The Kinetics of Formaldehyde Sulfonation
The Formaldehyde Clock Reaction

INSTRUCTOR RESOURCES

By

Dale A. Hammond, PhD, Brigham Young University Hawaii

Learning Objectives

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

Procedure Overview

- set up equipment, interface and computer.
- mix solutions and set up burets for dispensing.
- explore the variation of rate with a change of concentration of formaldehyde.
- explore the variation of rate with a change of concentration of HSO_3 /SO_3^{2} buffer.
- explore the variation of rate with change of temperature.
- use the ***MicroLAB*** spreadsheet to plot graphs to determine "clock" time.
- use an Excel spreadsheet to calculate log ratios to determine exponents, k values, ln k values, 1/T values (both C and K).
- use the ***MicroLAB*** spreadsheet to plot a graph of ln k vs. 1/T to determine E_a .

Name ____________________________ Section _____________ Date _________________

THE KINETICS OF FORMALDEHYDE SULFONATION
THE FORMALDEHYDE CLOCK REACTION

Report Sheet

Data Table 1: Variation of rate due to concentration of "B"

Experiment #	Drops indicator	Total mL water	mL "A"	mL "B"	Trial 1 --------	Trial 2 time(sec)-	Average ------	Rate s^{-1}
1	8	98	1	1	_______	_______	_______	_______
2	8	97	1	2	_______	_______	_______	_______
3	8	96	1	3	_______	_______	_______	_______
4	8	95	1	4	_______	_______	_______	_______

Average temperature of the reactions =

1. Consider the following questions in relation to the above experiments.
   a. What pattern was observed in the rate?

   b. Why was the amount of "A" unchanged throughout the four experiments?

2. Using the ***MicroLAB*** **Hand Entered** data mode, or an Excel spreadsheet, determine the exponent for variable "B" as discussed in the **Data Analysis** section of the experiment. What is the order of the rate expression in "B?"

3. Include properly labeled graphs of each of your runs as discussed in **Data Analysis** sections 2 ©) and (d) as a part of your report.

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Report Sheet (page 2)

Data Table 2: Variation of rate due to concentration of "A"

Experiment #	Drops indicator	Total mL water	mL "A"	mL "B"	Trial 1 -------	Trial 2 time(sec)	Average -------	Rate s^{-1}
5	8	98	.5	1	_______	_______	_______	_______
6	8	97	1	1	_______	_______	_______	_______
7	8	96	2	1	_______	_______	_______________	
8	8	95	3	1	_______	_______	_______	_______

Average temperature of the reactions =

4. Consider the following questions in relation to the above experiments.
   a. What pattern was observed in the rate?

   b. Why was the amount of "B" unchanged throughout the four experiments?

5. Using an Excel spreadsheet, determine the exponent for variable "A" as discussed in the **Data Analysis** section of the experiment. What is the order of the rate expression in "A?"

6. Compare the ORDER obtained for "A" and "B." How are they similar? How are they different? What causes this difference.

7. Include properly labeled graphs of each of your runs as discussed in **Data Analysis** sections 2 ©) and (d) as a part of your report.

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Report Sheet (page 3)

Data Table 3: Variation of rate due to temperature

Experiment #	Time (sec)	Temperature C (average)	Temperature K	Rate	"k" (1/sec)
9	______	______	______	______	______
10	______	______	______	______	______
11	______	______	______	______	______
12	______	______	______	______	______
13	______	______	______	______	______

8. Consider the following questions in relation to the above experiments.

   a. What pattern was observed in the rate as the temperature was varied?

   b. Why were the amounts of "A" and "B" unchanged throughout the six experiments?

9. Input the time/temperature data into the **Spreadsheet** function of ***MicroLAB*** , or into Excel, calculate the Kelvin temperature, and then determine the value of "k" for each of the six experiments. Record these in Table 3 and print out the computer data table.

10. Use the **Spreadsheet** to develop an algebraic expression that will give a linear relationship relating the "k" for each of the reactions to the temperature. (**Hint:** Recall how to obtain a linear plot from an exponential function, the Arrhenius equation.) Try using both the Celsius and Kelvin temperatures. Test linearity by the correlation value. Write the equations below with their corresponding correlation values, as well as writing them on the printed graphs.

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Report Sheet (page 4)

11. Which temperature scale gives the best results? Why?

12. In the space below, calculate the activation energy, E_a , from your data. Include a copy of your graph used to determine E_a with your report.

13. Is this reaction exothermic or endothermic? How can you tell? Any ideas as to why?

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Tips and Traps

1. Students should be instructed in the proper technique of using volumetric flasks in order to get accurate concentrations.

2. With the use of an indicator to produce the "clock" effect, and since the solution concentrations are very dilute, there is a tendency for dissolved CO2 from the atmosphere to lower the pH after the reaction has completed. This results in the indicator changing back to the acid form, and the pH vs. time plot showing a decrease after it levels out at the top. Students should be told about this in advance and the phenomenon explained so they don't think there is something wrong with their reaction.

3. Students at this level do not have that much facility with mathematics, especially logarithms. It is very helpful for the instructor to review the math involved to assist the students in understanding what they are doing. They seem to have an especially difficult time understanding how to get from the Arrhenius equation of $k = e^{-Ea/RT}$ to $\ln k = \ln A - Ea/RT$. They also have difficulty relating this to graphing ln k vs. 1/T to obtain Ea.

4. Students may need some help in understanding the relationship between the change in pH and change in temperature. Use of a sample graph could be helpful here.

5. **Sample Program**

pH and temperature versus time: pH, temperature and time are recorded automatically by the MicroLAB system every 100 seconds while maintaining a constant temperature bath at a specified temperature.
Purpose: **Example**: To measure the kinetics of an hydroxide producing reaction by monitoring pH at a fixed temperature.
Experiment name: ***sulfkin.exp***
Sensors: **Time**: X axis, Col. A, DD on top, units = sec; **pH**: Y1 axis, Col B, DD in middle, units = pH; **Temperature**: Not graphed, Col C, DD on bottom, units = °C.
Special Program:

Read Sensors (Reads all variables selected in Data Sensors/Variables and stores in a data grid.)
Repeat every 0.5 seconds
Repeat every 0.5 seconds
If TempIC < +/- value (Sets to hold water bath temperature at "value" °C.)
Output CAT-5B - ON (Turns Output ON, which turns ON the water bath heater)
Else
Output CAT-5B - OFF (Turns Output OFF, which turns OFF the water bath heater)
End If
Until Delta Time1 > +/- 100.00 (Sets to read temperature and pressure every 100 seconds)
Read Sensors (Reads all variables selected in Data Sensors and Variables and stores in a data grid.)
Until Stop Button is pressed

Comment: Temperature probe and pH calibration are required. To change the fixed value of the variable, double click the **If . . .** statement then click on **Condition True** and enter the variable value.

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Sample Data

Data Table 1: Variation of rate due to concentration of "B"

Experiment #	Drops indicator	Total ml water	ml "A"	ml "B"	Trial 1 -------	Trial 2 time(sec)	Average -------	Rate s-1
1	8	98	1	1	27.41			0.03648
2	8	97	1	2	17.71			0.05646
3	8	96	1	3	9.68			0.1033
4	8	95	1	4	7.79			0.1284

Average temperature of the reactions = ________________

1. Consider the following questions in relation to the above experiments.
   a. What pattern was observed in the rate?

   As the concentration of "B" was increased, the rate of reaction increased.

   b. Why was the amount of "A" unchanged throughout the four experiments?

   The amount of "A" remains unchanged throughout the four experiments because it is necessary to vary only one parameter at a time in order to see what effect that parameter has on the rate.

2. Using an Excel spreadsheet, determine the exponent for variable "B" as discussed in the **Data Analysis** section of the experiment. What is the order of the rate expression in "B?"

   The solution for the exponent of "B" from the ratio method should result in an order of +1.

3. Include properly labeled graphs of each of your runs as discussed in **Data Analysis** sections 2 ©) and (d) as a part of your report.

   See the separate sheet for the properly labeled graphs.

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Sample Data (page 2)

Data Table 2: Variation of rate due to concentration of "A"

Experiment #	Drops indicator	Total ml water	ml "A"	ml "B"	Trial 1 -------	Trial 2 time(sec)	Average -------	Rate s-1
5	8	98	.5	1	18.85			0.05305
6	8	97	1	1	33.14			0.03017
7	8	96	2	1	85.14			0.01175
8	8	95	3	1	137.6			0.007267

Average temperature of the reactions =

4. Consider the following questions in relation to the above experiments.

   a. What pattern was observed in the rate?

   As the concentration of "A" was increased, the rate of reaction decreased.

5. Why was the amount of "B" unchanged throughout the four experiments?

   The amount of "B" remained unchanged throughout the four experiments because it is necessary to vary only one parameter at a time in order to see what effect that parameter has on the rate.

6. Using an Excel spreadsheet, determine the exponent for variable "A" as discussed in the **Data Analysis** section of the experiment. What is the order of the rate expression in "A?"

   The solution for the exponent of "A" from the ratio method should result in an order of 1.

7. Compare the ORDER obtained for "A" and "B." How are they similar? How are they different? What causes this difference.

   The algebraic expressions obtained for [A] and [B] are similar in that they are both first order. They differ in that the order for "A" is negative, meaning that it is in the denominator and thus causes the rate to decrease as the [A] increases.

8. Include properly labeled graphs of each of your runs as discussed in **Data Analysis** sections 2 ©) and (d) as a part of your report. ***See the separate sheet for properly labeled graphs.***

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Sample Data (page 3)

Data Table 3: Variation of rate due to temperature

Experiment #	Time (sec)	Temperature C (average)	Temperature K	Rate	"k" (1/sec)
9	77.78	3.0	276	0.01286	0.01286
10	66.45	7.7	280.7	0.01505	0.01505
11	27.41	24.86	297.9	0.03648	0.03648
12	21.02	31.07	304.1	0.04757	0.04757
13	7.37	45.00	318	0.1357	0.1357

9. Consider the following questions in relation to the above experiments.

   a. What pattern was observed in the rate as the temperature was varied?

   The rate increased with an increase in temperature.

   b. Why were the amounts of "A" and "B" unchanged throughout the six experiments?

   The amount of "A" and "B" remained unchanged in order to have temperature as the independent variable and evaluate rate as the dependent variable.

10. Input the time/temperature data into the **Spreadsheet** function of ***MicroLAB*** , or into Excel, calculate the Kelvin temperature, and then determine the value of "k" for each of the six experiments. Record these in Table 3 and print out the computer data table.

    See Data Table 3 for this information.

11. Use the **Spreadsheet** to develop an algebraic expression that will give a linear relationship relating the "k" for each of the reactions to the temperature. (**Hint:** Recall how to obtain a linear plot from an exponential function, the Arrhenius equation.) Try using both the Celsius and Kelvin temperatures. Test linearity by the correlation value. Write the equations below with their corresponding correlation values, as well as writing them on the printed graphs.

    The proper relationship (and the one with the highest correlation value) to obtain a linear expression is to plot ln k vs. 1/T where T is the temperature in Kelvin.

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Sample Data (page 4)

12. Which temperature scale gives the best results? Why?

    The Kelvin temperature scale gives the best results because it is the natural temperature scale, i.e., it more accurately represents the energy of the molecules because a 0 K, the molecules have no translational, vibrational or rotational energy.

13. In the space below, calculate the activation energy, Ea, from your data. Include a copy of your graph used to determine Ea with your report.

    The activation energy should be approximately 54.7 kJ/mol.

14. Is this reaction exothermic or endothermic? How can you tell? Any ideas as to why?

    This reaction is exothermic. The graphs of temperature vs. time show an increase in temperature with time. The bond energies of the products are larger than the bond energies of the reactants.

Report Summary: check for the following information

Concentration experiments

1. Two graphs (pH and first derivative vs. time, and pH and temperature vs. time) for each experiment.
2. The spreadsheet calculations used to determine the order of the reaction for each reactant and the data to plot ln k vs. 1/T.
3. Completed Data Tables 1, 2 and 3 with the answers to all of the questions.

Temperature experiments

1. A data table relating time vs. C, with Kelvin temperatures (K) and rate constant (k) calculations.
2. Graphs showing a linear relationship between the rate constant (k) and temperature, both Celsius and Kelvin.

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Sample Data (page 5)

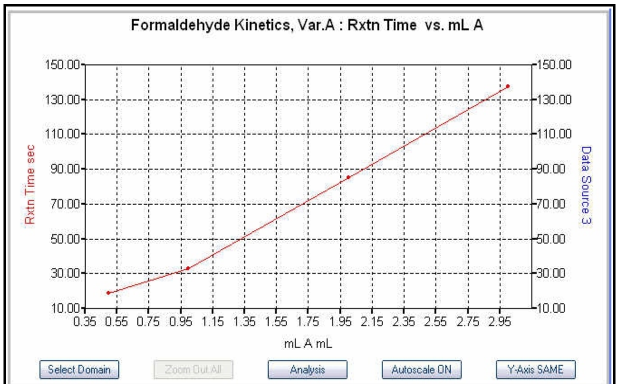

Figure 1. Reaction time verses concentration of SO_3^{2-} showing positive slope when the reaction order is positive.

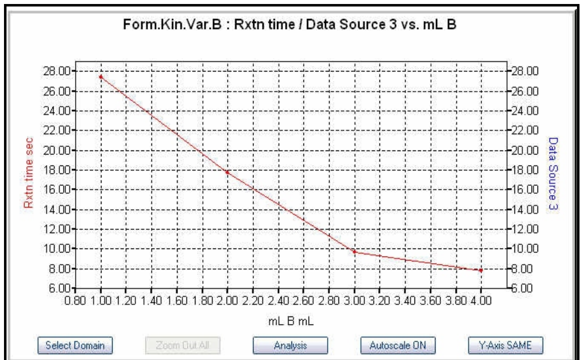

Figure 2. Reaction time verses concentration of formaldehyde, showing negative slope when the reaction order is negative.

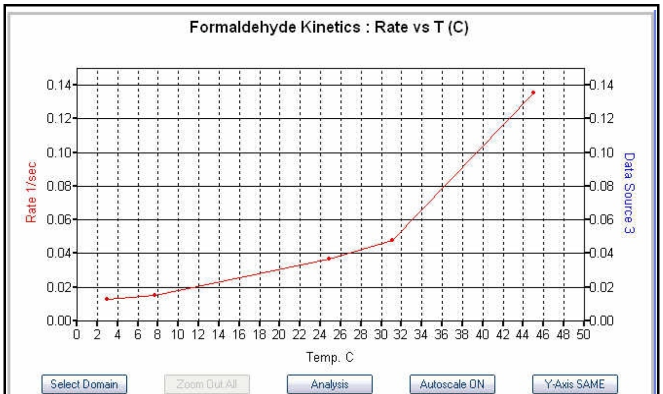

Figure 3. Graph of reaction rate versus temperature in °C.

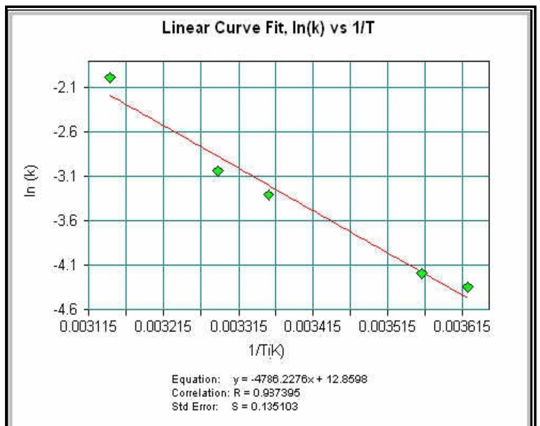

Figure 4. Graph of ln(K) versus 1/T (K). E_a is calculated as slope (-4786.2 K)*R(8.314 J/K mol)

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Laboratory Preparation (per student station)

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 250 ml Erlenmeyer flasks
- magnetic heater/stirrer with stirring bar
- pH probe
- thermistor probe
- ice
- ***MicroLAB*** interface with pH electrode
- AC controller 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

Supplies

- 5.00 g of $NaHSO_3$
- 0.75 g of Na_2SO_3
- 0.75 ml of 37% formaldehyde
- pH 4, 7 and 10 buffers for calibration of pH electrode

CAUTION:

- **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. 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.