THE KINETICS OF FORMALDEHYDE SULFONATION
THE FORMALDEHYDE CLOCK REACTION

By

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LEARNING OBJECTIVES

The objectives of this experiment are to . . .

- determine the rate law for the reaction between formaldehyde and bisulfite ion.
- determine the activation energy for the above reaction.
- understand the nature of a "pseudo" kinetic reaction.

BACKGROUND

Kinetics is the study of "how fast" and "how" a reaction occurs. This experiment will only deal with "how fast," accepting a previously defined three step mechanism. This particular type of experiment is normally a "clock reaction," in which one monitors the time required for a change to occur in the color of the solution, for example, from a light yellow green to deep blue due to the presence of bromothymol blue indicator. However, in this instance we will monitor the time required by a change in the acidity (PH) of the solution. The three step reactions that are believed to cause these changes were discussed by T. Cassen, *Journal of Chemical Education,* 1976, 53, 197. and are as follows:

(1) $HCHO + HSO_3^- \Longrightarrow HOCH_2SO_3^-$

(2) $H_2O + HCHO + SO_3^{2-} \Longrightarrow HOCH_2SO_3^- + OH^-$

(3) $OH^- + HSO_3^- \Longrightarrow SO_3^- + H_2O$

It is assumed that either both of the first two steps or at least the second step is "slow," and it is known that the third step is "fast." It is the second step that provides the means for monitoring the reaction. The initial mixture has a low acidity due to the HSO_3^-, a weak acid. The OH^- produced by step (2) immediately reacts with any HSO_3^- in solution, via reaction (3), thus preventing any accumulation of OH^- until all of the HSO_3^- is consumed. At that point in the reaction, OH^- accumulates in the solution causing the pH to increase. The time required for this to occur will be dependent upon the relative amounts of HCHO, HSO_3^-, and SO_3^{2-}. Because we are monitoring a change in the OH- at some time "t" after the reaction has started, and not a continuous change in a concentration of one of the reactants, this is known as a "pseudo" type kinetics reaction.

Reaction Order and Rate Constant

The rate of reaction between the formaldehyde and the HSO_3^-/ SO_3^{2-} buffer can be expressed as

$$\text{rate} = k\,[HCHO]^x\,[HSO_3^-/ SO_3^{2-}]^y$$

As seen by this equation, at a constant temperature, the rate of reaction will be influenced by the concentrations of the reactants, possibly in an exponential manner if *x* and *y* are other than 1. The constant "k" is a proportionality constant known as the rate constant, and it is constant at a given temperature, but varies with temperature. The values *of x* and y are termed the "order of the reaction" for each reactant, and their sum gives the overall order of the reaction. For example, if *x* = 2 and y = 1, the reaction would be second order in [HCHO], first order in [HS03/ S03], and third order overall. The task of the kineticist is to determine the order of the reaction for each reactant, i.e., determine *x* and y. Having done so, the rate constant may then be calculated, and all the factors are known for a given temperature.

Activation energy

Chemical reactions occur as a result of a collision between particles. However, all collisions

may not result in a chemical reaction because all the reacting species do not possess the certain minimum energy required in order for the reaction to proceed. This energy is known as the activation energy, Ea. The rates of most reactions increase as temperature increases. This is because as the temperature of the reactants increase, the average kinetic energy of the reactants increase and the number of molecules that possess that minimum "activation energy" increases. Thus, the reaction rate increases. As a rule of thumb, the reaction rate of most chemical reactions doubles or triples for every 10 °C increase in temperature.

In 1889, Svante Arrhenius discovered a relationship between the rate constant k, the temperature of the reaction, and activation energy. The equation is:

$$k = \mathbf{A}e^{-Ea/RT} \qquad (1)$$

in which k is the reaction rate constant measured at a specific temperature, A is a constant dependent upon the reaction, E_a is the activation energy, R is the gas constant (8.314 J/mole K) and T is temperature in K. Converting this to the logarithmic form by taking the natural log of both sides gives

$$\ln(k) = \ln(A) - \frac{E_a}{RT} \quad \text{or} \quad \ln(k) = \ln(A) - E_a\left(\frac{1}{R\,(T)}\right) \qquad (\text{of the } \textit{form}\ y = b + mx) \qquad (2)$$

For two rate constants at two different temperatures this becomes

$$\ln(k_2/k_1) = E_a/R(1/T_1 - 1/T_2) \qquad (3)$$

However, using only two temperatures can give rise to significant error in the value of E_a. Thus, in this experiment, we will determine the value of "k" for 5 or 6 different temperatures, plot this data using Equation (2) above, and determine E_a therefrom.

SAFETY PRECAUTIONS

Formaldehyde (HCHO) is a strong reducing agent whose vapors are irritating to the mucous membranes and may produce an irritant dermatitis if spilled on the skin. Use **ONLY** in the hood and use gloves when mixing the initial solution. Avoid prolonged exposure and flush with copious amounts of water if spilled on the skin. Avoid ingestion.

Sodium Bisulfite ($NaHSO_3$) and **Sodium Sulfite** (Na_2SO_3) are mild oxidizing agents. If spilled on the skin, flush with copious amounts of water. Avoid ingestion.

BEFORE PERFORMING THIS EXPERIMENT . . .

. . . you will need a ***MicroLAB*** program capable of monitoring pH, temperature and a timer set to collect data points every 100 milliseconds. This program may either be written by you, or provided by the instructor. The name of the program provided by the instructor is *sulfkin.exp*.

EXPERIMENTAL PROCEDURE

This experiment will make use of the computerized ***MicroLAB*** data collection system to collect the necessary data and assist in its analysis. You will collect time, temperature and concentration information, and use the pH probe to monitor the change in pH. You will then take the first derivative of the pH vs. time curve to determine the time required *for* the solution to reach the mid point of the steep portion of the curve (the equivalence point pH) after mixing the two reagents. Your instructor will assist you in setting up the system and in learning the operation if you need help.

Equipment

- two 25 ml burets for dispensing the reactant solutions
- 250 ml volumetric flask
- two 250 ml beakers
- two 400 ml Erlenmeyer flasks with rubber stoppers
- two 125 ml Erlenmeyer flasks
- magnetic heater/stirrer with stirring bar
- ***MicroLAB*** interface with pH electrode
- AC controller with cord with cord to accept a 2.0 V signal from the ***MicroLAB*** interface and a coffee cup AC heater or a 3 ft light socket cord and a small spotlight light bulb
- **OR**, separate temperature controlled water baths set at six temperatures between 10 and 50 °C
- pH probe

- two Temp(IC) probes
- lots of ice
- standard buffers of 4.0, 7.0 and 10.0 pH

System set-up

1. Connect the pH probe to the BNC connector in the back of the ***MicroLAB***.
2. Connect the Temp(IC) Bath probe to the CAT5-A input, the second Temp(IC) kin probe to the CAT5-B input
3. Calibrate the Temp(IC) probe at a minimum of three points using a well stirred ice bath, boiling water and a mixture of both. Calibrate the Temp(IC) kin probe against the Temp(IC) Bath probe at a minimum of three points. See the **Measurement Manual** for directions if you have not done this before.
4. Calibrate the pH probe using a standard pH buffer at 4.0, 7.0 and 10.0. Be sure to allow complete equilibration before entering the buffer value.

Mixing the solutions

1. Weigh out 5.00 g of $NaHSO_3$ and 0.75 g of Na_2SO_3, quantitatively transfer each to the 250 ml volumetric flask, fill about ½ full with distilled water and swirl until all solid has dissolved. Fill the flask with distilled water to within a few millimeters of the calibration line. Carefully dry the neck of the flask with a Kim Wipe wrapped around a heavy stirring rod, and then adjust the bottom of the meniscus just tangent to the calibration line by adding water with a beryl pipet. (Be careful not to wet the neck of the flask again.)
2. Mix the solution well by tightly holding the stopper in place, inverting the flask and swirling and shaking vigorously several times. Repeat the inversion process several times to insure complete mixing.
3. Transfer the solution to a clean 400 ml Erlenmeyer flask with a stopper and fill the 25 ml buret to the 0.00 mark. Label both the flask and the buret, **Solution A**.
4. Measure 22.5 ml of 37 % formaldehyde into a 50 or 100 ml graduated cylinder, and transfer this to a clean 250 ml volumetric flask. Dilute and mix this in the same manner as described above. Transfer this to a clean Erlenmeyer flask and buret as above, and label them both **Solution B.**

A. Initial investigation

In this part of the investigation, you will examine what reaction takes place, approximately how long it takes and the "clock" effect of watching the change from yellow green to blue for bromothymol blue, or from colorless to pink for phenolphthalein. Proceed as follows:

1. Rinse two 250 ml Erlenmeyer flasks several times with distilled water, then "shake" dry. Measure *exactly* 1.00 ml of Solution A into one flask and label it "A." Then, measure *exactly*

1.00 ml of **Solution** B into the other flask and label it "B." Add *exactly* 49.00 ml of distilled water to each of flasks A and B, and add 8 drops of bromothymol blue or 8 drops of phenolphthalein to **Solution** A. Mix each solution well with gentle swirling.

2. Setting up the experiment in the computer.

   a. Open the ***MicroLAB*** icon and select **Other** tab, then select *Sulfkin.exp*. (If you get an error message at this point, make sure the interface is connected and turned ON by pressing the POWER button on the right rear. Otherwise, see your instructor.)

   b. When everything is ready, gently swirl the two solutions in the Erlenmeyer flasks, mixing them together in a 250 ml beaker on the magnetic stirrer in which the pH probe is suspended and the stirring bar is on the bottom of the beaker. At the instant they are mixed, have one person click **Start** and turn on the stirrer. DO NOT STIR TOO RAPIDLY, as this will pull excess CO2 into the solution, reacting with OH^- ion and invalidating the data. Once the experiment has started, the computer will print and graph the data. *While this experiment is running, prepare the solutions for the next experiment.*

3. As soon as the graph flattens out at the top, click the **Stop** button. (*If you let the reaction continue, no harm will be done. If so, you will notice the curve slopes back down again due to neutralization by CO2 absorbed from the atmosphere.*)

4. Click the **Repeat Experiment** button, and save the data as *sulfkinR1.V1.DH*, where the R1 represents the run number, V1 represent the variable concentration, and DH represents the student's initials.

B. Quantitative variation of rate with a change in the concentration of "B"

Now that you have a feel for what is involved in the reaction, we can take additional quantitative data in a systematic way to determine how the time varies with concentration of the reactants.

Thoroughly rinse the two flasks with tap water and then rinse several times with distilled water from your wash bottle. Squirt all around the sides of the flask, swirl the flask several times, empty into the sink and "shake dry" after the last rinse. Repeat the experiment exactly as above, using the ml of "A" and "B" as indicated in Tables 1, experiments 1 - 4 on the results pages. Although you are collecting the data in the computer, **Be sure** to write down the reaction times and conditions in your lab notebook, and on the accompanying Data Tables just in case the computer data somehow gets lost or destroyed. (Use the run you did above as the first "B" run if you did it carefully.)

C. Quantitative variation of rate with a change in the concentration of "A"

Carry out experiments 5 - 8 exactly as you did experiments 1 - 4, this time varying the volume of "A" used as indicated in Table 2. Again, record your data.

D. Quantitative variation of rate with a change in temperature.

Select six temperatures ranging from about 10˚C up to about 50 ˚C to investigate the effect of temperature on this reaction. (Remember, you already have data for room temperature which can be

included as one of the six.) Use the concentration conditions set up for Experiment 1 in Table 1 in all six experiments.

1. For temperatures below 25 °C, unplug the AC controller from the ***MicroLAB*** interface.
2. Place both flasks (Solution A and Solution B) in an 800 ml beaker with a 50/50 ice slush, using the TempIC kin to read the temperature of the A solution, assuming the B solution will be the same. There should be a submerged platform in the beaker for the 125 ml Erlenmyer flasks to sit on. *Swirl the solutions frequently to facilitate thermal equilibrium. Do not let the temperature probe rest on the bottom of the beaker,* but suspend it with a split cork in the top of the flask, with the probe tip about midway in the solution.
3. At the desired temperature, remove both beakers from the ice bath,
4. While one student quickly, without spilling, mixes the two solutions into the "A" beaker, the other student clicks the **Start** button at the instant of mixing.
5. Swirl, the flask, place on the magnetic stirrer, re-insert the TempIC kin probe and monitor the reaction. *While this experiment is running, prepare the solutions for the next experiment.*
6. Keep the temperature probe suspended in the mixture beaker continuously so that you can determine the average temperature over the course of the experiment. Record the data in your lab notes and in Table 3.
7. Repeat steps two through four for a second temperature half way to 25 °C.
8. For temperatures above 25 °C, connect the AC controller to CAT5-C on the ***MicroLAB*** interface and connect the power cord to the wall socket. Connect the extension cord to the AC controller and place the bulb in an 800 ml beaker as a heating element. There should be a submerged platform in the beaker for the 125 ml Erlenmyer flasks to sit on.
9. Place both flasks (Solution A and Solution B) in the constant temperature bath, using the TempIC Bath probe in the constant temperature bath, and the TempIC kin probe to read the temperature of the A solution, assuming the B solution will be the same. *Swirl the solutions frequently to facilitate thermal equilibrium. Do not let the temperature probe rest on the bottom of the beaker,* but suspend it with a split cork in a utility clamp about midway in the solution.
10. As the temperature becomes greater than 29.5 °C, The program will pause, displaying the message “Mix solutions A and B, then press Enter.”
11. Remove both beakers from the temperature bath, and while one student mixes the two solutions into the "A" beaker, the other student presses **Enter**, at the instant of mixing.
12. Swirl the flask, place on the magnetic stirrer, and re-insert the TempIC kin probe.
13. Keep the temperature probe suspended in the mixture beaker continuously so that you can determine the average temperature over the course of the experiment. Record the data as before.
14. For each of two other temperatures above 30 °C, you will need to make changes in the program, as follows
    a. If the program steps are not showing, right click in the **Experiment Steps** view.
    b. Double click on the first **If . . .** statement, click on **Condition True**, and change the constant value to your new desired value, then press **Enter** twice to close out.

c. Do the same on the second **If. . .** statement, setting the temperature about 0.5 °C below your desired temperature.

15. Repeat steps six through 10 for all remaining temperatures.

16. If time allows, you may want to do some duplicate runs to verify the validity of your results . . .

DATA ANALYSIS

For each of the experiments, do the following:

1. Using the Analysis function of the Spreadsheet, calculate the first derivative of pH vs. time. Select this derivative from the Data Sources/Variables view, and "click-drag" it down to **Column F** and to the Y2 axis to see the overlay.

2. Approximate the time of the first derivative peak, then scroll down the **Spreadheet** to center the row containing the maximum of the first derivative. Record the time, pH and TempIC kin data from that row.

3. Right click on the TempIC kin column, select **Column Statistics** and print out the statistics data for that run.

4. Print your graph, then hand copy the above information on the graph. Make sure the **Header** caption includes which run, the concentrations, and both your initials.

5. "Click-drag" the TempIC kin column to the Y2 axis, then print out the graph so formed. Make sure the **Header** caption includes which run, the concentrations, and both your initials.

The rate of the reaction can be determined by dividing the observed change by the observed time of the change. In this instance, the observed change is the amount of hydroxide ion required to reach the equivalence point of the buffer reaction. We shall arbitrarily assign this a value of 1. This value "1" is then divided by the time in seconds to yield the rate for the reaction, i.e., the rate has the units, **unknown** units/second which equals l/seconds.

In a pseudo kinetic experiment, plotting the change in concentration vs. time is not an effective way to determine the reaction order. This is due to the fact that we are not continuously monitoring the change in concentration with time, but only looking at the time required to obtain a particular change. One can get around this by some mathematical manipulation of the rate equation as follows:

The general expression for the rate of a chemical reaction is

$$\text{Rate} = R = k\,[A]^m\,[B]^n \qquad (1)$$

Since we have rate values for four concentration values of each reactant, we can compare the rates by taking a ratio between them, e.g.,

$$\frac{R_1}{R_2} = \frac{k_1[A_1]^m\,[B_1]^n}{k_2[A_2]^m\,[B_2]^n} \qquad (2)$$

Since both reactions were carried out at the same temperature, kl = k2, and at a constant concentration of A, then these terms both divide out, leaving

$$\frac{R_1}{} = \frac{[Bl])^n}{} \qquad (3)$$

$$R_2 \qquad [B_2]^{\underline{n}}$$

One can now take the logarithm of both sides to obtain

$$\ln (R_1/R_{2)} = n*\ln([B_1]/[B_2]) \qquad (4)$$

This can be further simplified to

$$n = \frac{\ln((R_1/R_{2)})}{\ln([B_1]/[B_2])} \qquad (5)$$

Obtaining the "n" values for 1 and 4, 1 and 2, 1 and 3, 2 and 3, and 3 and 4, then averaging will give a good estimate of the order of the reaction. This can easily be accomplished using the ***MicroLAB*** **Hand Enter** mode, or another spreadsheet such as Excel.

REPORT SUMMARY

Concentration experiments

1. Two graphs (pH and first derivative vs. time, and pH and temperature vs. time) for each experiment.
2. A spreadsheet of calculations used to determine the order of the reaction with respect to HCHO and HSO_3^- .
3. Completed Data Tables I, 2 and 3 with the answers to all of the questions on them.

Temperature experiments

1. A data table relating time vs. Celcius (°C) and Kelvin (K) temperatures and rate constant (k) calculations.
2. One Celsius graph and one Kelvin graph showing a linear relationship between the rate constant (k) and temperature.