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Experiment #5 – Chemical Kinetics: Iodine Clock Reaction

In the previous experiment, we discussed the factors that influence the rate of a chemical reaction and presented the terminology used in quantitative relations in studies of the kinetics of chemical reactions. That material is also pertinent to this experiment and should be studied before you proceed further.

This experiment involves the study of the rate properties, or chemical kinetics, of the following reaction between iodide ion and bromate ion under acidic conditions:

$$6\ I^-(aq) + BrO_3^-(aq) + 6\ H^+(aq) \rightarrow 3\ I_2(aq) + Br^-(aq) + 3\ H_2O(l) \qquad (1)$$

This reaction proceeds at an easily measurable rate that depends on the concentrations of the I^-, BrO_3^-, and H^+ ions according to the rate law discussed in the previous experiment. For this reaction, the rate law takes the form

$$\text{rate} = k\,[I^-]^m\,[BrO_3^-]^n\,[H^+]^p \qquad (2)$$

The main goals of the experiment will be to evaluate the reaction orders m, n and p, the rate constant, k, and investigate the manner in which the reaction rate depends on temperature to solve for its activation energy, E_a, for the reaction.

Our method for measuring the rate of the reaction involves what is frequently called a "clock" reaction. In addition to Reaction 1, whose kinetics we will study, the following reaction will also be made to occur simultaneously in the reaction flask:

$$I_2(aq) + 2\ S_2O_3^{2-}(aq) \rightarrow 2\ I^-(aq) + S_4O_6^{2-}(aq)$$

As compared with (1) this reaction is essentially instantaneous above 10 °C. The I_2 produced in (1) reacts completely with the thiosulfate, $S_2O_3^{2-}$, ion present in the solution so that once all the thiosulfate ion has reacted, the concentration of I_2 is effectively zero. As soon as the $S_2O_3^{2-}$ is gone from the system, the I_2 produced by (1) remains in the solution, and its concentration begins to increase. The presence of I_2 is made strikingly apparent by a starch indicator which is added to the reaction mixture, since I_2 even in small concentrations reacts with starch solution to produce a blue color.

By carrying out Reaction 1 in the presence of $S_2O_3^{2-}$ and a starch indicator, we introduce a "clock" into the system. Our clock tells us when a given amount of BrO_3^- ion has reacted (1/6 mole BrO_3^- per mole $S_2O_3^{2-}$). The rate of reaction can be expressed in terms of the time it takes for a particular amount of BrO_3^- to be used up. In all our reactions, the amount of $S_2O_3^{2-}$ that reacts will be constant and small, therefore the amount of BrO_3^- to be used up is both constant and small as compared to the initial amounts of reactants. This means that the concentrations of all reactants will be essentially constant in Equation 2, and hence so will the rate during each reaction.

In our experiment, we will carry out the reaction between BrO_3^-, I^-, and H^+ ions under different concentration conditions. Measured amounts of each of these ions in water solution will be mixed in the presence of a constant small amount of $S_2O_3^{2-}$. The time it takes for each mixture to turn blue will be measured. The time obtained for each reaction will be inversely proportional to its rate. By changing the concentration of one reactant and keeping the other concentrations constant, we can investigate how the rate of the reaction varies with the concentration of a particular reactant. Once we know the order for each reactant, we can determine the rate constant for the reaction.

In the last part of the experiment we will investigate how the rate of the reaction depends on temperature. You will recall that in general the rate increases sharply with temperature. By measuring how the rate varies with temperature we can determine the activation energy, E_a, for the reaction by making use of the Arrhenius equation:

$$\ln k = -E_a / RT + \text{constant} \qquad (3)$$

In this equation, k is the rate constant at the Kelvin temperature T, E_a is the activation energy, and R is the gas constant. By plotting ln(k) against 1/T we should obtain, by Equation 3, a straight line whose slope equals $-E_a/R$. From the slope of that line, we can easily calculate the activation energy.

Procedure

Dependence of Reaction Rate on Concentration

In the following table, we have summarized the reagent volumes to be used in carrying out the several reactions whose rates we need to know in order to find the general rate law for Reaction 1.

Reaction Mixtures at Room Temperature (in mL)

Reaction Mixture	Reaction Flask I		
	0.010M KI	0.001 M $Na_2S_2O_3$	H_2O
1	5.0	5.0	5.0
2	10.0	5.0	0
3	5.0	5.0	0
4	5.0	5.0	0
5	4.0	5.0	6.0

Reaction Mixture		Reaction Flask II	
	0.040M $KBrO_3$	0.10 M HCl	starch
1	5.0	5.0	3 or 4 drops
2	5.0	5.0	3 or 4 drops
3	10.0	5.0	3 or 4 drops
4	5.0	10.0	3 or 4 drops
5	2.0	8.0	3 or 4 drops

Since there are several reagents to mix and we don't want the reaction to start until we are ready, we will put some of the reagents into one flask and the rest into another, selecting them so that no reaction occurs until the contents of the two flasks are mixed. For reaction mixture 1, measure out 5.0 mL 0.010 M KI, 5.0 mL 0.001 M $Na_2S_2O_3$, and 5.0 mL distilled water into a 125-mL Erlenmeyer flask (Reaction Flask I). Into a second 125-mL Erlenmeyer flask, measure out 5.0 mL 0.040 M $KBrO_3$, 5.0 mL 0.10 M HCl, and add 3 or 4 drops of starch indicator solution (Reaction Flask II).

Pour the contents of Reaction Flask II into Reaction Flask I and swirl the solutions to mix them thoroughly. Note the time at which the solutions were mixed. Continue swirling the solution. It should turn blue in about 2 minutes. Note and record the time at the instant that a blue color appears. Record the temperature of the blue solution to 0.2 °C.

Repeat the procedure with the other mixtures. *Don't forget to add the starch indicator before mixing the solutions* in the two flasks. The reaction flasks should be rinsed with distilled water and dried between runs. The temperature should remain about the same for all the runs. Repeat any experiments that did not appear to proceed properly.

Dependence of Reaction Rate on Temperature

In this part of the experiment, the reaction will be carried out at several different temperatures using Reaction Mixture 2 in all cases. The temperatures we will use will be room temperature (which you have already done), hot about 40 °C, and cold about 10 °C.

Use your Mixture 2 data for the time and temperature values in the room temperature column of table 2. To determine the time at hot temperature about 40 °C proceed as follows. Make up Reaction Mixture 2 as you did in Part A, including the indicator. However, instead of mixing the solutions in the two flasks at room temperature, place the flasks into hot tap water about 40 °C drawn from the hot water tap into a plastic tub. Check to see that the water is indeed at about 40 °C, and leave the flasks in the water for several minutes to bring them to the proper temperature. Then mix the two solutions, noting the time of mixing. Continue swirling the reaction flask in the warm water. When the color change occurs, note the time and the temperature of the solution in the flask.

Repeat the experiment at about 10 °C, cooling all the reactants in water with a bit of ice added before starting the reaction. Record the time required for the color to change and the final temperature of the reaction mixture.

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Dependence of the Reaction Rate on the Presence of Catalyst

Some ions have a pronounced catalytic effect on the rates of many reactions in water solution. Observe the effect on this reaction by once again making up Reaction Mixture 2. Before mixing, add 1 drop 0.5 M $[NH_4]_2MoO_4$, ammonium molybdate, and a few drops of starch indicator to Reaction Flask II. Swirl the flask to mix the catalyst thoroughly. Then mix the solutions, noting the time required for the color to change. Record this time in the data section.

Data and Calculations

Orders of the Reaction. Rate Constant Determination

For the reaction:

$$6\ I^-(aq) + BrO_3^-(aq) + 6\ H^+(aq) \rightarrow 3\ I_2(aq) + Br^-(aq) + 3\ H_2O(l) \qquad (1)$$

we have the rate law and reaction rate given by:

$$\text{rate} = k\,[I^-]^m\,[BrO_3^-]^n\,[H^+]^p = \frac{-\Delta[BrO_3^-]}{\Delta t} \qquad (4)$$

In all the reaction mixtures used in the experiment, the color change occurred when a constant predetermined number of moles of BrO_3^- had been used up by the reaction. The color "clock" allows you to measure the time required for this fixed number of moles of BrO_3^- to react. The rate of each reaction is determined by the time required for the color to change, since in Equation 4 the change in concentration is inversely proportional to the time, t. We are mainly concerned with relative rather than absolute rate; therefore, we will take all relative rates as being equal to 1 / t. Fill in the table on the next page, first calculating the relative reaction rate for each mixture.

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Table 1. Reaction Rate Data

Reaction Mixture	Time (sec) for color change	Relative Rate = 1/t	$[I^-]_{ini}$	$[BrO_3^-]_{ini}$	$[H^+]_{ini}$	Room Temp (°C)
1						
2						
3						
4						
5						

Varying conditions for Mixture 2	Time (sec) for color change	Temp (°C)
Hot: ~ 40 °C		
Cold: ~ 10 °C		
With a catalyst		

The reactant concentrations in the reaction mixture are not those of the stock solutions, since the reagents were diluted by the other solutions. The final volume of the reaction mixture is 25 mL in all cases. We can calculate the concentrations of all reactants in the table above ($M_1V_1 = M_2V_2$).

Determination of the Orders of the Reaction

Given the data in the table, the problem is to find the order for each reactant and the rate constant for the reaction. Since we are dealing with relative rates, we can modify Equation 2 to read as follows:

$$\text{relative rate} = k' [I^-]^m [BrO_3^-]^n [H^+]^p \qquad (5)$$

We need to determine the relative rate constant k' and the orders m, n and p in such a way as to be consistent with the data in Table 1.

The solution to this problem is quite simple once you make a few observations on the reaction mixtures. Each mixture (2 to 4) differs from Reaction Mixture 1 in the concentration of only one species (see table). This means that for any pair of mixtures that includes reaction Mixture 1, there is only one concentration that changes. We can then find the order for the reactant whose concentration was changed.

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Write Equation 5 below for Reaction Mixtures 1 and 2, substituting the relative rates and the initial concentrations of I^-, BrO_3^-, and H^+ from Table 1.

Relative rate 1 = _______________ = k [$]^m$ [$]^n$ [$]^p$

Relative rate 2 = _______________ = k [$]^m$ [$]^n$ [$]^p$

Solve for m, the order of the reaction with respect to the I^-, to two decimal places and then round off to the nearest integer.

m = ________ (2 decimal places) m = ________ (nearest integer)

Apply the same approach to find the value of n, the order of the reaction with respect to the BrO_3^- ion. Show your set-up.

n = _________ (2 decimal places) n = _________ (nearest integer)

Apply the method once again to find p, the order with respect to the H^+ ion. Show your set-up.

p = _________ (2 decimal places) p = _________ (nearest integer)

Having found m, n, and p (nearest integers, the rate law is written as:

rate = ____________________________________

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Determination of the Value of Relative Rate Constant

The relative rate constant, k' can be calculated by substitution of m, n, p and the known rates and reactant concentrations into Equation 5. Fill Table 2 below by calculating k for Reaction Mixtures 1 – 4.

Table 2. Reaction Constant, k

Reaction	1	2	3	4	Average	Units of k
k						

Calculations for each k value:

Briefly explain why k should have nearly the same value for each of the Mixtures 1 – 4.

Why? ____

Determination of Relative Rate and Reaction Time for Mixture 5

For Reaction Mixture 5, use k_{ave} from Table 2 above and the appropriate concentrations from Table 1 in Equation 5 to predict (calculate) the relative rate. Then use this value to predict (calculate) the reaction time, t, for Mixture 5. Show your calculations below.

relative $\text{rate}_{\text{predicted}}$ ___________ $t_{\text{predicted}}$ ___________ t_{observed} ___________

Calculate the percent difference of your reaction times.

% difference ____________

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The Effect of Temperature on Reaction Rate: The Activation Energy

To find the activation energy for the reaction, transfer the reaction times and temperatures onto Table 3 and fill in the remaining boxes using Mixture 2. Since the reactions at the different temperatures all involve the same reactant concentrations, the rate constants, k, for two different mixtures will have the same ratio as the reaction rates themselves for the two mixtures. This means that in the calculation of E_a, we can use the observed relative rates instead of rate constants.

Table 3. Reaction Rate at Different Temperatures for Mixture 2.

	Room Temp	Hot: ~ 40 °C	Cold: ~ 10 °C
Time (sec) for color change			
Actual Temp (°C)			
Actual Temp (Kelvin)			
1 / Temp (Kelvin^{-1})			
Relative Rate = 1/time			
ln (Relative Rate)			

Use the appropriate values from Table 3 and plot ln(relative rate) vs 1 / T in Microsoft Excel.® Insert a linear trendline and display both the equation and r^2 value of the trendline on the graph. Copy these in the space below. **Make certain to include your Arrhenius plot with this report**.

Trendline Equation: ________________________

r^2 = ________________

The slope of the line equals $-E_a / R$, where R = 8.314 Joules / (mole K). Use this relationship to calculate the activation energy, E_a, for your reaction in kJ/mol.

E_a = ________________ kJ / mol

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The Effect of a Catalyst on Reaction Rate

	Room Temperature Mixture 2	Catalyzed Mixture 2
Time for color to appear (sec)	____________________	____________________

Would you expect the activation energy, E_a, for the catalyzed reaction to be greater than, less than, or equal to the activation energy for the uncatalyzed reaction? Briefly explain.

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Pre-Lab Questions: Iodine Clock Reaction

1. A student studied the clock reaction described in this experiment. She set up a reaction mixture by mixing 10.0 mL of 0.010 M KI, 10.0 mL of 0.0010 M $Na_2S_2O_3$, 20.0 mL of 0.040 M $KBrO_3$ and 10.0 mL of 0.10 M HCl using the procedure given. It took 40.0 seconds for the color to turn blue.

   a. She found the concentration of each reactant in the reacting mixture by realizing that the number of moles of each reactant did not change when that reactant was mixed with the others, but that its concentration did. The volume of the mixture was 50.0 mL. Find the initial concentration of each reactant.

   $[I^-]_{ini}$ = __________ M; $[BrO_3^-]_{ini}$ = __________ M; $[H^+]_{ini}$ = __________ M

   b. What is the relative rate of the reaction (1/time)?

   ____

2. The student repeated the experiment using reaction mixture 1 by mixing 10 mL of 0.010 M KI, 10 mL of 0.0010 M $Na_2S_2O_3$, 10 mL of 0.040 M $KBrO_3$, 10 mL of 0.10 M HCl and 10 mL of H_2O. It took 75 seconds to turn blue.

   Find the initial concentration of each reactant after mixing:_

   $[I^-]_{ini}$ = __________ M; $[BrO_3^-]_{ini}$ = __________ M; $[H^+]_{ini}$ = __________ M

   What is the relative rate of the reaction (1 / time)?

   ____

3. Use the information above to determine the order with respect to BrO_3^-.

   n = ________ (2 decimal places) n = ________ (nearest integer)