

Experiment 13A

2/10/2021

THE KINETICS OF THE OXIDATION OF IODIDE ION BY HYDROGEN PEROXIDE

MATERIALS: 250 mL Erlenmeyer flasks (8), 500 mL Erlenmeyer flask, 25 mL graduated cylinder, 100 mL graduated cylinder, thermometer, 0.010 M Na₂S₂O₃ solution, 2% starch solution, buffer solution (1 M CH₃COOH and 1 M NaCH₃COO), 0.060 M KI solution, 0.040 M H₂O₂ 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.

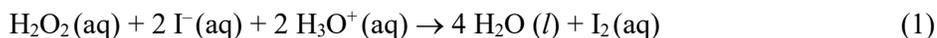
LEARNING OBJECTIVES: By the end of this experiment, the student should be able to demonstrate these proficiencies:

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 the reaction 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 is maintained at a constant value (approximately 2 × 10⁻⁵ M) by using a buffer solution. Therefore, the expression for the rate of the reaction simplifies to

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

where k' is the rate constant at a given hydronium ion concentration and is equal to $k[\text{H}_3\text{O}^+]^c$. The purpose of this experiment is to establish numerical values for k' , a , and b , from which the rate law for the reaction is determined.

B. Determining the Order of Reaction with Respect to [H₂O₂]

The order of the reaction with respect to hydrogen peroxide can 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:

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

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 a 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:

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

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

Because reaction (1) itself has no visible sign of completion, e.g., color change, we employ a secondary reaction that involves a color change. A small known quantity of sodium thiosulfate and starch indicator is added to the reaction mixture. The thiosulfate ion does not react to any appreciable extent with any of the reactants. However, it does react very rapidly with the iodine (I_2) produced in reaction (1) according to the equation



As the iodine produced by reaction (1) forms, it is immediately consumed by the thiosulfate ion. When the small quantity of thiosulfate present is consumed, iodine (I_2) will accumulate and form an intensely blue colored complex with the starch. Therefore, by noting the time required for the appearance of the blue complex after mixing the hydrogen peroxide and the iodide ion, the rate of the reaction can be established. In this experiment the rate is expressed as the rate of formation of iodine (I_2) in units of $\text{mol L}^{-1} \text{s}^{-1}$.

The concentration of thiosulfate ion used to measure the reaction rate is very small compared to the concentrations of hydrogen peroxide and the iodide ion. Therefore, it can be assumed that the concentrations of the reactants remain constant at their initial values during the reaction time period.

E. Determination of Activation Energy from Rate Constants

The activation energy, E_a , of the catalyzed and uncatalyzed reactions can be determined using the values for the rate constants, k_1 and k_2 , determined at two different temperatures, T_1 and T_2 , 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 2% 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 0.1% 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, 0.2% 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 $[\text{H}_2\text{O}_2]$ and $[\text{I}^-]$

- (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).

QUESTIONS
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1. Why can an average rate constant be calculated from the k' values for solutions 1-5 only? Why can't the rate constant values from solutions 2a-2c be included in the average?

2. If the procedure were repeated, using 0.120 M KI instead of 0.060 M KI, how would this affect the following:
 - a. rate of formation of iodine. Explain.

 - b. numerical value for the rate constant. Explain.

3. When a catalyst is added to a reaction mixture, what happens to the original pathway by which the reaction occurred without the catalyst?

4. What effect, if any, did lowering the temperature have on the rate of I_2 formation?

