CHEMICAL KINETICS: THE OXIDATION OF IODIDE TO TRIIODIDE

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INTRODUCTION

The rate at which chemical reactions proceed is often an important consideration in addressing chemistry in real systems. Some of the recent understanding of atmospheric chemistry comes from investigation of gas reaction rates. Biological systems are superbly balanced and regulated by enzymes that speed up reactions that would occur at a snail's pace without the enzymes. Geochemists think that the reason that $CaCO_3(s)$ disappears in the ocean at about a depth of 5 km may be related to a significant change in the rate at which $CaCO_3$ dissolves. Chemists often study reaction rates to get at least a partial handle on the *chemical mechanism* – the series of elementary steps at the molecular scale that lead from reactants to products. This kind of mechanistic information provides a molecular "glimpse" of the reaction and helps us to understand and predict patterns of reactivity.

For two weeks, you will investigate the reaction in water of I^- (iodide) and IO_3^- (iodate) to yield I_3^-

$$6\ H^+\ (aq) + IO_3^-\ (aq) + 8\ I^-\ (aq) \rightarrow 3\ I_3^-\ (aq) + 3\ H_2O(l)$$

Note the complexity of this reaction. It does not happen in one elementary step, as that would require simultaneous collision of 15 chemical species ($6H^+$, 1 IO_3^-, and 8 I^-) in one place -- a highly unlikely event! **Elementary steps** at the molecular level typically involve just one bond breakage and/or bond formation. In the reaction of I^- with IO_3^-, there are numerous bonds broken and formed, suggesting that the overall reaction occurs in a series of steps. Using data from kinetic studies, you will be able to postulate which reagents are involved in the slowest, rate-determining step. You will not be able to postulate the complete mechanism, as it is rarely possible to completely prove a mechanism for such a complex reaction.

This reaction has been chosen because it allows you to explore reaction rates using a method based on changes in color intensity. Here is the idea: Sometimes all the reactants are colorless and only one product is colored or vice-versa, so the reaction progress can be tracked by watching the product's color deepen (or the reactant's color fades) as the reaction proceeds forward. You can see the color change with your own detectors for visible light (your eyes), or you may require a more sensitive device for truly quantitative and detailed studies.

You will use a modern computer-controlled **UV-Vis spectrometer** (UV-Vis = Ultraviolet-Visible radiation) to monitor the speed at which color changes as the reaction takes place.

This experiment will be a class project in which you will split up the work with your peers so that when the period is over, you can all share everyone's data and get a fuller picture of what affects reaction rate. The second week of the lab is going to be dedicated to processing all the data acquired by all the members of the lab on week one; then you will have a chance to "play" with the data as well as get results.

QUICK COLOR STUDIES

These color studies should be done first by everyone.

This reaction has been chosen because it allows you to explore reaction rates using a method based on changes in color intensity. Sometimes all the reactants are colorless and only one product is colored or vice-versa, so the reaction can be tracked by watching the product's color deepen (or the reactant's color fade) as the reaction proceeds forward. The reaction we are studying is a case in point. You can see the color change with your own detectors for visible light (your eyes), or you may require a more sensitive device for truly quantitative and detailed studies.

Since color is a key player in our observations, you will first do a set of preliminary experiments. The goal is to associate colors with particular chemical species containing the element iodine (I^-, I_2, I_3^-, IO_3^- or I_3^- complexed to starch).

a. Look at a reagent bottle containing 0.1 M KIO3 contains solvated K^+ and IO_3^- ions. What color is K^+? What color is IO_3^-?
b. Look at a reagent bottle containing 0.16 M KI. What color is I^-?
c. Using your nickel spatula, add a tiny piece of I_2 (purple crystals) to a 50 mL beaker and add 15 mL of distilled water. Swirl the mixture for 3 - 4 minutes to mix. What do you observe?
d. Add 15 mL of the 0.16 M KI solution to the mixture above, making I_3^-. Swirl for 2 or 3 minutes to mix. What do you see?

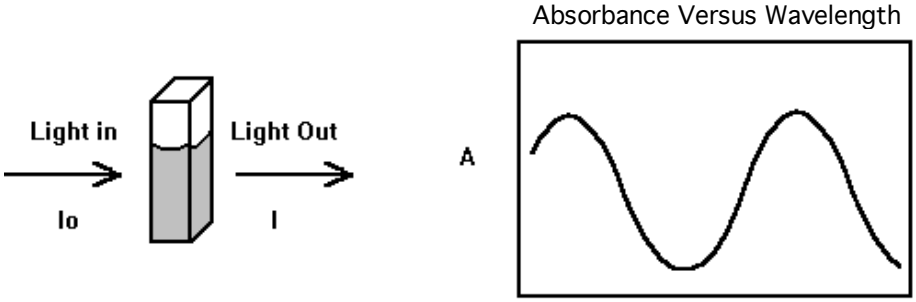
Don't proceed until you answer the following questions in your notebook.

- What color is I_2 in water?
- What color is I^- in water?
- What color is I_3^- in water?
- What color is IO_3^- in water?

UV-VIS ANALYSIS: THE INITIAL RATES METHOD

1. SPECTRA OF REACTANTS AND PRODUCTS

Here is a cartoon of the experiment you will perform to measure the spectrum of I_3^-. You will use a computer driven, diode array, UV-VIS spectrophotometer. Operating instructions for this instrument will be available close to the instrument.



A = Absorbance = $\text{Log}(I_o/I) = \varepsilon_o * \text{length} * \text{Concentration}$

(ε_o = molar absorptivity of analyte)

It is necessary to set a background reference to correct for the light absorbed by the cell and water. This "background" will be subtracted from your true signal for an accurate reading. Put a mark on one of the opaque faces of your cuvette and always keep that face oriented the same way when you insert the cell into the spectrophotometer. Always use the same cell for background reference and sample measurement. After setting a reference background, measure the spectrum of I_3^- from 340 to 800 nm (the visible region of the spectrum is 420-700nm). Dilute the I_3^- solution made in part 1 until the maximum absorbance is < 2 (when the absorbance is larger than two absorbance $\neq \text{Log}(I_o/I)$ and it becomes really hard to do any quantitative measurement). A dilution by a factor of 20 will get you close. Print a copy of the spectrum for each partner.

Looking at the transparent solutions with I^- or IO_3^- it appears that it is unlikely that either species absorbs light in 340 to 800 nm range (a range that mostly coincides with the visible region of the spectra). Measure the spectrum of these species as a check. Do not print this spectrum.

Discuss the following questions with your partner. We will talk about them together as a group.

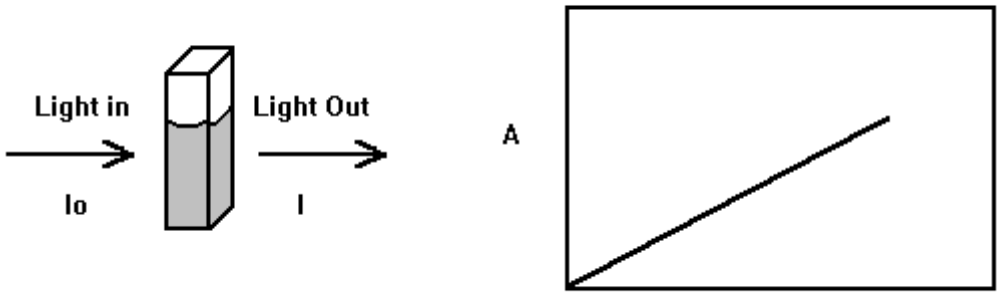
- Why can we ignore light absorption by I^- and IO_3^-?
- At what wavelength(s) does the colorful I_3^- absorb light? Look at the table below for the relationship between the color of absorbed light and the color you see with your eyes. We see the colors that are NOT absorbed. Predict the absorbed wavelength of I_3^- based on this table. Remember

that the absorption peak that complements the color we see does not need to be the maximum of your 340-800 nm spectra. Does your prediction agree with your spectrum?

Relationship of Wavelength to Color	
Wavelength Absorbed (nm)	Color Observed
400 (violet)	greenish yellow
450 (blue)	yellow
490 (blue green)	red
570 (yellow)	violet
580 (yellow orange)	dark blue
600 (orange)	blue
650 (red)	blue green

2. YOUR FIRST KINETICS STUDY

Your next step is to conduct a reaction and monitor the increase in color intensity of the reaction system. By Beer's law, Absorbance = ε_o * length * Concentration where ε_o is a constant characteristic of the substance being measured and the wavelength, length is the width of the cuvette (1 cm in our case) and concentration is the molarity (mol/Liter)of the substance being measured. Thus, absorbance is proportional to concentration.



Absorbance Versus Time

A = Absorbance = $\text{Log}(I_o/I) = \varepsilon_o$ * length * Concentration

You will monitor the change in absorbance <u>at a particular wavelength</u> as time goes on, and will use this information to calculate the rate of the reaction.

In Part 1 the spectrophotometer was set to measure absorbance as a function of wavelength. Now it must be modified to measure absorbance as a function of time at some specified wavelength. You and your partner will choose that wavelength. Pick a λ (wavelength) for monitoring the reaction where the ***reactant does not*** absorb and the ***product does*** – you many need to compromise. At the class discussion (see below), we will decide on one λ as a class for the following runs. Get the spectrophotometer ready to monitor your reaction by setting it to measure absorbance versus time, selecting a wavelength, and making a reference reading. Instructions for the use of the diode array UV-VIS spectrophotometer are available close to the instrument. Clean and dry your cuvette (your instructor will tell you how to do this.)

You will find the following prepared solutions in the lab.

~ 0.10 M KIO_3 (write down the exact concentration)
~ 0.16 M KI (write down the concentration)
distilled water (yellow center tap at end sinks)
2 buffers with fixed pH and therefore fixed $[H^+]$ (write down the exact pH)

All reagents can be easily and quickly dispensed from burettes and automatic dispensing pipettes. For the automatic dispensers, be sure to check the pre-set volume each time, in case someone has adjusted it. If you use pipetters, practice transferring colored water to a beaker 3-4 times. Your success as a class will depend on how exact you can be in delivering amounts to the reaction vessel.

Now you are ready. Prepare the following beakers:

BEAKER #1 (clean, dry 50 mL beaker)
- Pipette 1.00 mL of the 0.10 M KIO_3 solution using the automatic delivery system.
- Add 4.00 mL of the sodium acetate/acetic acid buffer **A** using the automatic delivery system. Since you are adding a buffer the $[H^+]$ written on the bottle will be the concentration of H^+ in your reaction mixture.
- Add 10.00 mL of distilled water from a buret (for easy dispensing).

BEAKER #2 (another clean, dry 50 mL beaker)
- Pipette 5.00 mL of the 0.16 M KI solution using the automatic delivery system.

Pour the KI solution into *BEAKER #1* and simultaneously start the data recording on the spectrophotometer. Mix the solutions by pouring the contents back and forth quickly between the two original beakers several times. Pour some of your sample into your clean, dry cuvette and insert it into the spectrophotometer. You will have to decide when to stop the reaction (see below). Usually 20 to 50 data points will suffice.

The spectrophotometer software will conduct a linear least squares analysis of your data over the range of data points you select. Choose a linear section of the data that is as close as possible to time equal zero. Record the calculated slope of the data and the estimated error.

Talk with your partner about the following questions (put initial answers in your notebook) and be prepared to share your ideas with the other teams.

- Are you satisfied with your choice of the wavelength used to monitor the $[I_3^-]$ growing in with time? We will have to decide this as a group so that later data can be compared among teams. Remember – you want a λ where I_3^- absorbs and I^- does not.
- The computer calculates a slope. What does this slope represents? How does it relate to a rate of appearance of I_3^-? (Hint: remember Beer's law)
- Why is it important to choose a linear region of the plot? Why is it important that the chosen region is very close to time equal zero?
- What would you like to vary in this reaction to see if a change affects the rate? We will negotiate this together so that several aspects get explored. For ideas, think about the concepts covered in lecture and the list of chemicals available in the lab.

3. CLASS DISCUSSION & MORE KINETICS STUDIES

After your team has developed a set of answers for the preceding questions all the teams will meet together. During the discussion, we will negotiate on which aspects will be studied next and by whom. The idea is to have a number of investigations ongoing so we can combine results at the end of the lab period. You will want to use the general procedure used in the first experiment, with some planned modifications. As a goal, every group should *repeat* the first run again to check for reproducibility. Then try to get *several more runs completed* by the end of the lab period.

4. TIPS FOR CAREFUL KINETICS STUDIES

1. If you vary the concentration of some reactant, keep the total reaction volume at 20 mL by adjusting the amount of water. This *constant volume* will allow you to vary the concentration of one reactant at a time while keeping the others at constant concentration.
2. Vary only one reactant at a time if you are changing the concentration. Otherwise, you won't be able to make sense of what is happening.
3. The reaction gets more complicated if $[I^-] < [IO_3^-]$ – the pathway of the chemistry could even change. You can explore this limit, but who knows what you will find. We don't want to actively discourage this direction, but your frustration level could increase if you opt for it – just so you know what you are getting into.
4. When you vary concentrations, it is always a good idea to vary reactants by at least a factor of two, so you have a chance to see an observable impact on the reaction rate.

5. The hydrogen ion concentration can NOT be changed by changing the volume of buffer. It can only be changed by switching from buffer A to buffer B. The [H^+] written on the bottle will be the concentration of H^+ in your reaction mixture.

A.5. PREPARATION OF A SUMMARY OF CLASS DATA

A computer will be set up to record all results. Be sure to enter your data before you leave the lab. At the end of the day the table will be available in the Moodle site.

DATA ANALYSIS (TO BE DONE IN THE 2ND WEEK OF THIS LAB)

Use ALL the class data collected in the first week of lab to answer the following questions

- Which reactants affect the reaction rate and thus appear in the overall rate law? Briefly note how you can tell by glancing at the class data tables.

- Obtain experimental orders and rate constant. Use the fact that rate=k [A] $^{\alpha}$ [B]$^{\beta}$ and therefore log(rate)=log(k [A] $^{\alpha}$) + β log [B] to learn β by graphing log(rate) vs log[B] and performing a linear analysis (the plot's slope is β). Do the same to calculate the orders on all reactants.

- How much can the quantitative order results be trusted? Since runs were repeated, find a simple way to quantify the error in orders. Using one set of the repeated data, estimate the error on the order for that reactant.

- Once you have calculated the order of all reactants calculate the rate constant (k) for the reaction. Write the full rate law you obtain, noting orders on all reactants and the units of your rate constant. Report your orders as integers (because of experimental error you can only be sure of one sig fig).

- Discuss how the assumptions of the initial rate method play out in your calculation of reactant orders. If you took rate data outside the initial rate regime (beyond the first 5% or so of the reaction), could you trust your order calculations? Why or why not?