total of 7 minutes (420 seconds). At the end of this time, click on the red **Stop** button, and save your data to the documents folder. Allow the cuvet to stand undisturbed at room temperature for at least one hour. You may proceed with the set-up of the spreadsheet for your data at this time.

After one hour, re-calibrate the SpectroVis Plus using deionized water. Return the cuvet containing the reaction mixture to the instrument and record the final absorbance value (A_{∞}) in your notebook. When you have completed the experiment, pour all solutions into the appropriate **Laboratory Byproducts Jar**.

Data Work-up (you do not need to outline the steps of this section for your pre-lab assignment)

You will use the spreadsheet program Excel to analyze your data (see TECH IV.C). Click on the button labeled Excel in the **Applications** folder. Under the **View** menu, make sure that **Formula Builder** has a check mark next to it.

Place your cursor in the first cell (A1) and type the word *Time* with the units in parentheses. Label the next column (B) with the heading A(t). In cell A2, enter 0 for the time, and in cell B2, enter the value that you recorded in your notebook which corresponds to the absorbance before ethanol was added to the dichromate solution.

Go back to the LoggerPro screen. Scroll through the data table to find the maximum absorbance value. This is the point at which the cuvet was inserted into the SVP. Highlight all the data from this point down in both columns. Once these values are highlighted, select **Copy** from the **Edit** menu. Go back to the Excel screen. Click in cell A3. Select **Paste** from the **Edit** menu, and all the data should appear in columns A and B. At this point, you should save the spreadsheet to the Documents folder.

You need to enter the value for the final absorbance reading, A_{∞} , somewhere in the table. Choose a cell that will not be used for any other data entries, such as a cell below the bottom of the data in column A, and type A(f) (for *final* absorbance reading, since the symbol ∞ is not available). In the next cell over (a cell in column B), type the value that you obtained for the final absorbance reading. [While you are waiting to obtain this value, type 0.05 as a “dummy” value in this cell for now. You can change it later.] Your sheet should look similar to the one shown at the top of the next page, except that your data table will be much longer.

You will need to plot three different graphs (or *charts*) in order to determine whether or not the reaction that you studied is zero, first or second order. Let's use the zero order case as an example to get you started. In the case of a zero order reaction, you need to plot $A_t - A_{\infty}$ as a function of time, t , in order to obtain a straight line (see equation 17).

You are now ready to define a column that will contain the values for $A_t - A_f$. First, place a heading at the top of column C for this data, $A(t) - A(f)$. We will now define a function for each cell in column C so that the computer will calculate the value $A_t - A_f$ for us. In cell C2 we would like the computer to subtract A_f (located in cell B11 in the example pictured on the next page) from the value for A_t , which is located in cell B2. To do this, you could place the cursor in cell C2 and type:

The screenshot shows an Apple Excel spreadsheet with the following data in columns A and B:

Time (sec.)	A(t)
0	0.602
60	0.505
120	0.403
180	0.301
240	0.251
300	0.202
360	0.154
420	0.111
A(f)	0.055

The formula bar at the top shows the formula `=B2-B11`.

$$=B2-B11$$

A number would appear in cell C2 that corresponds to the first value for A_t minus the value for A_f . You could continue to define a similar function in each individual cell of column C (e.g. cell C3 would be: $=B3-B11$).

Instead of typing a similar formula over and over, it is easier to use an **array** to define the whole column at once. To do this, simply highlight all the cells that will be defined with a similar function (cells C2 through C9, in this example). Then type:

$$=B2:B9-\$B\$11$$

Remember the equal sign! The dollar signs that precede the letter and number in the above formula ensure that the address of this cell (B11) remains constant throughout the array. Now *hold down the command key* (⌘), and then *press the return key*, and the appropriate numbers should appear in all the highlighted cells. (Array formulas must be locked in with the command-return keys.) [Note: To delete an array, all of the cells involved in the array must be highlighted, and then the command **Clear** is chosen from the **Edit** menu followed by pressing the command-return keys.]

You can complete the next columns on your own. Decide what you need to plot in the cases of a first order reaction and a second order reaction (see equations 18 and 19), and label the columns appropriately. Then, define the necessary functions for the cells in those columns. Be sure to *save* your data at some point. It is a good idea to save the data periodically as you work on your spreadsheet.

Some hints:

You *must* create an array. Do *not* simply use the copy and paste functions.

The value for A_0 is contained in one of the cells of the table. Which one?
 The command for obtaining the natural log of a value is simply LN followed by the argument in parentheses. For example, if you wanted to take the natural log of a value in cell A1 you would type: =LN(A1)
 The square brackets, [], should *not* be used when typing mathematical formulas in Excel. Use parentheses— these can be nested several times.
 Example: =(A1*(B1/(A2+B2)))

Charts

To obtain a graph of your data, you need to highlight the cells in the first column (the time values). Next, *hold down the command key* and highlight the cells in the column corresponding to the values necessary for a zero order plot (column C). It is important that the column containing the x values (time) is highlighted first. Do *not* highlight the text headings of the columns. Once both columns are properly highlighted, pull down the **Insert** menu and choose **Chart**. Click on the button **Scatter** from the **Charts** toolbar, then click on **Marked Scatter** (data points without a line drawn through them). A plot should appear on the spreadsheet. Pull down the **Chart** menu and select **Move Chart...** In the box, that appears, click in the circle next to “New sheet”, then click on **OK**. The chart will now fill the screen as it appears on its own page.

Click on the words **Chart Layout** in the toolbar. You will use the buttons that appear to give your plot a title and to label the axes. Click on the button **Chart Title** and choose **Title Above Chart**. Type in your title. Click on the button **Axis Titles** and choose **Horizontal Axis Title** followed by **Title Below Axis**. Type an appropriate label for the x -axis. Click on the button **Axis Titles** and choose **Vertical Axis Title** followed by **Rotated Title**. Type an appropriate label for the y -axis.

You can add a “best fit” line by placing the cursor on a data point of the graph and clicking once. All of the data points should now be highlighted. In the Chart Layout toolbar, click on the button **Trendline** followed by **Linear Trendline**. A line will appear on the graph. Click on **Trendline** again and choose **Trendline Options...** In the box that appears, click on **Options** from the list in the left-hand column. Click to put \checkmark 's in the boxes for “Display equation on chart” and “Display R-squared value on chart”, then click **OK**. Print your graph by choosing **Print** from the **File** menu.

To get back to the worksheet, click on the tab at the bottom of the screen that says **Sheet 1**. Use the same procedure to obtain plots and print-outs for the first and second order data as well. Determine which plot produced the straightest line, and thus, whether the reaction is zero, first or second order.

If you have trouble deciding which plot produced the straightest line, you can look at the value for R^2 , which is displayed on the chart. R is called the correlation coefficient and gives an indication of the “goodness” of fit of the data. The closer the R^2 value is to 1.00, the better the data fit, or correlate, to a straight line.

Once you have determined the order of the reaction rate, you can find the slope of this line and thus, the rate constant. The slope of the line is found in the equation that is displayed on the chart. Alternatively, you can use the **LINEST** function to perform a linear regression on the selected data and display the slope and the y -intercept on the worksheet.

When you have completed the worksheet, save it and print it out by choosing **Print** under the **File** menu. Print the worksheet (Sheet 1) as well.

Calculations

1. Hand in the three plots (zero, first and second order) and the Excel worksheet of your data and results.
2. Is the reaction zero, first or second order with respect to dichromate?
3. What is the value of the rate constant? What are the units? Use the value $3.58 \times 10^2 \text{ M}^{-1}$ for $\epsilon\ell$, if necessary.
4. Thermal decomposition of nitrogen dioxide to nitric oxide and oxygen occurs according to the following reaction:



The rate law is:

$$-\frac{d[\text{NO}_2]}{dt} = k[\text{NO}_2]^x$$

The equations corresponding to the possible orders of the reaction follow:

$$\begin{aligned} \text{zero order: } [\text{NO}_2] &= [\text{NO}_2]_0 - kt \\ \text{first order: } \ln([\text{NO}_2]_0/[\text{NO}_2]) &= kt \\ \text{second order: } 1/[\text{NO}_2] &= kt + 1/[\text{NO}_2]_0 \end{aligned}$$

Use Excel to determine the order and rate constant of the reaction given the following data:

Time (s)	[NO ₂] (M)
0	0.100
10	0.0506
20	0.0329
30	0.0253
40	0.0204
50	0.0163
60	0.0143

Note that in this problem you are given the *concentration* of NO₂ (in molarity), **not** the absorbance of a solution of NO₂. You do not need to use the Beer's law relationship between absorbance and concentration to solve this problem. Plot the "best fit" line. Hand in the relevant plots and data tables.

Questions

1. If the initial concentration of nitrogen dioxide in calculation 4 was doubled, what would be the effect on the rate of the reaction? What would be the effect on the rate constant?
2. Discuss the sources of error present in this experiment and how they would affect your results.