

Kinetics of an Iodine Clock Reaction

Objective:

Determine the experimental rate law for a peroxydisulfate decomposition reaction. Find its activation energy. Consider appropriate reaction mechanisms that match the experimental rate law.

Introduction:

Thermodynamics allows us to predict whether a reaction is favorable. Exactly how the reaction occurs on a microscopic level, however, cannot be determined from ΔG . The process by which a reaction occurs, what we call the reaction's mechanism, can often be deduced by measuring how fast the reaction occurs. We can do this because a reaction's rate depends on the rate of effective collisions between reacting species. This collision rate is directly related to the concentrations of those species. The overall reaction rate is obtained by appropriately combining the collision rates of species that participate in any step up to and including the slowest or rate-determining step. The relationship between the reaction's rate and the concentrations of species affecting the rate, R , is given by the rate law, which takes the general form

$$R = k[A]^\alpha \cdots [D]^\delta$$

where k is the reaction's rate constant and the terms in brackets, $[]$, are concentrations. The superscripts $\alpha \dots \delta$ are called reaction orders.

The purpose of this experiment is to characterize the reaction between iodide, I^- , peroxydisulfate (or persulfate), $S_2O_8^{2-}$, and thiosulfate, $S_2O_3^{2-}$. This reaction system is an example of what is commonly known as a "clock reaction." At one step during the reaction, a product is made which reacts with an indicator solution; the resulting change in color is used to time the reaction. Preliminary work will focus on identifying the individual steps comprising the overall reaction. An investigation of the reaction's kinetics provides additional information.

Solution Preparation

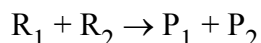
You will need to prepare 200 mL each of the solutions listed below. With the exception of the peroxydisulfate solution that must be prepared each week, these solutions, if well sealed, can be stored and used for several weeks. If you run out of any solution, you can prepare an additional amount. Be sure to note, however, the cautionary statements in Tasks I and II.

0.20 M KI	0.20 M KCl
0.0050 M $Na_2S_2O_3$	0.10 M Na_2SO_4
0.10 M $K_2S_2O_8$ (this must be prepared each week)	

Prepare these solutions using appropriate volumetric glassware. Two additional solutions – a saturated solution of I_2 and a starch indicator solution – are available in the lab.

Preliminary Investigations

Much of the chemistry in this system can be deduced using simple experiments in which two or more reagents are mixed together and the results recorded. Each preliminary investigation is followed by one or more questions. The answers to these questions are important so give them careful consideration. When asked to write tentative reactions, put them in the following general form:



where R represents a reactant and P represents a product. Whenever possible, replace R and P with known reactants and products. If you cannot identify a reactant or product (but know that one must be there) then retain the needed R and/or P designations in your reaction. If possible, balance your reactions.

Investigation 1. Place approximately 5 mL each of the KI, KCl, $K_2S_2O_8$, $Na_2S_2O_3$, and I_2 solutions in separate test-tube. To each test-tube, add a few drops of the starch indicator solution and record your observations.

Questions: What reagent is responsible for changing the indicator's color? Is this reagent a reactant or a product? Write a tentative reaction that explains your observations using $starch_I$ to represent the indicator's colorless form and $starch_C$ to indicate its colored form. We will assume that the starch indicator always reacts in a 1:1 stoichiometry.

Investigation 2. Mix together ten different combinations (two-at-a-time, about 5 mL each) of your reagents. Add a few drops of the indicator solution to each combination and record your observations.

Questions: Which combinations of reagents produce a change in the indicator's color? Write a tentative reaction that explains your observations.

Investigation 3. In separate test tubes place (a) about 5 mL of KI, (b) about 5 mL of KI and 1 mL of $Na_2S_2O_3$, and (c) 5 mL of KCl. Add a few drops of the indicator solution to each test tube. Finally, add about 5 mL of $K_2S_2O_8$ to each test tube and record your observations. As an additional experiment, try adding 1 mL of $Na_2S_2O_3$ to each test tube and recording your observations.

Questions: Which combinations of reagents produce a change in the indicator's color? For those combinations that provided a positive result, are there ways in which they behaved differently? How can you explain this difference? Write tentative reactions that explain your observations.

What have we learned to this point?

What is the chemical reaction with the $K_2S_2O_8$?

How does $Na_2S_2O_3$ participate? What is its role?

Measuring the Reaction's Rate – Task I

To study a reaction kinetically we must determine the reaction's rate. One approach is to measure the time required to react a known amount of reactant or the time required to make a known amount of product. This, of course, gives us an average rate, \bar{v} , over the elapsed time

$$\bar{v} = \frac{\Delta[\text{concentration}]}{\Delta t}$$

where $\Delta[\text{concentration}]$ is the change in concentration and Δt is the change in time.

The color change you observed in Task I can be used for this purpose. Use the following procedure as a guide. Use a thermistor-controlled water bath to maintain a constant temperature approximately at room temperature. Using appropriate volumetric glassware, transfer 20.0 mL of 0.20 M KI, 10.0 mL of 0.0050 M $\text{Na}_2\text{S}_2\text{O}_3$, and 3-4 drops of indicator into an Erlenmeyer flask. Into another Erlenmeyer flask, add 20.0 mL of 0.10 M $\text{K}_2\text{S}_2\text{O}_8$. Put both flasks in the water bath and allow them to come to thermal equilibrium. Mix the two solutions together and begin timing. While swirling the flask to ensure that the solutions are well mixed, observe the solution and note the time required for the indicator to change color. Repeat the procedure several times until you are confident that you can measure Δt reproducibly. Be sure to calculate your average value for Δt .

Now, calculate the reaction's rate. To do this you must determine the value for $\Delta[\text{concentration}]$. Think carefully about your results from the Preliminary Investigations and **decide which reactant is controlling the time required for the indicator's change in color**; once identified, the change in its concentration should be easy to determine. The rate you've determined will be called the "standard run." **Note:** – *the rate of a reaction depends on the concentrations of the reactants; consequently, you will need to repeat Task II each time you prepare a new solution of KI, $\text{Na}_2\text{S}_2\text{O}_3$, or $\text{K}_2\text{S}_2\text{O}_8$.*

Which Reactants Affect the Reaction's Rate? – Task II

A common method for studying kinetics is known as the **method of initial rates**. The rationale behind this approach is simple. First, the reaction's rate for a given set of initial concentrations is measured. (This measurement has been done on the standard run of Task I). Second, we change the concentration of one reactant, while holding the other reactants at their initial concentration, and measure the reaction's new rate. If, for example, you find that doubling a reactant's concentration leads to a doubling of the rate, then you know the reaction is first order in that reactant. This process can be extended one reactant at a time until each reactant's effect is known. When complete, you should be able to write down the rate law for the reaction and calculate the rate constant for the reaction.

Using the standard run from Task I as a starting point, design a set of experiments that will allow you to evaluate the effect of KI, $\text{Na}_2\text{S}_2\text{O}_3$, and $\text{K}_2\text{S}_2\text{O}_8$ on the reaction's rate. The simplest approach is to reduce the volume of one reagent, replacing it with an appropriate amount of an inert solution. For example, if you decide to use 15.0 mL of 0.20 M KI instead of the 20.0 mL used in the standard run, then add 5.0 mL of KCl to maintain the same total volume.

The following inert solutions should be used:

- Replace 0.20 M KI with 0.20 M KCl
- Replace 0.10 M $K_2S_2O_8$ with 0.10 M Na_2SO_4
- Replace 0.0050 M $Na_2S_2O_3$ with distilled water

(Why?! Why not use water instead?)

Repeat each trial until you get a consistent time change for each set of concentrations.

Use a thermistor-controlled water bath to maintain a constant temperature approximately at room temperature for each half of the reaction mixture.

Determine the rate law and rate constant for the reaction. Note – Be sure to use the same temperature for your Task II trial as was used for the standard run.

How Does Temperature Affect the Reaction's Rate? – Task III

The rate of a reaction is directly proportional to the reaction's rate constant, k , which, in turn, is related to the reaction's activation energy, E_a , by the Arrhenius equation

$$k = Ae^{-E_a/RT}$$

where A is a constant for a particular reaction. Increasing the temperature at which the reaction is done decreases the exponential term, thus increases the value of k . Simply put, most reactions go faster when the temperature is raised, and go slower when the temperature is decreased.

A useful feature of the Arrhenius equation is that it provides a means for determining a reaction's activation energy. Taking the natural logarithm of both sides of the Arrhenius equation

$$\ln k = \ln A - \left(\frac{E_a}{R}\right)\frac{1}{T}$$

shows that a plot of $\ln k$ vs. $1/T$ will be a straight line with a slope of $-E_a/R$. The slope, therefore, can be used to determine the activation energy.

To obtain the necessary data for determining the reaction's activation energy, repeat the standard run from Task I at five additional temperatures ranging from a low of 5 °C - 10 °C to a high of 50 °C. Mix the two solutions together, and record the time for the indicator to change color. Measure the temperature again and use the average temperature during the run as the reaction's temperature. Be sure to repeat the trials until you have reproducible times. Plot your data and determine the activation energy.

Creating a Reaction Mechanism

One of the goals of a kinetics study is to understand how reactions occur at the level of individual molecular collisions. Thus, we need to write a series of balanced elementary reactions (a reaction mechanism) that is consistent with your results from the Preliminary Investigations. In writing these reactions, you may assume that the reduction of $\text{S}_2\text{O}_8^{2-}$ results in the production of SO_4^{2-} and the oxidation of $\text{S}_2\text{O}_3^{2-}$ results in the production of $\text{S}_4\text{O}_6^{2-}$ (tetrathionate). Each elementary reaction should involve no more than two reactants (other than water and the hydronium ion). Next, examine your results from Tasks I and II and determine which step in your reaction scheme if your reaction mechanism is consistent with the reaction rate law. It may be helpful to try to determine a rate-determining step. It may be necessary to rewrite your reaction scheme to satisfy your rate law; don't be afraid to do so!

You need to construct at least **two** reaction mechanisms with at least one of the mechanisms having the correct experimental rate law. If you are unable to find a reaction mechanism that is consistent with your experimental rate law, then put **three** of your attempted mechanisms and their associated rate laws in an appendix.

Timetable for Completing the Lab

The Preliminary Investigations and Task I should be completed during the first lab period.

Task II should be completed during the second lab period.

Task III should be started during the second lab period and finished during the third lab period.

Waste Disposal

All solutions may be discarded in the sink along with generous water.

Other Questions to be Considered for Discussion

Did you expect the results you found, i.e., are your results reasonable? If not, explain.

Are there other methods that you could use to confirm your results?

What are good and bad points to the methods that were used?

What principles were confirmed (or not) by the results of your experiment?

How do your results compare to previously done work (primary sources)? If your results are significantly different, explain how the differences could have occurred.

What investigations can be done to improve the results?

Perform a propagation of error analysis on the determination of the rate constant and the activation energy and discuss the different sources of error.