Experiment 10 Kinetics of an Iodine Clock Reaction

Chemical Kinetics is the study of the rate of chemical reactions and the factors that influence that rate. In this experiment, you will be studying the kinetics of the reaction of iodide ion with bromate ion in acidic conditions:

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

The reaction rate depends on the concentration of reactants and temperature. The rate law for this reaction has the form:

$$\text{rate} = -\frac{\Delta[BrO_3^-]}{\Delta t} = k[I^-]^a[BrO_3^-]^b[H^+]^c$$

The value of the rate exponents a, b, and c and the rate constant k are determined by using the **method of initial rates**.

The method of initial rates is one way of determining the value of rate exponents and the rate constant for a chemical reaction. In this method, the reaction is performed several times with different initial conditions. The initial rate of the reaction is determined each time. In order to find the value of the rate exponents, the initial concentration of one species in the reaction varies at a time. For instance, let's say that two reactions are run where the initial concentration of iodide ion is change from $[I^-]_1$ to $[I^-]_2$ while keeping the other concentrations constant. According to the rate law above, the reaction rates will be:

$$\text{rate}_1 = k[I^-]_1^a[BrO_3^-]^b[H^+]^c$$

$$\text{rate}_2 = k[I^-]_2^a[BrO_3^-]^b[H^+]^c$$

Dividing the second equation by the first equation, we obtain:

$$\frac{\text{rate}_2}{\text{rate}_1} = \left(\frac{[I^-]_2}{[I^-]_1}\right)^a$$

This equation may be solved for the rate exponent a. After that a series of reactions in which $[BrO_3^-]$ is changed may be used to determine the rate exponent b and a series of reactions in which $[H^+]$ changes may be used to determine the rate exponent c. Once the values of the rate constants are known, the value of the rate constant is calculated from the experimental data.

Measuring the initial reaction rate uses an indirect method using the thiosulfate ion, $S_2O_3^{2-}$. Thiosulfate ion reacts with elemental iodine according to the reaction:

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

These reactions have excess concentrations of the iodide ion. In aqueous solution, I_2 combines with I^- to form the triiodide ion, I_3^-. Triiodide ions react in the same fashion as elemental iodine:

$$I_3^-(aq) + 2\,S_2O_3^{2-}(aq) \rightarrow 3\,I^-(aq) + S_4O_6^{2-}(aq)$$

The triiodide ion also forms an intensely blue complex with starch in aqueous solution. The presence of even trace amounts of triiodide ion gives a dark blue color in solution. The reaction of triiodide ion with thiosulfate ion occurs very rapidly compared to the reaction of iodide with bromate. Therefore, as long as there is thiosulfate ion present, the iodine (i.e., triiodide ion) produced by the first reaction is consumed by the thiosulfate ion. The moment that the thiosulfate ion is used up, the iodine forms the dark blue color of the starch complex. The rate of the reaction will be equal to the change in concentration of I_2 (or I_3^-) divided by the time required for the blue color to appear (Δt). Since the thiosulfate reaction is essentially instantaneous, the change in I_3^- concentration is related to the change in $S_2O_3^{2-}$ concentration by the reaction's stoichiometry:

$$rate = \frac{\Delta[I_3^-]}{\Delta t} = -\frac{1}{2}\frac{\Delta[S_2O_3^{2-}]}{\Delta t} = \frac{1}{2}\frac{[S_2O_3^{2-}]_0}{\Delta t}$$

Experimental

Equipment needed: 10-1000 μL digital pipettes, 10-mL beakers

Chemicals needed: DI water, 0.0100 M KI, 0.100 M HCl, 0.00100 M $Na_2S_2O_3$, 0.0400 M $NaBrO_3$, 1% starch solution

You will work in partners in this lab. If there is an odd number of students, there will be at most one group of three. 4 groups will share data and average their reaction times.

Table 9 Solution Aliquots for Method of Initial Rates

	Initial reagents					Final reagent
Exp	0.0100 M KI	DI water	0.100 M HCl	1% Starch	0.00100 M $Na_2S_2O_3$	0.0400 M $NaBrO_3$
A1	300 μL	600 μL	300 μL	150 μL	150 μL	300 μL
A2	600 μL	300 μL	300 μL	150 μL	150 μL	300 μL
A3	900 μL	---	300 μL	150 μL	150 μL	300 μL
A4	300 μL	300 μL	300 μL	150 μL	150 μL	600 μL
A5	300 μL	---	300 μL	150 μL	150 μL	900 μL
A6	300 μL	300 μL	600 μL	150 μL	150 μL	300 μL
A7	300 μL	---	900 μL	150 μL	150 μL	300 μL

I. In 6 separate clean 10-mL beakers, obtain enough of the solutions listed in **Table 9** to fill each beaker about two-thirds full.

II. Obtain 7 pipet tips that fit the digital pipets. Set them up so that you can dedicate one tip to each reagent that you will use during the experiment.

III. Measure the temperature of the starch solution. Assume that all reagents are at the same room temperature. Record this temperature.

IV. Obtain a clean 5-mL glass vial and label it A1.

V. Fill the vial with the "Initial Reagents" (or the first five columns) for Experiment A1 using the digital pipette.

VI. One partner should get ready to start a timer. The other partner should obtain the listed amount of $NaBrO_3$ solution in a digital pipet.

VII. The partner with the timer should start the timer while the other one adds the $NaBrO_3$ solution to the vial. Cap the vial and shake to mix the reagents. Place the vial on a white surface so you can see the color change.

VIII. The timer should be stopped when the first color (either blue or brown) appears.

IX. Record the time for the color to appear.

X. Label a 250- or 500-mL beaker as waste. Empty the contents of the vial into the waste beaker. Rinse it 3-4 times with DI water. The rinses can go down the sink. Drain the vial upside down on a paper towel for 30 seconds and then dry the interior of the vial with a cotton swab.

XI. Repeat steps 4-10 for vials A2 through A7.

Calculations

(Table B) Calculate the initial concentrations of each substance (except for DI water and starch) for each experiment using the following formulas and the data in **Table 9**:

$$[\mathrm{S_2O_3^{2-}}]_0 = \frac{(\text{Volume in } \cancel{\mu\mathrm{L}} \text{ of } \mathrm{Na_2S_2O_3} \text{ used})(0.00100\ \mathrm{M})}{1800\ \cancel{\mu\mathrm{L}}}$$

$$[\mathrm{I^-}]_0 = \frac{(\text{Volume in } \cancel{\mu\mathrm{L}} \text{ of KI used})(0.0100\ \mathrm{M})}{1800\ \cancel{\mu\mathrm{L}}}$$

$$[\mathrm{BrO_3^-}]_0 = \frac{(\text{Volume in } \cancel{\mu\mathrm{L}} \text{ of } \mathrm{NaBrO_3} \text{ used})(0.0400\ \mathrm{M})}{1800\ \cancel{\mu\mathrm{L}}}$$

$$[\mathrm{H^+}]_0 = \frac{(\text{Volume in } \cancel{\mu\mathrm{L}} \text{ of HCl used})(0.100\ \mathrm{M})}{1800\ \cancel{\mu\mathrm{L}}}$$

For example, the initial concentrations for Exp. A1 are:

$$[\mathrm{S_2O_3^{2-}}]_0 = \frac{(150\ \mu\mathrm{L}\ \mathrm{Na_2S_2O_3})(0.00100\ \mathrm{M})}{1800\ \cancel{\mu\mathrm{L}}} = 8.33 \times 10^{-5}\mathrm{M}$$

$$[\mathrm{I^-}]_0 = \frac{(300\ \mu\mathrm{L}\ \mathrm{KI})(0.0100\ \mathrm{M})}{1800\ \cancel{\mu\mathrm{L}}} = 1.67 \times 10^{-3}\mathrm{M}$$

$$[\mathrm{BrO_3^-}]_0 = \frac{(300\ \cancel{\mu\mathrm{L}}\ \mathrm{NaBrO_3})(0.0400\ \mathrm{M})}{1800\ \cancel{\mu\mathrm{L}}} = 6.67 \times 10^{-3}\mathrm{M}$$

$$[\mathrm{H^+}]_0 = \frac{(300\ \cancel{\mu\mathrm{L}}\ \mathrm{HCl})(0.100\ \mathrm{M})}{1800\ \cancel{\mu\mathrm{L}}} = 1.67 \times 10^{-2}\mathrm{M}$$

Please note that calculated concentrations need to have 3 significant figures. Cutting off these concentrations to the first non-zero digit will result in significant errors!

(Table C) The initial rate is calculated by dividing the initial thiosulfate ion concentration by the average reaction time in your group and multiply the result by ½ .

$$rate = \frac{1}{2}\frac{\left[\mathrm{S_2O_3^{2-}}\right]_0}{\Delta t}$$

(Table D) The order with respect to each substance is determined by comparing the ratios of the rates of two reactions in which only that substance is changed to the ratio of the initial concentrations of that reactant. For example, in the two reactions A1 and A2, $[\mathrm{I}^-]_0$ concentration changes while $[\mathrm{BrO_3}^-]_0$ and $[\mathrm{H}^+]_0$ remain constant. According to the rate law:

$$\frac{\mathrm{rate}_{\mathrm{A2}}}{\mathrm{rate}_{\mathrm{A1}}} = \left(\frac{[\mathrm{I}^-]_{\mathrm{A2}}}{[\mathrm{I}^-]_{A1}}\right)^{a}$$

If you take the natural log of both sides and use the property of logarithms, it would be true that:

$$\ln\left(\frac{\mathrm{rate}_{\mathrm{A2}}}{\mathrm{rate}_{\mathrm{A1}}}\right) = a\ln\left(\frac{[\mathrm{I}^-]_{0,\mathrm{A2}}}{[\mathrm{I}^-]_{0,A1}}\right)$$

The reaction orders will be small whole numbers such as 0, 1, or 2. Please round your result to the nearest whole number.