

Experiment 13A

THE KINETICS OF THE OXIDATION OF IODIDE ION BY HYDROGEN PEROXIDE

1/25/2023

MATERIALS: Eight 250 mL Erlenmeyer flasks, 500 mL Erlenmeyer flask, 25 mL graduated cylinder, 5 mL graduated cylinder, 100 mL graduated cylinder, thermometer, wall clock, 0.010 M $\text{Na}_2\text{S}_2\text{O}_3$ solution, starch solution, buffer solution (1 M CH_3COOH and 1 M NaCH_3COO), 0.060 M KI solution, 0.040 M H_2O_2 solution, 2.0×10^{-3} M sodium molybdate solution, distilled water, ice.

PURPOSE: The purpose of this experiment is to determine the rate law for the oxidation of iodide with hydrogen peroxide. The effect of temperature and a catalyst on the rate of the reaction will also be examined.

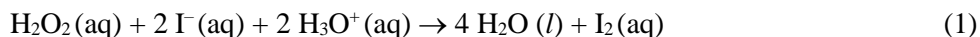
LEARNING OBJECTIVES: By the end of this experiment, the student should be able to demonstrate these proficiencies:

1. Construct a graph from experimental data using Microsoft Excel.
2. Determine the order of a reaction from graphical data.
3. Write a rate law expression from experimental data.
4. Determine the activation energy from experimental data.

DISCUSSION:

A. Introduction

Hydrogen peroxide oxidizes iodide ion (I^-) according to the equation:



A general expression for the rate of this reaction as a function of reactant concentrations (the “rate law”) can be written as:

$$\text{rate} = k [\text{H}_2\text{O}_2]^a [\text{I}^-]^b [\text{H}_3\text{O}^+]^c \quad (2)$$

In this experiment the concentration of the hydronium ion (H_3O^+) in the reaction mixture is maintained at a constant value (approximately 2×10^{-5} M) by using a buffer solution. This allows the rate law to be written in simplified form:

$$\text{rate} = k' [\text{H}_2\text{O}_2]^a [\text{I}^-]^b \quad (3)$$

where $k' = k[\text{H}_3\text{O}^+]^c$ is the rate constant at the given hydronium ion concentration. The purpose of this lab is to experimentally determine the rate law (Eq. 3) by establishing the numerical values for k' , a , and b .

B. Determining the Order of Reaction with Respect to $[\text{H}_2\text{O}_2]$

The order of reaction with respect to hydrogen peroxide will be determined by measuring the rates of reaction mixtures in which the concentration of the iodide ion is held constant while varying the initial concentration of the hydrogen peroxide. In this case, the rate expression becomes

$$\text{rate} = k'' [\text{H}_2\text{O}_2]^a \quad (4)$$

where $k'' = k' [\text{I}^-]^b = k [\text{I}^-]^b [\text{H}_3\text{O}^+]^c$, with $[\text{I}^-]$ held constant.

Taking the logarithm of both sides of equation (4) one obtains an equation for a straight line:

$$\begin{array}{l} \log (\text{rate}) = a \log [\text{H}_2\text{O}_2] + \log k'' \\ y = m x + b \end{array} \quad (5)$$

By plotting $\log (\text{rate})$ (on the y-axis) versus $\log [\text{H}_2\text{O}_2]$ (on the x-axis), the slope of the line equals a , the order of the reaction with respect to the hydrogen peroxide concentration.

C. Determining the Order of Reaction with Respect to $[\text{I}^-]$

In similar fashion, by measuring the rates of reaction mixtures in which the concentration of hydrogen peroxide is held constant while varying the initial concentration of the iodide ion, the rate expression becomes:

$$\text{rate} = k''' [\text{I}^-]^b \quad (6)$$

where $k''' = k' [\text{H}_2\text{O}_2]^a = k [\text{H}_2\text{O}_2]^a [\text{H}_3\text{O}^+]^c$, with $[\text{H}_2\text{O}_2]$ held constant. As before, taking the log of both sides of equation (6) gives an equation for a straight line:

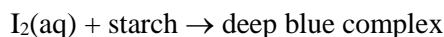
$$\begin{array}{l} \log (\text{rate}) = b \log [\text{I}^-] + \log k''' \\ y = m x + b \end{array} \quad (7)$$

The slope of the line obtained by plotting $\log (\text{rate})$ versus $\log [\text{I}^-]$ equals b , the order of the reaction with respect to the iodide ion concentration.

D. Monitoring the Rate of Reaction

Reaction (1) produces a faint yellow color in solution due to formation of I_2 product, but the color is too faint to be useful as a means of directly monitoring reaction progress. Instead, we will monitor the rate of the reaction indirectly, by linking it to a secondary reaction that produces an obvious visible color change **after a certain amount of I_2 product has been formed**. This is done by carrying out the reaction in the presence of a small, known quantity of sodium thiosulfate ($\text{Na}_2\text{S}_2\text{O}_3$), together with starch indicator.

To understand how this works, we first observe that in aqueous solution, starch reacts with even small concentrations of iodine to form a soluble, highly colored complex:



The color of this blue complex is so strong that iodine solution is commonly used to test for the presence of starch in foods. Now, if we were to conduct the hydrogen peroxide/iodide reaction in the presence of starch *alone*, the blue color would appear the instant that the first iodine product was produced; that would not be very useful! On the other hand, if we *also* add a small amount of sodium thiosulfate to the reaction mixture, then the thiosulfate ion reacts *very rapidly* with the iodine (I_2) as it is produced:



In this case, the iodine produced by reaction (1) is rapidly consumed by reaction with the added thiosulfate ions via reaction (8), so the blue color of the starch-iodine complex will not appear **until the thiosulfate runs out** and iodine (I_2) starts to accumulate in solution. The appearance of the blue color thus acts as a signal indicating that the reaction between the hydrogen peroxide and iodide has progressed to a certain point.

In this experiment, the rate of reaction (1) will be expressed as the rate of formation of iodine (I₂) in units of mol L⁻¹ s⁻¹. Another important detail is that the fixed amount of S₂O₃²⁻ added to each reaction mixture will be kept *very small* compared to the amounts of reactants H₂O₂ and I⁻ initially present. As a result, the absolute change in the concentrations of these reactants over the time period of the experiment will likewise be *very small*. This greatly simplifies the analysis by allowing us to assume that the concentrations of H₂O₂ and I⁻ reactants remain effectively constant at their initial values throughout the reaction period.

E. Determination of Activation Energy from Rate Constants

The activation energy, E_a, for reaction (1) can be determined using the values for the rate constants, k₁ and k₂, determined for runs carried out at two different temperatures, T₁ and T₂, respectively, using the following equation:

$$\ln \left(\frac{k_2}{k_1} \right) = -\frac{E_a}{R} \left(\frac{1}{T_2} - \frac{1}{T_1} \right) \quad (9)$$

PROCEDURE:

Part A. The Rate Law and the Reaction Order in $[H_2O_2]$ and $[I^-]$

1. The rate of this reaction is influenced greatly by small amounts of contaminants; extreme care must be taken to ensure the cleanliness of all glassware. Using tap water, thoroughly wash all of the glassware. Rinse several times with small quantities of distilled water and drain thoroughly but do not dry.
2. Prepare a $Na_2S_2O_3$ -buffer-starch stock solution by using the following procedure. Rinse a 25 mL graduated cylinder with a small quantity of 0.010 M $Na_2S_2O_3$ solution, then measure 25 mL of the 0.010 M $Na_2S_2O_3$ solution and pour it into a 500 mL Erlenmeyer flask. Using the same 25 mL graduated cylinder without further rinsing, measure 25 mL of the provided buffer solution and also add it to the 500 mL Erlenmeyer flask. Add 25 mL of the starch solution to the 500 mL Erlenmeyer flask and then add 175 mL of distilled water measured with a 100 mL graduated cylinder. Swirl the resulting solution to be certain it is homogeneous. The resulting mixture contains 0.0010 M $Na_2S_2O_3$, buffer, and starch.
3. Rinse a 25 mL graduated cylinder with a small quantity of the $Na_2S_2O_3$ -buffer-starch stock solution you prepared, then place 25 mL of this stock solution into *each* of eight 250 mL Erlenmeyer flasks labeled solution 1 through 5, 2a, 2b, and 2c. To each flask, add the quantities of 0.060 M KI solution and distilled water indicated in Table I below. **Do not add the 0.040 M H_2O_2 solution until the reaction time measurements are started.** Carefully add 1 mL (~20 drops) of sodium molybdate catalyst solution to solutions 2a and 2b. The eight solutions are now ready for the reaction time measurements.
4. Rinse a 50 mL graduated cylinder with a small quantity of 0.040 M H_2O_2 solution. Then measure 20 mL of the 0.040 M H_2O_2 solution. Note the time and quickly pour the H_2O_2 solution into the flask labeled solution 1. Swirl the solution and then place the flask on a white background. In Table II of the Data Section, record the time required for the entire solution to turn blue to the nearest second. Disregard a preliminary blue color, which may appear at the top of the solution where it contacts the flask.
5. Repeat the reaction time procedure using solutions 2 through 5. Use the volumes of H_2O_2 solution given in Table I and record the reaction times in Table II. Solutions 2a, 2b, and 2c will be investigated in Part B.

Table I: Quantities of Reagents Used in Reaction Mixtures

Solution Number	0.0010 M $Na_2S_2O_3$, buffer, starch stock solution (mL)	0.060 M KI (mL)	Distilled Water (mL)	2.0×10^{-3} M sodium molybdate (mL)	0.040 M H_2O_2 (mL)
1	25	25	30	0	20
2	25	25	20	0	30
3	25	25	0	0	50
4	25	15	10	0	50
5	25	10	15	0	50
2a (Room Temp)	25	25	19	1	30
2b (Low Temp)	25	25	19	1	30
2c (Low Temp)	25	25	20	0	30

Part B. Catalyst and Activation Energies

1. With the three remaining solutions (2a, 2b, and 2c), you will now investigate the effect of temperature and a catalyst on the reaction. Because all of the solutions have attained thermal equilibrium with the surroundings, it will be assumed that the temperature of solutions 2 and 2a are the same. Record this temperature. Now add 30 mL of the hydrogen peroxide to solution 2a and record the time required for the blue color to form.
2. Next place solution 2b in an ice-water bath until its temperature has been lowered to about 0°C. At the same time, place a 50 mL graduated cylinder containing 30 mL of 0.040 M H₂O₂ in the ice bath. (In order not to contaminate the H₂O₂ solution, do not measure its temperature.) Remove the H₂O₂ solution from the ice-water bath, quickly dry the outside of the graduated cylinder, note the time, pour the H₂O₂ solution into solution 2b, and swirl. Maintain the temperature of the solution at about 0°C by keeping it in the ice-water bath. In Table II, record to the nearest second the time required for the entire solution to turn blue. Record the temperature of solution 2b. Repeat this procedure with solution 2c.

Clean Up:

1. Rinse all solutions down the drain.
2. Wash your glassware.
3. Return equipment to the bins from which they were obtained.

Name _____

Section _____

Partner _____

Date _____

DATA SECTION
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Table II: Reaction Time Data

Solution Number	Time (s)
1	
2	
3	
4	
5	

Solution Number	Time (s)
2a	
2b	
2c	

Temperature of solutions 1 through 5 and 2a _____

Temperature of solution 2b _____

Temperature of solution 2c _____

DATA TREATMENT
Experiment 13A

Part A. The Rate Law and the Reaction Order in $[H_2O_2]$ and $[I^-]$

(A.1) Calculate the initial molarity of thiosulfate ion in each reaction mixture. (Note: it is the same for all eight solutions.) Show your work.

If the entire amount of thiosulfate ion reacts according to equation (8), what is the molarity of I_2 formed by reaction (1)?

(A.2) Complete Table III below. You may submit an Excel spreadsheet in lieu of completing this table by hand.

- a. For each reaction mixture, calculate the rate of iodine (I₂) formation in units of mol L⁻¹ s⁻¹:

$$\text{rate} = \frac{\Delta[\text{I}_2]}{\Delta t}$$

- b. For each reaction mixture, calculate the molarity of H₂O₂ and I⁻. (These are the same calculations as in Pre-Lab Question #1.)
- c. Calculate the log (rate), log [H₂O₂] and log [I⁻] for each solution.
- d. Calculate *k* after the orders of reaction are determined. Include units.

Table III: Summary of Data Treatment

Solution Number	Rate I ₂ Formation (mol L ⁻¹ s ⁻¹)	[H ₂ O ₂] (mol/L)	[I ⁻] (mol/L)	log (rate)	log [H ₂ O ₂]	log [I ⁻]	Rate constant
1							
2							
3							
4							
5							
2a							
2b							
2c							

(A.3) Using the values for solutions 1, 2, and 3, construct a single Excel plot of log (rate) versus log [H₂O₂]. Include the regression equation and R² value on your plot. Within experimental error, the slope of the line should be close to an integer. The integer value is the order of the reaction with respect to the hydrogen peroxide concentration.

Slope of log (rate) versus log [H₂O₂] plot = _____ Order with respect to [H₂O₂] = _____

(A.4) Using the values for solutions 3, 4 and 5, make a single Excel plot of log (rate) versus log [I⁻]. Include the regression equation and R² value on your plot. Determine the order of the reaction with respect to the iodide ion concentration.

Slope of log (rate) versus log [I⁻] plot = _____ Order with respect to [I⁻] = _____

- (A.5) Using the experimentally determined orders of reaction with respect to $[\text{H}_2\text{O}_2]$ and $[\text{I}^-]$, write the rate law expression for reaction (1), following the form of the simplified rate law given in equation (3).
- (A.6) For each of the eight solutions, calculate the rate constant and enter the values in Table III. Show work for your calculation for solution 1.

Using the values obtained for solutions 1 through 5, determine the average value of the rate constant, k' , for the uncatalyzed reaction at room temperature. Include units.

Average rate constant, k' , of uncatalyzed reaction at room temperature = _____

Part B. Catalyst and Activation Energies

- (B.1) Calculate the activation energy of the uncatalyzed reaction from the average value of k' at room temperature and the value obtained at a lower temperature (solution 2c) using equation (9).
- (B.2) Calculate the activation energy of the catalyzed reaction from its value of k' at room temperature (solution 2a) and the value obtained at a lower temperature (solution 2b) using equation (9).

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