A Kinetic Study of an Iodine Clock Reaction

Purpose

To investigate the kinetics of the reaction that occurs between iodide and persulfate ion. You will: (1) determine the rate law, (2) determine the numerical value of the rate constant at room temperature, (3) explore the effect of temperature on the reaction and determine the activation energy ($E_a$), and (4) investigate catalytic activity of selected metal ions on the reaction.

Introduction

Reaction times vary from picoseconds ($10^{-12}$ seconds) to years. It is an experimental challenge to design methods of studying reactions over such a wide range of rates. Reaction rates are similar to other rates: it is a change of something per unit time (like velocity - miles per hour, flow rate - liters per second, etc.). In reactions the rate is measured by changes in concentrations per unit time. For example, in the following reaction (all species are in aqueous solution):

$$S_2O_8^{2-} + 3 I^- \rightarrow 2 SO_4^{2-} + I_3^-$$  \hspace{1cm} (1)

the reaction rate could be determined by following a decrease in the concentrations of reactants ($S_2O_8^{2-}$ or $I^-$) or by the increase in the concentration of the products ($SO_4^{2-}$ or $I_3^-$). However, we need to recognize that these rates of change would all produce different numbers.

That is

$$\frac{-\Delta[S_2O_8^{2-}]}{\Delta t} = \frac{1}{3} \frac{\Delta[I^-]}{\Delta t} = \frac{1}{2} \frac{\Delta[SO_4^{2-}]}{\Delta t} = \frac{\Delta[I_3^-]}{\Delta t} = \text{rate of reaction.}$$  \hspace{1cm} (2)

We will investigate this reaction in the laboratory using the method of initial rates (consult your text if you are not familiar with this terminology) by measuring the amount of time required to produce a known amount of $I_3^-$. The presence of $I_3^-$ can be easily detected using a starch indicator. In order to understand how we will accomplish the measurement of the rate of production of $I_3^-$ it is important to understand some details of how this reaction proceeds. First recognize that this is an oxidation-reduction reaction with the half-reactions:

reduction: \hspace{1cm} $S_2O_8^{2-} + 2 e^- \rightarrow 2 SO_4^{2-}$  \hspace{1cm} (3)

oxidation: \hspace{1cm} $3 I^- \rightarrow 2 e^- + I_3^-$  \hspace{1cm} (4)

It will also become important to recognize that the overall reaction does not occur in a single step, but in a series of steps (or in a mechanism). This reaction can be broken down into at least two simple steps (rather than one overall reaction). One example (correct? or incorrect?) may be:

slow \hspace{1cm} $S_2O_8^{2-} + 2 I^- \rightarrow 2 SO_4^{2-} + I_2$  \hspace{1cm} (5)

fast \hspace{1cm} $I_2 + I^- \rightarrow I_3^-$  \hspace{1cm} (6)

fast \hspace{1cm} $I_3^- + \text{starch} \rightarrow \text{blue-black starch complex}$  \hspace{1cm} (7)

Thus, as the first reaction produces iodine, $I_2$, it is very rapidly converted into a blue-black complex which can be easily seen. The problem with this is that the color change will occur...
very quickly at the very beginning of the reaction. In order to produce reaction times that are easily measured, we will intervene in the normal sequence of reactions listed above in order to postpone the production of the blue-black color until a known quantity of I$_3^-$ has formed. In order to do this we will use another redox reaction:

\[
\text{very fast} \quad \text{I}_2 + 2 \text{S}_2\text{O}_3^{2-} \rightarrow \text{S}_4\text{O}_6^{2-} + 2 \text{I}^- \quad (8)
\]

This reaction prevents the iodine, I$_2$, from reacting to form the blue-black starch complex. Into each of our reaction mixtures, we will place the same known quantity of thiosulfate, S$_2$O$_3^{2-}$, and only after all of it is consumed will the iodine, I$_2$, be free to react further to form the blue-black starch complex. In this fashion, we will know how much iodine, I$_2$, has been formed when the color appears. By measuring the time this takes, the rate of reaction can be found.

**Experimental Determination of Rate Laws**

The rate of reaction is going to be determined indirectly by knowing how much thiosulfate, S$_2$O$_3^{2-}$, has been consumed. Reaction (8) allows us to relate this to the amount of I$_2$ produced in reaction (5) and consumed in reaction (8):

\[
\text{rate of reaction} = \frac{1}{2} \left( \frac{\text{moles S}_2\text{O}_3^{2-}}{\text{L seconds}} \right) \quad (10)
\]

Thus by knowing the initial concentration of thiosulfate in each reaction mixture, the rate of reaction can be found by measuring the amount of time for the blue-black color to appear. Note: in all of your experiments, the initial concentration of thiosulfate will be the same!

Once we have a way of measuring rates of reactions, we can experimentally determine the rate law for the reaction measured. In this case the rate law will look like:

\[
\text{rate of reaction} = k [\text{S}_2\text{O}_8^{2-}]^m [\text{I}^-]^n \quad (9)
\]

where \( k \) is the specific rate constant (which depends on temperature) and \( m \) and \( n \) reflect the order of reaction for each of the reactants. The rate of reaction depends on these values and on the concentrations of the reactants. In order to determine the values of \( m \) and \( n \) we will measure the initial rate of reaction while varying the concentration of each reactant individually. The concentration of the I$^-$ will be varied in three runs while the concentration of S$_2$O$_8^{2-}$ is held constant. Then, the concentration of the S$_2$O$_8^{2-}$ will be varied in three runs while the concentration of I$^-$ is held constant.

Equation (9) can also be rewritten in a logarithmic form to get an equation for a straight line:

\[
\log (\text{rate of reaction}) = \log (k) + m \log [\text{S}_2\text{O}_8^{2-}] + n \log [\text{I}^-] \quad (11)
\]
Since \( k \) is a constant, we can rewrite equation (11) in the two special cases found in our experiment:

When \([S_2O_8^{2-}]\) is held constant: \( \log (\text{rate of reaction}) = \text{constant} + n \log [I^-] \) (12)

When \([I^-]\) is held constant: \( \log (\text{rate of reaction}) = \text{constant} + m \log [S_2O_8^{2-}] \) (13)

By constructing two graphs, each \( \log (\text{rate of reaction}) \) vs. \( \log \) concentration, we can find the values of \( m \) and \( n \) from the slopes of these lines. Using this graphical approach allows us to find the best straight line through the data and thus minimize the error contributed by any single run.

In order to find \( k \), one simply uses the experimentally determined values of \( m \), \( n \), and rate of reaction in equation (9) to solve for \( k \). An average value of \( k \) can be found from all trials.

**Determining the Activation Energy for the Reaction**

Given that the value of \( k \) is the temperature dependent portion of the rate law, it should not be altogether surprising that the value of the activation energy, \( E_a \), (which causes this temperature dependence) can be found by determining the value of \( k \) at two or more temperatures. The relationship between temperature, \( k \), and \( E_a \) is given by the Arrhenius equation:

\[
k = A e^{-\frac{E_a}{RT}}
\] (11)

where \( R \) is the ideal gas constant, expressed as \( 8.314 \text{ J/K mole} \) and \( T \) and \( k \) are the Kelvin temperature and rate constant at that temperature, \( E_a \) is the activation energy, and \( A \) is a reaction specific constant (sometimes called the “collisional factor”). By taking the natural logarithm of the Arrhenius equation, a linear form of the equation is developed:

\[
y = m \ x + b
\] (12)

\[
\ln k = \left( -\frac{E_a}{R} \right) \frac{1}{T} + \ln A
\] (13)

As you can see, a plot of \( \ln k \) on the \( y \)-axis vs. \( 1/T \) on the \( x \)-axis will produce a line with a slope of \( \left( -\frac{E_a}{R} \right) \) and a \( y \)-intercept of \( \ln A \).

In our experiment we will use the average value for \( k \) found from the six trials discussed above for the room temperature value. We will then measure the reaction rate at other temperatures and then use the Arrhenius equation to find the activation energy and \( A \).

**Procedure**

**Part A: Reaction Rates at Room Temperature**

You and your partner will need to make the five solutions following the directions below and using the solutions listed in the table below. Recognize that the KCl and \((\text{NH}_4)_2\text{SO}_4\) solutions are added to keep the total volume constant at 50.0 mL and to maintain a constant concentration of ions (known as ionic
strength) in all reaction mixtures. This is done because reaction rates are known to depend upon ionic strength. For each trial do the following:

1. Into a clean 250 mL beaker, deliver 10.0 mL of the 0.0050 M Na$_2$S$_2$O$_3$ solution and add 4 drops of starch indicator.
2. Into one 50 mL Erlenmeyer flask, deliver the contents of Flask I from the table below.
3. Into another 50 mL Erlenmeyer flask, deliver the contents of Flask II from the table below.
4. Simultaneously mix the contents of the Erlenmeyer flasks into the beaker and immediately begin timing. You will need to measure the time required for the reaction to reach completion (blue-black color appearance) to the nearest second. Also, record the temperature these measurements are performed at (room temperature).
5. Repeat the above measurements to get two trials for each solution (average the two times if they match reasonably well).

<table>
<thead>
<tr>
<th>Trial #</th>
<th>Beaker</th>
<th>Flask I</th>
<th>Flask II</th>
</tr>
</thead>
</table>
|        | vol. of starch indicator | vol. of Na$_2$S$_2$O$_3$ 0.00500 M | vol. of 0.200 M KCl | vol. of 0.200 M KI | vol. of 0.100 M (NH$_4$)$_2$SO$_4$ | vol. Of 0.100 M (NH$_4$)$_2$S$_2$O$_8$
| 1      | 4 drops | 10.0 mL | 0 mL | 20.0 mL | 0.0 mL | 20.0 mL |
| 2      | 4 drops | 10.0 mL | 10.0 mL | 10.0 mL | 0.0 mL | 20.0 mL |
| 3      | 4 drops | 10.0 mL | 15.0 mL | 5.0 mL | 0.0 mL | 20.0 mL |
| 4      | 4 drops | 10.0 mL | 0.0 mL | 20.0 mL | 10.0 mL | 10.0 mL |
| 5      | 4 drops | 10.0 mL | 0.0 mL | 20.0 mL | 15.0 mL | 5.0 mL |

Part B: Catalytic Activity of Metal Ions:
In this part of the experiment, a series of reactions with trial 1 composition (or a slower reaction if appropriate) are run with different metal ion catalysts. Set up a reaction mixture as described for trial 1 in Part A, but before mixing add three drops of 0.10 M copper (II) sulfate to flask II. Mix and measure the time for the reaction (i.e. time required for the blue-black starch-iodine complex to appear). Repeat using a 0.10 M magnesium sulfate solution, 0.10 M chromium (III) sulfate, and 0.10 M nickel (II) sulfate.

Now repeat the same study for the fastest reaction but add five drops of 0.10 M EDTA to the solution before adding the three drops of best metal catalyst ion solution. Record the reaction time.

Part C: Measuring Reaction Rates at Different Temperatures
In this part of the experiment, a series of reactions with trial 1 composition (or a slower reaction if appropriate) are run at different temperatures. You may use the results from part A for the room temperature value in Part B. The other trials are to be done at other temperatures (above and below room temperature). Use a water bath and your own creativity to design a constant temperature set-up that will allow you to obtain data at 2 other temperatures over a range of 0 - 50°C. It would be nice if the temperature between these trials varied by roughly 20°C. Repeat the measurement of the rate of reaction at each new temperature following the directions used above. Show your results to your instructor to find out if any additional trials at other temperature need to be completed.

Prelab Questions:

1. Determine the molarity of Na$_2$S$_2$O$_3$, KI, and (NH$_4$)$_2$S$_2$O$_8$ in each reaction mixture listed in the table above.
2. Define the following terms: reaction rate, rate law, catalyst, and activation energy.