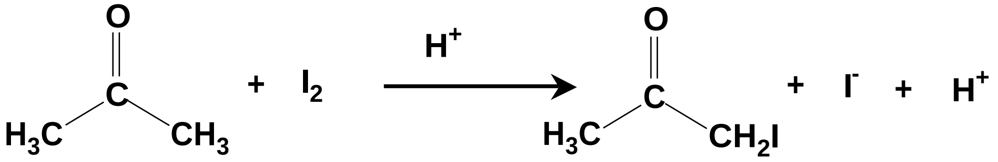
Rate and Activation Energy of the Iodination of Acetone

Introduction:

The rate law and the activation energy for this reaction will be determined by measuring the initial rates of the reaction while systematically varying the concentration of reagents and the temperature of the reaction of acetone with iodine.



The above reaction is catalyzed by hydrogen ions, H^+ (i.e. H_3O^+), so this ion appears in the rate law, which takes the form:

$$\text{rate} = k[\text{acetone}]^a[H^+]^b[I_2]^c$$

where a, b, and c are the reaction orders with respect to acetone, H^+ and I_2 respectively. This is a convenient reaction to study because the reaction order with respect to iodine is zero (c=0), so the reaction rate does not depend on the concentration of I_2. The reaction will proceed as long as iodine is present. Also note that I_2 has a characteristic yellow-brown color (especially in the presence of I^-, which forms I_3^- in solution). The experiment is designed so that a large excess of acetone and hydrogen ions is employed and a much smaller but known concentration of iodine is used. Using the following equation, the rate of the reaction can be calculated.

$$\text{rate} = -\frac{\Delta[I_2]}{\Delta t}$$

Safety Concerns:

CAUTION: Iodine will stain balances, skin, and clothing. If a small spill occurs, rinse with a solution of $Na_2S_2O_3$.

Experimental Procedure:

I. Stock Solutions

Obtain the following stock solutions, recording the exact, actual concentrations listed on the stock bottles:

20 mL of Acetone(aq) (approx. 4M)
20 mL iodine solution (approx. 5mM)
20 mL HCl(aq) (approx. 1M)

II. Preparation of Reaction Mixtures and Data Collection

A. Obtain ~250 mL of room temperature water in a 400 mL beaker and place it on a white sheet of paper to give a bright white background for observing the color of the solutions in the reaction tubes. In all the following runs use pipettes to dispense the solutions.

B. Prepare a blank or reference tube by adding 8.0 mL of distilled water to a clean large test tube. This tube will be compared with the reaction tubes to determine when the color of the I_2 solution has completely disappeared.

C. For Run #1 prepare the solutions as follows. Add 2.00 mL each of ~4 M acetone(aq), ~1 M H^+(aq) and distilled/deionized water to a large test tube (labeled 1A), and swirl to mix these reagents well. To a second large test tube (labeled 1B), add 2.00 mL of I_2 solution. Place tubes 1A and 1B in the water bath to allow their temperatures to equilibrate.

D. Data Collection: Run #1.

1. Using the clock on the wall (or a stop watch) note the starting time to the nearest second at the moment that you pour the contents of tube 1A into tube 1B. Pour the solution back and forth between the tubes at least twice to thoroughly mix the solutions. Be careful not to spill. Place the reaction tube and the blank side by side in the water bath. While looking down from the top at the tubes and comparing the colors, record the time it takes (in seconds) for the I_2 color to fade to the point that it looks like the blank. Repeat run #1 until the times for duplicate runs are within 10 percent of each other.

2. Repeat your data collection of Run #1 until your times agree within 10% of each other.

Q: What is the difference between a reaction time and a reaction rate? You have measured reaction times, what do you have to do to determine the reaction rate for each run? Does a long reaction time correspond to a "fast" or a "slow" reaction rate?

E. Data Collection: Cold Runs.
Once you have completed part D above and obtained reproducible reaction times you are ready to set up the cold runs. Prepare these samples in duplicate so you will have two sets of Cold Run data.

Prepare samples "CA" and "CB" with the same reagents and volumes as "1A" and "1B" above. You can use the same blank (or reference tube) for the low temperature run as you used for the room temperature run. Allow tubes CA, CB, and the blank to equilibrate in an ice/water bath (~0 ºC) for at least 5 minutes. Once the tubes are cold, quickly mix CA and CB. Record the time at the point of mixing to the nearest second and **return the tube to the ice/water bath**. Follow the course of the reaction by visually comparing the reaction solution with the blank. As the ice in the bath melts, continue to add ice and pour off water to keep the temperature at the bottom of the beaker constant at 0 ˚C. Record the time when the color due to I_2 has disappeared. The cold run takes a long time (more than a half hour). Leave the system to react and continue on with the room temperature runs. Keep an eye on this cold run reaction mixture and record the time required for the reaction to reach completion.

F. Data Collection: Cool Runs. Once your cold runs have been assembled and running, prepare a "Cool" water bath at approximately 10 ºC. You may choose to monitor this bath temperature by using the temperature probe and a temperature vs. time data collection in LoggerPro. Stirring the bath with a magnetic stir bar, try to keep the temperature within ±0.5 ºC by adding an ice chip or two when the bath starts to warm up. Prepare at least 2 "Cool" runs using the same volumes as the "Cold" runs. Monitor these reactions for completion visually as you did with the "Cold" run.

Q: Why does the cold run take longer than the room temperature runs? Explain your answer on a molecular level.

G. Data Collection: Additional room temperature runs

You will be determining the order of this reaction with respect to the various reactants by comparing additional reactions to the "standard" reaction you performed above (Run #1). Design a series of additional experiments that you can use to determine the order of this reaction with respect to acetone, acid and iodine concentrations using the following guidelines:

1. Change only 1 variable at a time. Changing multiple variables will make it more difficult (although not necessarily impossible) to interpret your results.

2. The total volume of your sample should always be 8.00 mL.

3. Distilled/deionized water is present only to make the total volume of the solution 8.00mL. For example, if you choose to double the amount of acetone in the experiment to 4.00mL, then you should omit the water. (4.00 mL acetone(aq) + 2.00 mL HCl(aq) + 2.00 mL I_2(aq) = 8.00 mL)

4. Consider the equipment that is already available in the lab. All measurements in your plan will have to be performed using the available equipment.

   We will set up a table of how to conduct this experiment together. You will need to repeat each experiment until you are confident of your results (until duplicates are within 10% of each other).

III. Data Analysis: This experiment generates a LOT of data; it is probably best to organize this data in a table or multiple tables to keep it straight. There are also quite a few repetitive calculations in this experiment; you may wish to use MS Excel or another spreadsheet to perform your calculations.

The second pre-lab video goes through the calculations needed for this lab.

A. Calculate the actual initial concentration of all reagents used in each reaction mixture.

   Q: What is the difference between an "initial concentration" and a "stock concentration"? What is the limiting reagent in each of the experiments you performed? Is this consistent with your observations? What would you observe if the limiting reagent were different?

B. Calculate the average rate of each experiment from your reliable trials.

C. Qualitative determination of order with respect to each reactant.
   Comparing your runs to Run #1, determine the order with respect to each reactant, assuming that the orders should (theoretically) be integers 0, 1, or 2. For example, if you double the concentration of iodine and the reaction rate is essentially unchanged, the order of the reaction with respect to iodine must be zero.

D. Quantitative determination of orders with respect to each reactant.
   The orders with respect to each reactant can also be determined mathematically. In theory, the values should be integers, so determining their exact mathematic value is not always necessary, but it does allow a more complete analysis of the experimental error. Set up a ratio of the rate equation for two runs, cancel everything you can cancel, and use a logarithm to solve for the exponent (reaction order) that's left over.

   Q: Why is there error in your result? Create a list of sources of error in this experiment and estimate the extent of each source. For example, if the HCl(aq) stock solution is listed as "1.00M", there is error in that last digit; the "real" concentration is somewhere between 0.99M and 1.01M. That's a 1% error. Is 1% a significant error in this experiment?

E. Calculate k, the rate law constant, for each of the runs, and the average value of k for all of your room temperature runs.

   Q: How much error is there in your average room temperature k? How does this error impact the number of significant figures you can legitimately report in your value of k?

   Q: How does your average room temperature value of k compare to the value of k for your cold run? Is this difference consistent with the rates you observed for the reaction?

F. The activation energy, E_a, may be determined using either the comparative form (for any 2 points) or the linear form (for all 3 points) of the Arrhenius equation. Calculate E_a mathematically for each pair of temperatures (Room/Cool, Room/Cold, Cool/Cold), and graphically using all three temperatures. See your text for details.

> ***Q: How do your pair-wise activation energies compare to one another? How do they compare to the graphically determined value? Which value do you prefer?***
>
> ***Q: You will be asked to calculate an average activation energy from the four calculated values (three by comparative and the one from graphical this a "large" activation energy? How does the activation energy of a reaction influence the rate of the reaction? Did this reaction seem very fast, very slow or somewhere in the middle of the road?***

Because there are so many calculations for this lab, the instructor will stay and help any who want to work on these calculations after lab. If you want to take advantage of that, please feel free to stay after lab to complete calculations needed for the handin.